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Los Angeles

Exposure Assessment for Toxic Vapors During Underground Storage Tank Inspections

A thesis submitted in partial satisfaction
of the requirements for the degree Master of Science
in Environmental Health Sciences

by

Ivan Jesse Torres

2017

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ABSTRACT OF THE THESIS

Exposure Assessment for Toxic Vapors During Underground Storage Tank Inspections

by

Ivan Jesse Torres

Master of Science in Environmental Health Sciences

University of California, Los Angeles, 2017

Professor Shane S. Que Hee, Chair

The purpose of this project was determining the exposure of toxic vapors, particularly benzene, toluene, ethylbenzene and xylene (BTEX), to workers during an underground storage tanks (UST) inspection process. BTEX are a group of hydrocarbons that are commonly found as volatile organic compounds (VOCs) in gasoline products. Thousands of other VOCs can also be found in gasoline, some that have been identified and others that have not. For this project, a total of 8 different filling stations were examined during a UST inspection with the help of a local regulatory agency. The project was conducted during the months of January to April 2017. The exposure assessment was divided into 4 phases (laboratory pre-calibrations, preliminary, secondary and personal sampling) to assess whether high air concentrations of VOCs and BTEX were present at the sites. A Photoionization Detector (ppbRAE 7240) was used to measure total VOC levels. A portable Gas Chromatography (GC) (PetroPRO) was used to measure the levels of BTEX. Integrated personal breathing zone sampling was also done at four sites with time ranges of 60-99 minutes. Personal samples were analyzed by GCMS after desorption of the charcoal tube with carbon disulfide.

VOC levels were at much higher concentrations when compared to the BTEX levels at concentrations ranging from 1.0 ppm to 200 ppm. BTEX concentrations levels decreased over time at constant cool temperatures and ranged from 118 to 340, 151 to 483, 276 to 926, and 249 to 869 ppb for BTEX, respectively. It was also observed that with higher increasing ambient temperatures, concentrations increased over time from 111 to 769, 81 to 504, 75 to 503, and 68 to 406ppb for BTEX, respectively. BTEX concentrations were overall below OSHA's PELs and STELs, and NIOSH STELs. For one particular site, concentrations of benzene did exceed NIOSH RELs of 0.1 ppm (100 ppb) and was above OSHA's Action Level (AL) at 0.5 ppm (500 ppb).

Overall, BTEX concentrations decreased over time with cooler temperatures and increased with warmer temperatures. VOCs were significantly high based on location and concentrations levels changed based on the time of the day related to temperatures. Turbine sumps showed the highest concentrations for VOCs and BTEX when compared to fillings sumps and dispenser sumps. Personal samples results were basically inconclusive because the samples were not analyzed until 6 months after sampling. Also, exposure assessment was not done for a total 8-hour exposure as required to compare with Cal/OSHA regulations and NIOSH guidelines. Similar concentrations were found for benzene and xylene (benzene being the highest concentration and xylenes being the lowest) as Site 4. All data were lower than 0.1 Cal/OSHA PELs, with the highest concentrations being 40.8 ppb for Site 5 and the lowest at 0.5 ppb for Site 6. In general, exposure levels to BTEX were not of immediate concern but it is still recommended for workers to take preventative measures to reduce exposures.

This thesis of Ivan Jesse Torres is approved.

Yifang Zhu

Michael Leo Brenna Jerrett

Shane S Que Hee, Committee Chair

University of California, Los Angeles

2017

DEDICATION

I will like to dedicate this thesis to all of the people who were involved with this study, all my professors and mentors who made this journey possible, the Los Angeles Fire Department Certified Unified Program Agency (CUPA), and most importantly to my family.

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ABBREVIATIONS

AL	Action Level
ATSDR	Agency for Toxic Substances and Disease Registry
AQMD	Air Quality Management District
ACGIH	American Conference of Governmental Industrial Hygienists
AIHA	American Industrial Hygiene Association
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
BEI	Biological Exposure Indices
CCR	California Code of Regulations
CUPA	Certified Unified Program Agency
CAA	Clean Air Act
CFR	Code of Federal Regulations
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
EPA	Environmental Protection Agency
FPM	Feet Per Minute
GC-MS	Gas Chromatography-Mass Spectrometry
HAP	Hazardous Air Pollutants
IDLH	Immediately Dangerous to Life or Health
ICC	International Code Council
LDL	Lower Detection Limits
LUST	Leaking Underground Storage Tank

LLD	Line Leak Detector
LEL	Lower Explosive Limit
LOAEL	Lowest Observed Adverse Effect Level
NESHAP	National Emission Standards for Hazardous Air Pollutants
NFPA	National Fire Protection Agency
NIOSH	National Institute for Occupational Safety and Health
NOAEL	No Observed Adverse Effect Level
NRC	National Response Center
OSHA	Occupational Safety and Health Administration
PPB	Parts Per Billion
PPM	Parts Per Million
PEL	Permissible Exposure Limit
PPE	Personal Protective Equipment
REL	Recommended Exposure Limit
RfC	Reference Concentration Dose
RCRA	Resource Conservation and Recovery Act
SB 989	Senate Bill 989
SOCMI	Synthetic Organic Chemical Manufacturing Industry
TLV	Threshold Limit Value
TWA	Time Weighted Average
UDL	Upper Detection Limit
UST	Underground Storage Tank

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INTRODUCTION

1.1 AIMS:

The aim of this research was to conduct an exposure assessment by (1) collecting data on the exposure of toxic vapors when working above underground storage tanks (UST) sumps, (2) to estimate the magnitude of exposure when working at or near USTs, and (3) to evaluate work practices to facilitate their improvement, provide recommendations to reduce exposure, and to provide better information to workers.

1.2 BACKGROUND:

1.2.1 Exposure to Gasoline Vapors

1.2.1.1. Introduction:

Gasoline fuel has volatile organic compounds (VOCs) that on exposure to humans are toxic to human health and the environment. Some of its most toxic constituents are benzene, toluene, ethylbenzene and xylene (3 isomers) (BTEX). The BTEX components are part of a group of aromatic hydrocarbons that are classified as human carcinogens (benzene), central nervous system depressors (all), reproductive toxins and overall toxic to the human body (toluene and *o*-xylene). Because of the toxic effects, it is important to understand the sources of exposure, the health impacts, controls for exposure and the interaction of BTEX with the environment.

USTs are one of many point sources of BTEX. In the U.S. there are approximately 561,000 USTs that contain petroleum or other hazardous substances⁽¹⁾. As tanks tend to leak over time, regulations require that USTs undergo maintenance services and inspections by local government agencies. Many of the exposures originate from the leak itself, the removal process, any fuel transfer operations, or during the inspection and maintenance process.

In this study, exposures to toxic gasoline vapors during UST inspections were assessed for the time of the duration of inspection. Most common exposures originate from spilled gasoline and from leaking pipes inside the sumps. The spilled gasoline inside the sumps evaporates eventually reaching a stable evaporation rate controlled by diffusion, and thus eventually leading to a constant headspace air concentration inside the sump. The continued evaporation of gasoline then causes a buildup of pressure inside the sumps as the head space inside the closed system becomes saturated. When the sumps are opened, the change in pressure, temperature and the pressure of a concentration gradient causes the release of vapors, thus causing direct exposures. Inspectors in particular are required to inspect the mechanical and electrical components (piping, sensors, pumps, etc.) inside the UST and dispenser sumps as part of the inspection process to verify that the equipment is in compliance with state regulations. Inspectors can spend 1-2 hours per site and complete about 2-3 sites per day. Direct exposures when inspecting the sumps are very short, durations lasting about a minute or less. During those short periods of exposure, inspectors are exposed to high levels of VOCs. Long term exposures to low doses of BTEX can have significant health effects to individuals.

In the present study, it was hypothesized that gasoline vapors from the sumps would initially be at high concentrations due to a vapor build up inside and then decrease as vapors escape from the sumps over time. Conducting exposure assessment during the inspection process can estimate the magnitude of exposure when working at or near USTs. It can help evaluate work practices, facilitate better work practices, provide recommendations to reduce exposure, and to provide educational information to workers to allow them to be self-initiating relative to their personal protective equipment (PPE). Whether it is an inspector, owner or designated contractor, it is important to be aware about the health and safety risks involved when working around USTs.

1.2.1.2. Vapor Generation

Vapor buildup is due to the evaporation of a solvent controlled by a diffusion rate based on a concentration gradient and temperature. The theory behind this is that evaporation of a solvent reaches a stable evaporation rate controlled by diffusion and thus eventually leading to a constant headspace air concentration. This *equilibrium vapor pressure* is defined as the pressure exerted by a vapor in thermodynamic equilibrium with its condensed phases (liquid) at a given temperature in a closed system⁽²⁾. In short, liquids emit vapors through evaporation and cause a buildup of pressure as the head space in a closed system becomes saturated. A closed system could be a container, a room or any space that is fully enclosed and no mass may be transferred in or out of the system boundaries.

For a UST, the sumps are considered closed systems because the sumps are enclosed by tight seal glass fiber walls and covered above with an iron lid. Inside the sump, small volumes of gasoline could be found usually from spills during the filling process or from leaking pipes. These gasoline liquids evaporate over time and thus vapors are collected and contained inside the sumps at a thermodynamic equilibrium. In a different situation, because gasoline has a low boiling point, vapors can be collected inside as they leak from the piping systems. When the equilibrium is disturbed, such as when temperatures change or when mass (vapors) escape, the vapor pressure changes inside and causes further evaporation as equilibrium is reestablished. For example, when a lid is removed from a sump, the concentrated vapors inside the sumps escape into the outside atmosphere due to a change in temperature and pressure inside caused by exposure to external conditions that also includes convective air currents. Vapors will continue to be emitted as it tries to reach a thermodynamic equilibrium or until all gasoline has been fully evaporated.

1.2.1.3. Theory

The theory behind this can be explained through the *Clausius-Clapeyron equation*⁽³⁾ (Eq. 1.0).

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (\text{Eq. 1.0})$$

This equation states that the equilibrium between a liquid and its vapor depends upon the temperature of the system. If the temperature increases, the saturation pressure of the water vapor increases, not linearly as expected from the Ideal Gas Law but exponentially. The rate of increase in vapor pressure per unit increase in temperature is given by the Clausius-Clapeyron equation. In general, this equation can be used to estimate the vapor pressure of a liquid at any temperature. To determine the vapor pressure inside a closed system, given the vapor pressure (P_1) of the liquid at temperature (T_1) and a second given temperature (T_2), Eq. 1.0 can be rewritten as Eq. 2.0:

$$P_2 = P_1 \exp\left[-\left(\frac{\Delta H_{vap}}{R}\right) \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] \quad (\text{Eq. 2.0})$$

Or, to also determine a temperature inside a closed system, given a pressure (P_1, P_2) and temperature (T_2), the Eq. 1.0 can be rewritten as Eq. 3.0:

$$T_2 = 1 / \left[\frac{1}{T_1} - \left(\frac{R \ln(P_2/P_1)}{\Delta H_{vap}} \right) \right] \quad (\text{Eq. 3.0})$$

Equations 1-3 are used to explain the theory behind the exponential proportional relationship between pressure and temperature of a liquid. This relationship can be viewed as such Fig. 1:

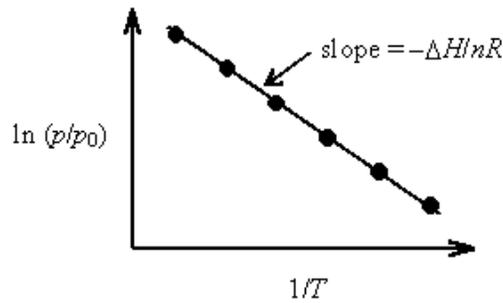


Figure 1. Exponential Proportional Relationship between Pressure and Temperature

The logarithm of the vapor pressure ($\ln(P_{\text{vap}})$) versus inverse absolute temperature ($1/T$) is a linear function⁽⁴⁾.

The rate of vapor diffusion can be explained by Fick's Law of Diffusion. Diffusion is the process by which molecules move through a medium in the absence of fluid flow by the kinetic energy of random motion⁽⁵⁾. Diffusion can function as a concentration gradient, from a higher concentration gradient to lower concentrations gradient, or as a thermodynamic process. Fick's first Law (Eq. 4.0) describes the rate at which a gas diffuses across a membrane given the properties of the membrane and the gas. For example, for exposure assessment, the medium of diffusion is air. As mentioned in Section 1.2.1.2., vapor pressure inside the headspace of the sumps exponentially increases with temperature. The vapor pressure is then proportional to the concentration found inside the sumps (assuming The Ideal Gas Law). Because this vapor buildup or pressure is within an enclosed system near equilibrium, concentrations will remain constant at undisturbed conditions. When the sumps are opened-because the concentrations inside are greater than outside concentrations-a transfer of mass (vapors) begins to diffuse outward exposing the inspectors. This is a flux diffusion based on a concentration gradient.

$$J = -D \frac{dC}{dx} \quad (\text{Eq. 4.0})$$

In Fick's First Law (Eq. 4.0), J represents the mass flux in mol/cm²-s or gm/cm²-s and D is the diffusion coefficient in m²/s (length² / time) which material a can diffuse into material b . The ratio of dC/dx is the concentration gradient (C represents the concentration of the species and x represents the distance of movement perpendicular to the surface of the barrier). The negative sign represents the down gradient concentration ⁽⁵⁾. In general, diffusion increases as temperature increases because of the increased motion of the molecules and because the Clausius-Clapeyron equation is obeyed. For a UST, when the sumps are opened on high temperature days, the diffusion of vapors to the outside increases. This was observed during the exposure assessment in this study (see results section). Vice versa reasoning can be applied for cool temperature days. In general, the greater the concentration gradient is relative the outside atmosphere concentration to the inside concentration in the sumps, the greater the mass flux J . Concentrations gradient will depend on high concentrations (C) and the shorter distances (x) that vapor will have to travel.

1.2.2 BTEX

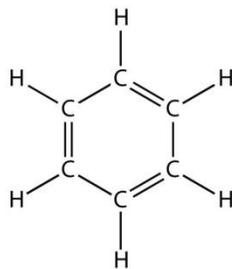
1.2.2.1 .Properties

The American Society for Testing and Materials (ASTM) defines very volatile organic compounds (VVOCs), as any organic compound with a low molecular weight and vapor pressures greater than 113 mmHg (15 kPa) at 25°C and boiling points below 30°C ⁽⁶⁾. EPA defines VVOCs as organic compounds with boiling points of < 0 to 100 °C ⁽⁷⁾. Since benzene, toluene, ethylbenzene, and *m*-, *o*-, *p*-xylene have boiling points of 80°C, 111°C, 136°C, 139°C, 144°C, 138°C, respectively, BTEX are volatile organic compounds (VOC).

Benzene

IUPAC name: Benzol, Benzole, Cyclohexatriene, Pyrobenzole, and Benzine ⁽⁹⁾. The benzene molecule is composed of 6 carbon atoms joined in a ring with 1 hydrogen atom attached to each with an alternating single and double carbon-carbon bonds. Because it contains only carbon and hydrogen atoms, benzene is classed as a hydrocarbon. Also, because of the cyclic continuous pi bond between the carbon atoms, benzene is classed as an aromatic hydrocarbon; it is the simplest such compound.

Its structural formula is:



Its characteristics include ⁽⁹⁾:

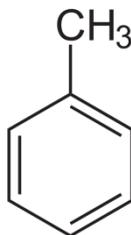
Empirical Formula: C₆H₆
CAS Registry Number: 71-42-2
Molecular Weight: 78.11 g/mol
Boiling Point: 80 °C
Vapor Density: 2.8 relative to air
Vapor Pressure: 94.8 mmHg at 25 °C
Relative Evaporation Rate: 2.8 (ether=1)
Odor Threshold in Air: 4.9 mg/ m³
Heat of Vaporization: 33.83 kJ/mol at 25 °C
Ionization Potential: 9.24 eV
Flash point (closed cup): -11°C
Lower Explosive Limit (LEL): 1.4 %/volume
Henry's law constant: 0.557 kPa m³/mol

Benzene is a colorless and highly flammable liquid with a sweet smell, and is responsible for the aroma around gasoline stations. Because of its low boiling point and high vapor pressure, benzene is a Volatile Organic Compound (VOC). The rate of evaporation increases with higher temperatures. Exposures to direct sunlight and to moving atmospheric air will cause evaporative increase during hot summer days. Benzene is very water soluble; its water solubility is 1.79×10^3 mg/L at 25 deg °C⁽⁹⁾.

Toluene

IUPAC Name: Methylbenzene, Toluol, Methylbenzol, and Phenylmethane. Toluene is a mono-substituted benzene derivative, consisting of a methyl group (CH₃) attached to a benzene ring with one hydrogen replaced. Because it contains carbons and hydrogen atoms and a benzene ring, toluene is an aromatic, hydrocarbon compound⁽¹⁰⁾.

Its structural formula is:



Its characteristics include ⁽¹⁰⁾:

Empirical Formula: C₆H₅-CH₃

CAS Registry Number: 108-88-3

Molecular Weight: 92.14 g/mol

Boiling Point: 110.7 °C

Vapor Density: 3.1 relative to air

Vapor Pressure: 28.4 mmHg at 25 °C

Relative Evaporation Rate: 6.1 (ether=1)

Odor Threshold in Air: 8 mg/m³

Heat of Vaporization: 38.01 kJ/mol at 25 °C

Ionization Potential: 8.82 eV

Flash point (closed cup): 4 °C

Lower Explosive Limit: 1.1 %/volume

Henry's law constant: 0.660 kPa m³/mol

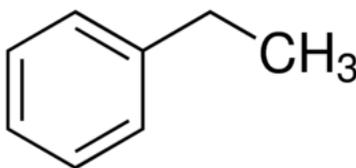
Toluene is a colorless liquid, water solubility at 25 deg °C is 526 mg/L, and has a smell associated with paint thinner or an aromatic odor. Toluene is also classified as a VOC. Toluene is soluble in acetone, absolute alcohol, ether, chloroform, benzene, petroleum ether, glacial

acetic acid, and carbon disulfide. The rate of evaporation increases with higher temperature. Exposures to direct sunlight and to atmospheric air cause an evaporation rate increase during hot summer days⁽¹¹⁾.

