

University of Alberta

**Atmospheric BTEX in Fort McKay, AB: A Comparison with Baseline
Measurements**

by

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Abstract

Fort McKay is a small community located in the oil sand industrial area in northeastern Alberta. Due to its close proximity to the expanding industrial activities, it is important to assess the health risk to the community's inhabitants.

Thirty-five randomly selected participants were measured for exposure to benzene, toluene, ethylbenzene, *m,p*-xylenes and *o*-xylenes (BTEX) volatile organic compound concentrations for a seven-day period in personal, indoor and outdoor sampling locations, using 3M OVM 3500 passive monitors.

Results show lower average concentrations than a baseline study performed in Fort McKay. Concentrations were lower than other urban locations and similar levels to other rural locations. Concentrations were found to be higher indoors than outdoors and lower in personal locations compared to indoor levels.

The results indicate that the BTEX concentrations found in Fort McKay are typical of a rural community and are not influenced by the oil sand industrial activities.

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List of Abbreviations

AH&W: Alberta Health and Wellness

ASTDR: Agency for Toxic Substances and Disease Registry

BTEX: Benzene, Toluene, Ethylbenzene and Xylene

CAPP: Canadian Associated Producers of Petroleum

CASA: Clean Air Strategic Alliance

CV: Coefficient of Variation

DAE: Department of Alberta Energy

EPA: Environmental Protection Agency

GC: Gas chromatography

MDL: Method Detection Limit

MS: Mass Spectrometer

NPRI: National Pollutant Release Inventory

OVM: Organic Vapour Monitor

TWA: Time weighted average

VOC: Volatile Organic Compound

List of Symbols

μm = micrometre

cm = centimetre

m = metre

km = kilometre

in = inch

μL = microlitre

mL = millilitre

m^3 = cubic metre

$^{\circ}\text{C}$ = degrees Celsius

s = second

min = minute

hr = hour

bpd = barrels per day

ng = nanogram

μg = microgram

mg = milligram

ppm = parts per million

1. Introduction

1.1. Background

It is widely known that industrial activities can result in the emission of atmospheric pollution and that these contaminants can have potentially adverse health effects on people. It is therefore important to study the link between industrial emissions of atmospheric pollution and how they contribute to the exposure of airborne contaminants for humans. A study performed through the fall of 1999 and winter of 2000 provided baseline measurements of airborne volatile organic compounds in Fort McKay, AB. With an increase in industrial activity since then, an opportunity for a reassessment of the exposure to these compounds the people living in this community is presented.

The small community of Fort McKay (population 521) (StatsCan, 2007) is located in northeastern Alberta, approximately 60 km north of Fort McMurray. This community is in relative close proximity to oil sand activities occurring in the region. These activities include oil sands mining, bitumen extraction and synthetic crude oil production. The two largest industrial facilities carrying out these activities in this area are Syncrude Canada Ltd. (Syncrude) and Suncor Inc. (Suncor). These facilities emit a wide variety of airborne pollutants, including volatile organic compounds (VOCs).

This study is the second phase of a survey with the first phase being completed in 1999 and 2000. The first phase of the study was to establish “baseline” concentrations to which the residents in this community were being exposed. Since the first phase of the study has been completed, there have been increases in the industrial activity in the

region. This presents an opportunity to determine if a relationship exists between the increase in industrial activity and the exposure to airborne pollution by the residents.

The main objectives of this study are to:

- obtain measurements of benzene, toluene, ethylbenzene and xylenes (BTEX) in personal, indoor and outdoor air;
- examine relationships between personal, indoor and outdoor BTEX concentrations;
- compare current BTEX levels to the past baseline study to determine if increases in industrial activity translate to increased exposure for residents; and
- increase understanding of the sources and causes of exposure of Fort McKay residents.

1.2. Study Area Description

1.2.1. Fort McKay, Alberta

Fort McKay is located approximately 60 km north of Fort McMurray and 500 km northeast of Edmonton. According to the last census (StatsCan, 2007), the population of Fort McKay is approximately 521 people. The community is located on the west banks of the Athabasca River, downstream from the Syncrude and Suncor facilities. The homes in the community consist mostly of single family detached homes including mobile homes.

The community of Fort McKay is located approximately 16.1 km away from the main stack at Syncrude and 22.6 km away from the main stack at Suncor. The marked arrow in Figure 1 shows the location of the oil sand activities in Alberta. Figure 2 shows

a close up map of the area marked by the arrow in Figure 1. Labeled on the map are Fort McKay, Syncrude and Suncor, and Fort McMurray.

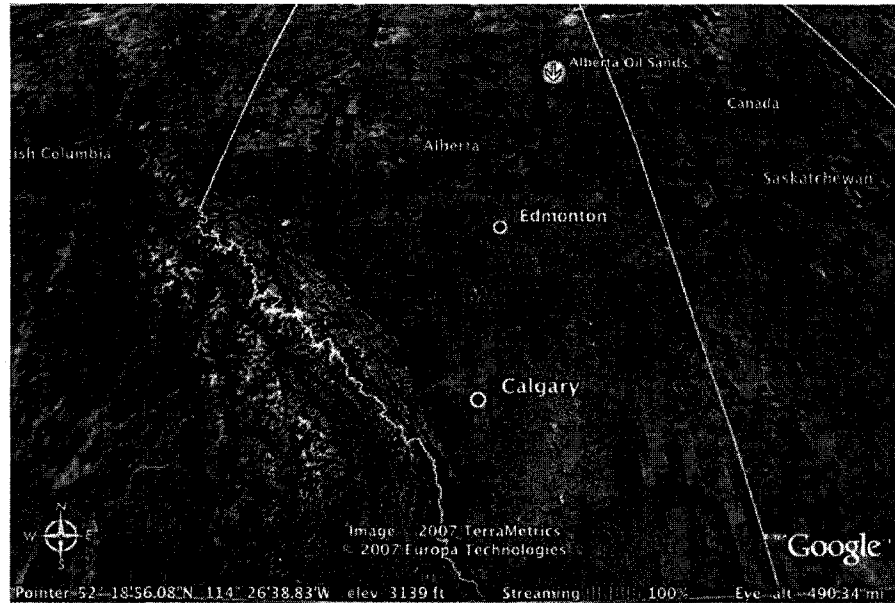


Figure 1: Location of oil sands in northeastern Alberta (Google Inc., 2007)

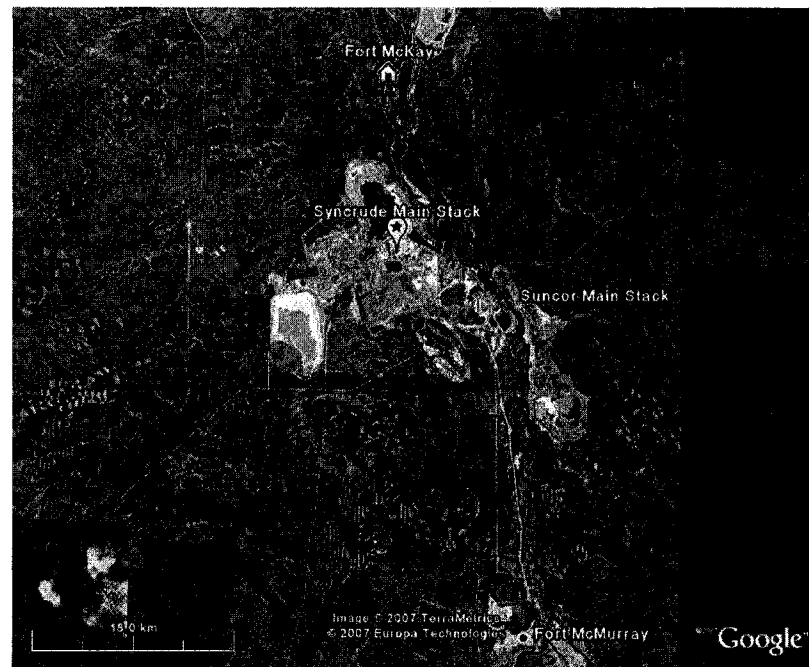


Figure 2: Close up of red highlighted area from Figure 1 (Google Inc., 2007)

1.3. Industrial Activity

Suncor and Syncrude are the two largest producers of oil in the region. According to the Department of Alberta Energy (DAE) (DAE, 2006), of the average 1, 063, 023 barrels of oil produced daily in all of Alberta in 2005, Suncor's portion constituted about 20% of this total while Syncrude produced approximately 25% of this total. This production is only expected to increase in the future with Suncor expected to double its oil production in the next 5 years. Shell Canada Ltd. has recently started operations in the region and is expected to increase production drastically over the next several years. Table 1 shows the oil sand production numbers for Suncor, Syncrude and Shell alongside the total VOC emissions from each operation.

Table 1: Oil sand production numbers and mass of VOC compounds released into the atmosphere

Year	Oil sand production ^a			Total VOC emissions ^b		
	(bpd)			(tonnes)		
	Suncor	Syncrude	Shell	Suncor	Syncrude	Shell
2002	269781	269810	< 100	21297	11666	8986
2003	273563	255498	51320	31666	11644	2117
2004	281711	287547	87930	21668	8592	4782
2005	214644	262401	101072	16599	7678	4941

^a based on data from the Department of Alberta Energy (2003; 2004; 2005; 2006)

^b based on data from the National Pollutant Release Inventory (2006)

As Table 1 shows, the amount of oil produced by Suncor and Syncrude remained relatively steady between 2002 and 2005. It can also be seen that the total VOC emissions from these industrial operations have dropped throughout this timeframe. However, the oil production from Shell has increased considerably over the last few years with production expected to continue in the future.

1.4. Research Hypotheses

The research conducted provides the opportunity to test several research hypotheses:

Hypothesis 1: Concentrations of indoor BTEX (benzene, toluene, ethylbenzene, and xylene) compounds are found to be greater indoors as compared to outdoor locations. Past research shows this trend is apparent due to the presence of indoor sources of these compounds (Davis and Otson, 1996).

Hypothesis 2: Past studies have shown that people generally spend most of their time indoors (Wallace et al., 1988; Kim et al., 2002; Edwards et al., 2005; Sexton et al., 2007). Therefore, personal exposure measurements of VOC compounds can be significantly correlated to concentrations found in their own homes. The hypothesis tested is firstly: that personal BTEX measurements are not significantly different from indoor measurements, and secondly: that personal BTEX concentrations are significantly correlated with indoor concentrations.

Hypothesis 3: Current BTEX concentration measurements taken have not significantly changed since the baseline study performed by Miyagawa (2001) was conducted. Even though oil sands activities have increased since the preliminary study was performed, VOC emissions have not (see Table 1), therefore, there is not expected to be a significant increase in ambient VOC concentrations found.

1.5. Methodology Overview

The measurements taken during the recent survey will compare concentrations of benzene, toluene, ethylbenzene, *m,p*-xylenes and *o*-xylene to measurements taken during

the baseline study. These concentrations of these compounds will also be compared to several other studies performed throughout Alberta, Canada, the United States and Europe.

The sampling period occurred between September 7, 2006 and November 1, 2006. The field staff consisted of two University of Alberta graduate students, namely Garrett Hoeksema and Laurie Cheperdak. Sampling methodology is also provided by Cheperdak (2007).

A probability sampling strategy was adopted, randomly selecting 35 homes throughout the community to participate. Before the recruitment process began, a pamphlet was delivered to each home in the community explaining the study. The recruitment process then involved the field workers going to the randomly selected participants' homes in order to explain the study and to determine if they were interested in participating. This process was repeated until 35 homes had agreed to participate in the survey.

Two visits to the participants' homes were made. During the first visit, the study was explained in greater detail, consent forms were administered and the home characteristics were documented. The participant's home was then outfitted with sampling stands and passive monitoring VOC badges were placed in the home, outside the home and on a necklace the participant wore for one week's time. During the second visit, the samples and any documentation was retrieved. After the sampling period had ended, the badges were collected and sent for analysis to the Centre for Toxicology in Calgary, AB.

All sampling design, participant recruitment and data collection was performed in cooperation with Laurie Cheperdak, fellow graduate student at the University of Alberta. Data analysis was performed separately with Cheperdak (2007) performing analysis on straight-chain aliphatic compounds (hexane, heptane, octane, nonane and decane) and 3-methylhexane. The concentrations of these compounds from each location were compared between locations as well as to baseline measurements from a study performed in 1999/2000 in Fort McKay, AB (Cheperdak, 2007). This study considers the analysis of benzene, toluene, ethylbenzene and xylenes, comparing them to the baseline study, as well as to the levels found in each location.

2. Literature Review

2.1. Volatile Organic Compounds

The focus of this study was on four volatile organic compounds, namely benzene, toluene, ethylbenzene and xylenes (BTEX). All four of these VOCs are variations of an aromatic carbon ring.

2.1.1. Chemical and Physical Properties

Benzene

Benzene is a clear, colourless, volatile and highly flammable liquid with a characteristic odour. It is a natural component of petroleum and was discovered by Faraday in 1825. Benzene has a boiling point and melting point of 80.1 °C and 5.5 °C, respectively. It is used in the manufacturing process of detergents, pesticides, pharmaceuticals and other industrial chemicals, as well as a gasoline additive (Budavari et al., 2001). The Alberta Air Quality Objective for benzene is 30 µg/m³ for a 1-hr average concentration.

Figure 3 shows the chemical structure of benzene, consisting of a single aromatic carbon ring.

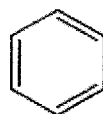


Figure 3: Chemical structure of benzene (C₆H₆) (Lide, 2007)

Toluene

Toluene is a flammable liquid with an odour similar to that of benzene. It is a substance mainly derived from tar oil. Physical properties of toluene include a melting point of $-95\text{ }^{\circ}\text{C}$, and a boiling point of $110.6\text{ }^{\circ}\text{C}$. In the manufacturing industry, it is used in the production of explosives, dyes and many organic compounds (Budavari et al., 2001). It is also used as a solvent for paints and lacquers; as a thinner for inks, perfumes and dyes; and as a gasoline additive (Budavari et al., 2001). The Alberta Air Quality Objectives for toluene are $1880\text{ }\mu\text{g}/\text{m}^3$ for a 1-hr average concentration and $400\text{ }\mu\text{g}/\text{m}^3$ for a 24-hr average concentration.

The chemical structure of toluene consists of a benzene ring with an attached methyl group, as shown in Figure 4.

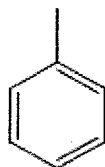


Figure 4: Chemical structure of toluene (Lide, 2007)

Ethylbenzene

Ethylbenzene has the chemical formula of $\text{C}_6\text{H}_5\text{C}_2\text{H}_5$ and has a molecular weight of 106.16 g/mol . It is a colourless, flammable liquid with a boiling point of $136.25\text{ }^{\circ}\text{C}$ and a melting point of $-95.01\text{ }^{\circ}\text{C}$. Ethylbenzene can be converted to a styrene monomer and can be used as a resin solvent (Budavari et al., 2001). The Alberta Air Quality Objective for ethylbenzene is $2000\text{ }\mu\text{g}/\text{m}^3$ for a 1-hr average concentration.

Figure 5 shows the chemical structure of ethylbenzene, consisting of a benzene ring with an attached ethyl group.

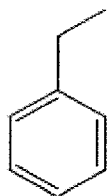


Figure 5: Chemical structure of ethylbenzene (Lide, 2007)

Xylenes

Xylene consists of two methyl groups attached to a benzene ring and has a chemical formula of $C_6H_4(CH_3)_2$. It has a molecular weight of 106.16 g/mol. Xylene naturally exists in three structural isomers each with its own chemical properties: ortho-xylene (*o*-xylene), meta-xylene (*m*-xylene) and para-xylene (*p*-xylene). *m*-xylene is a colourless liquid with a melting point of $-47.4\text{ }^\circ\text{C}$ and a boiling point of $139.4\text{ }^\circ\text{C}$. *o*-xylene is a colourless liquid with a melting point of $-25\text{ }^\circ\text{C}$ and a boiling point of $144\text{ }^\circ\text{C}$. *p*-xylene exists as colourless plates or prisms at low temperatures, has a melting point of $13\text{-}14\text{ }^\circ\text{C}$, and a boiling point of $137\text{-}138\text{ }^\circ\text{C}$ (Budavari et al., 2001). The Alberta Air Quality Objectives for xylenes are $2300\text{ }\mu\text{g}/\text{m}^3$ and $700\text{ }\mu\text{g}/\text{m}^3$ for 1-hr and 24-hr average concentrations, respectively.

The chemical structures of the three structural isomers of xylene are shown below in Figures 6, 7 and 8.

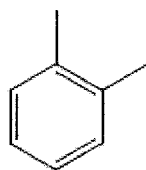


Figure 6: Chemical structure of *o*-xylene (Lide, 2007)

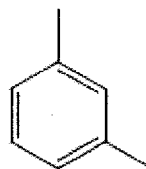


Figure 7: Chemical structure of *m*-xylene (Lide, 2007)

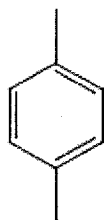


Figure 8: Chemical structure of *p*-xylene (Lide, 2007)

2.1.2. Sources of Volatile Organic Compounds

Volatile organic compounds have many different sources from which they are emitted into the atmosphere. These include natural and anthropogenic sources. Natural emissions generally include biogenic emissions and emissions from forest fires while anthropogenic emissions are a result of industrial activities and daily human activity. This section highlights the various types of VOC emissions, focusing on the aforementioned compounds.

Natural Emissions

On a global scale, biogenic emissions are the main natural source of volatile organic compounds in the atmosphere (Guenther et al., 1995; Filella and Peuelas, 2006). The main source of biogenic emissions is vegetation (Fall and Hewitt, 1999).

The combustion of wood from forest fires provides a significant source of benzene emissions (Naeher et al., 2007). Toluene emissions from the combustion of wood have been estimated at 3.75 percent mass toluene (Friedrich and Obermeier, 1999). This issue is particularly true for residents in northern Alberta as they are surrounded by boreal forest and therefore are susceptible to exposure of emissions from forest fires.

The ocean is another important source of atmospheric VOCs. The ocean is considered to be supersaturated with VOCs in comparison to the atmosphere and is therefore considered an emission source of VOCs (Guenther et al., 1995). This is due to the concentration gradient of the VOCs from the ocean to the atmosphere. Since there is a high concentration of VOCs in the ocean, through partition mixing, the VOCs will have a tendency to move from the ocean to the atmosphere.

Anthropogenic Emissions

Anthropogenic emissions also contribute to the concentration of VOCs in the atmosphere. These are made up of emissions from vehicles, industrial processes, use of solvents and biological processes (Friedrich and Obermeier, 1999).

Automotive Emissions

Benzene emissions from vehicles are a significant source, particularly in urban areas (Ilgen et al., 2001). Ilgen et al. (2001) found that vehicle emissions greatly

influenced both outdoor and indoor concentration measurements of VOCs, particularly benzene. Toluene, ethylbenzene and the isomers of xylene were also found to be influenced by the presence of vehicle exhaust, but to a lesser extent (Ilgen et al., 2001). Batterman et al. (2006) reported that the mean concentration of benzene in 15 garages of residential homes in the state of Michigan was $36.6 \mu\text{g}/\text{m}^3$ while outside the garages the mean concentration was only $0.4 \mu\text{g}/\text{m}^3$. The source of these benzene emissions was found to be from vehicles parking in the garage (Batterman et al., 2006). Another study performed in southeastern Michigan measured non-methane hydrocarbon (NMHC) emissions from vehicle fuel caps, and it was discovered that NMHC emissions increased as ambient temperature increased and as vehicle age and mileage increased (Batterman et al., 2005). These emissions are due to fugitive emissions from the gas tank (Batterman et al., 2005). Fugitive emissions are due to the vaporization of the gasoline in the car and then leaking out into ambient air through the gas tank cap. Benzene was found to constitute about 2.5% of these emissions (Batterman et al., 2005).

Vehicle emissions of toluene can come from the combustion of fossil fuels as well as evaporative emissions (Batterman et al., 2005; Kawashima et al., 2006). Evaporative emissions are due to the volatilization of gasoline into the atmosphere. A study performed in Japan estimated that the rate of emission from vehicles averages out to be $17 \text{ mg vehicle}^{-1} \text{ km}^{-1}$ (Kawashima et al., 2006).

The primary source of emission of ethylbenzene is from vehicle exhaust. The burning of hydrocarbon fuels results in the formation of ethylbenzene and its subsequent release into the atmosphere (Monod et al., 2001). An air quality study focusing on VOC emissions from vehicles in Algiers, Algeria detected ethylbenzene in the air by roadside

sampling (Kerbachi et al., 2006). The higher the traffic density, the larger the concentrations found (Kerbachi et al., 2006).

Xylene is also a product of the combustion of gasoline and is found in vehicle exhaust (Friedrich and Obermeier, 1999; Kawashima et al., 2006). Friedrich and Obermeier (1999) report that in a four Otto engine with the use of a three-way catalyst the mass percentage of xylene in the exhaust was on the order of 9.0 percent. Of the four aromatic hydrocarbon pollutants analyzed in this study, xylene was exceeded only by toluene at 10.0 mass percent (Friedrich and Obermeier, 1999).

Industrial Emissions

The Environmental Protection Agency (EPA) in the United States estimates that 17% of VOC emissions can be attributed to industrial processing and production activities (Cohen, 1996). In the Alberta oil and gas industry, the largest source of benzene is from glycol dehydrators (CAPP, 2007). In 2003, the total benzene emissions from glycol dehydrators in Alberta was 1,988 tonnes (CAPP, 2004).

The National Pollutant Release Inventory (NPRI) reports that for the year 2005, the emissions of benzene, toluene, ethylbenzene, and xylenes were 52, 218, 73 and 501 tonnes, respectively, for the Syncrude Mildred Lake facility in northern Alberta (NPRI, 2006). For the Suncor facility, the NPRI reports that for 2005 the emissions were 14 tonnes benzene, 132 tonnes toluene, 43 tonnes ethylbenzene and 211 tonnes xylenes (NPRI, 2006). It can therefore be seen that the oil extraction and refining process occurring in northern Alberta is a significant emission source of volatile organic compounds.

Industrial VOC emissions are produced from many other industrial processes. These include fugitive emissions from petrochemical and chemical facilities as well as from public treatment works (Cohen, 1996). The industrial use of organic solvents makes up a large part of industrial emissions (Friedrich and Obermeier, 1999; Monod et al., 2001). The use of paint, printing ink, adhesives or cleansing agents also contribute to the emission of VOCs into the atmosphere through the evaporation of these materials (Friedrich and Obermeier, 1999).

Volatile organic compounds are also released into the atmosphere by the evaporation of gasoline, and gas leakage from natural gas and liquefied petroleum gas storage facilities (Khoder, 2007).

Indoor Emissions

There are many studies that state that humans spend 90% of their time indoors, so this represents a significant source of human exposure to VOCs (Wallace et al., 1988; Davis and Otson, 1996; Edwards et al., 2001; Kim et al., 2002; Sexton et al., 2007). In some studies, it was found that there were higher concentrations of VOCs in the home compared to outside the home (Davis and Otson, 1996). This is due to the presence of indoor sources of VOC emissions from building materials, consumer and commercial product usage, and human activities such as residential water use and cooking (Davis and Otson, 1996).

The use of solvents and cleaning agents can also contribute to VOC concentrations in the home, particularly toluene, ethylbenzene and xylenes (Otson, 1996). Table 2 shows a list of potential sources of VOCs indoors and their components.

A study investigating how building materials and consumer products affect levels of indoor VOC concentrations was conducted by Wallace et al. (1987). It was found that paints, cleaners, glues and insecticide sprays significantly contributed to levels of VOCs in the indoor environments tested (Wallace et al., 1987).

Outdoor air also greatly contributes to concentrations of VOCs in the home (Ilgen et al., 2001). Indoor environments near busy roadways experience higher VOC concentrations than those in areas with less vehicle traffic (Isbell et al., 2002).

Table 2: Possible indoor sources and their components (adapted from Otson, 1996)

Source	Components
Latex paints	benzene, 1,2,4- & 1,3,5-trimethylbenzenes, toluene
Alkyd paints	1,1,2,2-tetrachloroethane, 1,2,4-trichlorobenzene
Carpets	1,2,4- & 1,3,5-trimethylbenzenes, benzene, toluene, styrene
Glued carpets	<i>p</i> -dichlorobenzene, <i>n</i> -decane
Wood burning	xylenes, 1,2,4- & 1,3,5-trimethylbenzenes, naphthalene, toluene, styrene
Foam board	dichlororomethane, dichlorobenzenes
Paint removers	dichlororomethane, toluene
Spray products	Dichloromethane, xylenes
Adhesives/tape	Trichloroethylene, <i>n</i> -decane, toluene, styrene
Room deodorizers	<i>p</i> -dichlorobenzene, limonene, decane
Detergents	limonene, pinene
Waxes	Pinene
Tobacco smoke	benzene, toluene, <i>m</i> - and <i>p</i> -xylenes, styrene, ethylbenzene
Gasoline/driving	benzene, toluene, xylenes, styrene, trimethylbenzene
Solvents	toluene, ethylbenzene
Dry cleaning	Tetrachloroethylene
Tap water	Chloroform

Higher concentrations of benzene and toluene have been found in homes with attached garages (Isbell et al., 2002). This is due to vehicle emissions and fugitive emissions from fuel storage in the garage that infiltrates the home (Naeher et al., 2007).

The combustion of fossil fuels inside the home also contributes as a source of VOCs to the indoor air. These emissions can come from either a natural gas or wood burning fireplace or a furnace (Edwards et al., 2001). In northern Alberta it may be common for houses to contain wood-burning fireplaces since wood is such a readily available source of fuel.

Tobacco smoke can also represent a large source of VOCs to the indoor environment, if present. Higher concentrations of VOCs have been measured and attributed to the presence of tobacco smoke (Edwards et al., 2001). Tobacco smoke has also been found to be a dominant source of indoor benzene concentrations (Edwards and Jantunen, 2001).

Personal Exposure

Since it is generally known that people spend upwards of 90% of their time in indoor environments, whether at home, work or elsewhere (Wallace et al., 1988; Edwards et al., 2001; Kim et al., 2002; Sexton et al., 2007), indoor environments and sources of VOCs in these environments contribute largely to personal exposure to volatile organic compounds. There are some potential sources that can only be attributed to personal activities. A study performed in Birmingham, UK by Kim et al. (2002) found the following sources to contribute to exposure to VOCs: exposure to tobacco smoke, use of vehicles, space heating, cooking, moth balls, hair sprays, cleaning and painting. Another study, performed in several communities in California as part of the Total Exposure Assessment Methodology (TEAM) study, found that the three leading contributing sources to personal VOC exposure are tobacco smoke, employment and auto-related

activities such as driving, pumping gas and visiting service stations (Wallace et al., 1988).

2.1.3. Health effects

Acute Exposure

The main potential pathways for benzene to enter the human body include inhalation, oral and dermal (ATSDR, 2005a). Possible symptoms of acute overexposure to benzene by either inhalation or ingestion include dizziness, vomiting, fatigue, anorexia, loss of consciousness and respiratory arrest (Budavari et al., 2001). Death by inhalation of benzene generally occurs due to exposure to high concentrations for a period of time. It has been estimated that exposure to concentrations of 20,000 ppm (333 $\mu\text{g m}^{-3}$) benzene in air for a period of 5 to 10 minutes is fatal (ATSDR, 2005a).

A potential health effect due to acute overexposure to toluene by inhalation is central nervous system excitation and depression (Budavari et al., 2001). Exposure to low concentrations can result in mild upper respiratory tract irritation, mild eye irritation, slight nausea and drowsiness (Budavari et al., 2001). Exposure to high concentrations can cause vision disturbances, dizziness, nausea, headaches and death from respiratory failure or sudden ventricular fibrillation (ATSDR, 2000).

Short term overexposure to ethylbenzene by inhalation has been known to cause eye, skin, throat and mucous membrane irritation; headache; and coma (Budavari et al., 2001). There were cases reported where people exposed to higher levels showed more severe effects such as decreased movement and dizziness (ATSDR, 1999). There have been no reported cases of death related to overexposure to ethylbenzene (ATSDR, 1999).

Some of the potential symptoms of acute overexposure to any of the three isomers of xylene by inhalation are flushing and reddening of the face, a feeling of increased heat, disturbed vision, dizziness, drowsiness, and confusion and coma (Budavari et al., 2001). In some rare instances, people were exposed to very high concentrations of xylene for a short period of time and died as a result (ATSDR, 2005b).

Chronic Exposure

Chronic exposure to benzene through inhalation has been found to cause respiratory, gastrointestinal, hermatological, musculoskeletal, renal, dermal, ocular, immunological, lymphoreticular, neurological, reproductive and cancer effects (ATSDR, 2005a).

Studies have also shown that toluene exposure affects the blood, however it is not a critical target tissue (ATSDR, 2000).

The health effects of long term exposure to ethylbenzene are not known due to lack of information on this subject (ATSDR, 1999).

Potential symptoms of chronic exposure to xylenes by inhalation include respiratory irritation, central nervous system excitation followed by depression, tremors, apprehension, impaired memory, headache, anorexia and nausea (Budavari et al., 2001).

2.2. *Passive Sampling*

By definition, passive sampling involves the transport of contaminated air to a collector without the use of an air-moving device (Rose and Perkins, 1982). Passive monitors are small, lightweight, require no maintenance and are easy to use (Rose and Perkins, 1982). These characteristics make them appropriate to use for personal air

contaminant or indoor monitoring as they do not hinder the person wearing them, or can be easily placed inside a home.

2.2.1. Theory of Passive Monitors

Passive monitoring is also referred to as diffusive monitoring. This is due to the fact that there is no air forced upon them by the use of a mechanical device. Diffusion, when it comes to air contaminants, is the process by which particles in the air travel across a concentration gradient. This process is governed by Fick's First Law of Diffusion (Lautenberger et al., 1981; Rose and Perkins, 1982; Posner and Moore, 1985), which states:

$$J = -D \left(\frac{\Delta C}{\Delta x} \right), \quad (\text{Equation 1})$$

where J is the mass flux, D is the diffusion coefficient of the contaminant of interest, and $\Delta C/\Delta x$ is the concentration gradient (Lautenberger et al., 1981). The presence of the negative sign indicates the direction the particles will travel, from high concentration to low concentration.

By multiplying both sides of the equation by the cross-sectional area of the passive monitor the equation becomes:

$$JA = -DA \left(\frac{\Delta C}{\Delta x} \right), \quad (\text{Equation 2})$$

and since

$$JA = \frac{M}{t}, \quad (\text{Equation 3})$$

where M/t is the mass collection rate, Equations 2 and 3 combine to give:

$$\frac{M}{t} = -DA \left(\frac{\Delta C}{\Delta x} \right). \quad (\text{Equation 4})$$

Figure 9 is a schematic diagram illustrating the derivation of Fick's Law. The sorbent is located on the right, indicating the boundary of the monitor. The left side is a permeable boundary, which restricts the convective airflow but allows diffusion of the contaminant to still occur. The region between the permeable boundary and the sorbent is assumed stagnant air space without convection currents (Lautenberger et al., 1981).

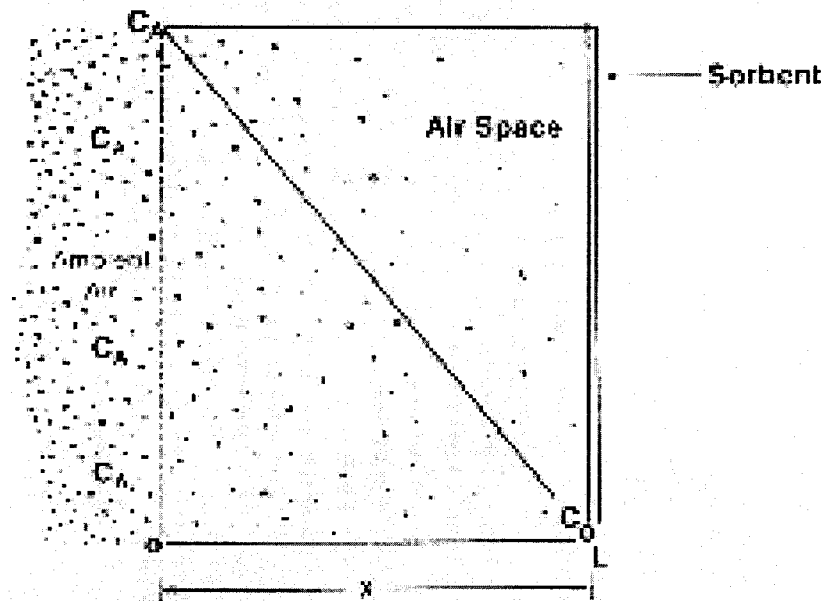


Figure 9: Derivation of Fick's First Law of Diffusion (Lautenberger et al., 1981)

As Figure 7 shows, the ΔC can be substituted as:

$$\Delta C = C_A - C_0, \quad (\text{Equation 5})$$

where C_A is the concentration of the contaminant in the ambient air and C_0 is the concentration of the contaminant at the sorbent.

Figure 7 also shows the following:

$$\Delta x = L, \quad (\text{Equation 6})$$

where L is the length of the diffusion path.

Therefore,

$$\frac{\Delta C}{\Delta x} = \frac{C_A - C_o}{L}, \quad (\text{Equation 7})$$

and if the assumption is made that the concentration at the sorbent is zero (Lautenberger et al., 1981), then $C_o = 0$ and the expression becomes:

$$\frac{\Delta C}{\Delta x} = \frac{C_A}{L} \quad (\text{Equation 8})$$

Substituting Equation 8 into Equation 4 gives

$$\frac{M}{t} = DA \frac{C_A}{L} \quad (\text{Equation 9})$$

Rearranging this equation gives the expression:

$$M = \frac{DA}{L} C \times t \quad (\text{Equation 10})$$

The term DA/L is known as the sampling rate and has the units of cm^3/sec , the same units associated with active sampling methods (Rose and Perkins, 1982). Equation 9 describes the mass deposited on the passive monitor as a function of the sampling rate, the concentration of the contaminant and the time of the exposure.

2.2.2. Factors affecting passive monitor performance

Passive monitor performance can be affected by the environmental conditions the monitors are placed in. The OVM 3520 passive monitor, manufactured by 3M™, was tested under varying concentrations, temperatures and relative humidities (Chung et al., 1999). The concentrations varied from 10 to 200 $\mu\text{g}/\text{m}^3$, while the temperature varied between 10, 25 and 40 °C and the relative humidity was changed between 12, 50 and 90 % (Chung et al., 1999). It was found that the passive monitor performed best at the

lowest temperature (10 °C) and performance dropped off at higher temperatures as the humidity increased (Chung et al., 1999).

Fellin and Otson (1994) investigated the effect of varying climatic conditions had on the performance of the OVM 3500 passive monitor. The researchers found that the climatic factors, specifically the temperature and relative humidity, were only weakly correlated with VOC concentrations (Fellin and Otson, 1994). It was concluded that the climatic factors did not affect the concentrations of the VOCs measured using the passive monitors but that a more important factor was the presence of sources of VOC emissions (Fellin and Otson, 1994).

2.3. Case Studies

2.3.1. EXPOLIS – Helsinki, Finland

The EXPOLIS (Air Pollution Exposure Distributions of Adult Urban Populations in Europe) study was a large initiative aimed at assessing the exposure to major air contaminants in six major urban centres across Europe (Jantunen et al., 1998; Jantunen et al., 2004). The study involved measuring concentrations from the personal sampling location, the interiors and exteriors of homes, and the interior of work environments (Jantunen et al., 1998). Several key air contaminants were analyzed in these locations including: particulate matter smaller than 2.5 µm (PM_{2.5}), volatile organic compounds (VOCs) and carbon monoxide (CO) (Jantunen et al., 1998). The sampling occurred between the fall of 1996 and the winter of 1997-1998 in the cities of Athens, Basel, Grenoble, Helsinki, Milan and Prague (Jantunen et al., 1998).

The VOC results from the city of Helsinki, Finland were published by Edwards et al. (2001). For this component of the EXPOLIS study, the researchers looked at VOC concentrations in residential environments (indoor and outdoor), at the workplace (indoors) and personal airspace (Edwards et al., 2001). This was done using an active sampler which was placed in these microenvironments and sampled only when the participant was present in each microenvironment and by using an active sampler that the participant carried around with them (Edwards et al., 2001). Questionnaires and time activity diaries were also completed by the participants to collect information on their personal activities, commuting behavior and residential/workplace characteristics (Edwards et al., 2001). These characteristics included the type of building, ventilation, traffic volume, type of stove, heating type and exposure to tobacco smoke (Edwards et al., 2001).

The investigators found that outside of residential homes, the mean concentrations of benzene, toluene, ethylbenzene, *o*-xylene and *m,p*-xylenes were 1.7, 1.0, 5.6, 1.3 and 3.1 $\mu\text{g m}^{-3}$, respectively (Edwards et al., 2001). These concentrations were found to be relatively low compared to residential indoor concentrations. The indoor residential home concentrations were reported to be 2.2 $\mu\text{g m}^{-3}$ for benzene, 2.9 $\mu\text{g m}^{-3}$ for ethylbenzene, 20 $\mu\text{g m}^{-3}$ for toluene, 2.5 $\mu\text{g m}^{-3}$ for *o*-xylene, and 7.8 $\mu\text{g m}^{-3}$ for *m,p*-xylenes (Edwards et al., 2001). This suggests that there are sources for these aromatic VOCs within the home.