Ethylbenzene

IUPAC Name: Phenylethane, Benzene, Ethylbenzol, and Aethylbenzol. Ethylbenzene is a derivative of benzene and it is classified as a monocyclic aromatic hydrocarbon consisting of a CH₂-CH₃ group attached to a benzene ring with one hydrogen replaced by the ethyl group⁽¹²⁾. Ethylbenzene is water soluble at 25 °C of 170 mg/L. It is also a colorless and highly flammable liquid. It has a sweet odor like gasoline⁽¹³⁾.

Its structural formula is:



Its characteristics include⁽¹³⁾:

Empirical Formula: C₈H₁₀, or C₆H₅C₂H₅, or CH₃CH₂C₆H₅

CAS Registry Number: 100-41-4

Molecular Weight: 106.17 g/mol

Boiling Point: 136.2 °C

Vapor Density: 3.7 relative to air

Vapor Pressure: 9.6 mmHg at 25 °C

Relative Evaporation Rate: 0.84 (butyl acetate=1 min.)

Odor Threshold in Air: 2-3 mg/ m³

Heat of Vaporization: 42.24 kJ/mol at 25 °C

Ionization Potential: 8.76 eV

Flash point (closed cup): 15 °C

Lower Explosive Limits (LEL): 1.2 %/volume

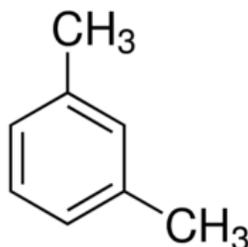
Henry's law constant: 0.843 kPa m³/mol

Ethylbenzene is slightly soluble in water at 25 °C⁽⁵⁷⁾. It is also a colorless and highly flammable liquid. It has a sweet odor like gasoline. Ethylbenzene is classified as a VOC.

m-Xylene

IUPAC Name: 1,3-Dimethylbenzene, M-Xylol, 1,3-Xylene, M-Dimethylbenzene , and Meta-Xylene. *M*-Xylene is an aromatic hydrocarbon, based on benzene with two methyl substituents replaced by two hydrogens. It is an isomer of *o*-xylene and *p*-xylene. The *m* stands for *meta*, meaning the two methyl substituents are at locations 1 and 3 on the aromatic ring⁽¹⁴⁾.

Its structural formula is:



Its characteristics include ⁽¹⁴⁾:

Empirical Formula: C₈H₁₀ or C₆H₄(CH₃)₂

CAS Registry Number: 108-38-3

Molecular Weight: 106.17 g/mol

Boiling Point: 139.1 °C

Vapor Density: 3.7 relative to air

Vapor Pressure: 8.29 mmHg at 25 °C

Relative Evaporation Rate: 9.2 (ether=1)

Odor Threshold in Air: 0.05-1 ppm

Heat of Vaporization: 42.65 kJ/mol at 25 °C

Ionization Potential: 8.56 eV

Flash point (closed cup): 25 °C

Lower Explosive Limit: 0.9 %/volume

Henry's law constant: 0.730 kPa m³/mol

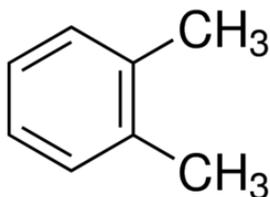
m-Xylene is a clear, colorless liquid with a sweet or aromatic odor. *M*-Xylene is also flammable and classified as a VOC. Water solubility is 1.61X10² mg/Lat 25 °C ⁽¹⁵⁾.

o-Xylene

IUPAC Name: 1,2-dimethylbenzene; 1,2-xylene; 2-xylene, *o*-xylol; and *ortho*-xylene. *o*-

Xylene belongs to the family of aromatic hydrocarbons with a benzene ring and two adjacent methyl substituents. It is a positional isomer of *m*-xylene and *p*-xylene. The *o*- stands for *ortho*, meaning the two methyl substituents are located at locations 1 and 2 on the benzene ring ⁽⁵⁸⁾.

Its structural formula is:



Its characteristics include ⁽⁵⁸⁾:

Empirical Formula: C₈H₁₀ or C₆H₄(CH₃)₂

CAS Registry Number: 95-47-6

Molecular Weight: 106.168 g/mol

Boiling Point: 144.5°C

Vapor Density: 3.7 relative to air

Vapor Pressure: 6.65 mmHg at 25 °C

Relative Evaporation Rate: 9.2 (ether=1)

Odor Threshold in Air: 0.05 ppm

Heat of Vaporization: 43.43 kJ/mol at 25 °C

Ionization Potential: 8.56 eV

Flash point (closed cup): 31°C

Lower Explosive Limit: 0.9 %/volume

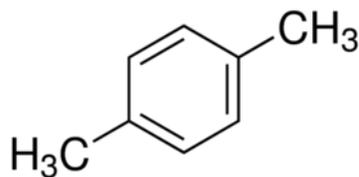
Henry's law constant: 0.551 kPa m³/mol

O-Xylene is a colorless liquid with a sweet or "aromatic" odor. *O*-Xylene is also flammable and classified as a volatile organic compound (VOC). Water solubility is 1.78X10² mg/L at 25 °C ⁽⁵⁸⁾.

p-Xylene

IUPAC Name: 4-xylene, P-xylol, Para-xylene, and Paraxylene. *O*-Xylene is one of the three dimethylbenzene positional isomers. *O*-Xylene is an aromatic hydrocarbon with a benzene ring and two methyl substituents. The *p*- stands for *para*-, meaning the two methyl groups are located at locations 1 and 4 on the benzene ring ⁽⁵⁹⁾.

Its structural formula is:



Its characteristics include ⁽⁵⁹⁾:

Empirical Formula: C₈H₁₀ or C₆H₄(CH₃)₂

CAS Registry Number: 106-42-3

Molecular Weight: 106.168 g/mol

Boiling Point: 138.3 °C

Vapor Density: 3.7 relative to air

Vapor Pressure: 8.84 mmHg at 25 °C

Relative Evaporation Rate: 9.9 (ether=1)

Odor Threshold in Air: 0.05 ppm

Heat of Vaporization: 42.40 kJ/mol at 25 °C

Ionization Potential: 8.44 eV

Flash point (closed cup):25 °C

Lower Explosive Limit: 1.1 %/volume

Henry's law constant: 0.690 kPa m³/mol

p-Xylene is a colorless liquid with a sweet odor or aromatic odor. *p*-Xylene is also flammable and classified as a VOC. Water solubility is 1.62X10² mg/L at 25 °C ⁽⁵⁹⁾.

1.2.2.2. Process and Use

BTEX is a group of aromatic compounds composed of hydrocarbons, with benzene as the primary aromatic ring. BTEX is naturally found in crude oil and are also byproducts in petroleum products such as gasoline and diesel. In the refining process, toluene is used to produce benzene and used as a solvent ⁽¹⁶⁾. Xylenes are produced by the methylation of toluene and benzene ⁽¹⁷⁾. Some of these compounds are also added as additives to increase the octane rating of the gasoline products and as anti-knocking agents. The amount of BTEX in gasoline varies based on the crude oil used, the refining process, the overall balance of product demand and the desired fuel properties. Gasoline contains higher concentrations of benzene by volume when compared to diesel. According to the EPA Mobile Source Air Toxics 2 final rule, published in 2007, gasoline can have an annual average benzene content of 0.62 volume percent (vol%) or less and for diesel a fuel content of 0.02 volume percent (vol%) or less ⁽¹⁸⁾. This is the standard given by the EPA's Gasoline Benzene Program. This is why benzene content is regulated in gasoline but not in diesel. Currently, composition of BTEX as a whole in gasoline (w/w) is composed of about 11% benzene, 26% toluene, 11% ethylbenzene, and 52% for xylene isomers (total equaling 100%) (Fig. 2) ⁽⁵²⁾.

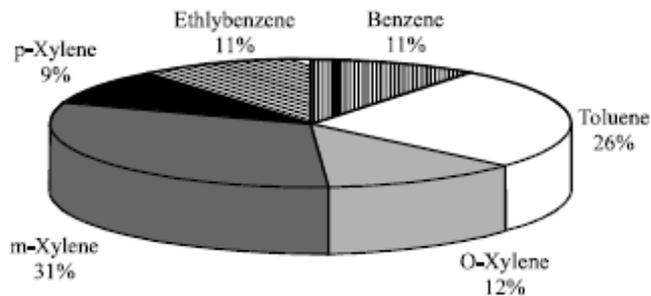


Figure 2. percentage (weight) of BTEX components of gasoline

1.2.2.3. Toxic Effects

BTEX compounds are well absorbed by inhalation and skin routes and can also be easily distributed to lipid and vascular tissues (e.g. brain, bone marrow, and body fat) in humans and animals because of their lipophilicity⁽¹⁹⁾. The most common exposure route for BTEX is through inhalation. Other routes of exposure are through dermal contact, the eyes in spill accidents and the least common route of exposure is through ingestion (cross contamination). BTEX are rapidly eliminated from the body. Exposure to BTEX as a whole has not been studied on the relative health effects and dose-response relationships⁽²⁰⁾. Despite the lack of research on health hazards and BTEX as a whole, there are numerous data on health hazards for each individual hydrocarbon.

1.A. Benzene

Lethal Concentration (LC50): Acute inhalation lethal concentration (LC50) for rats is calculated as 13,700 mg/kg (13,700 ppm) for a 4-hour exposure. A study showed that 4 of 6 rats died following a 4-hour exposure to 16,000 ppm of benzene. In addition, another study showed intermediate exposures of male CD-1 mice to benzene at doses of 302 ppm for 6 hours/day, 5 days/week for 26 weeks total showed mortality approaching 50%⁽⁹⁾⁽²¹⁾.

Carcinogenicity: Benzene is known to cause leukemia and it is classified as a human carcinogen by the National Institute for Occupational Safety and Health (NIOSH), the Environmental Protection Agency (Group A) and by the International Agency for Research on Cancer (Group 1)⁽⁹⁾. Benzene is listed as a carcinogen in the proposition 65 list.

Species: Rat Sex: female Dose: 0, 25, 50, 250 mg/kg, Exposure time: 103 weeks Number of exposures: daily, 5 days/week, Remarks: zymbal gland carcinomas, squamous cell papillomas; male Dose: 0, 50, 100, 200 mg/kg, Exposure time: 103 weeks, Number of exposures: daily, 5 days/week, Remarks: zymbal gland carcinomas, squamous cell papillomas⁽⁹⁾.

Species: Mouse Sex: male and female Dose: 25, 50, 100 mg/kg, Exposure time: 103 weeks, Number of exposures: daily, 5 days/week, Remarks: Clear evidence of multiple organ carcinogenicity⁽⁹⁾.

Short term effects or acute effects: Exposure to high concentration levels of benzene can affect the nervous system and cause drowsiness, dizziness, rapid or irregular heartbeat, headaches, tremors, confusion and loss of consciousness⁽²²⁾.

Biomarkers and BEIs: There are several biomarkers for benzene exposure: t, t-muconic acid results from ring opening; S-phenylcysteine (SPC) in hemoglobin (Hb), from the reaction of benzene oxide with a cysteine sulfhydryl group; and SPC in albumin. Workers exposed to average concentrations of 0, 4.4, 8.4, and 23.1 ppm benzene, 8 h/d, 5 d/week, showed SPCHb linearly increased in the exposed groups⁽²³⁾. The BEI for benzene is 25 µg/g creatinine for S-phenylmercapturic acid in urine. For t,t-muconic acid in urine, the BEI is 500 µg/g creatinine⁽²⁴⁾. Both are sampled at the end of the shift.

Reference Concentration (RfC): $3 \times 10^{-2} \text{ mg/m}^3$ based on an occupational epidemiologic study in which workers were exposed to benzene by inhalation that resulted in decreased lymphocyte count⁽²⁵⁾.

1.B. Toluene

Lethal Concentration (LC50): Acute inhalation lethal concentration (LC50) for mice is calculated as 5,320 ppm for 7-hour inhalation period⁽¹¹⁾.

Short term effects or acute effects: Short period exposures to high concentrations of toluene vapors may cause drowsiness, headache, nausea, visual changes, muscle spasm, dizziness, and loss of coordination⁽²⁶⁾. EPA established a Reference Concentration (RfC) of 5 mg/m³ based on neurologic effects in occupationally exposed workers (i.e., impaired color vision, impaired hearing, decreased performance in neurobehavioral analysis, changes in motor and sensory nerve conduction velocity, headache, dizziness) as the most sensitive endpoint.

Neurotoxicity: Based on occupational studies, long term inhalation exposure to toluene can cause adverse effects to the nervous system such as reductions in thinking, memory, and muscular abilities, as well as some losses in hearing and color vision. Permanent toxicity to the brain can occur from inhalation exposures to high levels of toluene⁽²⁶⁾.

Two studies showed neurological effects and color vision impairment from toluene inhalation in occupational workers at the lowest observed adverse effect level (LOAEL) of 97ppm and 40ppm, respectively. Other studies have shown LOAELs to cause neurological effects at exposure levels as low as 42 ppm and as high as 132 ppm⁽²⁷⁾.

Reproductive Effects: There is current disagreement on whether or not toluene is a reproductive toxin. Some studies in people have shown reproductive effects such as an increased risk of spontaneous abortion from exposure to toluene in the workplace. Toluene is also known to cross the placenta and to be excreted in breast milk of lactating mothers. In some animal studies, toluene has been shown to be fetotoxic, but not teratogenic⁽¹¹⁾. Toluene is listed as a developmental toxic in the proposition 65 list.

Biomarkers and BEIs: Toluene in blood (Toluene-B), toluene in urine (Toluene-U) and o-Cresol (o-C) in urine are all used as biomarkers for toluene exposure. BEIs for Toluene-B, Toluene-U and o-C are 0.02 mg/L, 0.03 mg/L and 0.3 mg/g creatinine, respectively⁽²⁴⁾. Toluene-B should is

sampled prior to last shift of workweek. Toluene-U and O-Cresol are both sampled at the end of shift.

Reference Concentration (RfC): 5 mg/m³ based on neurologic effects in occupationally exposed workers (i.e., impaired color vision, impaired hearing, decreased performance in neurobehavioral analysis, changes in motor and sensory nerve conduction velocity, headache, dizziness) as the most sensitive endpoint ⁽²⁷⁾.

LOAEL and NOAEL: One study showed to find a LOAEL of 300 ppm and a NOAEL of 30 ppm after exposing male and female CD-1 mice and Sprague-Dawley rats to 0, 1, 10, 30 or 300 ppm of benzene, 6 hours/day, 5 days/week for 91 days and measuring various hematological endpoints ⁽²⁷⁾. Other animal studies have reported significant hematological effects at benzene exposures of 10-25 ppm. Another study reported a LOAEL of 7.6 ppm after a significant reduction of absolute lymphocyte count (ALC) in a group of 11 workers after exposed to a median 8-hour TWA of 7.6 ppm of benzene ⁽²⁷⁾.

1.C. Ethylbenzene

Lethal Concentration (LC50): Acute inhalation lethal concentration (LC50) for rats is calculated as 13,367 ppm at a 2-hour exposure and 4,000 ppm at a 4-hour exposure. Studies in rabbits indicate that ethylbenzene is irritating to the skin and eyes ⁽³⁰⁾.

Short term effects or acute effects: Systemic health effects from inhalation exposure of ethylbenzene can cause general weakness, nausea, headaches, dizziness, disorientation, and unconsciousness. Acute inhalation exposure to high concentrations can cause upper respiratory irritation, than can lead to asphyxia, muscular weakness, coma and untimely death from respiratory failure. In other instances, chronic exposure to elevated concentrations of ethylbenzene can cause damage to the liver ⁽³¹⁾.

Respiratory effects: In a study, male volunteers were exposed to 2,000 ppm of ethylbenzene for a 6-minute inhalation period and all reported throat and nasal irritation and feelings of “chest

constriction” during the exposure. In other studies, humans acutely exposed to air concentrations of ethylbenzene ranging from 2,000 to 5,000 ppm for 6 minutes reported symptoms of dizziness followed by vertigo⁽³²⁾.

Neurotoxicity: A study showed that workers exposed, to a mean exposure level of 1.8 ppm for a mean of 13 years, to solvent mixtures that include ethylbenzene showed a 58% incidence of hearing loss compared to the reference group⁽³²⁾.

Ocular effects: observed in humans and animals after inhalation exposure are assumed to be due to exposure of the mucous membranes of the eye to ethylbenzene vapor. Volunteers reported eye irritation and burning, and profuse lacrimation, which gradually decreased with continued exposure to 1,000 ppm for 1–6 minutes⁽³²⁾. Upon entering the chamber with an ethylbenzene concentration of 2,000 or 5,000 ppm, the volunteers also experienced severe eye irritation. Eye irritation in humans after exposure to ethylbenzene vapor was observed at 10,000 ppm⁽³²⁾.

Biomarkers and BEIs: Biomarkers for ethylbenzene exposure are the sum of mandelic acid and phenylglyoxylic acid in urine. The BEIs guideline has mandelic acid and phenylglyoxylic acid together in urine at 0.15 g/g creatinine and sampled at the end of shift at the end of workweek⁽²⁴⁾.

Reference Concentration (RfC): 1.0 mg/m³ based on inhalation exposures in animal studies (rats and rabbits) in which developmental toxicity was found in maternal organs (liver, lungs, kidney, heart, spleen, adrenals, ovaries, and brain)⁽²⁸⁾.

LOAEL: One study showed developmental effects in rabbits from ethylbenzene inhalation in at the lowest observed adverse effect level (LOAEL) of 100 ppm⁽²⁸⁾

1.D. Xylene

Lethal Concentration (LC50): Xylene isomers: Acute inhalation lethal concentration (LC50) for rats ranges from 6,350 ppm to 6,700 ppm for 4-hour exposures. *P*-xylene: LC50 in rats is 4,740

ppm for a 4-hour exposure. *M*-, *O*-, and *P*-xylene: LC50 for a 4-hour exposure in mice are 5,267, 4,595, and 3,907 ppm, respectively. *P*-xylene may be slightly more toxic than the other xylene isomers. According to the toxicity classification system these values indicate that mixed xylene and its isomers are slightly toxic by acute inhalation. Mice appear to be more sensitive than rats to the lethal effects of the *m*- and *o*-isomers of xylene⁽³³⁾.