The authors came to the conclusion that traffic and smoking influenced the concentrations of VOCs individuals were exposed to (Edwards et al., 2001). Participants exposed to tobacco smoke were also exposed to elevated concentrations of benzene,

toluene, and xylenes as well as marginal changes in the concentration of ethylbenzene (Edwards et al., 2001).

2.3.2. Fort McKay, AB – Background Study

In the fall of 1999 and the winter of 2000 a study was performed in Fort McKay, Alberta to determine baseline concentrations of VOCs both inside and outside of participants' homes (Miyagawa, 2001). The passive sampling performed was done using the 3M™ OVM-3500 samplers and analyzed at the Centre for Toxicology at the University of Calgary (Miyagawa, 2001). The samples were placed both inside and outside of approximately 30 participants' homes for approximately 96 hours at a time (Miyagawa, 2001). A 24 hour sampling period was used to measure the personal sampling location of the participants (Miyagawa, 2001). The sampling population was stratified to account for differences in the type of housing and were randomly chosen throughout the community in order to get an accurate representation from all homes in the community (Miyagawa, 2001).

This study was completed in both the fall season and the winter season, and the results from each portion of the study will be reported here. Table 3 shows the 96-hour time weighted average indoor and outdoor concentration statistics for the fall sampling period, while Table 4 shows the 96-hour time weighted average indoor and outdoor concentration statistics for the winter sampling period.

**Table 3: 96-hour time weighted average concentrations for fall 1999 sampling period ($\mu\text{g}/\text{m}^3$)
(adapted from Miyagawa, 2001)**

VOC	Location	Median	90th Percentile	Maximum	Geometric Mean	Geometric s.d.
Benzene	Indoor	4.1	9.1	26	4.1	2.2
	Outdoor	0.8*	1.5	5.2	N/A	N/A
Toluene	Indoor	11	37	170	13	2.4
	Outdoor	0.5*	5.3	7.4	N/A	N/A
Ethylbenzene	Indoor	1.8	5.3	20	1.4	3.6
	Outdoor	0.0*	0.1*	1.1	N/A	N/A
<i>m,p</i> -Xylenes	Indoor	5.2	20	84	5.7	2.4
	Outdoor	1.3	2.9	8	1.5	1.9
<i>o</i> -Xylene	Indoor	1.8	7.9	29	1.5	4
	Outdoor	0.0*	0.1*	1.3	N/A	N/A

** denotes concentration is below the mean detection limit
N/A denotes data is not available*

The results in Table 3 show that for all the compounds listed above, the indoor concentrations are higher than outdoor concentrations. This shows that there are sources of volatile organic compounds in the homes of participants. Toluene had the highest indoor concentration in the participants' homes (Miyagawa, 2001). A Wilcoxon signed rank test was also performed and provided statistical evidence that the concentrations of VOCs were higher indoors than outdoors (Miyagawa, 2001). The indoor/outdoor ratios were also analyzed and were found to be higher than one, again indicating higher concentrations of VOCs indoors as compared to outdoors (Miyagawa, 2001).

**Table 4: 96-hour time weighted average concentrations for winter 2000 sampling period ($\mu\text{g}/\text{m}^3$)
(adapted from Miyagawa, 2001)**

VOC	Location	90th			Geometric Mean	Geometric s.d.
		Median	Percentile	Maximum		
Benzene	Indoor	5.3	9.8	13	5.1	1.6
	Outdoor	2.3	3.8	4.6	2.3	1.4
Toluene	Indoor	18	30	80	16	1.9
	Outdoor	3.6*	10	18	N/A	N/A
Ethylbenzene	Indoor	2.8	7.1	17	3.1	2.1
	Outdoor	1.3	2.7	4.1	0.9	2.8
<i>m,p</i> -xylenes	Indoor	8.7	26	71	10	2.1
	Outdoor	3.9	8	15	3.9	1.8
<i>o</i> -xylene	Indoor	3.3	9.1	24	3.5	2.7
	Outdoor	1.6	3.4	5.6	1	3.5

N/A denotes data not available

Table 4 results show that the concentrations are found to be higher indoors than outdoors, again indicating that indoor sources contribute to the levels found there. The highest concentration found was for toluene in the indoor sampling location with a maximum value of $80 \mu\text{g}/\text{m}^3$ (Miyagawa, 2001).

3. Methods and Materials

All sampling, sample selection procedures as well as sampling design were carried out in cooperation with Laurie Cheperdak, graduate student at the University of Alberta in Edmonton, AB (Cheperdak, 2007). Analysis of the results was carried out and discussed separately.

3.1. Sample Selection Procedures

3.1.1. Sampling Design

Probability Sampling

In order to be able to make inferences about the target population every individual element of the population must have a chance of being selected for participation in the sampling selection (Whitmore, 1988). The population can be broken down into different subgroups in order to get a statistical representation of each sub-population within the total population. This technique of probability sampling is called stratified sampling and can be used when there is variability between groups in the population and an accurate representation of each subgroup (or strata) is required (Whitmore, 1988). A stratified probability sampling strategy was applied for this study in order to minimize the amount of bias introduced into the study.

For this study, the target population was divided into two strata, namely, single family detached homes and mobile homes (trailers). The reason this stratification was chosen was because it was thought that these different types of homes have different

characteristics. Detached houses and mobile homes were hypothesized to have different ventilation properties as well as different building materials. This would lead to different concentrations of VOCs within the homes.

3.1.2. Sample Selection

The target population for the sampling frame was all the single family homes located in the community of Fort McKay, AB. Unoccupied dwellings were excluded from the target population since the focus of the study was on the quality of indoor and outdoor air. A requirement of the participant was that they had to be over the age of 18. In order to apply the sampling selection strategy, a map of Fort McKay was obtained from the Fort McKay Industrial Relations Corporation. Since this map did not list whether a home was a detached house or a mobile home, the community was surveyed prior to the study in order to determine the number of houses and the number of mobile homes in the community as well as the number of unoccupied homes.

Sample Size

According to the Central Limit Theorem, as the sample size increases the distribution of the sample means will approach a normal distribution. It is also generally accepted that a sample size of 30 is sufficient to approximate a normal distribution (Stuart, 1984). Therefore, if the distribution of the sample means follows a normal distribution, any inferences made from the sample population can be assumed to be true for the entire population. For this study, a sample size of 35 was chosen. These extra samples allowed for a small margin of error in the event that some participants wished to

drop out of the study or the passive monitors were damaged and were not able to be analyzed.

The sizes of the two strata were proportional to the percentage of each type of home in the community. After the community was surveyed, a fraction of each type of dwelling was calculated, and from the sample size of 35, the required number of samples from each type of home was calculated. The survey of the community showed that there were 156 homes in Fort McKay with 137 of them being single detached homes and 19 being mobile homes. From this data, the percentage of the number of single detached homes in Fort McKay was found to be 87.8%, and the percentage of mobile homes in the community was 12.2%. Therefore, for the required sample size of 35, the required number of houses for sampling was 31 and the required number of mobile homes for sampling was four. The strata sizes and representative fractions of the population of homes are shown in Table 5.

Table 5: Sampling strata and corresponding fractions in Fort McKay, AB

<i>Stratum</i>	<i>Population</i>	<i>Sample Size</i>	<i>Sampling Fraction</i>
Houses	137	31	0.878
Mobile Homes	19	4	0.122
Total	156	35	1.0

Random Selection Procedures

After surveying the community, an identifier was assigned to each home which identified whether the home was a detached house or a mobile home. Each home on this list was then given number and a random list of these assigned numbers was generated in

Microsoft Excel[®] (Microsoft, 2003). If the house was randomly selected more than once, the repeat selections were deleted and another house was randomly selected in its place. This generated a random list of the houses and mobile homes in the community. Even though the houses and mobile homes were both included in the list, they were treated separately for the purpose of sampling in order to obtain the correct numbers of detached houses and mobile homes as calculated by the fractions of each strata.

3.2. Participant Recruitment Procedures

The first step in the recruitment process was the delivery of an information pamphlet on the field study. The informational letter informed the households why the study was being performed as well as what would be involved in the participation of the study.

After the delivery of the pamphlets, a door-to-door campaign was conducted to recruit participants for the study. This involved approaching homes selected at the top of the randomly selected list of households. The field staff would further explain the study to the residents and answer any questions the residents might have. If the residents of the home were interested in participating, a tentative time was scheduled for setting up the monitoring equipment.

If no one was home at the selected home, the field staff returned in order to obtain a positive or negative response up to a maximum of three visits. If, after three visits, the field staff were unable to obtain a positive or a negative answer, the house was counted as a negative answer. Once an answer was determined from a selected household, the field staff moved to the next randomly selected home on the list. This process was repeated

throughout the study until the number of willing participants was equal to the sample sizes for houses and for mobile homes.

3.2.1. Recruitment Response Rates

According to the sampling fractions, the required number of houses to be sampled was 31 and the required number of mobile homes was 4. The response rates for the community are shown below in Table 6.

Table 6: Response rates for sampling

	<i>Houses</i>	<i>Mobile Homes</i>	<i>Overall</i>
Total households in community	137	19	156
Total households approached	76	19	95
Percentage of households approached	55.5%	100%	60.9%
Number of households sampled	31	4	35
Response rate	40.8%	21.1%	36.8%

3.3. Sample Collection Procedures

3.3.1. Equipment

OVM 3500

The collection of the volatile organic compound measurements was obtained using the 3M™ OVM-3500 passive monitors. The primary usefulness of passive monitors are for industrial hygienic purposes, however it is possible to use them for the monitoring of ambient air (Coutant and Scott, 1982). They have been used by other researchers in order to obtain concentrations of VOCs in the air (Davis and Otson, 1996; Otson, 1996).

The small size and ease-of-use make the OVM 3500 desirable to use for monitoring VOCs in air. It can easily be clipped to a shirt to monitor personal exposures or placed in a home on a small stand. Figure 10 shows a picture of the OVM 3500.

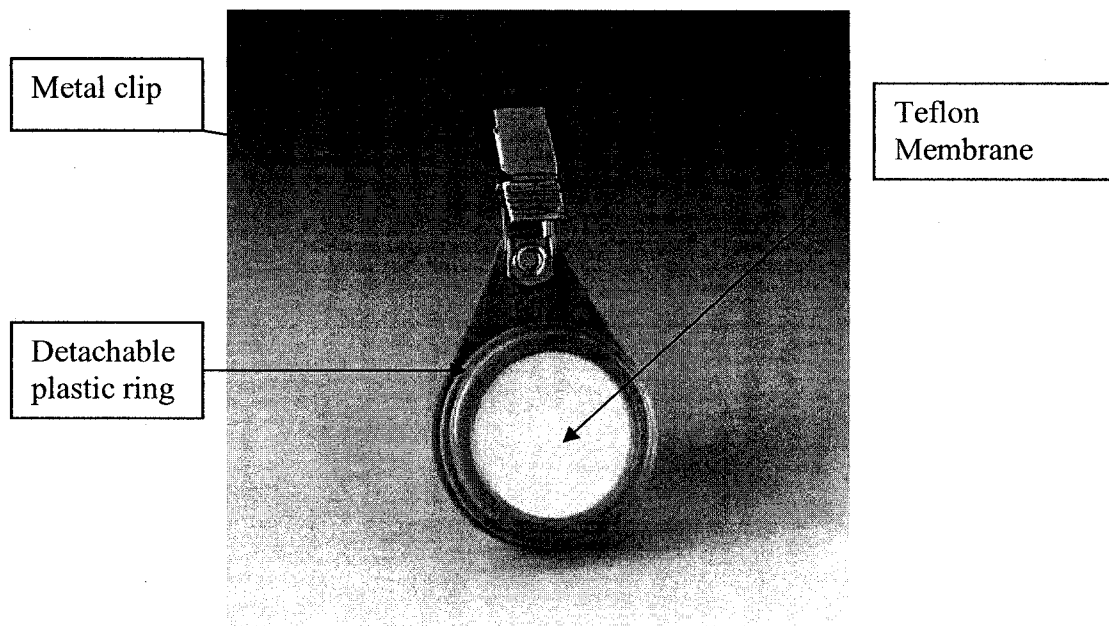


Figure 10: 3M OVM 3500 passive VOC monitor (3M™, 2006)

The OVM 3500 has a charcoal badge beneath the orange casing and is protected by a thin Teflon membrane held on by a detachable plastic ring. Beneath the membrane there is a plastic spacing device to separate the membrane from the charcoal surface. The attached clip is suitable for attaching the badge to a shirt or to a lanyard string that can be hung either around a person's neck or on a small stand for either indoor or outdoor monitoring. The device is contained in a small sealed aluminum can and is provided with a closure cap with two ports for analyzing the sorbent charcoal.

Sampling Stands

The passive monitors were attached to sampling stands when collecting measurements on the interiors and exteriors of homes. The indoor stands were constructed of 1.9 cm (0.75 in.) diameter PVC piping. They had a small base into which screwed a T-shape that stood upright reaching a sampling height of 1.2 metres. The top of the stand had a lanyard string across, to which the monitors could be attached. The

outdoor stands were very similar with the difference being that they had a larger base that was secured to the ground in order to prevent the wind from blowing it over and an attached plastic rain shield to prevent the passive monitors from getting wet.

The personal measurements were obtained by attaching the passive badges to a break-away lanyard necklace which the participant could wear around their neck. This ensured that the person's breathing zone was being monitored.

3.3.2. Sampling Locations

The sampling locations were chosen based on guidelines determined from past studies performed by Alberta Health & Wellness (AH&W). Prior to the beginning of the study, an employee of Alberta Health & Wellness gave a training session on the use of the equipment as well as on the placement of the monitors. A field manual was also provided with required specifications on the placement of the monitors. There were occasional instances where the guidelines could not be completely met due to spatial restrictions and/or the presence of small children and pets. A floor plan of the home was also taken to later reference where the monitors were located and any potential sources (stoves, fireplaces, windows, doors) were also marked. The placement of the monitors on the sampling stands guaranteed a constant sampling height of 1.2 metres.

The following list shows the guidelines used for the placement of the indoor sampling stands.

Guidelines for choosing the Sampling Location of Indoor Monitors

1. Place the indoor samplers in the primary living area of the home.
2. Place the indoor samplers at least 2 metres away from exterior doors, windows and ventilation registers.

3. Avoid placing the monitors adjacent to exterior walls and corners.
4. Avoid placing the monitors in areas that receive direct sunlight.
5. Avoid placing the indoor samplers where there are noticeable drafts (near open windows, etc.).
6. Avoid placing the monitors in well-trafficked locations.
7. Avoid placing the indoor samplers in areas that receive a direct impact from indoor sources (ie. Gas stoves, furnaces, etc.).

When small children or pets were present, the potential for the damaging of the monitors was assessed. If there was a significant threat to the monitors, they were placed on a lanyard string and hung at a height of 2 metres in a location the children or pets could not reach them.

The outdoor monitors were placed using the guidelines in the following list.

Guidelines for choosing the Sampling Location of Outdoor Monitors

1. Place the outdoor samplers at least one metre away from any trees or bushes.
2. Place the outdoor monitors at least five metres away from any type of air exhaust (clothes dryer vents, air conditioning, heating, etc.).

If there was a deck or patio present, the monitors were generally placed in that location if the above criteria were met. This was done to prevent the vandalism of the monitors and to reduce the risk of the monitors being stolen.

3.3.3. Sampling Protocols

Sampling protocols were provided by Alberta Health & Wellness based on guidelines from 3M™ and past monitoring studies. These protocols were also covered in the training session. Table 7 shows the sample deployment procedures. Table 8 highlights the preparation of the VOC air monitor blanks. Table 9 shows the protocols used in the retrieval of the VOC air monitors.

Only one blank was performed for each participant, rather than for each location of monitoring carried out for each participant.

Table 7: Guidelines for Sample Deployment of VOC monitors

-
- 1) Choose sampling location based on guidelines for choosing the Sampling Location.
 - 2) Remove plastic lid from the aluminum can and ensure the label on the outside of the can matches the labels inside the lid.
 - 3) Carefully pull the tab to open the aluminum lid and remove the air monitor from the can.
 - 4) Affix one of the labels to the back of the VOC sampler and one to the appropriate space on the data log sheet. Place the remaining two labels back into the container. Leave the plastic closure cap and the plastic tube in the container.
 - 5) Record the participant number, site description, date and time of sample initiation, and any other relevant comments on the data log sheet.
 - 6) Inspect the monitor to ensure that it is not damaged. Check that the clip is operable and the Teflon membrane is intact.
 - 7) Attach the air monitor to the appropriate stand.
-

Table 8: Guidelines for the Preparation of the VOC blank

-
- 1) Follow the steps for the Sample Deployment of VOC monitors except for steps 1 and 7. The blank is not to be exposed for any relevant length of time. It is also not necessary to record the time on the data log sheet. It is important to handle the blank in the same way as the exposed monitors.
 - 2) Continue to the retrieval of VOC air monitor procedures (as listed in Table 9). Be sure to parafilm the monitor as soon as it is returned to the container.
-

Table 9: Guidelines for the retrieval of VOC air monitors

-
- 1) At the end of the sampling period, remove the plastic ring and the Teflon membrane from the face of the sampler.
 - 2) Snap the plastic closure cap from the container onto the face of the sampler gently, starting at one end of the cap and working around the cap.
 - 3) Ensure that the two port plugs on the closure cap are firmly seated.
 - 4) Turn the metal clip to the side and return the monitor to the appropriate container as marked with the label matching the label on the back of the monitor. Place the plastic lid on the container and seal the lid with parafilm tape.
 - 5) Record the time and date of sample termination on the data log sheet. Record any comments such as damage, discolouration, movement of the sampling stand, or relevant participant comments.
 - 6) Collect the exposed monitors at the field office and ship them to the Centre for Toxicology in Calgary at the appointed time.
-

3.4. Field Sampling Procedures

During the field sampling time frame the sampling field staff completed the recruiting, the deployment and the retrieval of the monitors. The deployment times were arranged during the recruiting and then confirmed on the phone the day before. If the participant needed to reschedule the appointment, that was done.