Short term effects or acute effects: Xylene vapor is heavier than air and thus may cause asphyxiation in enclosed, poorly ventilated, or low-lying areas. Acute exposure (<14 days) to xylene can cause irritation to the respiratory tract⁽³⁴⁾. Irritation of the nose and throat can occur at approximately 200 ppm after 3–5 min. At 200 ppm, xylene can also irritate the lungs leading to chest pain. No studies have found that chronic exposures to low-levels of xylene have any long-term effects on the lung. In an occupational study, it was observed that at very high vapor levels (unspecified concentration) of exposure workers experienced symptoms of nausea, vomiting and gastric discomfort⁽³³⁾.

Neurotoxicity: Exposures to xylene can cause depression to the central nervous system (CNS). Such symptoms of CNS depression include dizziness, ataxia, drowsiness, excitement, tremor, and coma. At exposures of 100-200 ppm symptoms of nausea and vomiting can occur; at concentrations of 200-500 ppm symptoms of dizziness, general weakness, irritability, vomiting, slowed reaction time; at exposures of 800-10,000 ppm symptoms of dizziness, confusion, clumsiness, slurred speech, loss of balance, ringing in the ears; and concentrations of >10,000 ppm sleepiness, loss of consciousness, and death can occur⁽³⁵⁾.

Biomarkers and BEIs: The biomarkers for xylenes exposure are methylhippuric acids in urine. The BEI is 1.5 g/g creatinine measured at the end of shift. Measurement of blood levels of xylene is limited by the rapid metabolism of xylene. Detection of methylhippuric acids as biomarkers in the urine is only valid soon after exposures⁽²⁴⁾.

Reference Concentration (RfC): Xylene (all isomers) of 0.1 mg/m³ based on inhalation exposures in rat studies in which impaired motor coordination (decreased rotarod performance) was observed⁽²⁹⁾.

LOAEL: Two studies showed impaired motor coordination (decreased rotarod performance from xylene exposure in a rat study at the lowest observed adverse effect level (LOAEL) of 50 ppm. Another study reported an LOAEL of 100 ppm in an inhalation rat study to significantly decreased rotarod performance and decreased spontaneous activity ⁽²⁹⁾.

1.2.2.4. Fate in the Environment

BTEX is normally found in petroleum products such as gasoline and diesel and has been found after spills and leaks in the environment such as in air, water and soil. At gas stations, BTEX can be introduced into the environment via motor vehicle exhaust, from the evaporation of spilled gasoline and from leaking underground storage tanks (LUSTs). USTs tend to leak over time with age of the tank. Prior to 2003, USTs were not mandated to today's regulations of the double wall system ⁽³⁶⁾. Today, many old, damaged, rusty and poorly maintained tanks pose a potential environmental threat. In fact, in 2010, over 491,000 leaking underground storage tanks (LUSTs) were confirmed ⁽³⁷⁾. Under the new Senate Bill 445 (SB 445) (Stats. 2014, Ch 547), effective September 25, 2014, The State Water Boards has notified all single wall tank owners of the mandatory permanent closure for all single wall tanks by December 31, 2025. This law is covered under the Health and Safety Code, chapter 6.7, Section 25292.05. Despite guidelines to prevent releases from USTs and innovations in leak detection methods, leaks, spills, and overfills still occur which may lead to environmental contamination.

The main concern of LUSTs, according to The State Water Resources Control Board (SWRCB), is the contamination of groundwater. Because gasoline is more volatile than diesel, infiltration through soil is greater for diesel spills and evaporation is greater for gasoline spills. As a result, diesel has a higher potential for soil contamination and gasoline has a greater potential to evaporate into the atmosphere. The evaporated gasoline can eventually makes its way into the ambient air as it makes its way through soil sediments and crack openings in the cement linings covering UST tanks ⁽³⁸⁾. LUSTs are required to be monitored ⁽³⁸⁾ by conducting water, soil and air monitoring ^{(40) (36)}.

Leaks can originate from the piping systems or from the tank itself. Until the mid-1980s, most USTs were made of bare steel that corroded over time and allowed to leak into the environment ⁽⁴⁰⁾. The average life expectancy for a steel tank is 30 to 50 years ⁽⁴¹⁾. Also, faulty installation or inadequate operating and maintenance procedures also can cause USTs to release gasoline into the environment. In piping, most of the leaks occur at the connection joints and additional connections added to the piping or modifications and alterations done to the system that affects the integrity of the UST.

BTEX does not react in the air with other compounds after being released and thus can remain stable in the environment. Because benzene and toluene have a long half-lives air concentrations can increase in ambient air ⁽⁵⁶⁾. Overtime, BTEX will degrade in the atmosphere by reactions with hydroxyl radicals with half-lives of 13, 2, 2.3days and 16-28 hrs, respectively⁽⁴²⁾. At much lower degradation rates, BTEX can also be degraded by ozone molecules and nitrate radicals present in the atmosphere (half-lives of 56 days and 65-183 days for ethylbenzene and xylenes)⁽⁴²⁾. Also, because toluene, ethylbenzene, and xylenes do not absorb light at wavelengths >290 nm, these compounds are not susceptible to photolysis by sunlight ⁽⁴²⁾. Benzene has a half-life of 16.9 days for a photolysis reaction at 253 nm ⁽⁴²⁾. In addition, because BTEX compounds are relatively water soluble, rain can remove benzene from the atmosphere ⁽⁴²⁾.

1.2.2.5. BTEX Guidelines and Regulations

The American Conference of Governmental Industrial Hygienists (ACGIH) has set Threshold Limit Values (TLVs) for an 8hr TWA of 0.5, 20, 20 and 100 ppm for BTEX, respectively, where each xylene isomer has the same guideline. ACGIH has also set TLVs for Short-Term Exposure Limits (STELs) of 2.5ppm for benzene and 100ppm for xylene (all isomers). NIOSH has also set RELs for IDLH, TWA and STEL conditions. For IDLH conditions, NIOSH has set RELs of 500, 800, 500 and 900 ppm for BTEX, respectively. For 8-hr TWA conditions, RELs have been set

at 0.1, 100, 100, and 100ppm for BTEX, respectively. Short Term Exposures Limits have been set at 1, 125, 150, and 150 ppm for BTEX, respectively. The California Occupational Safety and Health Administration have set regulations for Permissible Exposure Limits and for Short-Term Exposure Limits. PELs are set at 1, 5, 10, and 100ppm for BTEX, respectively. STELs are set at 5, 30, 150, and 150 ppm for BTEX, respectively. No current guidelines and regulations are available for total VOC concentrations

Table 1. Occupational Guidelines and Regulations for BTEX

<u>Chemical Name</u>	Exposure Limits in Air (PPM)							
	ACGIH TLV		Cal/OSHA			NIOSH REL		
	TWA	STEL	PEL	Ceiling	STEL	IDLH	TWA	STEL
Benzene	0.5 (Skin)	2.5 (Skin)	1	NE	5	500	0.1	1
Ethylbenzene	20	NE	5	22	30	800	100	125
Toluene	20	NE	10	500	150	500	100	150
Xylene (All isomers)	100	150	100	300	150	900	100	150

NE=Not Established

EPAs National emission standard for equipment leaks (fugitive emission sources) of benzene prohibit detectable benzene emissions from processing equipment (e.g., pumps, valves) that contains materials which have a benzene concentrations of 10% or more by weight ⁽⁴²⁾.

Under CERCLA for hazardous chemical spills, all individuals in charge of vessels or facilities are required to notify the National Response Center (NRC) immediately, when there is a release of this designated hazardous substance, in an amount equal to or greater than its reportable quantity of 10 lbs. or 4.54 kg for benzene, 1000 lbs. or 454 kg for toluene and ethylbenzene, and 100 lbs. or 45.4 kg for xylene ⁽⁴²⁾.

1.2.3 Underground Storage Tanks

An underground storage tank (UST) refers to a tank and any underground piping connected to it that has at least 10% of its combined volume underground⁽⁴⁰⁾. USTs are used to store petroleum products and other hazardous substances. USTs are mainly found at gasoline stations and other types of filling stations. Nationwide, there are approximately 561,000 UST's⁽¹⁾. In the Los Angeles basin, there are approximately 3,140 retail gas stations, all containing USTs⁽⁴³⁾. During use, the petroleum product is mechanically pumped out of the tank. USTs are made up many mechanical components and complex piping systems. Tanks can be made of steel, fiberglass reinforced plastic (FRP), or composite (FRP-clad steel). Piping can be made of steel or FRP and can be under pressurized or suction systems⁽⁴⁴⁾.

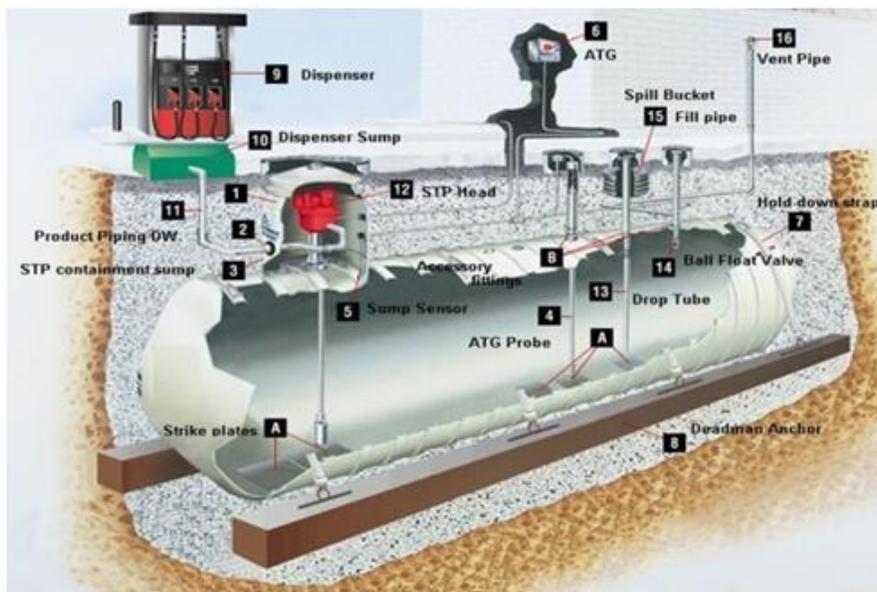


Figure 3. A Schematic Diagram of a UST System with Components: (10) Dispenser sump; (9) gasoline dispenser; (1) Turbine containment sump; (12) Turbine; (15) Spill bucket sump and filling port; (11) Product piping; (13) Drop tube. (EPA, 2016)

Above the tanks there are normally two sumps-or manholes -that house the main filling station (Fig. 4) and the turbine. Turbine sumps are designed to provide access to the turbine area

above the tank. The turbine area may house the submersible turbine pump head, piping, line leak detectors, interstitial monitoring devices, wiring, and other equipment ⁽⁴⁴⁾. Sumps may or may not be contained. Fill port sumps house and provide access to the filling port where the delivery driver connects the product and/or vapor recovery hoses to the tank. Contained sumps have sides and a bottom, are designed to be liquid tight, and may have a special cover designed to keep out water.

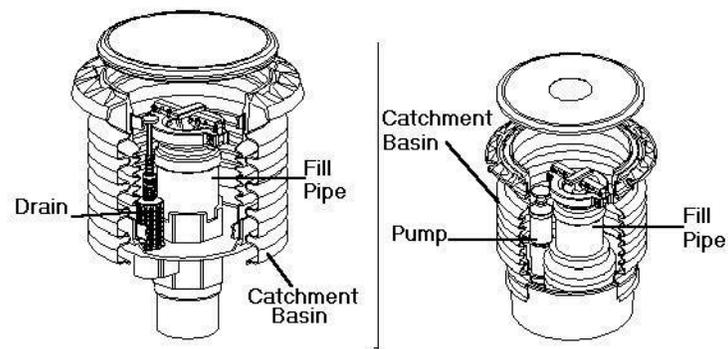


Figure 4. Fill sumps and Fill Pipe.

Depending on the UST design, some manholes or sumps may range from 3 feet to 10 feet deep below ground. Because of environmental regulations, USTs have been mandated to have secondary containment and spill preventive measures ⁽³⁷⁾. Filling ports are mandated to be contained by the installation of spill buckets that encapsulate the filling port and thus prevent any spilled products from reaching soils ⁽⁴⁵⁾. USTs are also now required to be double tank walled to provide additional spill prevention. Piping also is required to be double walled, or flexible double-walled for containment purposes ^{(45) (37)}.

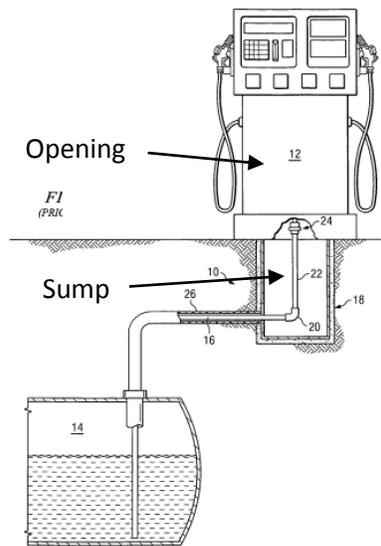


Figure 5. Gas Dispenser and Dispenser Sump.

At gas stations, USTs are connected to the gasoline dispensers through underground piping (Fig. 5). At the dispenser, there is a sump located underneath the dispenser. The sump houses piping connections and sensors and thus it is designed to provide access to piping, flex connectors, shear valves, and other equipment located beneath the dispenser⁽⁴⁴⁾. It also functions as a containment system to contain any spilled gasoline from the piping connections.

1.2.3.1 .UST Guidelines and Regulations.

USTs in California are regulated under the Underground Storage of Hazardous Substances California Health & Safety Code, Division 20, Chapter 6.7, section 25288(a) and under Chapter 6.11 of the Unified Hazardous Waste and Hazardous Material Management Regulatory Program, Section 25404. Local agencies involved are the State Water Resources Control Board, Certified Unified Program Agencies (CUPA), and the Air Quality Management District (AQMD). California's Health and Safety Codes provide guidance for regulatory bodies and business to comply with current regulations.

UST Regulations are provided under California Code of Regulations (CCR), Title 23, Division 3, Chapter 16; and Tank Tester Licensing Regulations are found under CCR, Title 23, Division 3, Chapter 17. Regulations on storage of combustible materials are found under the Liquids Code of the Code of Federal Regulations, Title 49, Chapter 1, Part 192.701-192.755, Subpart M-Maintenance. Unified Program Regulations are under CCR, Title 27, Division 1, Subdivision 4, Chapter 1, Sections 15100 – 15620. Local regulatory agencies have amended authority and jurisdiction under Code of Federal Regulations (CFR), Title 40, Part 280; California Health & Safety Code, Division 20, Chapter 6.7 & 6.75; California Code of Regulations, Title 23, Chapters 16 & 18; and under the Los Angeles Municipal Code (for the City of Los Angeles), Article 7 of Chapter V, Section 120, 5003, & 2301.

Senate Bill No. 989 (SB 989) requires all UST owners to conduct testing of secondary spill containment every three years. Complete versions of the laws that govern underground storage tanks (USTs) are available in CFR, Title 42, Chapter 82, Subchapter IX. Guidelines to reduce the hazards associated with the storage, handling, and use of flammable and combustible liquids are found in the National Fire Protection Agency 30 (NFPA 30). The International Code of Council's (ICC) also provides guidelines for Fuel Oil Piping and Storage of USTs under Chapter 13, Sec. 1300-1305 General.

1.2.4 Inspection Process

UST inspections assess the level of compliance within the regulated facilities, in order to eliminate economic incentives to violate and to ensure public safety and the protection of the natural environment. The role of the inspector (regulator) is to determine and ensure compliance by persons, businesses, and all facilities and entities. All USTs and ASTs are subjected to regulation under the California Code of Regulations, title 27, section 15110, and SWRCB Local Guidance 159 (LG 159) (see Sec. 1.2.3.1). This gives inspectors authority and jurisdiction over tanks within their designated jurisdiction. Parties involved in the inspection process are the contractors that perform the testing, the regulated business and the regulatory agency doing the inspections. They can be onsite during maintenance of the tanks, the installation and removal of new equipment and tanks or during the testing of the spill prevention equipment. In general, inspectors are required to be on site during such procedures for compliance purposes, and without the approval of an inspector a UST could not be certified and thus must be placed out of service.

For this study, exposures were assessed during a three year testing process of the spill prevention equipment (SB 989) and during an annual monitoring certification process (see 1.2.3.1.). During these testing processes spill prevention equipment were tested for performance and integrity. Inspections are normally conducted in the morning and latest in the afternoons. Usually the inspector arrives before the contractors. This step is important because it is crucial that the inspector arrives before and inspects the equipment before any testing procedures take place to verify that no equipment has been tampered with and corrected before the inspector's arrival. The turbine, fill and dispenser sumps are the main areas inspected (see Fig. 3-5). During the annual monitoring certification process required by The Health and Safety Code 6.7, Title 23, the automatic line leak detector (LLD) is tested for performance and accuracy. The purpose of the line leak detector is to detect leaks from any portion of the tank or its piping that routinely contains gasoline or diesel and to record it in the monitoring panel normally located in an adjacent building(see Fig. 6) ⁽⁵³⁾. Inspectors inspect the LLD and other secondary containments and equipment.

The inspection process normally begins with the contractors removing the sump lids upon the arrival of the inspector. The inspector then proceeds to stand directly over the sumps to inspect. Inspectors verify that sensors are placed correctly, look for any leaks or water intrusion, examine the integrity of the spill buckets, look for any open electrical circuitry, and verify if the LLD is electronic or mechanical. Inspectors continue the same process for every UST sump. Every UST contains 2 sumps and each site can have 1-4 USTs. After inspecting the UST sumps, the inspector then proceeds to inspect the dispenser sumps. For these sumps, inspectors also verify that the sensors are placed correctly, look for any leaks or water intrusion, any open electrical circuitry, make sure that the dispensers are bolted correctly to the ground, no smoking stickers are correctly placed on the dispensers and examine the integrity of the sumps. Any faulty equipment found during the process is required to be replaced immediately or be placed out-of-service.

Once the sumps have been inspected, the inspector then reviews the alarm history of any past detected leaks recorded in the monitoring panel (see Fig 6). The inspector also reviews the company's log book for any documented leaks recorded by employees and to make sure that the leaks recorded by the employees match the leaks recorded by the monitoring panel. After reviewing all records, inspectors then return back to the testing process and perform any final inspections, provide any final signatures, and answer any final questions. Inspectors normally do not stay on site for the whole testing process that could take 3-4 hours, unless the business has a history of repeated violations or of illegally tampering with equipment then the inspector might stay throughout the whole testing process to monitor the process and to assure the business is not performing any illegal procedures. Normally, an inspection process can last 1-2 hours, depending on the inspector. Inspector can also complete 2-3 sites per day for 3 days a week, up to 5 days a week on a busy month.



Figure 6. Monitoring Panel for UST Automatic Line Leak Detector.

Senate Bill 989 (SB 989) testing is a mandatory testing procedure of the secondary containment spill prevention equipment done every three years. During this process all leak detecting sensors or float and chains (found in older USTs) are tested and sumps and spill buckets are filled with water and tested by very sensitive equipment to detect any small leaks. This process is called *spill bucket testing* and it is done by using very sensitive sensors that can sense any change in liquid volume. The spill buckets are filled with water and sensors are placed inside the bucket submerged in the water. The sensors will then detect and record any small spills up to a rate of 0.1 gallons per hour for single wall tanks. In this process inspectors spend limited time to no time inspecting equipment, as the purpose of these inspections is to monitor the testing process done by the contractors. Most of the exposures mainly happen during the monitoring certification process. UST sites can be temporarily placed out of service if any leaks are detected in any secondary containment equipment.

UST inspectors can also be involved in hazmat inspections. Many of the UST sites also generate and store hazardous materials so they are also required to be regulated as a hazmat site. Hazmat inspections are normally scheduled the same day of the monitoring certification but could also be scheduled at different times during busy months. During the inspection process, inspectors review emergency business plans, and review the business hazmat inventory.

1.2.4.1 . Evaluation of Work Practices and Exposures

Most of the exposures originate from the direct inspections of USTs and dispenser sumps. During this process, inspectors are required to inspect the sumps directly for compliance purposes (see Sec. 1.2.4). For UST sumps, inspectors stand directly in front and above the sumps. In investigative situations, inspectors have to kneel down to floor level and look directly above the sump to have a better visual examination or to take photographs of the inside of the sump. For the dispenser sumps, inspectors also inspect the sumps but need to get closer. Because of the relatively small opening, the size of the sump (smaller than UST sumps), the vertical opening (Figure 5), this process requires inspectors to protrude their head almost inside the sumps to see the inside. In general, such inspections cause the most exposure, especially after opening the sumps because of the buildup of vapors inside the sumps is released by diffusion. Inspectors do not wear personal protective equipment (PPE) during inspections nor are they provided with PPE.

Exposures can also vary between sites. Some sites can be well maintained and clean. At such sites, sumps will be free of any gasoline at the bottom of the sumps, grime, or gasoline odors. Other sites might not be well maintained or clean and inspectors will be exposed to liquids containing gasoline at the bottoms of the sumps, grime all over the mechanical components, pipes also covered in grime, and potentially extremely strong gasoline odors. Inspection per site can vary between 30 min – 4 hrs. and inspectors can complete 2-3 sites per day at 3-4 days per week. At times, inspection periods might be extended because of technical issues with the UST system that require inspectors to be on site or during the installation of new equipment, repairs, or decommissioning.

Other exposures include those to hazardous materials (HAZMAT) during hazmat inspections at facilities. Every business in California that generates, stores, recycles, or treats hazardous waste of any kind or handles hazardous materials at threshold quantities set by the agency is required under the state law to be inspected. Inspectors additionally are required to inspect business also for hazmat. During that time, exposures can vary based on the kind of

business being inspected, types of chemicals that are used, and their quantities. The number of facilities inspected also range from 2-3 per day and take 1-2 hrs. per site. In this process, exposures vary on the amount of time that inspectors are exposed to chemicals, the quantity of chemicals stored at the facility, the size of the facility, or the amount of time spend inside a business office meeting with business operators and reviewing paper work. It was shared by an inspector that one inspector had to be hospitalized due to a severe exposure to hazardous materials during an inspection that led to respiratory distress. It is important to understand that most inspectors are exposed to multiple hazardous substances and not only are they exposed during UST inspections but also during inspections of non-UST areas.

All inspectors are International Code Council (ICC) certified. The ICC certification program provides training related to standards and codes to contractors and various types of safety industry professionals who work with USTs ⁽⁴⁶⁾. Also, all inspectors receive training at first hire. Training consists of learning the inspections process, regulations, and understanding the different UST systems and devices. No training is provided on health and safety. It is important to note that in some departments inspectors are sworn-in firefighters and so most of them have prior background training in health and safety from that avenue. Work practices do vary per inspector.

1.2.5 Previous Literature on UST Emission of BTEX

Much attention has been given to gasoline infiltration to groundwater. Little attention has been given to the release of toxic vapors from the USTs and no research is available for the health hazards involved in the inspection process of USTs. Starting in 2018, all employers will be required to conduct monthly walk through as set forward by the EPA⁽⁴⁷⁾. This can potentially result in more frequent exposures. Studies have covered research areas related to emissions of toxic fumes from USTs during the filling process of gasoline, removal process of USTs, and for leaking USTs. The Air and Waste Management Association published a journal titled, *Emissions from Underground Gasoline Storage Tanks*⁽⁴⁸⁾. The emission of gasoline vapors from an underground storage tank during the filling process was reported. A test design was developed to apply the most recent technology and knowledge on emissions from USTs. The study was divided into a two phase process. In the first phase, researchers obtained background information on tank breathing (inhaling of air and exhaling of a vapor-air mixture through the vent pipe during normal pumping operations) and filling losses from USTs without vapor control equipment. Because the filling method might result in vapor emissions, phase two was then performed to obtain comparative information on emissions when using splash filling or submerged filling and for tanks equipped with control valves and vapor return system.

For every 1000 gallons of gasoline delivered, for gas filling there was a loss of gasoline vapors 73 ft³, 11.5 lbs., or 0.19 %wt. For submerged filling, there was a loss of gasoline vapors of 46 ft³, 7.3lbs., or 0.12 %wt. The submerged filling procedure reduced vapor loss by approximately 37%. In normal filling operations, vent pipes (external ventilation pipe that extend from inside the UST out to the atmosphere, which help to draw in air or allows air to escape during displacement of gasoline) are left open to help relieve pressure inside the tanks as gasoline occupies the head space inside. In combination with a vapor recovery system, it was found that when the vent line was left open during the filling process, 5 ft³, 0.8 lbs., or 0.013 %wt. of gasoline vapor was lost. When the vent line is closed, 100% of vapors are recovered. Overall, the study showed that having a vapor recovery system can significantly reduce vapor losses.

Having the vent lines opened in combination with a vapor recovery system reduced vapor losses by 93% and 100% for closed vent lines.

In a different study, *Benzene Exposure Assessment of Underground Storage Tank Contractors*, an exposure assessment was conducted to measure benzene and total hydrocarbons during a UST removal ⁽⁴⁹⁾. Sampling was done on laborers and the observer. The removal process required the contractors to enter the tanks and clean the interior of the tank. Other tasks included cutting the tanks, tank testing, and transferring gasoline from the UST to a tank truck. It was found that during the removal process (cutting and cleaning) exposures to the observer were 0.12 to 0.43 ppm at sampling times ranging from 4.75 to 6.5 hours. Benzene exposure to the contractors were 0.43 to 3.84 ppm at sampling times ranging from 1.5 to 6 hours. The highest short-term benzene exposure was 9.14 ppm (15 minutes) for during cleaning. Benzene concentrations during the cutting process ranged from 2.16 to 4.57 ppm for a sampling range of .5 to 3 hours. Benzene exposure during a tank testing process was 0.23 ppm for a sampling time of 4.75 minutes. Total mean ratio of benzene to total hydrocarbons concentrations was 0.028.

Hilpert et al., *Hydrocarbon Release During Fuel Storage and Transfer at Gas Stations: Environmental and Health Effects*, examined the behavior characteristics of gasoline and diesel fuel during soil penetration from leaking underground storage tanks (LUST) ⁽⁵⁰⁾. In a laboratory experiment, fuel droplets were spilled into small concrete samples. Evaporation was greater for gasoline, while infiltration was greater for diesel spills. This is because gasoline is more volatile than diesel and diesel had a higher potential for soil contamination because of the higher infiltrated mass. In LUSTs, spilled fuel must first penetrate relatively impermeable pavement underneath. Released fuel may also evaporate within the soil, and a portion of it can also move downward as a vapor.

1.2.6 Occupational Incidents Related to USTs

According to a Cal/OSHA report, a UST contractor died of asphyxia in El Monte, California while working inside a toxic vapor-filled sump. The body of the worker was found inside a fill sump that measured 36 inches by six feet deep in diameter. It was later discovered that the worker had been working inside the sump without any protection and thus asphyxiated after inhaling gasoline vapors. The employer was cited for failing to conduct or provide (1) a written permit-required confined space program; (2) a hazard evaluation; (3) adequate training; and (4) protective equipment or clothing ⁽⁵⁴⁾.

In another incident, a UST worker was severely injured by a vapor explosion from an underground gasoline tank in Troy, Missouri. The worker was conducting some maintenance on a 6,000 gallon tank when the heat from the workers halogen work light ignited the gasoline vapors inside the tank causing the explosion. The workers sustained severe burns to multiple areas of his body and sustained a head injury. The worker did survive the incident and was rushed to Mercy Hospital St. Louis in Creve Coeur. The incident was later investigated by OSHA and the Troy Fire Department ⁽⁵⁵⁾.

2.0 EXPERIMENTAL:

2.1 Rationale

2.1.1. Selection of UST Locations:

USTs can be found in public gas stations or private filling stations. Public gasoline stations usually distribute more gasoline than any other filling stations, especially gasoline stations located in busy streets or highly populated cities. Privately own station may distribute less gasoline per day when compared to public stations. More distribution of gasoline can result in more wear and tear on the gasoline distribution system (piping, turbines, sensors, spill sumps, etc.) that can eventually lead to leakages and releases of gasoline vapors. For this reason, busy gasoline stations tend to be less maintained and clean. When inspecting some of the busiest gas stations, inspectors find gasoline at the bottom of the sumps, grime as a mixture of gasoline and dirt, and strong gasoline smell. Often, some equipment needs to be replaced. Private filling stations in most cases are better maintained.

UST sites that were scheduled for an SB 989 testing and monitoring certification (see Sec. 1.2.4 and 1.2.3.1) were randomly selected to be assessed for this study. Inspectors have authority to inspect both private and public sites and thus during the assessment both types of sites were assessed. All sites were filling sites for transportation, to be distinguished from back generators USTs. All sites also contained diesel and unleaded gasoline USTs. Verbal consent for assessment was given upon entry of inspection. All sampling and assessments were completed with the assistance of the local regulatory agency.

2.1.2 Selection of Gasoline Vapor Analytes

Air BTEX was chosen as the gasoline parameter to be assessed in this study because of the known toxic effects of these components to human health and to the environment (see Sec. 1.2.2.3. & 1.2.2.4.) and because they are ubiquitous VOCs from gasoline products regulated under EPA and OSHA. Benzene, toluene and xylene (3 isomers) are all in the List of Hazardous

Air Pollutants under the Clean Air Act (CAA), Section 112(b). Benzene is covered under the National Emission Standards for Hazardous Air Pollutants (NESHAP) and classified under the list of hazardous air pollutants (HAP), or “air toxics” which includes specific compounds that are known or suspected to cause cancer or other serious health effects. Under RCRA, benzene and toluene are listed in the Hazardous Constituents List under Title 40 CFR Part 261, Appendix VIII. Also, under the Clean Water Act, benzene, toluene and ethylbenzene are listed in the Toxic Pollutant List and Priority Pollutant List 40 CFR 401.15. Section 307 (a) (1); 33 U.S.C. 1317(a) (1). Lastly, for BTEX fugitive emissions under the USEPA Atmospheric Standards, all newly constructed, modified, and reconstructed Synthetic Organic Chemical Manufacturing Industry (SOCMI) process units are required to use the best demonstrated system of continuous emission reduction for equipment leaks of VOCs, considering costs, non-air quality health and environmental impacts and energy requirements. For occupational exposures, benzene, toluene and xylenes (isomers) are regulated under the Occupational Safety and Health Administration (OSHA) Air Contaminants Limits list. Occupational exposure guidelines and regulations are provided in Section 1.2.2.5. (Guidelines and Regulations).

2.2 Sampling Equipment

For the detection of total VOCs a photoionization detector (PID) the ppbRAE 7240 was selected. The PID showed whether high VOC in air concentrations were present. For the detection of BTEX, a portable BTEX Gas Chromatography (GC-PID) PetroPRO, by Photovac was used to measure the concentration levels of BTEX in air grab samples. The portable GC allowed screening for BTEX since it may have detected other chemicals too. For integrated personal sampling, an SKC pump (model 210-1002) was used. Solid sorbent tubes (coconut shell charcoal) of size 100 mg/50 mg by SKC were used for collection of BTEX along with Tygon tubing. All pumps were calibrated with a miniBuck calibrator. A Kanomax Climomaster (Model A533) was used to measure atmospheric flow rate, temperature and relative humidity.

2.3 Methods

A total of 8 different gas stations were examined. This project was divided into four phases and was conducted from January to April 2017. The first phase was the laboratory standardization of the equipment before and after field visits (see Sec. 2.3.2.). The first field phase was a pilot study to assess if high levels of VOCs were present at the sites. Having the data from the pilot assessment provided direction for the sites chosen for the detailed exposure assessment. For field phases two and three, two separate sites for each phase were assessed for a total of four sites. BTEX levels were measured 2.5-3 feet directly above open sumps and 1 foot or less in front of the dispenser sumps. All tanks contained different grades of unleaded gasoline. Pilot screening of total VOCs was conducted with the calibrated ppbRAE 7240. For the detailed field assessment, the calibrated PetroPRO was used to measure BTEX. For the personal sampling phase, integrated personal sampling in the breathing zone was done to capture the time-weighted average exposure. This was done with a solid sorbent charcoal tube attached to a sampling pump, following NIOSH Method 1501. Four sites were assessed for the personal sampling phase. All sampled data for this study was collected from gasoline public stations and private stations in West Los Angeles, CA and in San Fernando, CA. Sites contained both unleaded gasoline and diesel. Both, gasoline and diesel sumps were inspected, as well as the dispenser sumps. For the primary and secondary assessment, only USTs and dispenser sumps containing gasoline were sampled. For personal sampling, both diesel and unleaded gasoline were captured during the sampling for sampling times of 60-99 minutes.

2.3.1 Field Procedures

2.3.1.1. Preliminary Field Assessment

Two different sites were assessed during a one day period during the month of January 2017. The first site contained 4 USTs (3 gasoline & 1 diesel fuel) and the second site contained 2 unleaded gasoline tanks. The PID was used as the direct reading devices. Each site was separately assessed and individual readings were collected from two USTs and two dispenser sumps for a sampling time of one minute each. Each sump was re-sampled over a 23-30 minute time interval. Samples were taken 2.5-3 ft. above the sump. The time spent at each site was approximately one hour. All gas station operations were temporarily stopped during the inspection.

2.3.1.2. Secondary Field Assessment

For the secondary assessment, two separate gasoline stations were assessed from January to February 2017. The PetroPro was used as the direct reading device. Samples were collected approximately 2.5-3 feet above the tank to simulate the distance to a tank during the inspection process. A total of six samples were collected for site 3 and four samples for site 4. Each sump was re-sampled after 23-32 minute intervals to assess concentrations over time and sampling times are provided in Table 19. All gas station operations were temporarily stopped and closed to the public during the inspection. Site 3 contained one diesel fuel and two gasoline USTs. Site 4 contained two gasoline USTs.

2.3.1.3. Personal Sampling

A total of four sites were assessed over a two day period, completing two sites per day during the month of April 2017. Personal sampling was not done on inspectors but instead was done on the observer who shadowed the inspector. The observer followed the inspector throughout the process and performed the same task to simulate the inspector's task and exposure. A

sampling pump and absorbent charcoal tube was used as the sampling equipment. Sampling pump was set at 0.2 L/min following NIOSH Method 1501 for BTEX and calibrated using a mini-BUCK calibrator (model: m-30) (see Table 2). Sampling conditions are provided in Table 27. Sampling was done at four different gas stations in San Fernando Valley, CA. All gas station operations were temporarily stopped and closed to the public during the inspection. Both, UST and dispenser sumps were assessed.

Table 2. Calibration of Pumps Before and After Sampling

	1/19/2017				2/01/2017			
	Site 5		Site 6		Site 7		Site 8	
	Before (LPM)	After (LPM)						
1	0.198	0.194	0.201	0.198	0.202	0.196	0.997	0.189
2	0.195	0.193	0.203	0.196	0.198	0.208	0.995	0.191
3	0.202	0.192	0.199	0.192	0.201	0.198	0.996	0.194
Average	0.198	0.195	0.201	0.195	0.200	0.198	0.190	0.191
% Error	-1	-2.5	0.5	-2.5	0	-1	-5	-4.5

Sampling was done for 1.5 hours for site 5 and 1 hr. and 40 min for site 6. Sampling was not done for full length of inspection due to max volume restrictions for the sorbent tube (see limitations section). Site 5 was a private police station site and contained one diesel and one unleaded gasoline UST. Site 6 was a public gasoline station and contained two unleaded gasoline USTs and one diesel UST. Site 6 was located on a corner street between two busy intersections and site 5 was located inside a private property. Site 7 was a public gas station and only contained unleaded gasoline grade 87, 89 and 91. Sampling was done for 1 hr. Site 7 was located on a main road with heavy vehicle traffic. Site 8 was located in a private location at a packing delivery facility and contained one unleaded gasoline UST and one diesel fuel UST. No vehicle traffic was observed during sampling that might interfere with exposure results.