3.4.1. Sample deployment visit

On arrival at the participants' homes, an explanation of what would be occurring during the visit was made to the participants. The administration of the registration and consent forms was completed by one of the field workers while the other field worker completed the sketch of the floor plan. When the registration forms were complete and

the study was fully explained, a suitable sampling location was chosen, with help from the participant, and noted on the floor plan. The indoor sampling stand was assembled and placed in the chosen location. The VOC monitors were deployed as to the guidelines presented in the previous section. The blank monitors and the replicates were deployed at this time as well. The passive badges were also deployed according to the guidelines of sample deployment and attached to a lanyard necklace the participant could wear around their neck. The field staff then assembled the outdoor sampling stand and deployed the samples as well as any replicates. The location of the outdoor sampling location was chosen based on the guidelines mentioned in the previous section and noted on the floor plan of the house. The sample retrieval appointment was then scheduled with the participant.

3.4.2. Sample Retrieval Visit

After the sampling time of seven days, the monitors were then retrieved. The participant was reminded of their appointment with a phone call the day before to ensure that they would be home. There were two cases when the samples could not be retrieved on the seventh day of sampling and had to be made on day six of the sampling.

On arrival at the participants' homes, the field staff collected the VOC monitors from the indoor location and the personal necklace as per the guidelines listed in the previous section. The sampling stand was disassembled and the equipment was removed from the home. The seven day samples collected outside were also retrieved and the stand was disassembled. The samples were then taken to the field office where they awaited shipping to the lab. The equipment was taken back to the field office for storage.

3.4.3. Co-location Monitoring

Samples were also deployed at the Fort McKay Air Quality Monitoring Station. The purpose of this was to determine the accuracy of the measurements being recorded by the OVM 3500 passive monitors by comparing the results with the readings obtained by the equipment at the monitoring station. A blank was also carried out during the deployment at this location.

It was discovered after the sampling timeframe that the sampling for VOCs at the monitoring station was not constant but worked on a rotation that was not consistent to the sampling performed with the passive monitors. Therefore this data was not used to estimate the accuracy of the monitors.

3.5. *Sample Analysis*

Although there were twelve VOCs chosen for analysis by Alberta Health & Wellness, the target compounds analyzed for the purpose of this report was benzene, toluene, ethylbenzene, *o*-xylene and *m,p*-xylenes. The characteristics and the health effects of these compounds are described in the literature review.

3.5.1. Laboratory Analysis Procedures

After the samples had been exposed, they were stored at the field office and shipped to the Centre for Toxicology at the University of Calgary for analysis. The following procedures were provided by Lorinda Butlin, Lab Manager at the Centre for Toxicology (Butlin, 2007).

Analytical Procedure

The VOCs were desorbed from the charcoal sorption pad in the monitor by the process of solvent extraction. This process involves inserting 1.5 mL of carbon disulphide solvent through the sampling port onto the charcoal sorption pad. The sample was then left to sit for 30 minutes. After this time, the carbon disulphide solution was then transferred into a glass vial and capped securely.

The carbon disulphide solvent was then injected onto a gas chromatograph (GC) for compound separation and was detected by a mass spectrometer (MS). The system used is a Hewlett-Packard GC-6890/MS-5973. The separation was performed on an HP 19091V-402 capillary column, 25m x 200 μ m x 1.12 μ m at an oven temperature range of 40°C – 140°C. The amount of solvent injected is 1 μ L and the total run time of the instrument is 17.5 minutes.

The lab detected the following 14 compounds:

- ⇒ Hexane
- ⇒ 3-Methylhexane
- ⇒ Benzene
- ⇒ Heptane
- ⇒ Toluene
- ⇒ Octane
- ⇒ Ethylbenzene
- ⇒ *m,p*-Xylenes
- ⇒ Nonane
- ⇒ *o*-Xylene
- ⇒ *n*-Propylbenzene
- ⇒ Decane
- ⇒ Limonene
- ⇒ *n*-Butylbenzene

Calculations

The results from the GC/MS analysis consist of a VOC concentration in $\mu\text{g}/\text{mL}$. The concentration values are then multiplied by the extraction volume of 1.5 mL and a conversion factor of 1000 to give concentrations in the units of ng/badge.

The following formula was then used to convert the concentration in ng/badge to $\mu\text{g}/\text{m}^3$.

$$\text{Analyte}(\mu\text{g} / \text{m}^3) = \frac{\text{Mass}(\text{ng}) \times \frac{1\mu\text{g}}{1000\text{ng}}}{\text{Time}(\text{min}) \times \text{Rate}(\text{mL} / \text{min})} \times (1 \times 10^6 \frac{\text{mL}}{\text{m}^3})$$

(Equation 11)

Where:

- Analyte is the atmospheric concentration of the analyte in $\mu\text{g}/\text{m}^3$
- Mass is the mass of analyte on the badge in ng
- Time is the amount of time the monitor was exposed for in minutes
- Rate is the sampling rate for the analyte in mL/min

The sampling rates were provided by the manufacturer of the VOC badges, 3M™ (3M™, 2007). These sampling rates are empirical constants derived by the manufacturer of the passive monitors. These are presented for each compound that the laboratory analyzed, in Table 10.

Table 10: Sampling Rates for VOCs (adapted from 3M) (3M™, 2007)

<i>Compound</i>	<i>Sampling Rate (mL/min)</i>
Hexane	32.0
Methylhexane	28.9
Benzene	35.5
Heptane	28.9
Toluene	31.4
Octane	26.6
Ethylbenzene	27.3
m, p-Xylenes	27.3
o-Xylene	27.3
Nonane	24.6
Decane	23.1
Limonene	21.9
N-Propylbenzene	24.6
N-Butylbenzene	22.4

4. Results and Discussion

4.1. *Overview of Sample Collection*

This section presents the results of the sampling survey. The raw data are located in Appendix 2. The sampling period occurred between September 7, 2006 and November 1, 2006. During this sampling period, samplers were deployed in 35 homes in Fort McKay. This allowed some room for error in case some participants decided to drop out of the study or damage occurred to some of the sampling badges. This way the Central Limit Theorem could be met with a sample size of at least 30. Sampling was performed in personal, indoor, and outdoor air locations, as well as at the Fort McKay Air Quality Station. In total 179 3MTM OVM-3500 passive monitoring badges were deployed, including field blanks and replicates. Sampling was carried out in cooperation with Laurie Cheperdak (2007).

Once the passive monitors were exposed, they were stored at the field office and shipped once per week to the Centre for Toxicology at the University of Calgary for analysis. A number of monitors were deployed in the field for quality assurance and quality control purposes. The field blank monitors deployed were to assess the method detection limit, and the replicate measurements were performed in order to assess the precision of the method.

4.2. Field Blank Analysis

In total throughout the study, there were 47 field blank monitors deployed and collected. All of the blanks were analyzed at the Centre for Toxicology in Calgary, Alberta.

The purpose of the field blanks was to quantify the amount of background contamination that is present in the sampling badges. Background contamination can come from manufacturing of the badges as well as exposure during storage, handling and shipping of the monitors. The level of background contamination can be determined by analyzing the amount of each compound present on the blank monitors. For this analysis, the lab detected no amounts of background contamination of the compounds greater than the limit of quantitation. The limit of quantitation is the limit at which the instrument can detect the presence of the specific compound under analysis. Therefore the method detection limit for the study is reported as the same as the limit of quantitation. The method detection limits for the compounds of interest are reported in Table 11.

Table 11: Method detection limits for compounds of interest (Butlin, 2007)

<i>Compound</i>	<i>Method Detection Limit</i>	
	<i>Analyte per badge (ng/badge)</i>	<i>7-day TWA ($\mu\text{g}/\text{m}^3$)</i>
Benzene	150	0.42
Toluene	150	0.47
Ethylbenzene	150	0.55
o-Xylene	150	0.55
m,p-Xylenes	300	1.09

4.3. Precision

The precision of a passive monitor as used in the context of this study can be defined as the ability of a set of monitors to absorb the same amount of analyte when exposed to the same ambient concentration. Duplicate measurements were used in order to assess the precision of the passive monitors. Five sets of VOC duplicate measurements were taken for personal VOC concentrations, five sets were taken for indoor concentrations, and five sets for outdoor VOC levels. The identities of the duplicate measurements were “disguised” from the laboratory in order to prevent bias from occurring during the analysis.

4.3.1. Intraclass Correlation Coefficients

An effective method of representing the precision of passive monitors is to calculate an intraclass correlation coefficient (Lee et al., 1995). The purpose of the intraclass correlation coefficient is to provide a measure of the variability between members within the same class, in this case the same location (Lee et al., 1995). For this study, the number of sampling locations was fifteen, with five being personal, five being indoor locations, and five being outdoor locations. Only pairs of monitors with both measurements above the detection limit were included in the calculation.

The intraclass correlation coefficient is usually a positive value, between 0 and 1, with a 1 meaning an ideal precision has been met and the two duplicate measurements are identical to each other. Table 12 below shows the calculated estimators of intraclass correlation coefficients for the compounds of interest. The calculations were performed in Microsoft Excel[®] and were based on equations taken from Lee et al. (1995) which are listed in Appendix 4.

As can be seen from Table 12, all the intraclass correlation coefficients calculated are very close to 1. This shows excellent sampling precision of the passive monitors.

Table 12: Intraclass correlation coefficients

<i>Compound</i>	<i>Number of duplicate pairs >MDL</i>	<i>Intraclass Correlation Coefficient</i>
Benzene	10	0.9984
Toluene	15	0.9961
Ethylbenzene	10	0.9987
<i>o</i> -Xylene	8	0.9965
<i>m,p</i> -Xylenes	15	0.9981

4.3.2. Coefficient of Variation

The coefficient of variation, also known as the relative standard deviation, is another common measure of precision. The coefficient of variation (CV) is defined as the ratio of the standard deviation to the mean of a group of measurements. The values for the CV vary between 0 and 1 with a greater degree of precision as the CV approaches 0. The coefficients of variation were calculated only for the duplicate pairs for which both monitors had concentrations above the mean detection limit. Table 13 shows the median values of the calculated coefficients of variation.

Table 13: Median Coefficients of Variation

<i>Compound</i>	<i>n</i>	<i>Median Coefficient of Variation</i>
Benzene	20	0.030
Toluene	30	0.165
Ethylbenzene	20	0.042
<i>o</i> -Xylene	16	0.039
<i>m,p</i> -Xylenes	30	0.039

From the data presented in Table 13, it can be seen that the passive monitors have relatively low coefficients of variation. Aside from the coefficient of variation for toluene, the other coefficients were all below 0.1. This shows that the VOC passive monitors are relatively precise. Although the CV value for toluene is comparatively high with respect to the other chemicals, the precision of the passive monitors for measuring toluene is still acceptable. The relatively higher CV for toluene can be attributed to a larger difference between paired measurements recorded for toluene.

4.4. Accuracy

The Fort McKay air quality station routinely tests for VOCs in the air. These compounds are not continuously monitored and therefore testing for accuracy on the passive monitors was not possible. This test would have been performed by setting up passive VOC monitors near the air quality station and comparing those values with the measured values from the air quality station in Fort McKay. When the VOCs are

measured at the air quality station, they are only measured for a 24-hour period. The logistics were found to be too great to coordinate the testing for accuracy and therefore this was not performed.

A study performed to evaluate the applicability of using passive monitors to monitor organic compounds in air, reports a comparison between an active sampling device and the OVM 3500 (Partyka et al., 2007). The researchers report that when measuring microbial VOCs, the OVM 3500 was $\pm 30\%$ of the values of the active sampling device (Partyka et al., 2007).

4.5. Climate and Weather Conditions

Past monitoring studies have shown that climatic conditions can have an effect on the concentrations measured using a passive monitoring device such as the OVM-3500 (Fellin and Otson, 1994; Chung et al., 1999). When measuring indoor concentrations in Canadian homes, Fellin and Otson (1994) investigated the effects of outdoor relative humidity and temperature on VOC concentrations inside the home. They found that there was a low correlation between the outdoor conditions and the concentration readings found in the home (Fellin and Otson, 1994). A more significant factor was the presence of sources of VOC compounds inside the home (Fellin and Otson, 1994). Chung et al. (Chung et al., 1999) found that passive monitoring devices work relatively well under a large range of temperatures and relative humidity values. It was discovered that the influence of temperature and relative humidity on measured concentrations were compound specific and generally only had an effect under extreme conditions (Chung et

al., 1999). For the present study, only the outdoor VOC concentrations from the passive devices would be affected by a larger variation of climatic conditions.

The wind speed and direction would have an effect on the concentrations on the VOC monitors. Due to the oil sand extraction and refining processes occurring near Fort McKay, the wind could carry the pollution from these activities to the community depending on where the wind is coming from and at what speed.

Fort McKay has a meteorological station and all the data was downloaded from the Clean Air Strategic Alliance's on-line data warehouse. There was a large range of meteorological conditions throughout the sampling period and these are shown in the following tables and graphs. Table 14 displays the mean, minima and maxima of the temperature, relative humidity and wind speed over the sampling period which ranged from September 7 – November 1, 2006.

Table 14: Means, minima and maxima of temperature, relative humidity and wind speed during the sampling period (September 7 - November 1, 2006) (CASA, 2007)

<i>Meteorological Condition</i>	<i>Mean</i>	<i>Minimum</i>	<i>Maximum</i>
Temperature (°C)	5.1	-8.7	25.7
Relative Humidity (%)	70	23	95
Wind Speed (m/s)	3.0	0.1	8.5

Figure 11 shows the trends of the daily mean, minimum and maximum temperatures throughout the sampling period. As can be seen from the graph and the data in Table 14, there was a great variation in the temperature occurring over a 34.4 °C range. The relative humidity also varied greatly, ranging from 23% to 95%.

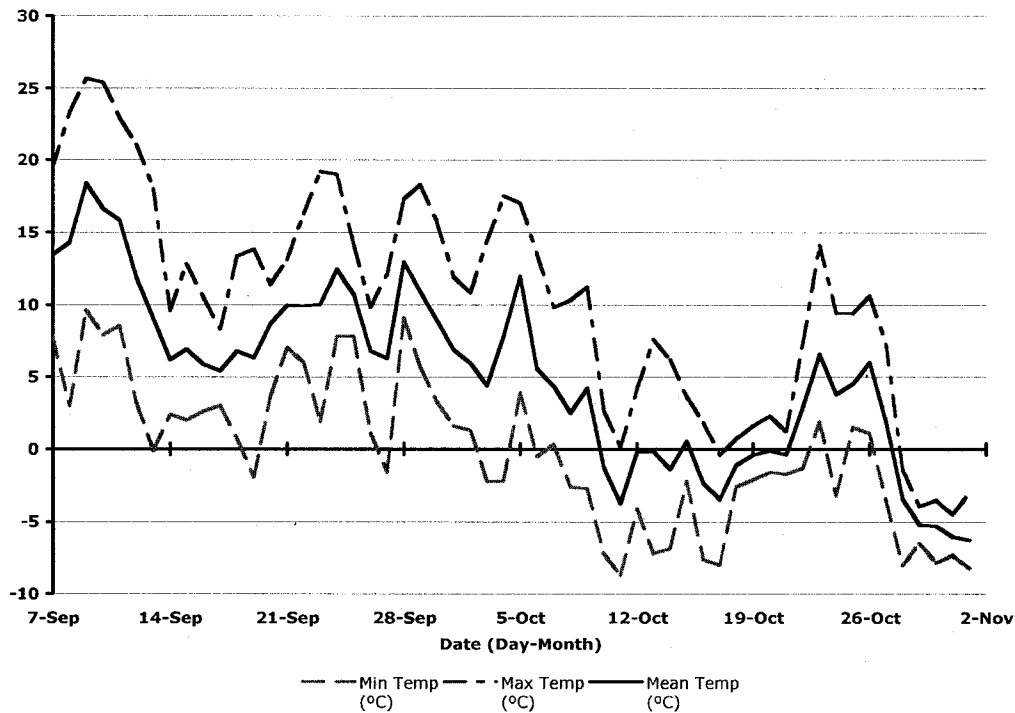


Figure 11: Daily mean, minimum and maximum temperatures (CASA, 2007)

The wind speed class frequency distribution is shown in Figure 12. It shows that the wind speed was mostly flowing in the 2.1 – 4.2 m/s range. The minimum wind speed was 0.1 m/s while the maximum was 8.5 m/s. Figure 13 contains a wind rose plot showing the direction the winds generally blow from for the meteorological station in Fort McKay. From this plot it can be seen that the wind commonly flows from the north and northwest directions although it is not uncommon for the wind to blow from the south. The mean directional vector is from the west-northwest direction.

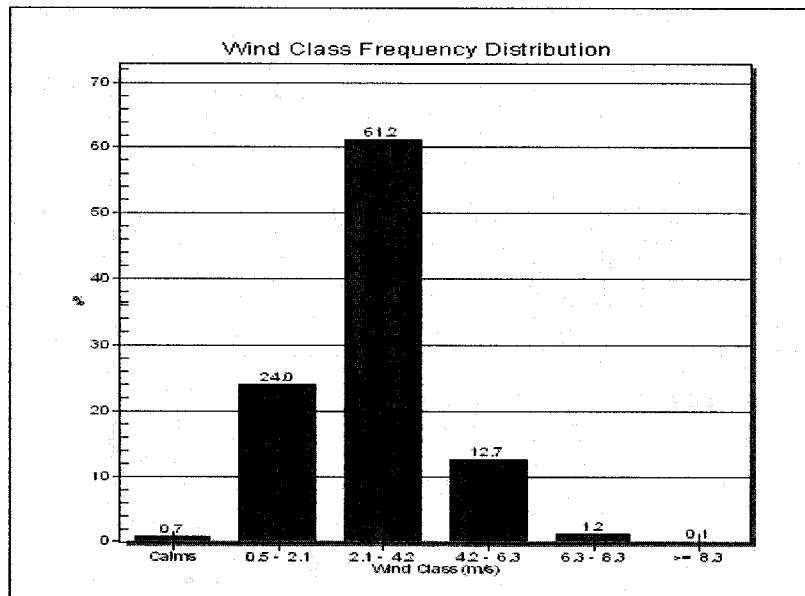


Figure 12: Wind Speed Frequency Distribution Plot (CASA, 2007)

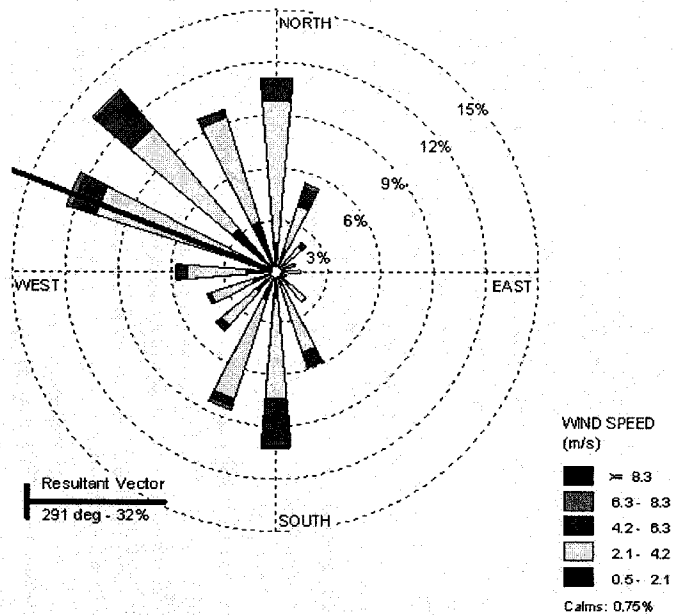


Figure 13: Wind Rose Plot of Fort McKay, AB from September 7 - November 1, 2006 (CASA, 2007)

4.6. *Detectable Measurements*

Non-detect measurements are defined as measurements that are below the method detection limit. In environmental monitoring, non-detect measurements are common and cause problems when performing statistical tests (Zhang et al., 2004). If a reasonable percentage of the measured values are below the method detection limit (MDL), it can be a challenge to analyze datasets using statistical tests (Gleit, 1985). The usual method of dealing with data below the detection limit is to censor it and report it as non-detect or below method detection limit.