2.3.2 Laboratory Procedures

2.3.2.1. Calibration of Portable Devices

ppbRAE:

The ppbRAE was calibrated to manufacturer’s specifications using isobutylene at 10ppm (cylinder). As a secondary calibration method and for quality assurance, the ppbRAE was also calibrated by a four point calibration using four generated Tedlar gas bags of benzene at 0, 0.5, 1, and 1.5 ppm concentrations (see appendices for calculations and Figure 8). Benzene was chosen as the calibration gas due to it being found in gasoline and its low PEL of 1.0 ppm and TLV of 0.5 ppm.

A rotameter was used to measure flow rate of pure air and a mini-BUCK calibrator (model: m-30) was used to calibrate the flow rate (Table 3). Before sampling, the gas bags were filled and emptied with pure air three times to remove any previous residues. First, 4L of air was inserted into a 10 L Tedlar gas bag at 2.0 LPM for 2 minutes. Then, 3.2 µL of liquid benzene in a 10 µL syringe was injected into the gas bag. To accelerate the vaporization process and to evenly mix the benzene inside the bag, a blow-dryer was used to provide heat. After injecting the liquid benzene, another 4L of air was inserted into the bag to generate a gas bag of 100ppm of benzene after another blow dry treatment.

Table 3. Calibration of Flow Rate for Pure Air for 100 ppm Bag using a Mini-BUCK Calibrator.

Pure Air for 100ppm Bag (8 L)		
	First 4 liters	Second 4 liters
Mini-Buck Calibrator M30 (LPM)	2.064	2.160
	2.035	1.847
	2.074	2.043
	2.063	1.914
	1.994	2.015
	1.987	1.990
Average LPM=	2.036	1.994
SD	0.038	0.099
% Error=	1.8	-0.3

A volume of 80 μL of benzene vapor was extracted from the 100ppm bag and injected with a 100 μL gas tight syringe into 8L of air in another 10 L Tedlar gas bag to generate 1.0ppm of benzene vapor. Similarly, 40 μL of benzene vapor created 0.5ppm concentration, 8.0 μL produced 0.1 ppm, and 120 μL generated 1.5ppm. The volumes of benzene injected into the bags were negligible. Table 4 displays the flow rates of pure air inserted into the diluted 8L gas bags to generate the 0.5, 1.0 and 1.5ppm concentrated benzene in air.

Table 4. Flow Rates of Pure Air Inserted Into 8 L Diluted Benzene Bag Using a Mini-BUCK.

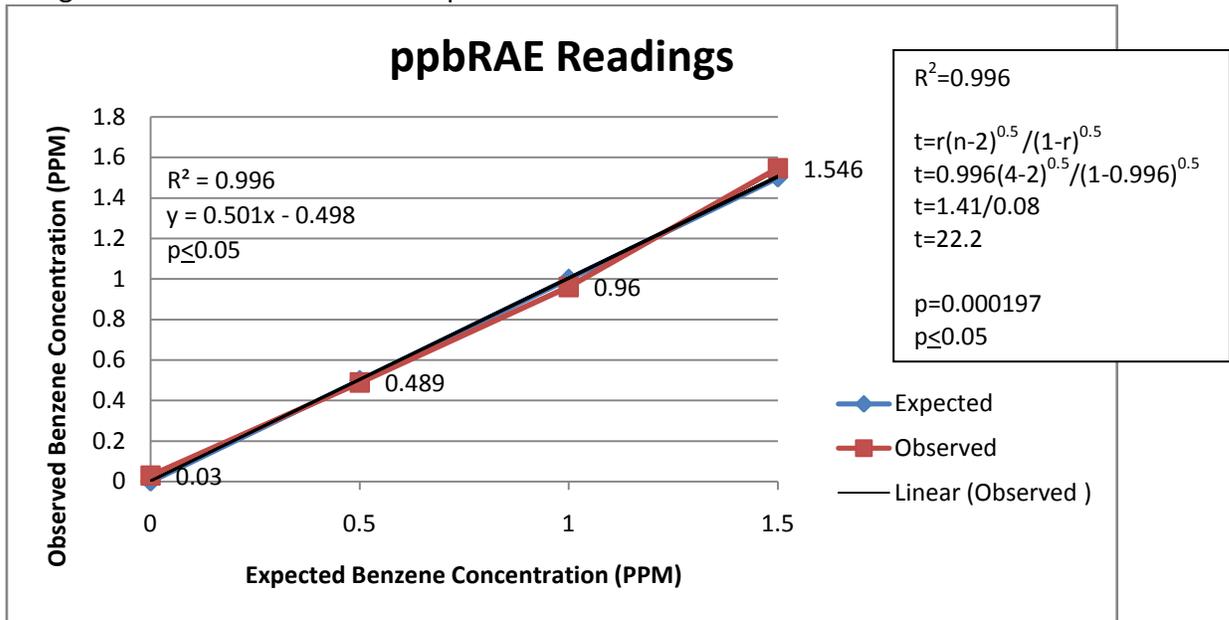
Gas Bag Concentration	Pure Air (LPM)						Average (LPM)	% Error	SD
0.5ppm	1.985	2.103	1.980	1.968	1.965	1.968	1.994	-0.3	0.054
1.0ppm	2.017	1.982	1.999	2.045	2.003	1.996	2.007	0.35	0.022
1.5ppm	1.978	2.137	1.904	2.046	1.906	1.408	1.885	-5.75	0.25

For the calibration process, the ppbRAE was directly connected to the benzene 0.5, 1.0 and 1.5 ppm Tedlar gas bags using a butt-to-butt joint of tygon tubing. The ppbRAE was allowed to stabilize to a constant reading then the direct measurements of benzene were recorded. For consistency, every reading was recorded at a 5 second interval for three readings for each concentration. Observed benzene concentrations in ppm were plotted as a linear regression versus the expected benzene concentrations in ppm. The increased concentration shown in the Figure 7 at 1.5ppm can be explained by the -5.75 percent error on Table 4. A negative percent error means less air was inserted than the expected volume and thus less volume of air inside the bag resulted in a slight increase in concentration as shown in the graph at the 1.5 ppm reading. Calibration data are presented below:

Table 5. Calibration Data for ppbRAE

ppbRAE						
Gas Bag Concentrations (Expected) (ppm)	Direct Readings (Observed) (ppm)			Average (ppm)	% Error	SD
0	0.031	0.030	0.032	0.030	----	0.001
0.5	0.519	0.520	0.518	0.519	3.80	0.001
1.0	0.988	0.990	0.992	0.990	-1.00	0.002
1.5	1.592	1.565	1.572	1.576	5.06	0.014

Figure 7. Calibration Data for Expected Concentrations vs. Observed Concentrations



All percent errors were below NIOSH's $\pm 25\%$ maximum error and below the desired $\pm 10\%$ error. Standard deviations are presented in Table 5. Observed benzene concentrations in ppm were

plotted as a linear regression versus the expected benzene concentrations in ppm. R^2 for the regression line was 0.996, with a p-value of 0.000197 which is ≤ 0.05 .

Portable GC:

The portable GC was first calibrated to the manufacturer's specifications by using a gas cylinder containing concentrations of: benzene at 0.534 ppm, ethylbenzene at 1.67 ppm, toluene at 0.843 ppm and *m*-xylene at 1.76 ppm. As a secondary calibration method and for quality assurance, the PetroPRO was also calibrated by a four point calibration method using four generated Tedlar gas bags containing benzene, toluene, ethylbenzene and *m*-xylene at 0, 0.5, 1.0, and 1.5 ppm concentrations, respectively (see appendices for calculations and Table 8). Because the portable GC measures *m*-xylene from all isomers, *m*-xylene was used for calibration in this study. The same laboratory procedures from the ppbRAE were used to generate the gas bags for the PetroPro, so the procedures and the data tables will be presented only. For each bag an amount of the compound was injected using the appropriate syringe volume into a 10LTedlar gas bag to generate 8L of 100ppm concentrations. Each bag was then used to generate a diluted second 8L gasbag. Table 6 displays the amount of the compound injected to generate a 100ppm of each concentrate to be diluted into 0.5, 1.0, and 1.5ppm concentrated gas bags.

Table 6. Amount of The Compound Injected to 100ppm Gas Bag of Each Concentrate

Compound	Benzene	Toluene	Ethylbenzene	<i>m</i>-Xylene
Injected(μL)	3.2	3.2	4	4

Calibration data is presented below:

Table 7. Calibration of Flow Rate for Pure Air for 100ppm 8 L Bag Using a Mini-BUCK Calibrator

Pure Air		
	First 4 liters	Second 4 liters
LPM	Benzene bag	
	2.054	2.098
	2.044	2.117
	2.088	2.055
Average LPM=	2.062	2.090
% Error=	3.1	4.5
SD	0.23	0.032
	Toluene bag	
LPM	1.996	1.967
	2.014	1.976
	1.922	2.074
Average LPM	1.977	2.005
% Error	-1.2	0.3
SD	0.049	0.060
	Ethylbenzene bag	
	2.034	2.075
	1.856	2.055
	2.171	2.032
Average LPM	2.020	2.054
% Error	1.000	2.700
SD	0.16	0.022
	m-Xylene bag	
LPM	2.073	1.904
	1.996	2.022
	1.978	1.980
Average LPM	2.015	1.968
% Error	0.750	-1.600
SD	0.050	0.060

Table 8. Flow Rates of Pure Air Inserted Into the Diluted 8L Gas Bag Using a Mini-BUCK.

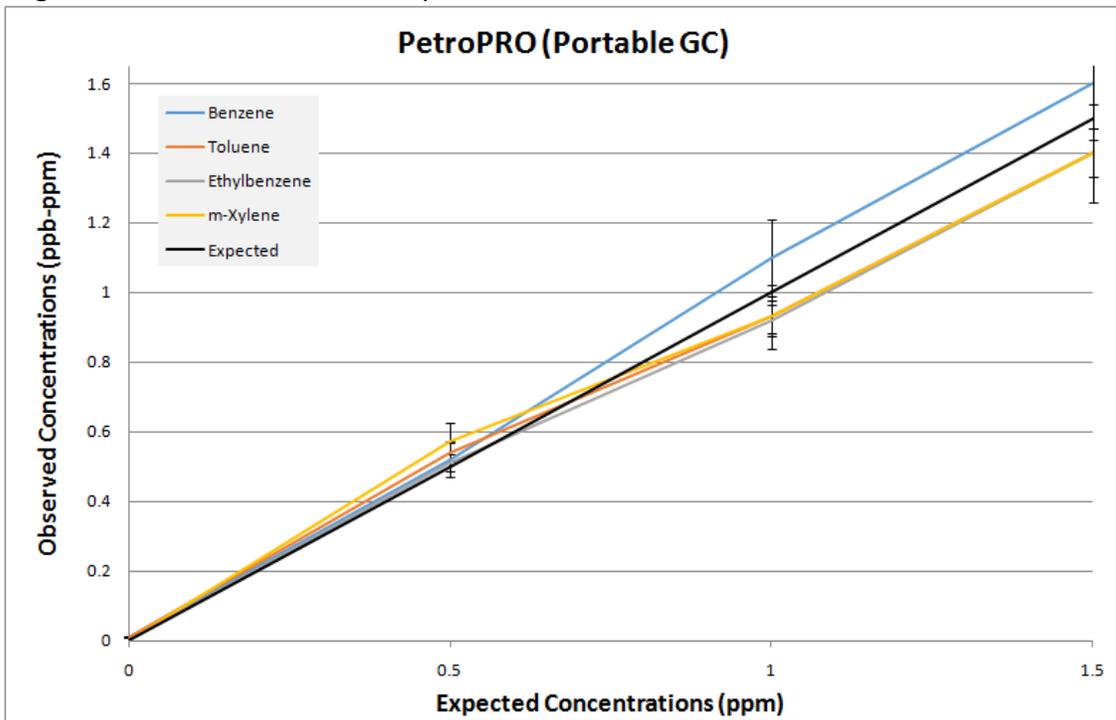
Gas Bag Concentration	Pure Air (LPM)						Average (LPM)	% Error	SD
	Benzene bag								
0.5ppm	1.992	1.967	1.964	1.969	1.982	1.986	1.976	-1.2	0.012
1.0ppm	1.997	2.004	2.046	1.998	1.983	2.016	2.007	0.35	0.022
1.5ppm	1.507	1.905	2.057	1.903	2.138	1.906	1.902	-4.9	0.22
	Toluene bag								
0.5ppm	2.012	2.077	2.053	2.077	2.074	2.097	2.065	-3.25	0.029
1.0ppm	2.967	1.902	1.923	2.088	2.072	1.995	2.157	7.85	0.40
1.5ppm	2.005	2.001	1.948	2.098	1.953	2.096	2.016	0.8	0.070
	Ethylbenzene bag								
0.5ppm	1.913	1.977	1.955	1.976	1.984	1.986	1.965	1.75	0.028
1.0ppm	2.076	2.003	2.022	1.988	2.972	2.086	2.191	9.55	0.38
1.5ppm	1.904	1.903	2.037	1.989	2.042	1.988	1.977	-1.15	0.061
	m-Xylene bag								
0.5ppm	1.982	1.977	1.954	1.979	1.972	1.996	1.976	-1.2	0.014
1.0ppm	1.987	2.103	2.022	1.988	1.993	2.005	2.016	0.8	0.044
1.5ppm	1.606	1.901	2.048	1.899	2.142	1.895	1.915	-4.25	0.18

Table 9. Calibration Data for PetroPRO

Portable GC-MS (PetroPRO)						
Benzene						
Gas Bag Concentrations (ppm)	Direct Readings (ppm)			Average (ppm)	% Error	SD
0	0.007	ND	0.007	0.007	----	0.001
0.5	0.40	0.52	0.61	0.52	4.00	0.001
1.0	1.1	1.2	1.1	1.10	10.00	0.002
1.5	1.70	1.40	1.60	1.60	6.66	0.014
Toluene						
0	0.02	ND	0.01	0.01	---	0.007
0.5	.54	.53	.55	0.54	8.00	0.005
1.0	.910	.931	.956	0.93	-7.00	0.023
1.5	1.30	1.70	1.30	1.4	-6.66	0.230
Ethylbenzene						
0	0.001	ND	0.002	0.001	---	.71x10 ⁻³
0.5	.51	.49	.52	0.51	2.00	0.015
1.0	.931	.915	.922	0.92	-8.00	0.008
1.5	1.20	1.40	1.70	1.4	-6.66	0.205
m-Xylene						
0	0	ND	0	0	---	0
0.5	.57	.54	.61	0.57	14.0	0.035
1.0	.927	.938	.934	0.93	-7.00	0.005
1.5	1.40	1.50	1.50	1.4	-6.66	0.057

ND=No Detection

Figure 8. Calibration Data for Expected Concentrations vs. Observed Concentrations



10% errors are shown as error bars.

Benzene: $Y = 0.535x - 0.533$ $R^2 = 0.999$ $p \leq 0.05$	Toluene: $y = 0.456x - 0.42$ $R^2 = 0.996$ $p \leq 0.05$
Ethylbenzene $y = 0.460x - 0.444$ $R^2 = 0.998$ $p \leq 0.05$	Xylene: $y = 0.456x - 0.415$ $R^2 = 0.992$ $p \leq 0.05$

All percent errors were below NIOSH's $\pm 25\%$ maximum error. The 0.1ppm benzene and 0.5ppm *m*-xylene gas bag were above the desired $\pm 10\%$ error at 10% and 14%. Standard deviations are presented in Table 9. Observed BTEX concentrations in ppm were plotted as a linear regression versus the expected BTEX concentrations in ppm in Figure 8. R^2 for the regression line were all at 0.99, with p-values of ≤ 0.05 .

2.3.2.2. GC-MS

Gas chromatography–mass spectrometry (GC-MS) was the analytical method used for the analysis of the personal samples. The gas chromatograph was an Agilent 6890 model, with a stationary phase moderately polar HP-5MS capillary column with dimensions of 60.0 m x 320 μm inner diameter x 1.00 μm film thickness. The mass spectrometer (MS) was an Agilent 5973 model. Following NIOSH analytical method 1501, a flow rate of 2.6 mL/min was set for the Helium carrier gas. Oven temperatures were set to an initial temperature of 40 °C 10 min, then increased to 140 °C at 7.50 °C/min, and then increased to 280 °C at 50.0 °C/min, and holding it for 5.80 minutes, for a total of 31.93 minutes. The link to the link to the mass spectrometer was at 280 °C. The 70 eV electron impact ion source was at 230 °C, and quadrupole temperature was 150 °C. The injector temperature was set at 250 °C.

Preparation of Samples:

Samples were prepared by removing the absorbent charcoal from inside the tube by breaking the ends of the tube and using a paperclip end to manually remove the filters and charcoal from inside. The charcoal was then placed into a 2.0 mL vial and adding 1.0 mL of carbon disulfide following NIOSH method 1501. The charcoal was allowed to sit in the carbon disulfide for approximately one hour with constant agitation for complete desorption of analytes.

Preparation of External Standards:

Calculations for external standards are provided in the appendices section. Following the calculated quantities provided in Table 10, four concentrates were first prepared to create a total volume of 1000 μL (1.0 mL) for each compound diluted with carbon disulfide. Following the quantities in Table 11, final standards were created by making up four cocktails containing all four compounds (BTEX) by adding the appropriate volumes of the concentrates to generate each standard to 1.0 mL total volume with carbon disulfide as in Table 11. This was continued

for each integer to make four total cocktails. Integers were chosen based on their OSHA's PELs. In addition, a 0.0 integer standard was prepared by using pure carbon disulfide. Aliquots 2.0 μL of each standard mixture and samples were injected to obtain integration areas of the appropriate peaks as identified by retention time of the component in carbon disulfide.

Table 10. Diluted Concentrations per Compound

Benzene				
Integer Value	μg	μL	Concentrate μL	$\text{CS}_2 \mu\text{L}$
2	76.8	0.0896	4.38=4.4	995.62
1	38.4	0.0438	4.38	995.62
0.5	19.2	0.0219	4.38	995.62
0.1	3.84	0.00438	4.38	995.62
0	0	0	0	1,000
Toluene				
2	909	1.04	5.2	994.8
1	452	0.52	5.2	994.8
0.5	226	0.26	5.2	994.8
0.1	45.2	0.052	5.2	994.8
0	0	0	0	1,000
Ethylbenzene				
2	522	0.60	3.0	997
1	261	0.30	3.0	997
0.5	130.5	0.15	3.0	997
0.1	26.1	0.030	3.0	997
0	0	0	0	1,000
Xylene (all isomers)				
2	10422	12.118	6.06	994
1	5211	6.059	6.06	994
0.5	2605.5	3.0295	6.06	994
0.1	260.55	0.30295	6.06	994
0	0	0	0	1,000

Table 11. Integer Values for External Standards

Integer Value	Benzene μL	Toluene μL	Ethylbenzene μL	Xylene μL	Total μL BTEX	μL of CS_2	Total Vol μL
2	20	200	200	12x3=36	456	544	1000
1	10	100	100	6x3=18	428	572	1000
0.5	5	50	50	3x3=9	114	886	1000
0.1	1.0	10.0	10.0	100x3=300 (diluted of 6 μL of 1.0 mL)	321	679	1000

Analysis:

Mass spectrometer auto tune and an air & water check were done prior to any injection to detect any air leaks or water inside the GC-MS. A volume of 2.0 μL of carbon disulfide in a 10 μL syringe was first injected to elute any contaminants left on the column. Carbon disulfide was injected until consistent peaks were observed, but at least 3 times. Only the front sections of the charcoal absorbent tubes were analyzed as no breakthrough was suspected due to low concentrations. 2.0 μL was injected per sample. Also, field blanks were not analyzed. The RTE Integrator was used to integrate mass chromatograms to find signal peaks. Because the corrected areas for total xylenes at integer 0.1 were higher than expected they were not used in the calibration data. Calibration linear regression data for each compound are provided in the following Figures 9-12 where the peak area was plotted against mass in μg in 1 mL.

Table 12. Corrected Areas for Each Compound Using RTE Integrator

		Corrected Areas			
Compound	Ret. Time (min)	0.1 / mass (µg)	0.5/mass (µg)	1/mass (µg)	2/mass (µg)
Benzene	23.673	36,116/3.84	258,376/19.2	578820/38.4	978,876/76.8
Toluene	16.923	593,212/45.2	2,314,168/226	5,509,602/454	8,013,510/904
Ethylbenzene	20.306	548,721/26.1	2,533,931/130.5	5,194,574/261	7,398,190/522
<i>M+P</i> -xylene	20.625	12,160,461	765,969	1,569,217	2,680,160
<i>O</i> -xylene	21.478	6,978,278	389,708	652,618	1,311,216
Total =Xylenes		19,138739/781.65 Not Included	1,155,677/7,816.5	2,221,835/15,633	3,999,376/31,266

Figure 9. GC-MS External Standard Curve for Benzene

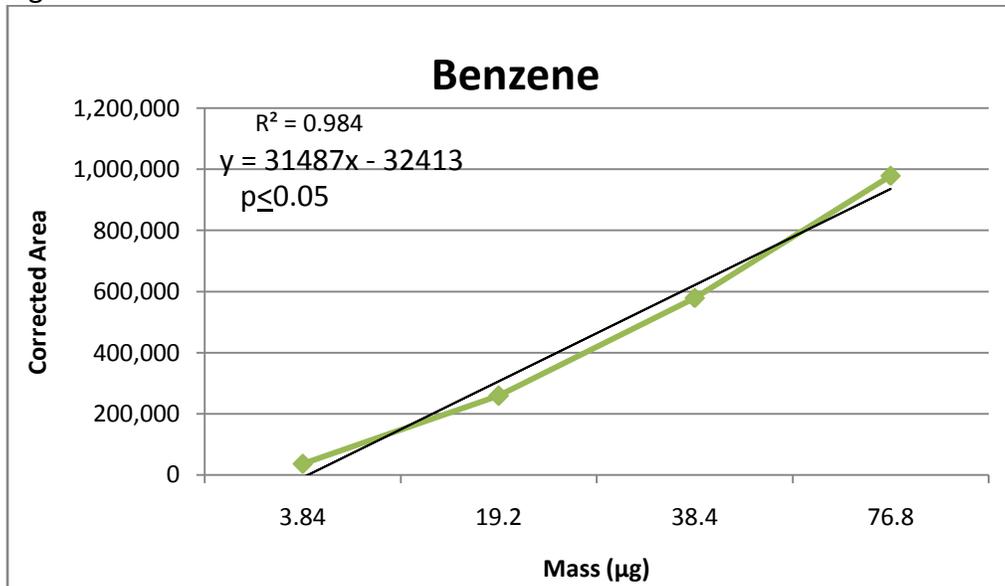


Figure 10. GC-MS External Standard Curve for Toluene

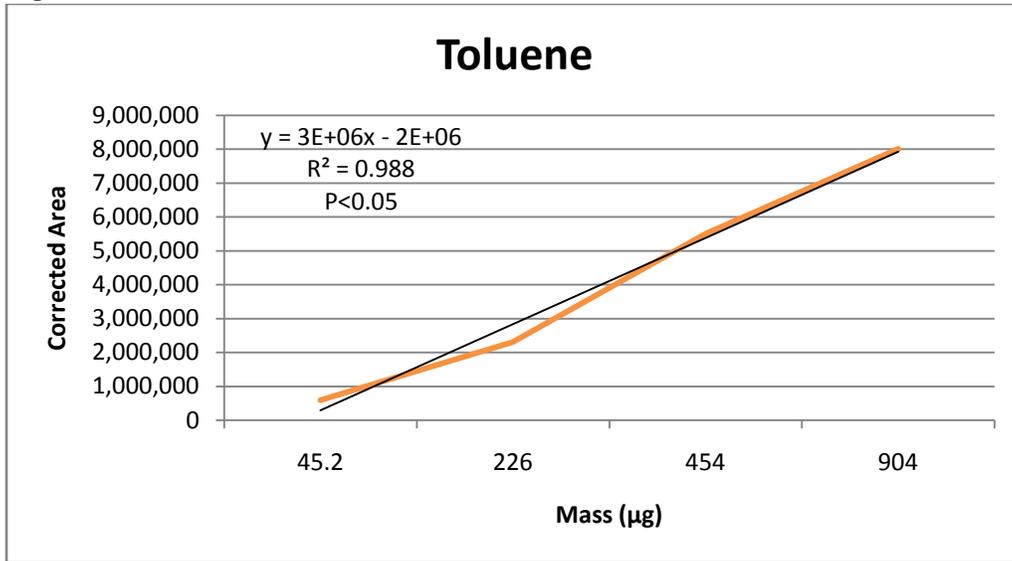


Figure 11. GC-MS External Standard Curve for Ethylbenzene

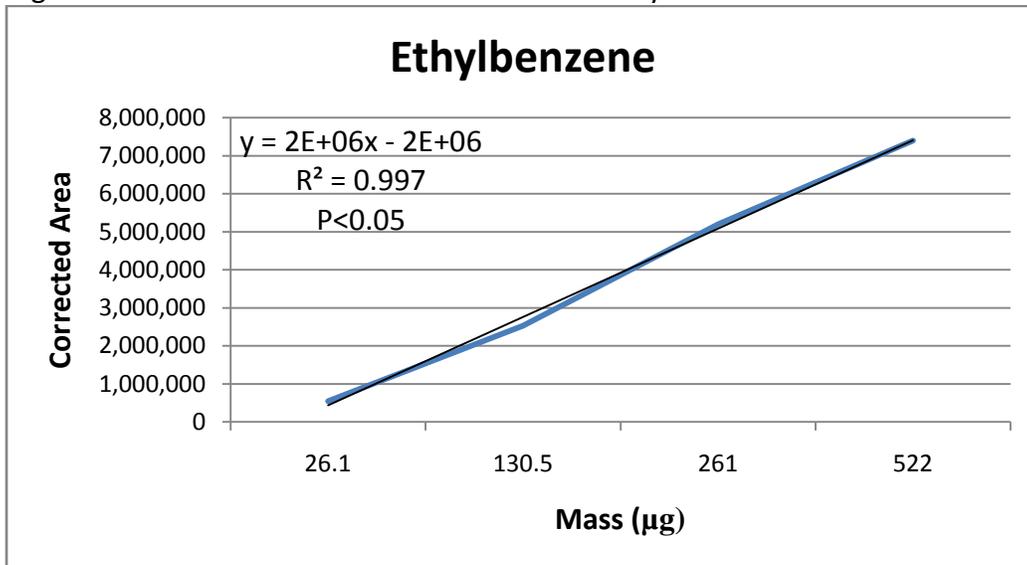
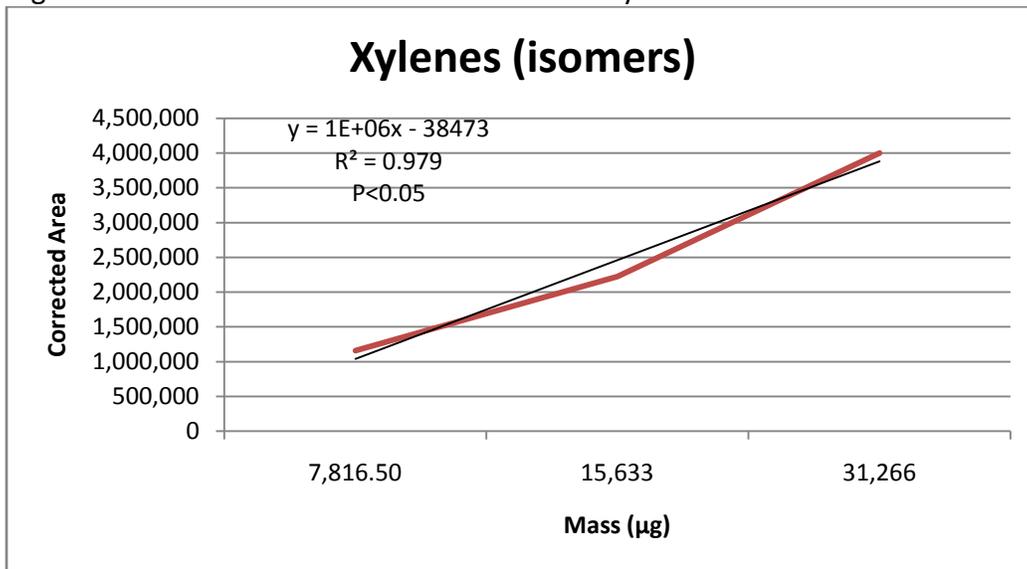


Figure 12. GC-MS External Standard Curve for Xylenes



The mass on the charcoal tube section was found by interpolation on the appropriate regression equation. The mass was then divided by the volume of the corresponding air sample and the concentration converted to ppb at the conditions of sampling using the relation below:

$$c (\mu\text{g}/\text{m}^3) = (M/V_m) \cdot c (\text{ppb}) \quad (\text{Eq. 5.0})$$

Where M is the molecular weight and V_m is the Ideal Gas molar volume in L at the temperature (Kelvin) and pressure conditions of sampling. The R^2 for the linear regressions were approximately 1 for all curves, with p-values of ≤ 0.05 . Below are the chromatograms for the external standards (0.1, 0.5, 1.0, and 2.0), carbon disulfide and the personal samples in Figures 13-21.