The United States Environmental Protection Agency (EPA) (2000) has produced guidelines for dealing with non-detect data. For data with less than 15% non-detects, they suggest replacing the non-detects with the detection limit divided by 2 and performing nonparametric tests on the data (EPA, 2000). For datasets containing between 15% and 50% non-detects, more complex methods are suggested such as: Cohen's method for adjusting the estimated sample mean and standard deviation, the trimmed means method, winsorizing or Atchinson's Method (EPA, 2000). For data with 50% to 90% non-detects, the EPA (2000) recommends using the Test of Proportions and for data that has greater than 90% non-detects, it is recommended that no further statistical tests are performed.

There are, however, other methods of dealing with values found below the detection limit. The above method of substituting non-detect values with 0.5 of the detection limit was evaluated by Helsel (2006). It was found that this method is not an accurate way of representing the non-detect values (Helsel, 2006). Since non-detect values are a typical result in environmental data, Helsel (2006) presents another method called the maximum likelihood estimation method for dealing with non-detect data.

However, it is stated that this recommended method does not work well on small datasets, with fewer than 30 – 50 detected values (Helsel, 2006).

Table 15 shows the percent of measurements detected for the compounds under analysis. A high percentage of measurements were found for all the compounds for the personal measurements and within the indoors environment. Outdoors, there was a high occurrence of readings for toluene and *m,p*-xylenes, but a low detection for benzene, ethylbenzene, and *o*-xylene.

Table 15: Percentage of measurements above the method detection limit

<i>Compound</i>	<i>Sampling Location</i>		
	<i>Personal</i>	<i>Indoors</i>	<i>Outdoors</i>
Benzene	97.5%	92.3%	10.3%
Toluene	100%	100%	76.9%
Ethylbenzene	100%	100%	17.9%
<i>m,p</i> -Xylene	100%	100%	94.9%
<i>o</i> -Xylenes	95%	87.2%	10.3%

For this analysis, it was decided to only perform detailed statistical analyses and hypothesis testing on datasets containing greater than 50% of its measurements above the detection limit.

4.7. Normality

For each compound and sampling location, the dataset was tested for normality using histograms and normal probability plots. Histograms are presented in Appendix 6. Histograms showed that distributions of the data were positively skewed. This indicates that there is a possibility the data follows a lognormal distribution. Lognormal distributions have been commonly used to describe air quality data in past studies (Gokhale and Khare, 2007). A logarithmic transformation was performed on the concentrations and plotted against the z-scores in normal distribution plots. The normal probability plots can visually show whether the data follows a normal distribution. The normal probability plots of the log-transformed data are shown in Appendix 6. These plots showed that the data, when transformed, have the possibility of following a normal distribution. Tests for normality were also carried out and are presented in Section 4.7.2.

4.7.1. Outliers

The log transformed data, when plotted on the histograms and normal probability plots, show possible outliers in the dataset. A useful way to determine outliers is to plot the data in box and whisker plots. Box and whisker plots are based on the median and interquartile range (iqr) and can show the spread of the data and any possible outliers. Based on the box and whisker plot definitions, an outlier is a value that is more than $1.5iqr$ away from the nearest end of the box and an extreme outlier is a value that is more than $3.0iqr$ away from the nearest end of the box (Devore and Peck, 2005). The box on a box and whisker plot represents the interquartile range, or where 25 to 75 % of the measurements fall (Devore and Peck, 2005). The whiskers represent the range of measurements that are not outliers while the vertical line through the box represents the

median (Devore and Peck, 2005). Based on the box and whisker plots shown in Appendix 3, the outliers can be seen and were disregarded in the data analysis hereby following. A limitation of removing outliers from small datasets is that the small dataset may not adequately represent the expected variability within an actual sample population with outliers removed, particularly for indoor or personal air concentrations. High indoor or personal air concentrations may be a result of rare but actual activities or sources associated with a specific subject or household. Notwithstanding this limitation, a decision was made to identify and remove outliers from the datasets obtained.

4.7.2. Test for Normality

The data were tested to determine if a lognormal distribution is present. There are several tests available to test for normality. A common method is to use the Shapiro-Wilk test for normality (Shapiro and Wilk, 1965). The D'Agostino-Pearson test for normality is another test that can be used to evaluate the normality of the data (D'Agostino et al., 1990). The Shapiro-Wilk test for normality can be negatively influenced by concentration measurements of the same magnitude (D'Agostino, 1986). Since this is the case with the dataset for this analysis, the D'Agostino-Pearson test for normality is a better choice for analyzing the data in this case (D'Agostino, 1986). An explanation of the D'Agostino-Pearson test is included in Appendix 10 and the results of the test are shown in Appendix 11. The D'Agostino-Pearson test for normality was performed on data with greater than 50% of the measurements above the method detection limit. The results of the test showed that on the log transformed data, normal distributions are likely for all BTEX compounds for the personal measurements and the indoor environment, as well as for the outdoor *m,p*-xylenes distribution, when tested using a significance level of 0.05.

4.8. *Summary Statistics*

To calculate the summary statistics shown, the EPA's method of replacing the non-detect values with half the method detection limit was used (EPA, 2000). For locations where there were replicate measurements performed, the mean of the two measurements were taken and that value was used as the concentration for that location.

The data were summarized using the median, maximum, geometric mean, geometric standard deviation, and 90th percentile. The data were positively skewed and therefore the arithmetic mean would be heavily influenced by concentrations near zero. Therefore the median would be a better measure of the central tendency of the data. The geometric mean and the geometric standard deviation were only calculated for compounds and locations where greater than half the measurements were above the method detection limit. Statistics that are below the MDL are marked with an asterisk (*). Table 16 shows the 7-day time weighted average (TWA) summary statistics for the personal measurements. The statistics (7-day TWA) for the indoor location are summarized in Table 17. Table 18 displays the summary statistics (7-day TWA) for the outdoor monitoring locations.

Table 16: 7-day time weighted average personal summary statistics

<i>Compound</i>	<i>Median ($\mu\text{g}/\text{m}^3$)</i>	<i>Maximum ($\mu\text{g}/\text{m}^3$)</i>	<i>90th Percentile ($\mu\text{g}/\text{m}^3$)</i>	<i>Geometric Mean ($\mu\text{g}/\text{m}^3$)</i>	<i>Geometric St. Dev. ($\mu\text{g}/\text{m}^3$)</i>
Benzene	1.7	27.7	5.3	1.8	12.6
Toluene	9.1	48.4	22.3	10.1	4.8
Ethylbenzene	1.6	5.5	2.4	1.6	6.6
<i>o</i> -Xylene	1.3	4.6	2.9	1.3	9.9
<i>m,p</i> -Xylenes	3.8	13.5	8.2	3.7	9.4

For the personal monitors, toluene was found to have the greatest number of high concentrations as seen through the measures of central tendency, the median and the geometric mean. The highest overall concentration of toluene was $48.4 \mu\text{g}/\text{m}^3$. *o*-Xylene had the lowest distribution of concentrations for the personal measurements. All of the VOCs under analysis were measured with a high degree of frequency in the personal measurements.

Table 17: 7-day time weighted average indoor summary statistics

<i>Compound</i>	<i>Median ($\mu\text{g}/\text{m}^3$)</i>	<i>Maximum ($\mu\text{g}/\text{m}^3$)</i>	<i>90th Percentile ($\mu\text{g}/\text{m}^3$)</i>	<i>Geometric Mean ($\mu\text{g}/\text{m}^3$)</i>	<i>Geometric St. Dev. ($\mu\text{g}/\text{m}^3$)</i>
Benzene	1.9	31.9	6.6	1.7	3.5
Toluene	10.7	58.7	23.6	10.7	2.0
Ethylbenzene	1.7	5.8	3.3	1.6	1.8
<i>o</i> -Xylene	1.2	6.2	3.2	1.2	2.2
<i>m,p</i> -Xylenes	3.3	19.7	9.5	3.8	2.0

In the indoor environment, toluene was found to have the greatest number of high concentrations with the highest measurements of central tendency and the maximum concentration. The highest geometric mean and median were for toluene with values of 10.7 and 10.7 $\mu\text{g}/\text{m}^3$, respectively. The greatest number of low concentrations was for *o*-xylene with a median of 1.2 $\mu\text{g}/\text{m}^3$ and a geometric mean of 1.2 $\mu\text{g}/\text{m}^3$. All of the five VOCs were measured with a high degree of frequency in indoor air.

Table 18: 7-day time weighted average outdoor summary statistics

<i>Compound</i>	<i>Median ($\mu\text{g}/\text{m}^3$)</i>	<i>Maximum ($\mu\text{g}/\text{m}^3$)</i>	<i>90th Percentile ($\mu\text{g}/\text{m}^3$)</i>	<i>Geometric Mean ($\mu\text{g}/\text{m}^3$)</i>	<i>Geometric St. Dev. ($\mu\text{g}/\text{m}^3$)</i>
Benzene	0.2*	0.8	0.3*	-	-
Toluene	0.5	1.5	0.9	0.5	3.7
Ethylbenzene	0.3*	0.9	0.7	-	-
<i>o</i> -Xylene	0.3*	0.8	0.5*	-	-
<i>m,p</i> -Xylenes	0.7*	2.0	1.6	0.8*	2.4

For the measurements made outside of the homes, benzene, ethylbenzene and *o*-xylene had very low values with the majority of the measurements made being below the method detection limit. Toluene and *m,p*-xylenes were detected with relatively high frequency but the distribution of concentrations were found to be low as compared to the indoor and personal concentrations.

4.9. Comparison to other Studies

The results obtained from the field sampling in Fort McKay were compared to values obtained from similar studies performed. Alberta Health & Wellness (AH&W) has performed several studies throughout Albertan communities and several communities were chosen for comparison (AH&W, 2002; AH&W, 2003; AH&W, 2006). The AH&W studies only reported summary statistics for benzene, no calculated statistics were reported for toluene, ethylbenzene, *o*-xylene and *m,p*-xylenes. The values were also compared to the results from Helsinki as part of the larger EXPOLIS study previously

discussed (Edwards et al., 2001), as well as to the background study performed in Fort McKay were also compared to current values. These studies were compared for personal, indoor, and outdoor locations for the BTEX compounds and are summarized in Tables 19, 20, and 21, respectively. The indoor and outdoor measurements were also compared to the results from a survey performed in Los Angeles, California as part of the Total Exposure Assessment Methodology (TEAM) study performed in the 1980's across the United States (Pellizzari et al., 1986). The indoor concentrations were also compared to data collected from Canadian residences across the country by Otson et al. (1994).

Table 19: Comparison of Personal Sample VOC Concentrations

	Fort McKay^a Fall 2006	Fort McKay^b Fall 1999	Fort McKay^b Winter 2000	Wabamun^c	Fort Saskatchewan^c	Grand Prairie^c	Helsinki, Finland^d
Personal Air Concentration ($\mu\text{g}/\text{m}^3$)							
N	35	29	29	193	172	132	183
Benzene	1.7	7	7.8	1.7	1.6	1.5	2.5
Toluene	8.7	21.1	23.7	n/a	n/a	n/a	16.3
Ethylbenzene	1.6	< 1.1	1.3	n/a	n/a	n/a	2.8
<i>m,p</i> -Xylenes	3.7	10.2	12.2	n/a	n/a	n/a	8.7
<i>o</i> -Xylene	1.1	< 1.1	4.9	n/a	n/a	n/a	2.9

^a median of 7-day personal air samples

^b median of 24-hour personal air samples from the baseline study (Miyagawa, 2001)

^c median of 7-day personal air samples from communities across Alberta (AH&W, 2002; AH&W, 2003; AH&W, 2006)

^d geometric mean of 48-hour personal air samples from Helsinki, Finland (Edwards et al., 2001)

n/a = data not available

Table 20: Comparison of Indoor Sample VOC Concentrations

	Fort McKay^a Fall 2006	Fort McKay^b Fall 1999	Fort McKay^b Winter 2000	Wabamum^c	Fort Saskatchewan^c	Canadian Homes^d	Helsinki, Finland^e	Los Angeles^f
	Indoor Air Concentration ($\mu\text{g}/\text{m}^3$)							
N	35	30	29	193	172	757	183	25
Benzene	1.9	4.1	5.3	1.0	0.3	5	1.6	18
Toluene	11	11	18	n/a	n/a	41	15	n/a
Ethylbenzene	1.8	1.8	2.8	n/a	n/a	8	2.2	9.7
<i>m,p</i> -Xylenes	3.7	5.2	8.7	n/a	n/a	20	6.1	26
<i>o</i> -Xylene	1.3	1.8	3.3	n/a	n/a	6	1.9	11

^a median of 7-day indoor air samples

^b median of 96-hour indoor air samples from the baseline study (Miyagawa, 2001)

^c median of 7-day indoor air samples from communities in Alberta (AH&W, 2003; AH&W, 2006)

^d mean of 24-hour indoor air samples from across Canada (Otson et al., 1994)

^e geometric mean of 48-hour indoor air samples from Helsinki, Finland (Edwards et al., 2001)

^f median of overnight indoor air samples from Los Angeles, California (Pellizzari et al., 1986)

n/a = data not available

Table 21: Comparison of Outdoor Sample VOC Concentrations

	Fort McKay^a Fall 2006	Fort McKay^b Fall 1999	Fort McKay^b Winter 2000	Wabamum^c	Fort Saskatchewan^c	Helsinki, Finland^d	Los Angeles^e
Outdoor Air Concentration ($\mu\text{g}/\text{m}^3$)							
N	35	29	29	193	172	183	25
Benzene	< 0.4	< 1.0	2.3	0.4	0.6	1.4	17
Toluene	0.6	< 3.6	< 3.6	n/a	n/a	3.7	n/a
Ethylbenzene	< 0.6	< 0.3	1.3	n/a	n/a	0.8	11
<i>m,p</i> -Xylenes	< 1.1	1.3	3.9	n/a	n/a	2.4	30
<i>o</i> -Xylene	< 0.6	< 0.3	1.6	n/a	n/a	1.1	11

^a median of 7-day outdoor air samples

^b median of 96-hour outdoor air samples from the baseline study (Miyagawa, 2001)

^c median of 7-day outdoor air samples in communities across Alberta (AH&W, 2003; AH&W, 2006)

^d geometric mean of 48-hour outdoor air samples from Helsinki, Finland (Edwards et al., 2001)

^e median of overnight outdoor air samples from Los Angeles, California (Pellizzari et al, 1986)

n/a = data not available

The AH&W studies along with the current study all had 7-day TWA concentrations from which the statistics were calculated (AH&W, 2002; AH&W, 2003; AH&W, 2006). The monitoring performed in Fort McKay in 1999 and 2000 consisted of 4-day TWA measurements (Miyagawa, 2001). The EXPOLIS study performed in Helsinki, Finland consisted of 2-day (48-hour) TWA measurements (Edwards et al., 2001). The study performed in Los Angeles consisted of overnight measurements both indoors and outdoors of participants' homes (Pellizzari et al., 1986).

For the personal benzene measurements, Table 19 shows that the median benzene concentration was lower than what was found for the baseline fall and winter studies by factors of 4.1 and 4.6, respectively, and by a factor of 1.5 for the Finnish study. Personal median levels were similar to the other Albertan communities. Comparing the measurements of central tendency of indoor benzene in Table 20, it can be seen that the concentrations were lower than the baseline study by a factor of 2.2 for the survey performed in 1999 and by a factor of 2.8 for the survey performed in 2000. The indoor concentrations were found to be slightly higher than the studies performed in Wabamun and Fort Saskatchewan and similar to concentrations found in Helsinki, Finland during the EXPOLIS study. Current indoor levels were found to be lower by a factor of 2.6 for benzene as compared to the Canadian homes survey and lower by a factor of 9.5 than those found in Los Angeles' homes. Comparing outdoor benzene concentrations in Table 21, the concentration for the current study was below the detection limit and contained a large number of non-detections and therefore is not able to be numerically compared to the values presented from other studies. The concentrations from the current study do appear to be lower than those obtained from the other surveys.

Table 19 shows that the calculated median personal toluene value for the current study is lower by factors of 2.4 and 2.7 than the median from the 1999 and 2000 Fort McKay surveys, respectively, as well as by a factor of 1.8 for the Helsinki, Finland study. Indoor toluene concentrations were similar with the baseline study's fall 1999 reported value, and lower by a factor of 1.6 for the baseline study's winter 2000 value, as seen in Table 20. The EXPOLIS study's concentrations were found to be higher by a factor of 1.4. The highest indoor levels for toluene were found for the Canadian national survey, which was found to be higher than the current study's by a factor of 3.7. Table 21 shows the comparison of outdoor toluene levels and it can be seen that low values are found for both the current and baseline studies in Fort McKay, with slightly higher measurements for the Helsinki study.

The ethylbenzene comparison for personal measurements is shown in Table 19. It can be seen that concentrations are very similar to those from the baseline study and the Helsinki survey. The central tendency measurement for indoor concentrations from Table 20 shows that the values are similar with both the past Fort McKay study and the Helsinki study. The Canadian national survey and the Los Angeles study were both considerably higher, by factors of 4.4 and 5.4, respectively. Table 21 shows that the outdoor concentration of ethylbenzene was lower than the detection limit. The study conducted in Helsinki has a low value ($0.8 \mu\text{g m}^{-3}$) while a higher median of ethylbenzene measurements was found in the Los Angeles survey ($11 \mu\text{g m}^{-3}$).