Figure 13. Selective Ion Monitoring Chromatogram for Carbon Disulfide

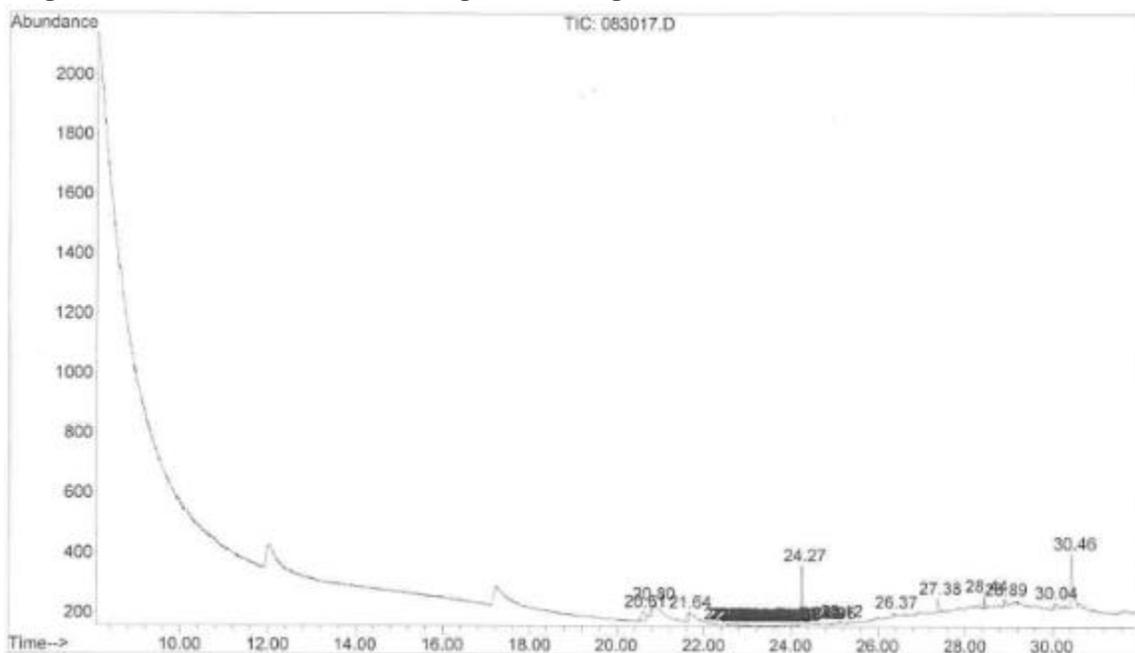


Figure 14. Selective Ion Monitoring Chromatogram for Integer 0.1 BTEX

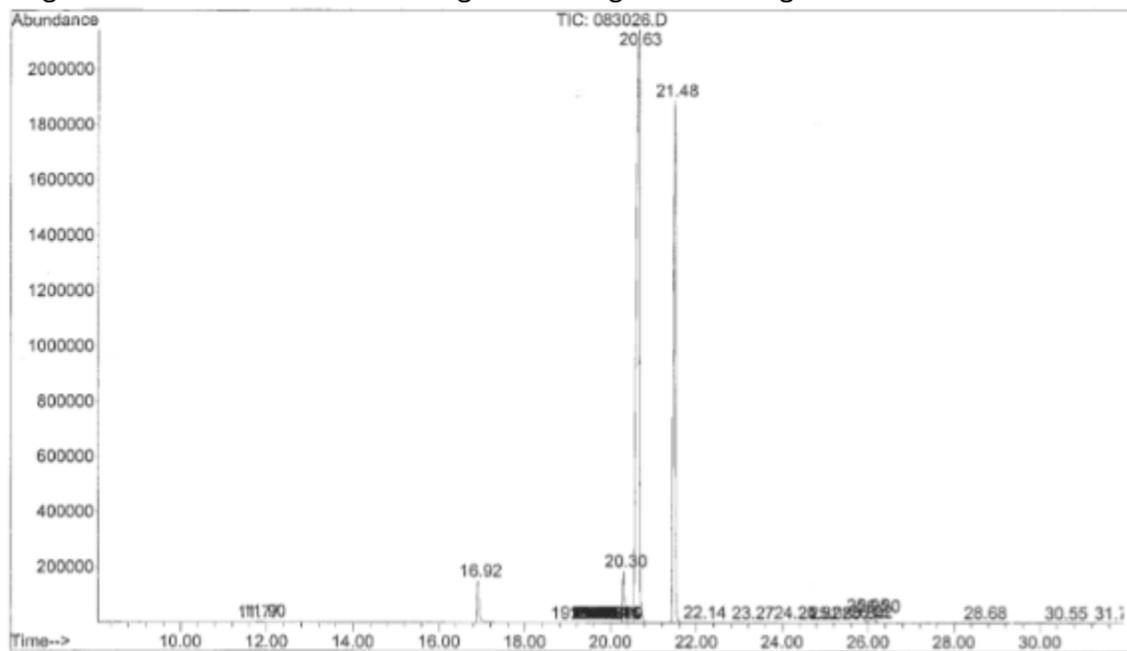


Figure 15. Selective Ion Monitoring Chromatogram for Integer 0.5 BTEX

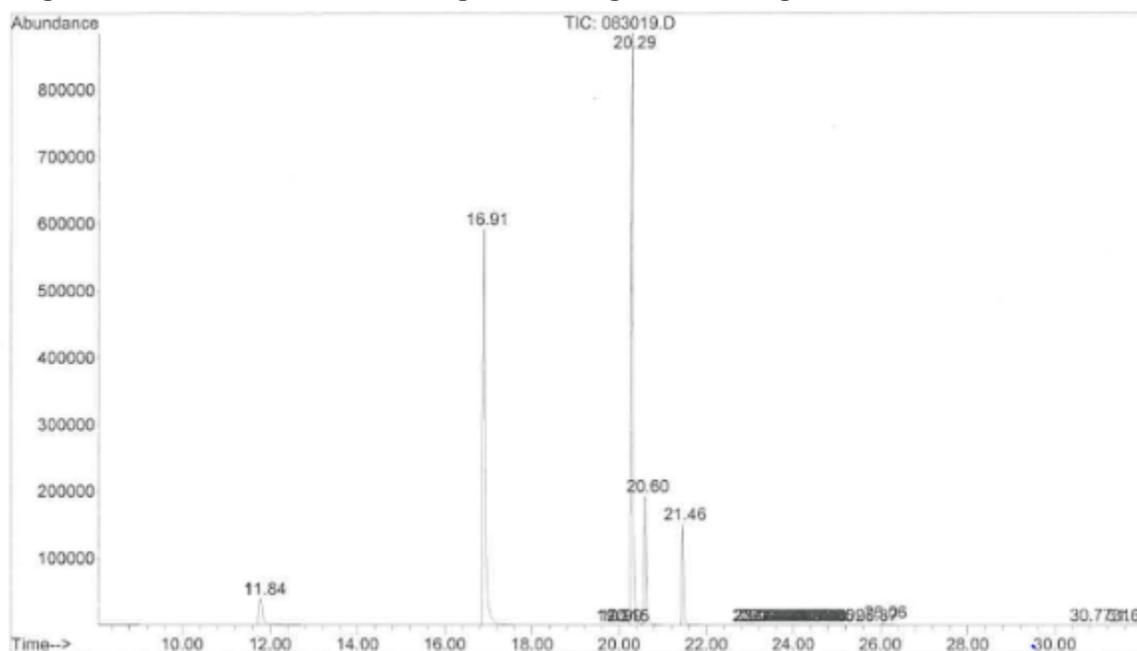


Figure 16. Selective Ion Monitoring Chromatogram for Integer 1.0 BTEX

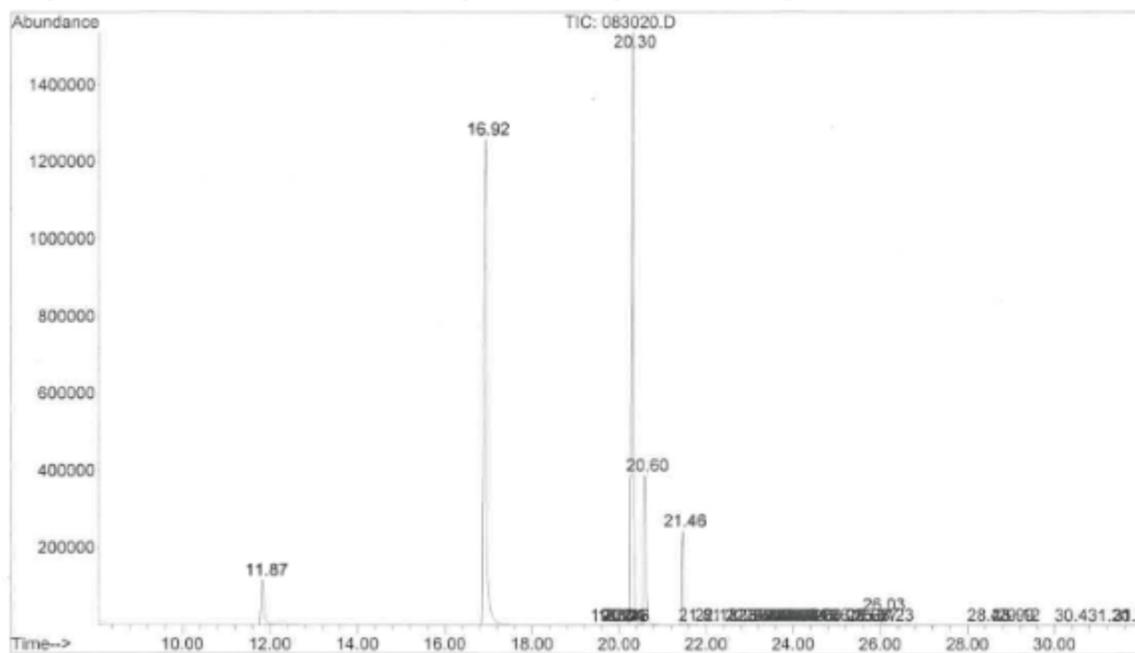


Figure 17. Selective Ion Monitoring Chromatogram for Integer 2.0 BTEX

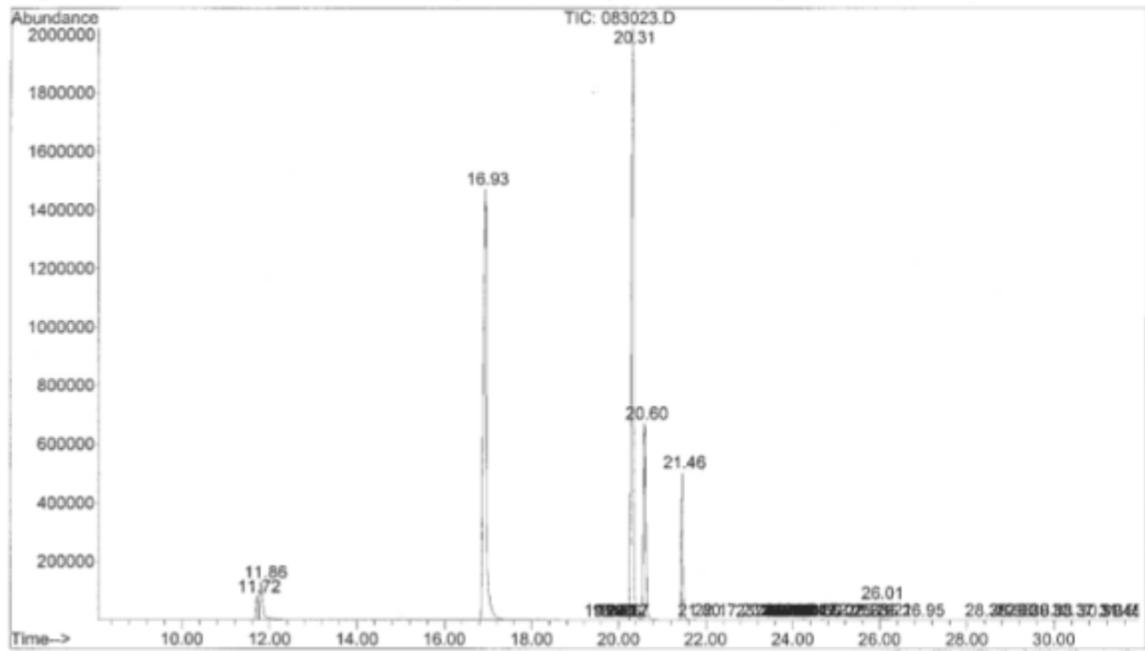


Figure 18. Selective Ion Monitoring Chromatogram for Sample 1A Front

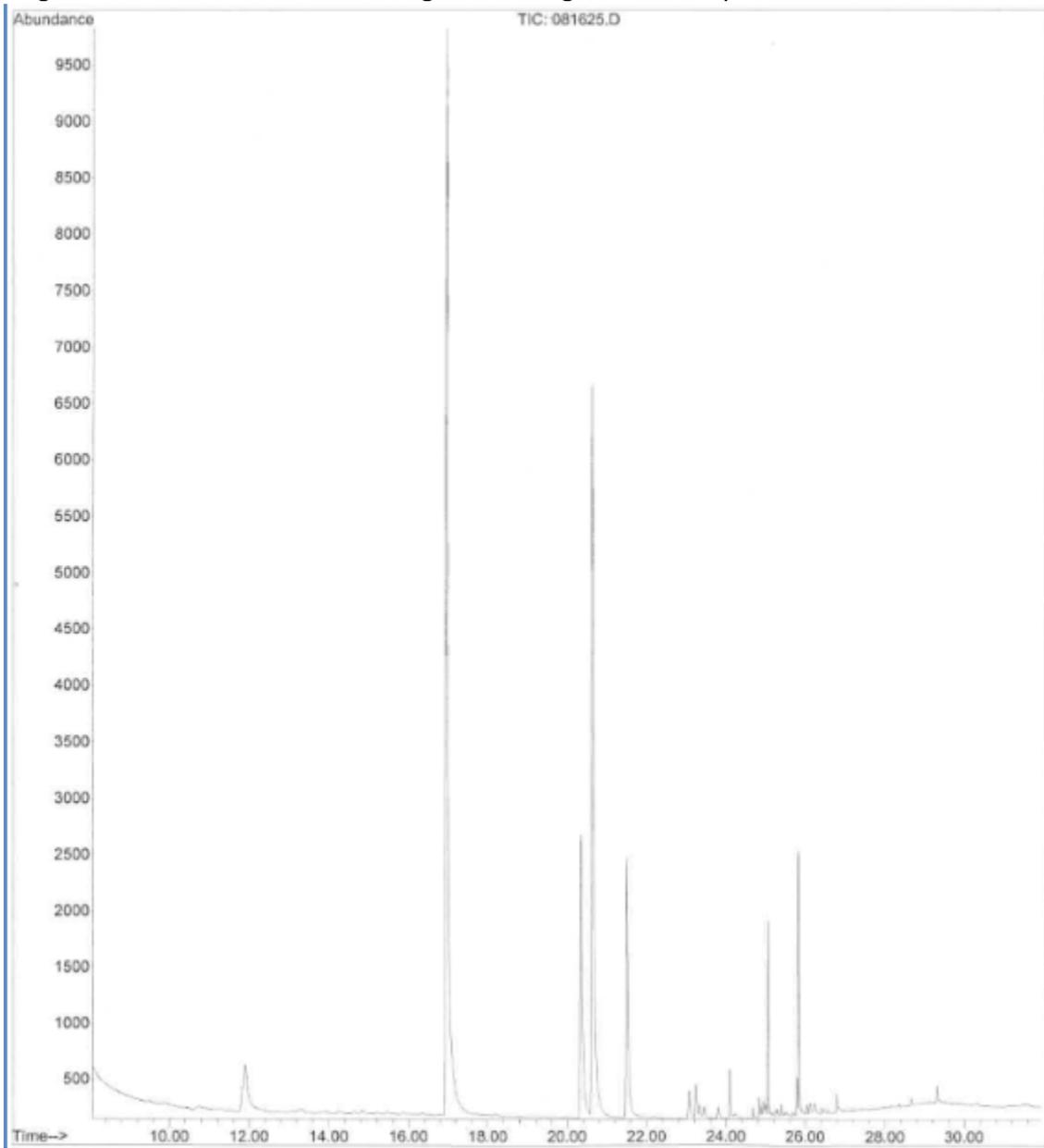


Figure 19. Selective Ion Monitoring Chromatogram for Sample 2A Front

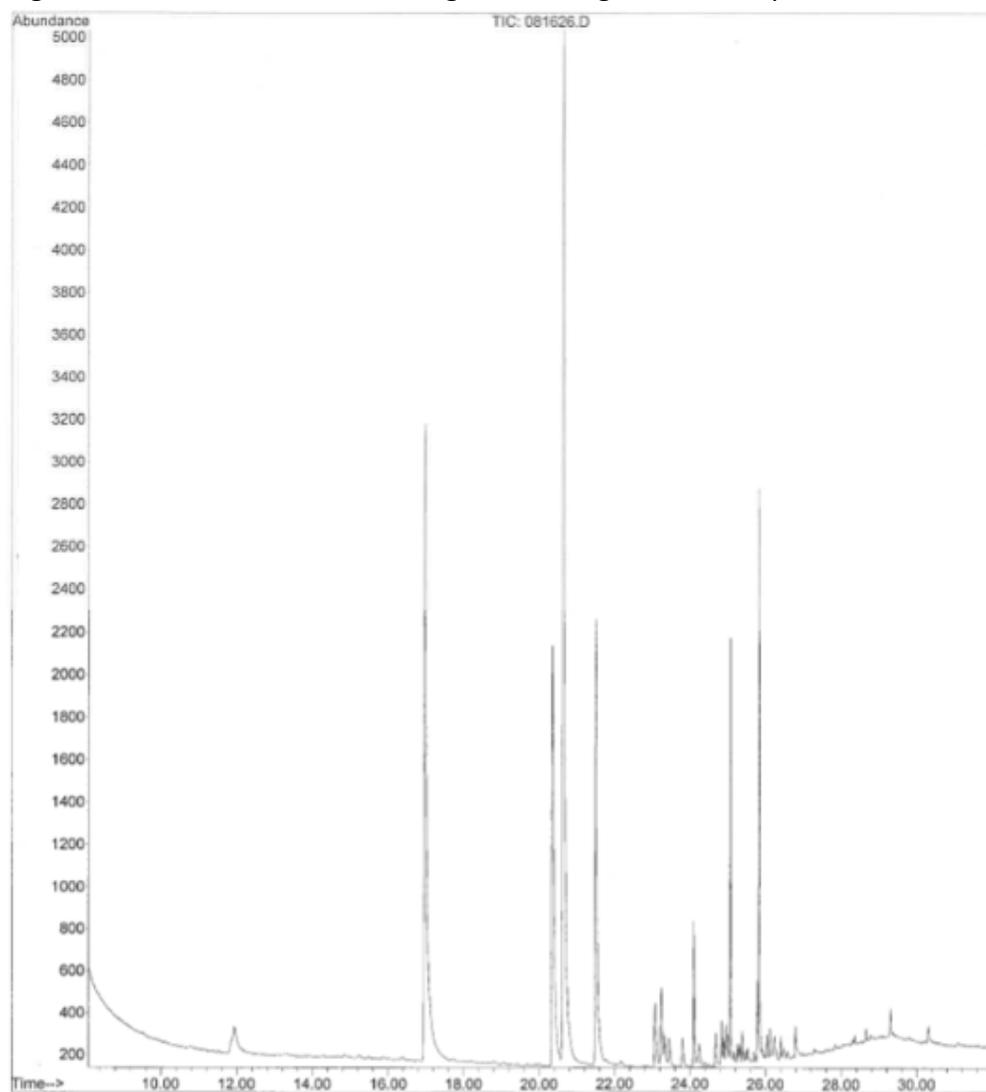


Figure 20. Selective Ion Monitoring Chromatogram for Sample 1B Front.

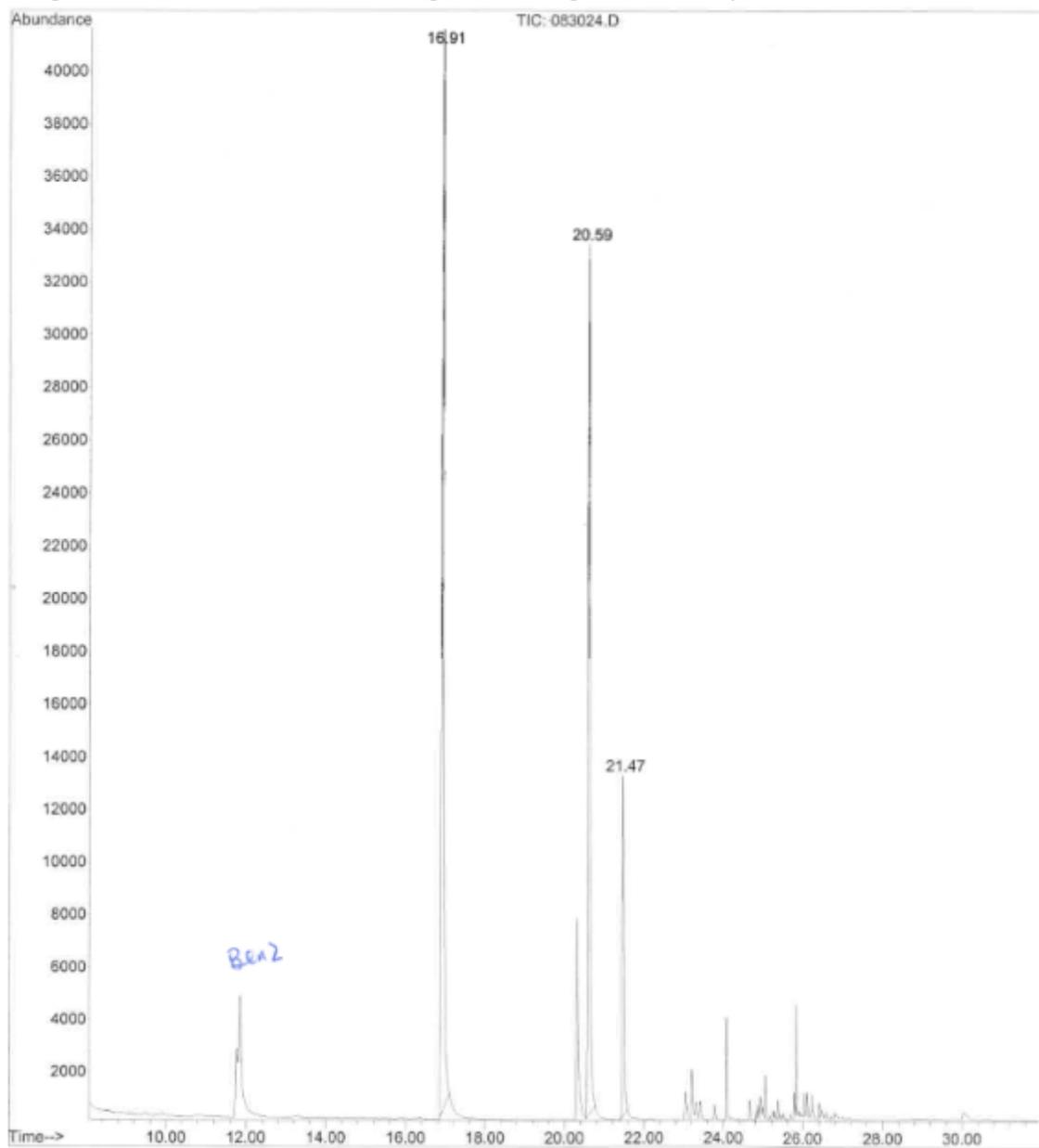
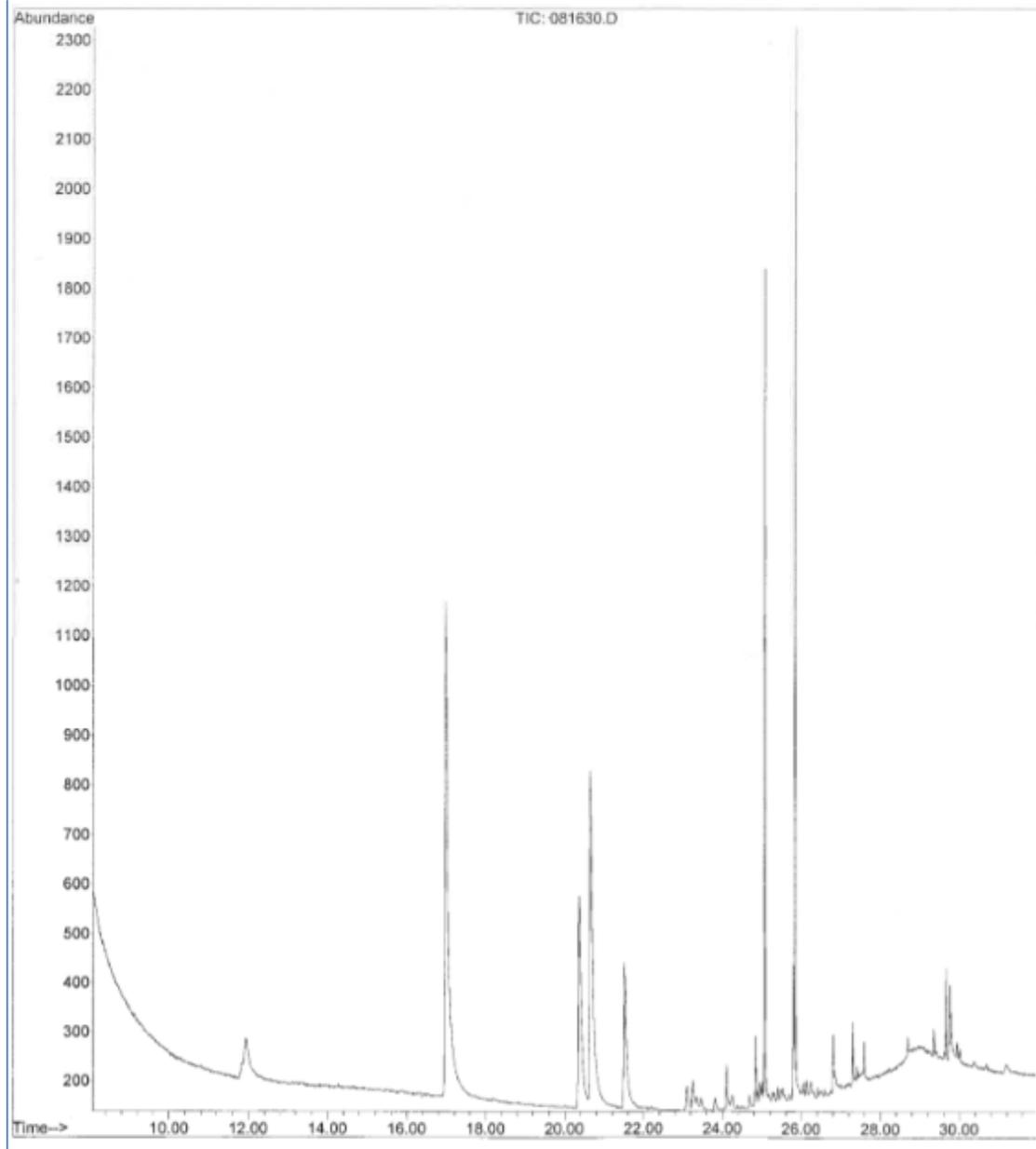