As shown in Table 19, the median concentrations of personal *m,p*-xylenes measurements are lower for the current study by a factor of 2.8 as compared to the baseline fall 1999 measurements and by a factor of 3.2 as compared to the winter 2000

values. Comparing the current study measurement of central tendency for *m,p*-xylenes to the study performed in Helsinki, Finland, the value is lower by a factor of 2.4. In Table 20, the median concentrations can also be seen to be relatively low for the current and baseline studies. As compared to the Canadian, Los Angeles and Finnish studies, the concentrations of *m,p*-xylenes from the current Fort McKay study were lower by factors of 5.4, 7 and 1.6, respectively. The median outdoor *m,p*-xylenes concentrations were lower than the detection limit for the current study. Higher concentrations were found for the baseline, the EXPOLIS and the Los Angeles studies, as is shown in Table 21. Table 19 shows that the medians for *o*-xylene is low for all the studies presented in the personal sampling location. Table 20 shows low indoor concentrations of *o*-xylene for the current, baseline and Finnish studies. Comparing indoor *o*-xylene concentrations for the Canadian homes and the Los Angeles surveys, the current Fort McKay levels are lower by factors of 3.2 and 8.5, respectively. Outdoors (Table 21), the concentrations were relatively low or below the detection limit for all the communities listed with the exception of Los Angeles, which had a concentration of $11 \mu\text{g m}^{-3}$.

4.10. Hypothesis Testing

Through statistical hypothesis testing, it is possible to formally test the hypotheses of this study. From the data collected, three hypotheses were tested:

- 1) Increased industrial activity did not significantly affect BTEX concentrations in Fort McKay between 1999/2000 and 2006.
- 2) Concentrations of indoor BTEX compounds are not significantly greater than outdoor VOC concentrations.

- 3) Concentrations of personal BTEX compounds are not significantly greater than indoor BTEX concentrations.

4.10.1. Indoor – Outdoor Relationships

There have been studies performed that document higher VOC concentrations in indoor environments as compared to outdoor environments (Pellizzari et al., 1986; Wallace et al., 1986; Edwards et al., 2001; Miyagawa, 2001; AH&W, 2002; AH&W, 2003; AH&W, 2006). A common method to show this is through the use of ratios of indoor and outdoor concentrations. If the samples are paired, for example, measurements taken from both indoor and outdoor locations, a Wilcoxon Signed Ranks test (Siegel and Castellan, 1988) can also be used. These two methods were used to compare indoor and outdoor measurements taken in Fort McKay.

Ratios of indoor and outdoor median concentrations were calculated in order to effectively compare the concentrations from the indoor and outdoor locations. These were compared to ratios from other studies performed. Since indoor and outdoor paired measurements were taken at each participants home, the Wilcoxon Signed Ranks Test was performed to test the difference of the means between the two samples. The formal hypothesis testing was only performed for the compounds that had greater than 50% of measurements above the detection limit at both locations. Therefore the hypothesis testing was only performed for toluene and *m,p*-xylenes.

Indoor/Outdoor Ratios

The ratios of Indoor/Outdoor median concentrations were calculated. For concentration readings less than the method detection limit, the U.S. EPA method of

substituting with half the detection limit was used (EPA, 2000). The resulting ratios were compared to ratios obtained from the baseline study performed in 1999/2000 (Miyagawa, 2001) as well as with several studies performed by Alberta Health and Wellness, although only the ratios for benzene were provided (AH&W, 2002; AH&W, 2003; AH&W, 2006).

If the Indoor/Outdoor ratios are greater than 1, the median concentration is found to be greater for the indoor environment. The resulting calculated ratios and comparisons are shown in Table 22. It can be seen from the table that for the current study, all the compounds show higher median indoor concentrations than found outdoors. This is consistent as compared to the baseline study results. The Alberta Health and Wellness studies also show a higher median benzene indoor concentration than found outdoors although the ratios are smaller. This could indicate that for the current study either:

- i) The median indoor benzene concentration is higher than for the other studies, or
- ii) The median outdoor benzene concentration is lower than for the other studies.

It seems more likely that the latter is more consistent with the results since for the current study there were a large number of non-detections for benzene in the outdoor environment.

Table 22: Comparison of Indoor/Outdoor Median Concentration Ratios

	Fort McKay^a Fall 2006	Fort McKay^b Fall 1999	Fort McKay^b Winter 2000	Wabamun^c	Fort Saskatchewan^c	Grand Prairie^c
Benzene	8.5	5.1	2.3	2.4	1.5	1.7
Toluene	21	22	5	n/a	n/a	n/a
Ethylbenzene	3.2	6.3	2.2	n/a	n/a	n/a
m,p-Xylenes	3.0	3.9	2.2	n/a	n/a	n/a
o-Xylenes	2.2	6.4	2.1	n/a	n/a	n/a

^a Indoor/Outdoor ratio of median of 7-day air samples

^b Indoor/Outdoor ratios of median of 96-hour air samples from the baseline study (Miyagawa, 2001)

^c Indoor/Outdoor ratios of median of 7-day air samples from communities in Alberta (AH&W, 2002; AH&W, 2003; AH&W, 2006)

n/a = data not available

Wilcoxon Signed Ranks Test

The Wilcoxon Signed Ranks test was carried out in Microsoft Excel[®] based on the procedure outlined by Siegel and Castellan (1988). The indoor and outdoor paired measurements were tested using the nonparametric analysis to test the following hypotheses:

- H_0 : there is no significant difference between indoor and outdoor BTEX concentrations.
- H_a : indoor BTEX concentrations are significantly greater than outdoor BTEX concentrations.

Results of the analysis are provided in Table 23. The table provides the value of N (number of non-zero differences between location concentrations); T+ (the test statistic); Z (calculated Z-score); and P (associated probability that T+ is greater than or equal to the calculated value when H_0 is true). The test was carried out with a significance level, ($\alpha = 0.05$) and the test is one sided since the direction of the difference is predicted.

Table 23: Wilcoxon Signed Ranks test results for Indoor-Outdoor Paired Measurements

	N	T+	Z	P
Toluene	31	482	4.60	2.1E-06
<i>m,p</i> -Xylenes	33	561	5.01	2.7E-07

The analysis was only carried out on two compounds, toluene and *m,p*-xylenes since these compounds had more than 50% of measurements above the method detection limit. These results (Table 23) show from the calculated P-value that the null hypothesis

can be rejected and it can be concluded that the indoor concentrations are greater than the outdoor concentrations for the tested volatile organic compounds ($\alpha = 0.05$).

4.10.2. Personal – Indoor Relationships

Wilcoxon Signed Ranks Test

The Wilcoxon Signed Ranks test was carried out in Microsoft Excel[®] according to the procedures outlined in Siegel and Castellan (1988). The following hypotheses were tested:

- H_0 : there is no significant difference between personal and indoor VOC concentrations.
- H_a : there is a significant difference between personal and indoor VOC concentrations.

The results are tabulated in Table 24. The table provides the values of N (number of non-zero differences between location concentrations); T+ (sum of the ranks of the positive differences); T- (sum of the ranks of the negative differences); Z (calculated Z-score); and P (associated probability that T+ is greater than or equal to, or T- is less than or equal to, the calculated value when H_0 is true). The test was carried out with a significance level $\alpha = 0.05$, and the test is one sided since the direction of the difference is predicted.

The results in Table 24 show that the null hypothesis must be accepted for all the tested compounds except for ethylbenzene. For ethylbenzene it can be seen that at $\alpha = 0.05$ the null hypothesis must be rejected. Therefore it can be stated that there is a

significant difference between personal and indoor ethylbenzene concentrations. By looking at the calculated Z statistic for ethylbenzene, it can be seen from its negative value that the measured personal concentrations are in fact lower than the indoor concentrations. For all the other compounds, it can be concluded that there is no significant difference between personal and indoor concentrations.

Table 24: Wilcoxon Signed Ranks Test results for Personal-Indoor paired measurements

	N	T+	T-	Z	P
Benzene	34	289	-306	-0.15	0.4420
Toluene	34	222.5	-372.5	-1.29	0.0993
Ethylbenzene	32	164.5	-363.5	-1.92	0.0276
<i>m,p</i> -Xylenes	32	225	-303	-0.74	0.2310
<i>o</i> -Xylene	30	238	-227	0.12	0.4541

Spearman Rank Order Correlation Coefficients

The Wilcoxon signed ranks test was used above to determine whether there was a difference between personal and indoor concentrations for the compounds under analysis in this study. As it can be seen from the results of the analysis, only personal ethylbenzene concentrations were found to be significantly lower than the paired indoor concentration. By calculating the Spearman rank order correlation coefficient (Siegel and Castellan, 1988), it can be statistically shown whether the personal and indoor concentrations for the BTEX compounds are correlated. The Spearman rank order correlation coefficient test requires that the two measurements be paired. Since the personal and indoor measurements were paired by participant, the test can be used to show if the two concentration measurements are related.

The hypotheses for the Spearman rank order correlation coefficients test in this case are:

- H_0 : Personal and Indoor BTEX measurements are not correlated
- H_a : Personal and Indoor BTEX measurements are positively correlated

The Spearman rank order correlation coefficient test was performed on the paired personal and indoor measurements. The test was carried out in Microsoft Excel[®] according to the procedures presented by Siegel and Castellan (1988) at a significance level $\alpha = 0.05$. Results of the test are shown in Table 25. The table shows N (number of matched pairs); r_s (calculated Spearman rank order correlation coefficient); Z (calculated z-score); and P (probability that r_s is greater than or equal to the calculated value when H_0 is true).

Table 25: Spearman rank order correlation coefficient analysis results for Personal-Indoor paired measurements

	N	r_s	Z	P
Benzene	35	0.9226	5.38	3.7E-08
Toluene	34	0.8298	4.77	9.4E-07
Ethylbenzene	33	0.8121	4.59	2.2E-06
m,p-Xylenes	33	0.8745	4.95	3.8E-07
o-Xylene	33	0.8728	4.94	4.0E-07

It can be seen from Table 25 that the probabilities of the Spearman rank order correlation coefficients are all considerably smaller than the significance level of 0.05. Therefore, the null hypothesis can be rejected for all the compounds under analysis. It can be concluded that the personal and indoor measurements of the analyzed VOC compounds are positively correlated and significantly related.

4.10.3. Comparison to the Baseline study

The results collected from the current study were compared to those of the study performed in 1999 and 2000 in the community of Fort McKay. In this way it is possible to infer whether concentrations of the BTEX compounds have increased or decreased since the original measurements were taken. The method used to compare the two results is the Wilcoxon-Mann-Whitney test (Siegel and Castellan, 1988).

Wilcoxon-Mann-Whitney Tests

The Wilcoxon-Mann-Whitney tests were performed in Microsoft Excel[®] according to the procedures outlined in Siegel and Castellan (1988). Data collected from personal, indoor and outdoor locations were compared between the present study and the study performed by Miyagawa (2001). Since the baseline study was carried out in both fall and winter seasons, datasets collected from each season were separately compared to data collected from fall of 2006. The hypothesis tests were carried out separately for each location, testing the following hypotheses:

- H_0 : there is no significant difference of concentrations between 1999/2000 and 2006 for the compounds under analysis.
- H_a : there is a significant difference of concentrations between 1999/2000 and 2006 for the compounds under analysis.

Results from the tests are presented in Tables 26 through 28. These tables provide values of W_x (sum of the ranks from either the fall or winter study); Z , (calculated Z-score); and P (associated probability that W_x is greater than or equal to the calculated value when H_0 is true). The tests were carried out at a significance level $\alpha = 0.05$ and the test is one sided as the direction of the difference is predicted.

Table 26: Wilcoxon-Mann-Whitney test results for personal locations

	Fall 1999 vs. Fall 2006			Winter 2000 vs. Fall 2006		
	W _x	Z	P-value	W _x	Z	P-value
Benzene	1316	5.03	2.4E-07	1175.5	4.61	2.0E-06
Toluene	1227	3.38	3.6E-04	1072.5	2.69	3.6E-03
Ethylbenzene	786	-1.20	0.114	872.5	0.06	0.4768
<i>m,p</i> -Xylenes	1155	4.92	4.3E-07	1164	5.05	2.2E-07
<i>o</i> -Xylene	660	-2.48	6.6E-03	975	2.97	1.5E-03

Table 27: Wilcoxon-Mann-Whitney test results for indoor locations

	Fall 1999 vs. Fall 2006			Winter 2000 vs. Fall 2006		
	W _x	Z	P-value	W _x	Z	P-value
Benzene	1083	2.58	4.9E-03	1174	3.84	6.1E-05
Toluene	909	0.36	0.3613	909	1.75	0.0404
Ethylbenzene	814	-0.15	0.4408	1014	3.57	1.8E-04
<i>m,p</i> -Xylenes	785	0.74	0.2302	921.5	3.64	1.4E-04
<i>o</i> -Xylene	768.5	0.48	0.3153	1002	4.15	1.7E-05

Table 28: Wilcoxon-Mann-Whitney test results for outdoor locations

	Fall 1999 vs. Fall 2006			Winter 2000 vs. Fall 2006		
	W _x	Z	P-value	W _x	Z	P-value
Toluene	906.5	1.02	0.1547	1068	5.88	2.1E-09
<i>m,p</i> -Xylene	982	3.08	1.0E-03	1200.5	6.42	6.8E-11

As it can be seen by the P-values in Table 26, the null hypothesis must be rejected for benzene, toluene, *m,p*-xylenes and *o*-xylenes indicating that the concentrations of these compounds are different for the two studies. The positive Z-scores show that the concentrations for benzene, toluene and *m,p*-xylenes are higher for the fall 1999 study and the negative Z-score for *o*-xylene is indicative of a higher concentration for the current study. The concentrations of ethylbenzene were not found to be significantly different between the two studies since the null hypothesis is accepted. As compared to the winter 2000 concentrations, the P-values in Table 26 indicate that the alternative hypothesis must be accepted for all the compounds with the exception of ethylbenzene

for which the null hypothesis must be accepted. By looking at the Z-scores, it can be seen that for benzene, toluene, *m,p*-xylenes and *o*-xylene the concentrations were found to be higher for the winter 2000 survey.

For the comparison for the indoor location between the fall 1999 and fall 2006 measurements, the P-values in Table 27 show that for all the compounds except benzene, the null hypothesis must be accepted. This indicates that the concentrations of toluene, ethylbenzene, *m,p*-xylenes and *o*-xylene were found to not be significantly different for both studies. For benzene, it was found that the concentrations were higher for the fall 1999 than found in the fall of 2006. The P-values from the comparison of the winter 2000 study to the fall 2006 study show that the alternative hypothesis must be accepted for all compounds. By looking at the Z-scores, it can be determined that the concentrations measured during the winter of 2000 study were higher than for the current study.

For the comparison of the outdoor location measurements taken during the sampling periods, only toluene and *m,p*-xylenes were tested against the hypotheses since they had >50% of the measurements above the detection limit. The P-values in Table 28 indicate that only the concentrations of *m,p*-xylenes were found to be significantly different between the fall 1999 and fall 2006 studies. The corresponding Z-scores indicate that the concentration was greater for the fall 1999 study. Toluene was not found to have significantly differing concentrations between the two studies. Comparing the winter 2000 and fall 2006 data, the corresponding P-values indicate that there is a significant difference in concentrations between the two sampling events. It is determined from the Z-scores that the concentrations for both toluene and *m,p*-xylenes were

significantly higher in the winter 2000 study as compared to the fall 2006 study for the outdoor location measurements.

As it can be seen from the above results, the statistical comparison tests show that there are: 1) no significant differences between the 1999/2000 and the 2006 BTEX concentration levels or; 2) higher concentrations found from the survey performed in 1999/2000. Therefore, the general hypothesis that outdoor, indoor and personal air concentrations have increased due to the increased oil sand development activity between 1999/2000 and 2006 is false.

5. Conclusions and Recommendations

5.1. *Conclusions*

The results from the sampling of the BTEX compounds in Fort McKay show several trends, based on hypotheses testing.

The first is that the concentrations of the BTEX compounds found in indoor air were higher than those found in the outdoor air. The compounds were detected in indoor air with higher frequency and at higher concentrations. This can be seen through the Indoor-Outdoor concentration ratios which were found to be greater than 1 in all cases and in fact much higher than 1.

The second noticeable trend is that the personal samples collected do not show a significant difference in concentration measurements from the indoor samples. This trend was shown through the results of Wilcoxon Signed Ranks and Spearman Correlation Coefficient tests performed on the paired indoor and outdoor measurements. The Spearman Correlation Coefficient hypothesis test showed that the personal and indoor BTEX measurements were significantly related and positively correlated. This suggests that the personal monitors were present inside participant's homes most of the time.

Thirdly, the last trend shown is that – compared to the baseline study performed in Fort McKay several years ago – concentrations have either remained similar or have in fact decreased. This could be attributed to several possible factors. The first is that the meteorological conditions throughout the sampling periods were different for this study as compared to the baseline study. Another possible explanation is that the analysis was performed differently between the two studies. In the current study, outliers were

removed from the analysis in order to describe a more accurate representation of the concentrations throughout the population. This was possible due to the fact that 35 samples were obtained, leaving room to remove these outlying samples while still fulfilling the requirements of the Central Limit Theorem. The baseline study did not obtain the correct amount of samples to fulfill the requirements of the Central Limit Theorem, therefore every sample measurement was necessary to include in the analysis. Another possibility is that since the emissions of VOCs from the oil sand activities have decreased over the last few years, the impact of these industrial emissions is significantly smaller now as compared to during the baseline study.

Concentrations of BTEX compounds obtained from this study were similar to the results found from other studies across Canada, the United States and Europe. The outdoor concentrations found in Fort McKay were found to be considerably lower as compared to larger urban and industrial centres of population. This can be attributed to the fact that Fort McKay is largely isolated and free of heavy traffic as compared to more urban locations. The pollution from the nearby industrial sources appears to either be diluted by the time it reaches Fort McKay.

The findings also suggest that indoor sources of the selected VOC compounds are a greater influence on personal air measurements than outdoor sources are. The BTEX compounds were all found with higher frequency and concentrations in the indoor environment than the outdoor environment. This indicates that household items, building materials, and activities are a greater influence on the concentrations found in peoples' homes. The indoor concentrations were similar to or less than concentrations found in other surveys performed. This could be attributed to the fact that the outliers were

removed from the survey data, which would affect the distribution of the sample means, shifting it towards the lower concentrations. The indoor concentrations were also found to range by large orders of magnitude between homes, further indicating that indoor sources are important to concentration levels found there.

Personal concentrations were found to be not significantly different from indoor concentrations. This contradicts the findings of many studies that indicate that concentrations of personal measurements significantly exceed indoor concentrations. Several explanations may exist. On the one hand, it may be an indication that subjects wearing the personal monitors spent significant amounts of time in their home. On the other hand, the outcome obtained for this study could be a result of the method of sampling. Since personal sampling was also performed for other air pollutants (NO_2 , SO_2 , and O_3) along with the VOCs and any replicates, the number of badges on the participants' necklaces may be too much of a burden for them to wear for a 7-day period. As a result, some subjects may not have worn their assigned monitors at all times. If in fact the participants left their monitors at home most of the time, the concentration readings would be similar to the indoor concentration levels obtained. It was observed on several participants that they were seen around the town without their monitors during their deployment period.

Although questions remain about similarities in personal air and indoor air concentrations measured in the study, these questions do not detract from the importance of other results observed. That is indoor air concentrations tended to be higher than outdoor concentrations – consistent with findings of previous studies in the community and elsewhere. Further, outdoor, indoor, and personal air concentrations remained

unchanged or decreased from fall 1999/winter 2000 to fall 2006 in the community. Thus changes in oil sands development activity from fall 1999/winter 2000 to fall 2006 did not result in increases in outdoor, indoor, and personal air concentrations of the compounds measured.

5.2. Recommendations

Although the industrial emissions have increased in the region since the baseline study was performed, there was no significant increase found in the concentrations of BTEX compounds found for Fort McKay. It would be beneficial to perform the survey again in a few years time in order to compare with both the baseline study and the recent study performed in order to obtain repeat measurements as well as to gain a better understanding of the sources of BTEX compounds in the community.

If the study were to be performed again, the number of compounds sampled for the personal measurements should be decreased in order to simplify the process for the participants. Since the participants are volunteers, it should not be made too difficult for them to take part in the study.

The analysis here only presents the data for VOC compounds. Since VOCs have several sources that can be found in and around the home, it can be difficult to attribute the concentration readings to the oil sand industrial activities. Ambient monitoring of VOCs should be constantly performed at the air quality monitoring station in order to provide continuous data. The data can be analyzed and compared to the passive monitor readings to get an idea of the accuracy of the monitors as well as an understanding of the VOC pollution transport from the oil sand activities.

Although not a specific objective of this study, extra information was obtained from the participants, such as time activity diaries. This information could be analyzed in order to obtain a better understanding of the potential sources affecting the personal measurements.

Finally, air quality is only one of several ways that people are exposed to VOCs in the environment. If there is interest in analyzing the risk to human health as a result of industrial activity, other methods of sampling should occur, such as water and food testing.

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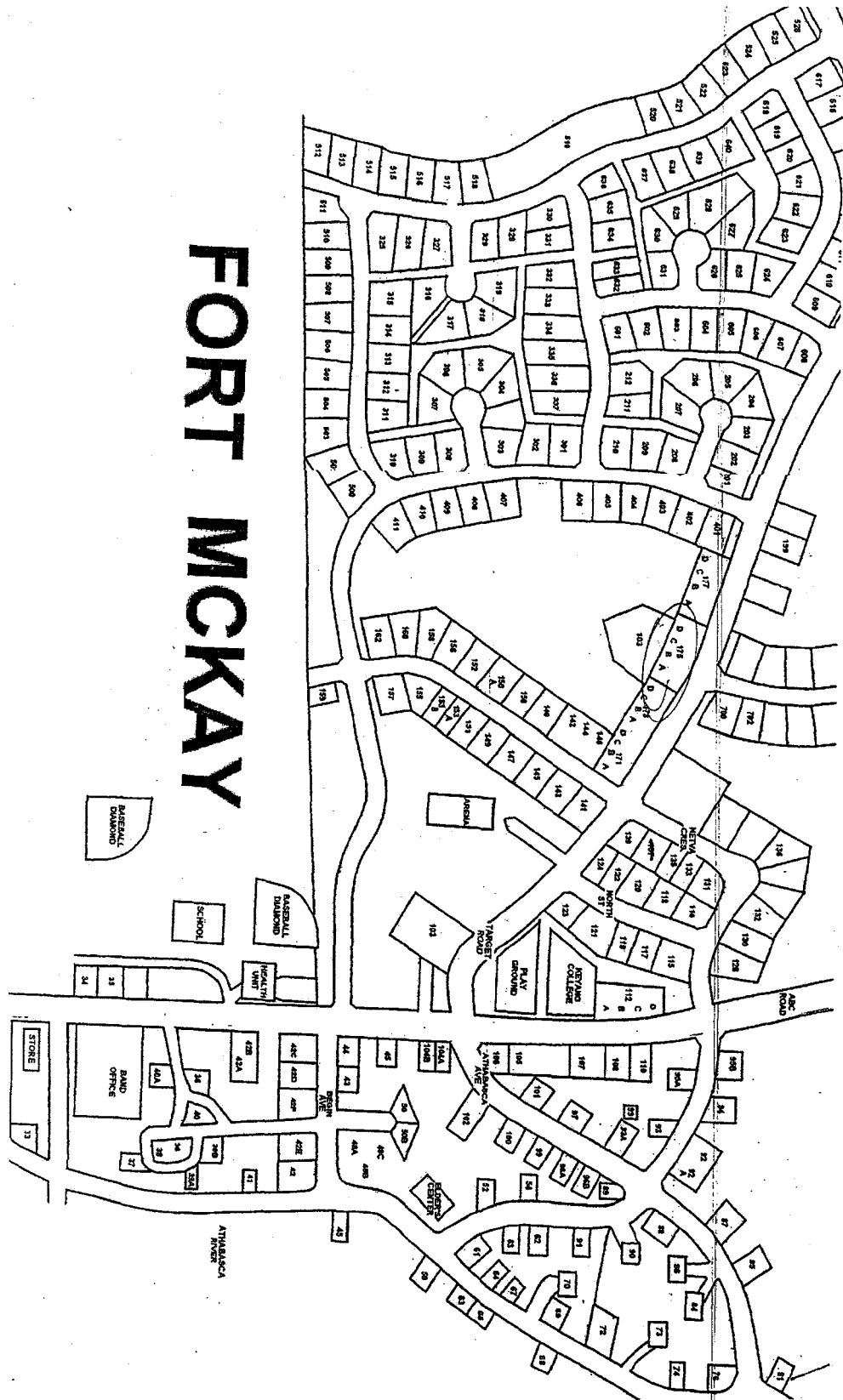
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Appendix 1 – Map of Fort McKay, AB



FORT MCKAY

Figure 14: Map of Fort McKay, AB

Appendix 2 - Raw data

Table 29: Blank monitor raw data results

Monitor	House ID	Benzene (ug/m3)	Toluene (ug/m3)	Ethylbenzene (ug/m3)	m,p-Xylenes (ug/m3)	o-Xylene (ug/m3)
VOC 6054	1201	0.00	0.00	0.00	0.00	0.00
VOC 6047	1202	0.00	0.00	0.00	0.00	0.00
VOC 6009	1203	0.00	0.00	0.00	0.00	0.00
VOC 6028	1204	0.00	0.00	0.00	0.00	0.00
VOC 6026	1205	0.00	0.00	0.00	0.00	0.00
VOC 6040	1206	0.00	0.00	0.00	0.00	0.00
VOC 6039	1207	0.00	0.00	0.00	0.00	0.00
VOC 6052	1208	0.00	0.00	0.00	0.00	0.00
VOC 6033	1209	0.00	0.00	0.00	0.00	0.00
VOC 6055	1210	0.00	0.00	0.00	0.00	0.00
VOC 6084	1211	0.00	0.00	0.00	0.00	0.00
VOC 6107	1212	0.00	0.00	0.00	0.00	0.00
VOC 6082	1213	0.00	0.00	0.00	0.00	0.00
VOC 6112	1214	0.00	0.00	0.00	0.00	0.00
VOC 6087	1215	0.00	0.00	0.00	0.00	0.00
VOC 6083	1216	0.00	0.00	0.00	0.00	0.00
VOC 6102	1217	0.00	0.00	0.00	0.00	0.00
VOC 6119	1218	0.00	0.00	0.00	0.00	0.00
VOC 6101	1219	0.00	0.00	0.00	0.00	0.00
VOC 6149	1220	0.00	0.00	0.00	0.00	0.00
VOC 6126	1221	0.00	0.00	0.00	0.00	0.00
VOC 6165	1222	0.00	0.00	0.00	0.00	0.00
VOC 6077	1223	0.00	0.00	0.00	0.00	0.00
VOC 6175	1224	0.00	0.00	0.00	0.00	0.00
VOC 6174	1225	0.00	0.00	0.00	0.00	0.00
VOC 6158	1226	0.00	0.00	0.00	0.00	0.00
VOC 6137	1227	0.00	0.00	0.00	0.00	0.00
VOC 6166	1228	0.00	0.00	0.00	0.00	0.00
VOC 6136	1229	0.00	0.00	0.00	0.00	0.00
VOC 6157	1230	0.00	0.00	0.00	0.00	0.00
VOC 6184	1231	0.00	0.00	0.00	0.00	0.00

Monitor	House ID	Benzene (ug/m3)	Toluene (ug/m3)	Ethylbenzene (ug/m3)	m,p-Xylenes (ug/m3)	o-Xylene (ug/m3)
VOC 6140	1232	0.00	0.00	0.00	0.00	0.00
VOC 6201	1233	0.00	0.00	0.00	0.00	0.00
VOC 6176	1234	0.00	0.00	0.00	0.00	0.00
VOC 6127	1235	0.00	0.00	0.00	0.00	0.00

Table 30: Personal monitors raw data results

Monitor	House ID	7-day Time-Weighted Average Concentration (µg/m ³)				
		Benzene	Toluene	Ethylbenzene	m,p-Xylenes	o-Xylene
VOC 6038	1201	4.74	9.05	1.74	4.20	1.14
VOC 6048	1202	0.50	7.11	0.76	1.53	0.55
VOC 6006	1203	0.50	8.20	1.25	3.43	0.93
VOC 6043	1204	0.59	20.14	0.76	2.02	0.71
VOC 6022	1205	0.54	8.06	1.85	3.76	1.36
VOC 6051	1205	0.54	8.63	1.96	3.65	1.42
VOC 6017	1206	2.52	11.14	0.93	2.02	0.65
VOC 6029	1207	4.69	14.50	1.85	4.52	1.31
VOC 6053	1208	2.98	23.74	5.45	11.66	4.63
VOC 6027	1209	4.44	14.12	2.13	6.21	1.91
VOC 6044	1210	3.48	9.95	2.40	6.70	2.56
VOC 6086	1211	8.64	21.37	3.33	10.47	4.03
VOC 6111	1212	4.36	7.49	1.09	2.45	0.71
VOC 6078	1213	0.98	9.29	1.27	2.48	0.89
VOC 6114	1213	1.03	9.01	1.34	2.48	0.89
VOC 6106	1214	0.46	8.34	0.93	1.80	0.71
VOC 6064	1215	12.07	13.36	2.29	5.94	1.74
VOC 6090	1216	27.75	65.45	46.17	187.51	63.72
VOC 6099	1217	2.52	14.17	1.85	2.13	0.65
VOC 6088	1218	0.59	4.64	0.89	1.84	0.00

Monitor	House ID	7-day Time-Weighted Average Concentration ($\mu\text{g}/\text{m}^3$)				
		Benzene	Toluene	Ethylbenzene	m,p-Xylenes	o-Xylene
VOC 6105	1218	0.59	4.37	0.89	1.78	0.64
VOC 6096	1219	0.75	8.25	1.64	2.45	0.98
VOC 6097	1219	0.71	8.25	1.58	2.34	0.98
VOC 6095	1220	0.00	8.10	0.60	1.20	0.00
VOC 6171	1221	0.50	10.47	12.86	43.99	12.65
VOC 6133	1222	0.80	18.44	1.64	3.82	1.53
VOC 6063	1223	0.84	2.84	1.14	2.83	1.09
VOC 6134	1224	4.07	33.03	4.14	13.52	4.42
VOC 6173	1225	2.35	22.65	1.31	3.82	1.64
VOC 6135	1226	0.96	5.40	1.14	2.89	1.09
VOC 6168	1226	1.01	5.50	1.09	2.89	1.04
VOC 6163	1227	2.47	6.54	1.04	2.40	0.82
VOC 6164	1228	4.78	6.07	1.36	3.49	0.98
VOC 6132	1229	1.47	5.97	1.69	4.96	1.91
VOC 6170	1230	1.59	5.26	1.53	5.29	1.85
VOC 6178	1231	1.72	7.35	2.13	6.60	1.91
VOC 6154	1232	0.46	4.93	1.31	2.18	0.82
VOC 6198	1233	2.56	48.39	2.45	7.63	2.62
VOC 6144	1234	1.26	6.07	2.34	8.34	3.00
VOC 6145	1235	5.58	16.02	1.91	4.91	1.42

Table 31: Indoor monitors raw data results

Monitor	House ID	7-day Time-Weighted Average Concentration ($\mu\text{g}/\text{m}^3$)				
		Benzene	Toluene	Ethylbenzene	m,p-Xylenes	o-Xylene
VOC 6037	1201	6.04	11.09	1.91	4.36	1.09
VOC 6058	1202	0.46	8.25	0.76	1.47	0.00
VOC 6005	1203	0.00	7.20	3.43	9.76	1.91

Monitor	House ID	7-day Time-Weighted Average Concentration ($\mu\text{g}/\text{m}^3$)				
		Benzene	Toluene	Ethylbenzene	m,p-Xylenes	o-Xylene
VOC 6020	1204	0.50	10.14	0.55	1.04	0.00
VOC 6021	1204	0.50	10.66	0.55	1.09	0.00
VOC 6030	1205	0.54	13.51	2.23	4.63	1.64
VOC 6015	1206	3.86	15.35	1.42	3.05	0.87
VOC 6018	1207	4.57	14.22	1.80	4.42	1.25
VOC 6032	1208	3.56	26.44	5.83	8.83	3.16
VOC 6011	1208	3.60	25.83	6.00	8.83	3.05
VOC 6046	1209	1.55	10.14	1.20	3.27	1.04
VOC 6059	1210	2.81	8.48	2.56	7.63	3.11
VOC 6076	1211	9.35	23.13	3.43	9.65	3.76
VOC 6108	1212	3.86	6.35	0.98	2.34	0.65
VOC 6113	1212	3.81	6.49	1.09	2.29	0.71
VOC 6110	1213	0.93	16.09	2.48	3.69	1.34
VOC 6109	1214	0.00	8.10	0.87	1.69	0.65
VOC 6066	1215	13.25	13.51	2.56	6.21	1.80
VOC 6092	1216	31.90	71.42	55.33	218.85	78.38
VOC 6072	1217	4.15	15.31	1.25	2.45	0.71
VOC 6073	1217	4.40	16.49	1.36	2.62	0.76
VOC 6118	1218	0.54	3.98	0.76	1.21	0.00
VOC 6098	1219	0.75	8.63	1.74	2.56	1.04
VOC 6162	1220	0.42	11.09	0.65	1.04	0.00
VOC 6123	1221	0.00	11.28	14.01	48.35	12.70
VOC 6179	1222	0.75	22.61	1.80	4.09	1.64
VOC 6181	1222	0.80	24.88	1.85	4.47	1.74
VOC 6061	1223	0.67	2.56	1.20	2.83	1.20
VOC 6172	1224	5.16	45.88	5.18	19.73	6.16
VOC 6156	1225	2.10	21.14	1.09	2.89	1.31
VOC 6183	1226	0.96	5.17	1.04	2.78	0.98
VOC 6150	1227	2.56	5.97	1.09	2.34	0.82
VOC 6167	1228	4.02	4.98	1.20	3.05	0.87
VOC 6182	1229	0.92	3.84	1.14	2.67	0.98
VOC 6177	1230	7.00	20.09	2.34	5.89	1.64

Monitor	House ID	7-day Time-Weighted Average Concentration ($\mu\text{g}/\text{m}^3$)				
		Benzene	Toluene	Ethylbenzene	m,p-Xylenes	o-Xylene
VOC 6139	1231	1.93	8.44	2.34	7.41	2.56
VOC 6131	1232	0.50	5.07	1.42	2.56	0.98
VOC 6129	1233	2.26	58.67	2.56	8.01	2.51
VOC 6141	1234	1.09	5.73	2.73	10.47	3.71
VOC 6169	1235	5.45	12.80	2.02	4.58	1.42

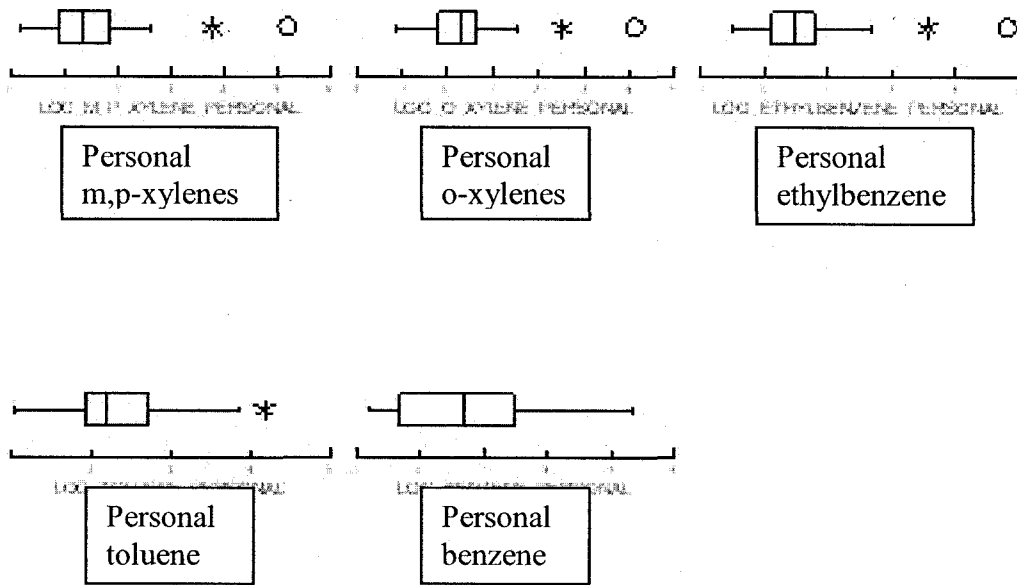
Table 32: Outdoor monitors raw data results

Monitor	House ID	7-day Time-Weighted Average Concentration ($\mu\text{g}/\text{m}^3$)				
		Benzene	Toluene	Ethylbenzene	m,p-Xylenes	o-Xylene
VOC 6036	1201	0.00	0.00	0.00	0.60	0.00
VOC 6049	1202	0.00	0.00	0.00	0.55	0.00
VOC 6013	1203	0.00	0.52	0.00	0.87	0.00
VOC 6014	1204	0.00	0.57	0.00	0.60	0.00
VOC 6007	1205	0.00	0.00	0.60	1.47	0.00
VOC 6025	1206	0.00	0.52	0.00	0.65	0.00
VOC 6012	1207	0.00	0.62	0.00	0.87	0.00
VOC 6060	1207	0.00	0.81	0.55	1.04	0.00
VOC 6056	1208	0.00	0.76	0.00	0.87	0.00
VOC 6004	1209	0.46	1.52	0.71	1.85	0.65
VOC 6016	1210	0.00	0.57	0.00	0.87	0.00
VOC 6041	1210	0.00	0.66	0.00	0.93	0.00
VOC 6104	1211	0.00	0.57	0.00	0.65	0.00
VOC 6116	1212	0.00	0.00	0.00	0.65	0.00
VOC 6075	1213	0.00	0.00	0.00	1.02	0.00
VOC 6080	1214	0.00	0.00	0.00	0.55	0.00
VOC 6094	1215	0.00	0.00	0.00	0.60	0.00
VOC 6062	1216	0.00	0.00	0.00	0.65	0.00
VOC 6070	1217	0.00	0.81	0.00	0.82	0.00
VOC 6079	1218	0.00	0.77	0.00	1.08	0.00

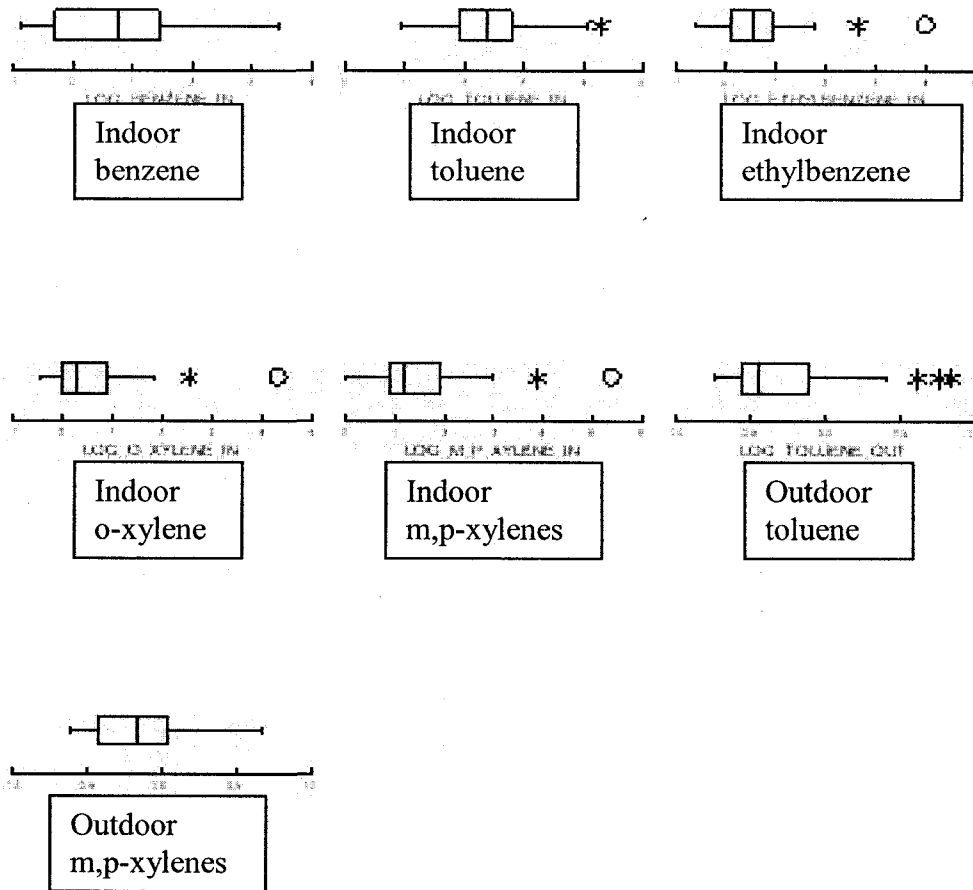
Monitor	House ID	7-day Time-Weighted Average Concentration ($\mu\text{g}/\text{m}^3$)				
		Benzene	Toluene	Ethylbenzene	m,p-Xylenes	o-Xylene
VOC 6103	1218	0.00	0.77	0.00	1.08	0.00
VOC 6071	1219	0.00	0.90	0.00	1.04	0.00
VOC 6146	1220	0.00	0.00	0.00	0.00	0.00
VOC 6121	1221	0.00	0.62	0.00	0.55	0.00
VOC 6151	1222	0.00	0.81	0.00	0.60	0.00
VOC 6089	1223	0.00	0.90	0.00	0.93	0.00
VOC 6091	1223	0.00	1.09	0.00	0.93	0.00
VOC 6153	1224	0.00	0.00	0.00	0.00	0.00
VOC 6128	1225	0.00	0.62	0.00	0.65	0.00
VOC 6124	1226	0.00	0.62	0.00	0.71	0.00
VOC 6180	1226	0.00	0.57	0.00	0.65	0.00
VOC 6147	1227	0.00	0.52	0.00	0.65	0.00
VOC 6138	1228	0.00	0.52	0.00	0.60	0.00
VOC 6152	1229	0.75	2.13	0.71	1.80	0.65
VOC 6142	1230	0.00	0.47	0.00	0.55	0.00
VOC 6130	1231	0.46	2.32	0.87	1.96	0.76
VOC 6143	1232	0.42	1.85	0.82	1.64	0.65
VOC 6186	1233	0.00	1.52	0.71	1.20	0.00
VOC 6125	1234	0.00	0.52	0.00	1.04	0.00
VOC 6148	1235	0.00	0.52	0.00	0.76	0.00

Appendix 3 – Box and Whisker Plots

Personal Box and Whisker Plots



Indoor and Outdoor Box and Whisker Plots



Appendix 4 – Description of Statistics

D’Agostino – Pearson Test for Normality.....97

Intraclass Correlation Coefficient.....98

D'Agostino-Pearson Test for Normality

In order to test for normality of the data, the D'Agostino-Pearson Test for Normality was used. This test was carried out as described below according to the procedures outlined by D'Agostino (1986) and D'Agostino et al. (1990).

The D'Agostino-Pearson chi square test involves calculating the statistic:

$$K^2 = X^2(\sqrt{b_1}) + X^2(b_2)$$

- where $\sqrt{b_1}$ is a measure for symmetry
- and b_2 is a measure for kurtosis.

The K^2 value can be seen as a chi square variable with two degrees of freedom. From this, a p-value can be calculated. At a significance level of $\alpha = 0.05$, a p-value smaller than this indicates a non-normal distribution, while a p-value larger than 0.05 indicates a normal distribution.

References:

D'Agostino, R. B. 1986. Tests for Normal Distribution. In: R. B. D'Agostino and M. Stephens, A. (eds.). Goodness-of-fit Techniques: New York: Marcel Dekker, Inc.

D'Agostino, R. B., Belanger, A. and D'Agostino, R. B., Jr. 1990. A Suggestion for Using Powerful and Informative Tests of Normality. The American Statistician 4: 316-321.

Intraclass Correlation Coefficient

Lee et al. (1995) demonstrated an effective method of determining the precision of passive monitors. This method is by calculating the intraclass correlation coefficient.

This statistic is calculated as follows:

$$r_I = \frac{s_a^2 - s_w^2}{s_a^2 + s_w^2},$$

- where r_I is the estimator of the intraclass correlation coefficient,
- s_a^2 is the between-classes mean square,
- and s_w^2 is the within-classes mean square.

The s_a^2 and s_w^2 statistics are calculated as follows:

$$s_a^2 = (2 \times (\sum_{i=1}^n \frac{(\bar{X}_i - \bar{X})^2}{(n-1)})),$$
$$s_w^2 = (\sum_{i=1}^n \sum_{j=1}^2 \frac{(X_{ij} - \bar{X}_i)^2}{n}),$$

- where X is the sample measurement,
- \bar{X} is the total mean of all samples,
- \bar{X}_i is the mean of the duplicate measurements for sample i ,
- n is the number of samples
- and j is the number of duplicates.

Reference:

Lee, K., Yanagisawa, Y., Spengler, J. D. and Davis, R. 1995. Assessment of precision of a passive sampler by duplicate measurements. Environment International 4: 407-412.

Appendix 5 – D’Agostino – Pearson Test for Normality Results

D'Agostino – Pearson Test for Normality Results

Table 33: D'Agostino - Pearson Test for Normality Results

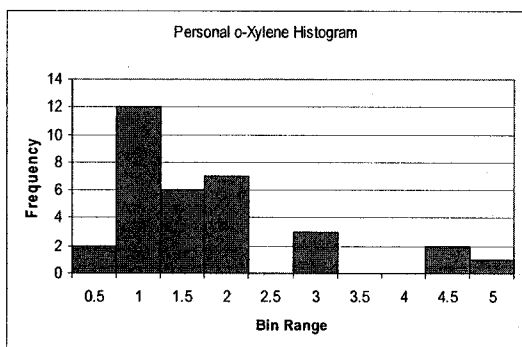
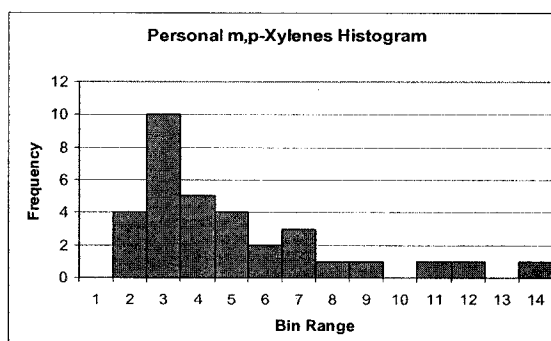
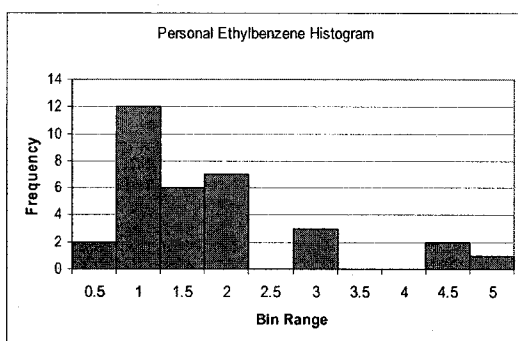
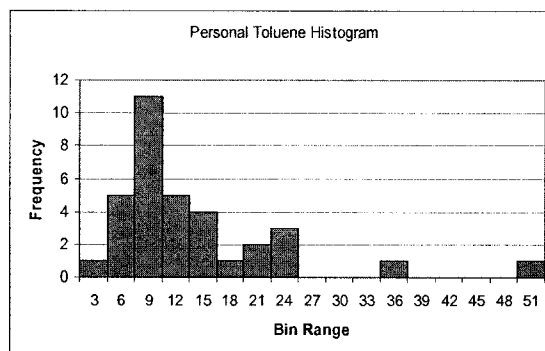
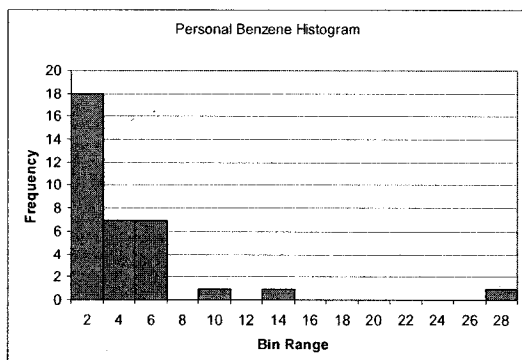
Compound	Personal	Indoor	Outdoor
Benzene	0.433	0.474	-
Toluene	0.382	0.587	0.020
Ethylbenzene	0.453	0.722	-
o-Xylene	0.759	0.214	-
m,p-Xylene	0.478	0.792	0.100

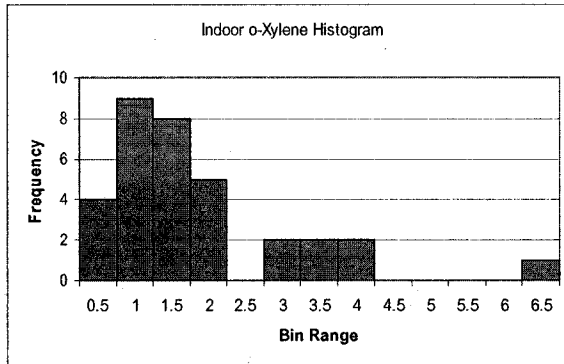
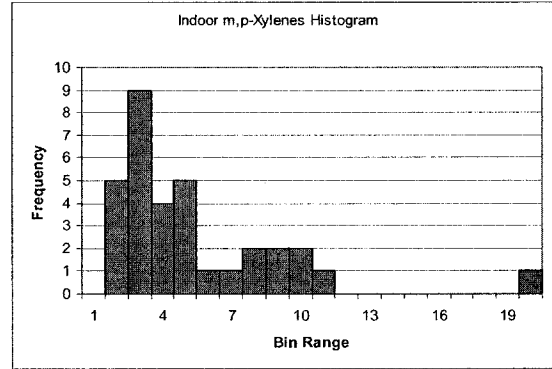
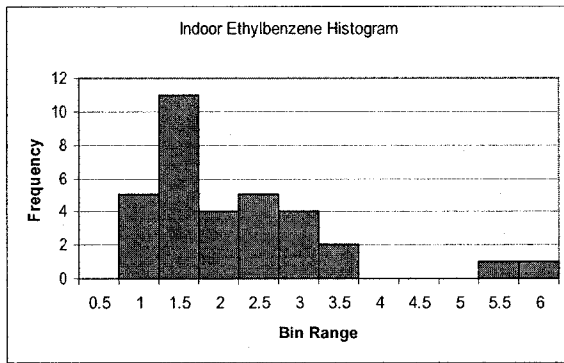
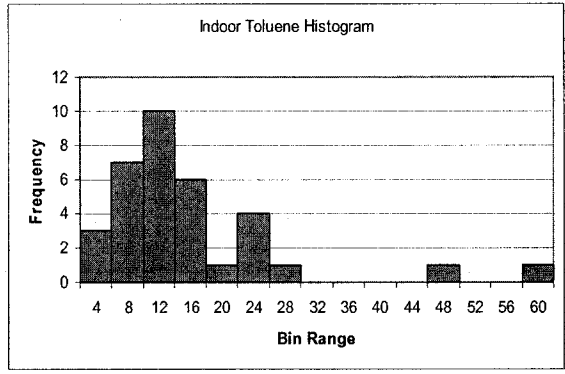
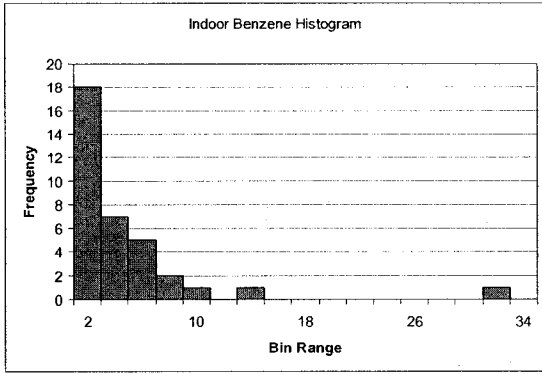
Appendix 6 – Histograms and Normal Probability Plots

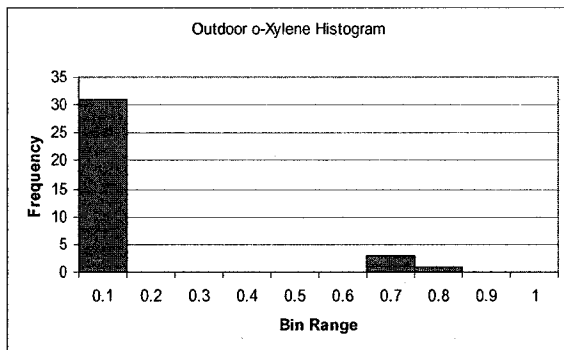
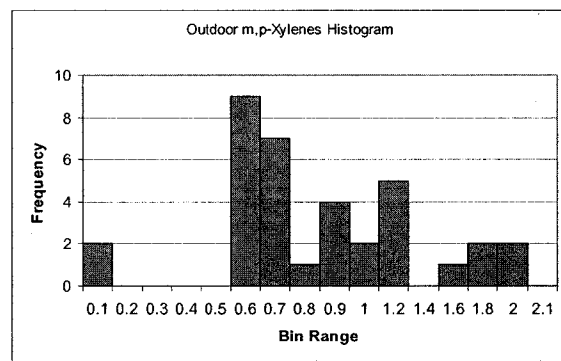
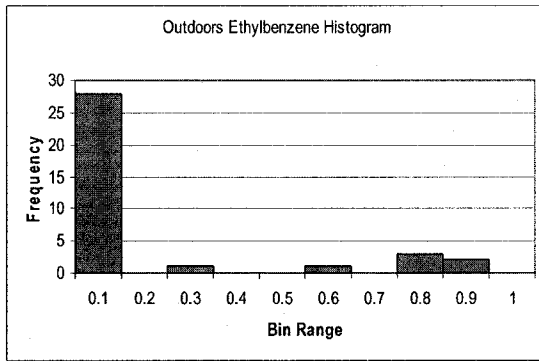
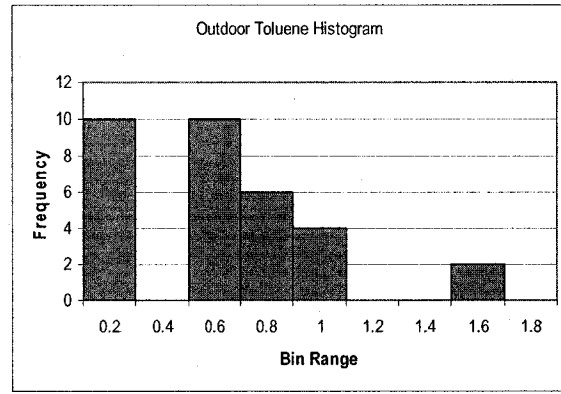
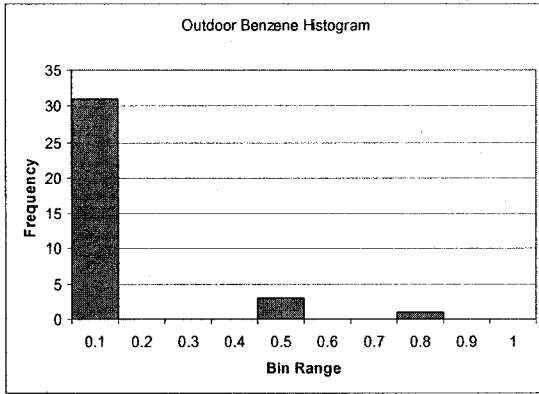
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Histograms







Normal Probability Plots