Figure 21. Selective Ion Monitoring Chromatogram for Sample 2B Front.



3.0 RESULTS AND DISCUSSION:

3.1 Findings

3.1.1 Preliminary Assessment:

Site 1.

Total (including all sumps) maximum, average and minimum VOC concentrations during the sampling process for Site 1, using the ppbRAE, were: 200,000ppb, 93,046ppb, and 533ppb, respectively (Table 13). These concentrations are a total average, maximum, and minimum concentrations of all sumps sampled (before and after) during the site assessment and only represent a snapshot of VOC exposures during the sampling times, as sampling was not continued for the total time spent at the site. All data were log transformed because the percentage relative to its standard deviation of the log transformed values were 0.29-15% and lowest % relative standard deviation of the untransformed data was 18-95%.

Table 13. Total VOC Concentrations for Site 1

Site 1 Total Concentrations in ppb				
Maximum	Minimum	Average	Mode	Median
200,000	533	93,045	200,000	63,650

Total VOC concentrations for each sump are provided below in Table 14. The turbine sumps emitted the highest average concentrations from all the sumps at 179,566 ppb \pm 0.11 (180 ppm) and 40,316 \pm 0.24 (40 ppm) after 26 time-lapses ($p \leq 0.05$). Turbine sumps contain the distribution piping and pump that transfer gasoline from the tank to the dispenser and thus there is a consistent flow of gasoline through the pipes when fueling gasoline. Also, UST sumps are much larger in depth and diameter compared to dispenser sumps and thus the larger size of the UST sumps can contribute to higher VOC concentrations as shown in Fig. 3. The lowest

average concentrations were emitted by the dispenser sumps. Dispenser sump 1 emitted the lowest average concentrations at 3876 ppb (4.0 ppm) and 1541 ppb (2.0 ppm) after 23 minutes. There was a concentration difference between dispenser sump 1 and dispenser sump 2, as dispenser 1 had a higher before and after average concentrations ($p < 0.05$). Even though both sumps are similar in design, cleanliness differs for each sump which will result in varying concentrations emitted.

Table 14. Measured Total VOC Concentrations in ppb for Site 1.

	Fill Sump 1		Turbine Sump 1		Dispenser Sump 1		Dispenser Sump 2	
	Before 0800	After 0825	Before 0804	After 0830	Before 0812	After 0835	Before 0814	After 0840
Min	4,017	401	52,210	12,229	907	147	377	50,390
Max	93410	200,000	200,000	200,000	200,000	200,000	200,000	200,000
Aveg	31,445	1,033	179,566	40,316	3,876	1,541	781	15,921
Median	26,554	852	199,990	35,335	3,292	1,009	740	199,990
Mode	14,135	401	199,990	12,229	9,33	1,49	411	199,990

When comparing VOC concentrations from each sump over time, concentrations decreased by average concentration differences of 30412 ppb \pm 0.34(97% decrease) ($p \leq 0.05$) for fill sump 1 over a 25 minute period, 139250 ppb \pm 0.11 (78% decrease) ($p \leq 0.05$) for turbine sump 1 over a 26 minute period, 2335 ppb \pm 0.25 (60% decrease) ($p \leq 0.05$) for dispenser sump 1 over a 23 minute period. There was an increase in VOC concentrations for dispenser sump 2 at 0840 hours due to sample being collected during a sensor testing process where gas was dispensed causing elevated concentrations (Figure 22). Dispenser sump 2 was not then calculated due to its skewed effect of a high concentration reading. Temperatures during the sampling time began to increase as the sampling time started early in the morning and continued onto a later time and thus affecting the vaporization rates of the gasoline compounds found inside the sumps.

Table 15. Atmospheric Conditions for Site 1.

Sample Location	Sample time	Temperature °C	Wind Speed FPM	Relative Humidity %
1/19/2017				
Site 1	0800-0842	13.7	110	79.9

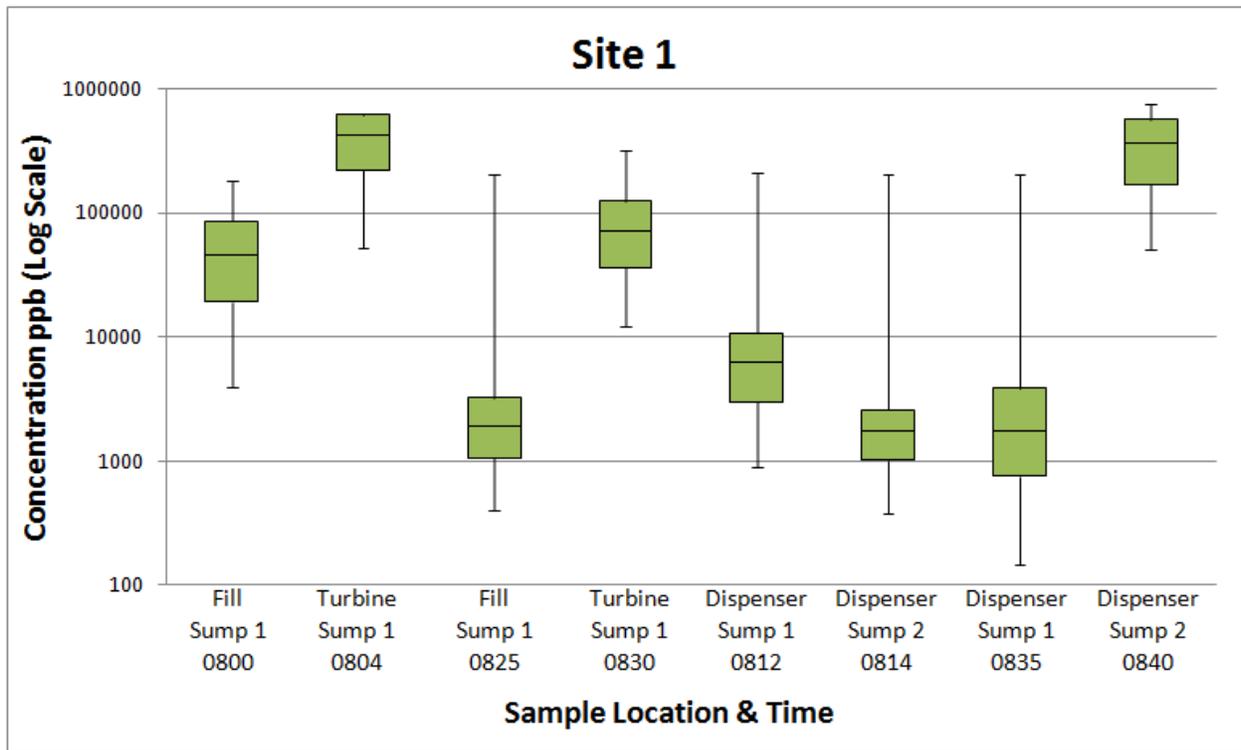


Figure 22. Total VOC concentrations measured directly 2.5-3 ft. above the sumps containing unleaded gasoline and collected over 23-26 minute intervals. Data is arranged in time sequence order.

As the closed system or the *equilibrium vapor pressure* in the headspace is disturbed when the lids were opened, concentration diffusion occurred and thus decreased the total VOC concentrations over time inside the sumps (see Sec. 1.2.1.3.). During this inspection process, the sump lids were removed and left opened for a period of time. Over an average of 25 minutes, these VOC concentrations inside the sumps decreased greater than 50% in

concentrations. This is important for inspectors to allow enough time for vapors to escape before beginning the inspection process and thus to significantly reduce vapor exposures.

Site 2.

For site 2, the maximum, average and minimum total VOC concentrations were: 147, 52,181 and 200,000 ppb, respectively (Table 16). As site 1, these concentrations do not represent an inspector’s total VOC exposure for the total average time spent at site 2 and only be viewed as a snapshot.

Table 16. Total VOC Concentrations for Site 2

Site 2 Total Concentrations in ppb				
Maximum	Minimum	Average	Median	Mode
200,000	147	8,304	8,304	200,000

Comparable to Site 1, VOC concentrations from each sump also decreased over time by an average concentration difference of 92365 ppb \pm 0.37 (53% decrease) ($p \leq 0.05$) for fill sump 1 over a 30 minute period, 130613 ppb \pm 0.12 (66% decrease) ($p \leq 0.05$) for turbine sump 1 over a 29 minute period, and 29892 ppb \pm 0.18 (97% decrease) ($p \leq 0.05$) for dispenser sump 1 over a 29 minute period. Over an average of 30 minutes, VOC concentrations inside all sumps decreased by greater than 50%. Despite Site 2 having higher temperature conditions, decreased concentration differences were not as significant as Site 1. It is possible that time between the time the sumps were first opened to the time sampling started was greater than site 1 which could explain why it took less time for concentrations to decrease by 50%.

Table 17. Site 2 Measured Total VOC Concentrations in ppb.

	Fill Sump 1		Turbine Sump 1		Dispenser Sump 1	
Time	Before 0933	After 1003	Before 0940	After 1009	Before 0952	After 1021
Min	28,947	3,163	150,280	11,569	9,225	533
Max	200,000	200,000	200,000	150,240	77,260	1,123
Aveg	175,619	83,254	199,218	68,605	30,734	842
Median	200,000	58970	200,000	64589	28047	824
Mode	200,000	3163	200,000	19033	1307	770

Also, when comparing the Fill, Turbine, and Dispenser sumps from both sites, Site 1 had lower concentrations and site 2 had higher concentrations. There were temperature differences between Site 1 and Site 2. The temperature at Site 2 was 0.4 °C greater. This temperature difference can cause higher evaporation rates and thus cause higher concentrations (see Sec. 1.2.1.3.). Turbine sumps released the highest concentrations, compared to filling sumps and dispenser sumps during the initial (before) assessment ($p \leq 0.05$). Turbines sumps did release higher concentrations in the second assessment (after) when compared to the dispenser sump ($p \leq 0.05$) but there was no statistical differences in concentrations when compared to the fill sump 1 (after) ($p=0.79$).

Understanding how the concentrations inside the sumps can decrease over time at constant temperatures can allow workers to better protect themselves from high exposure concentrations by allowing enough time for VOC levels to decrease before entering the work area. Also, because turbine sumps seemed to release higher VOC levels, workers can also be aware on which sumps can contribute to higher exposures and thus can minimize time spent at each sump.

Table 18. Atmospheric Conditions for Site 2.

Sample Location	Sample time	Temperature °C	Wind Speed FPM	Relative Humidity %
1/19/2017				
Site 2	0933-1022	14.1	108	77.6

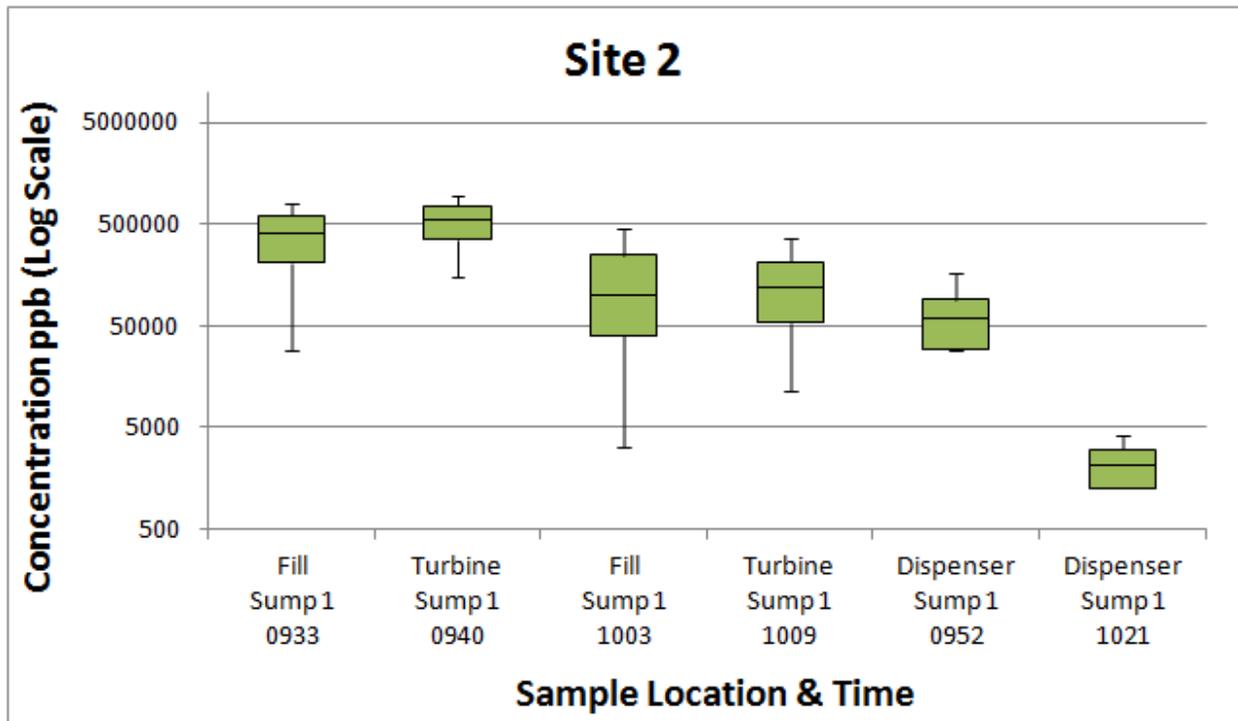


Figure 23. Total VOC concentrations measured at the second site containing unleaded gasoline. Samples were collected in 30 minute intervals. Data are arranged in time sequence order.

In general, the total VOC levels collected in this sampling phase could represent a true occupational exposure when standing directly in front of the sumps during inspections. There are no regulations for total VOC concentrations but there is scientific evidence that VOC exposures are dangerous to human health, depending on the composition. Occupational exposures to VOCs from petroleum products involve multiple chemicals. Breathing in low levels of VOCs for long periods of time may increase some people’s risk of health problems, such as for people with asthma or who are particularly sensitive to chemicals⁽⁵¹⁾. Some acute exposures

to VOCs can cause eye, nose and throat irritation, headaches, nausea/vomiting, and dizziness (51).

3.1.2 Secondary Assessment:

Site 3

For all sumps, before and after, the lowest concentrations were recorded for benzene and the highest recorded for ethylbenzene (Table 20). Because gasoline contains low additive concentration of benzene compared to toluene, ethylbenzene and xylenes; benzene concentrations appeared to be the lowest in all samples (see Sec 1.2.2.2.). *m*-xylene and ethylbenzene were similar in concentrations. This is possibly due to their relatively close vapor pressures of 9.6 mmHg at 25 °C for ethylbenzene and 8.29 mmHg at 25 °C for *m*-xylene. Vapor pressures for benzene and toluene are 94.8 and 28.4 mmHg at 25 °C. It is evident that ethylbenzene and *m*-xylene concentrations are related more closely and as expected for xylenes when compared to benzene and toluene.

Table 19. Atmospheric Conditions for Site 3.

Sample Location	Sample time	Temperature °C	Wind Speed FPM	Relative Humidity %
01/26/2017				
Site 3	0805-0938	7.8	203	56.2

Table 20. BTEX Concentrations in ppb for Site 3.

	Turbine Sump 1		Fill Sump 1		Area Sample (0855)	Dispenser Sump (0937)
	Before (0805)	After (0836)	Before (0808)	After (0840)		
Benzene	340	311	289	267	283	118
Toluene	483	428	397	337	366	151
Ethylbenzene	926	803	697	584	653	267
<i>m</i>-Xylene	868	752	633	518	585	249

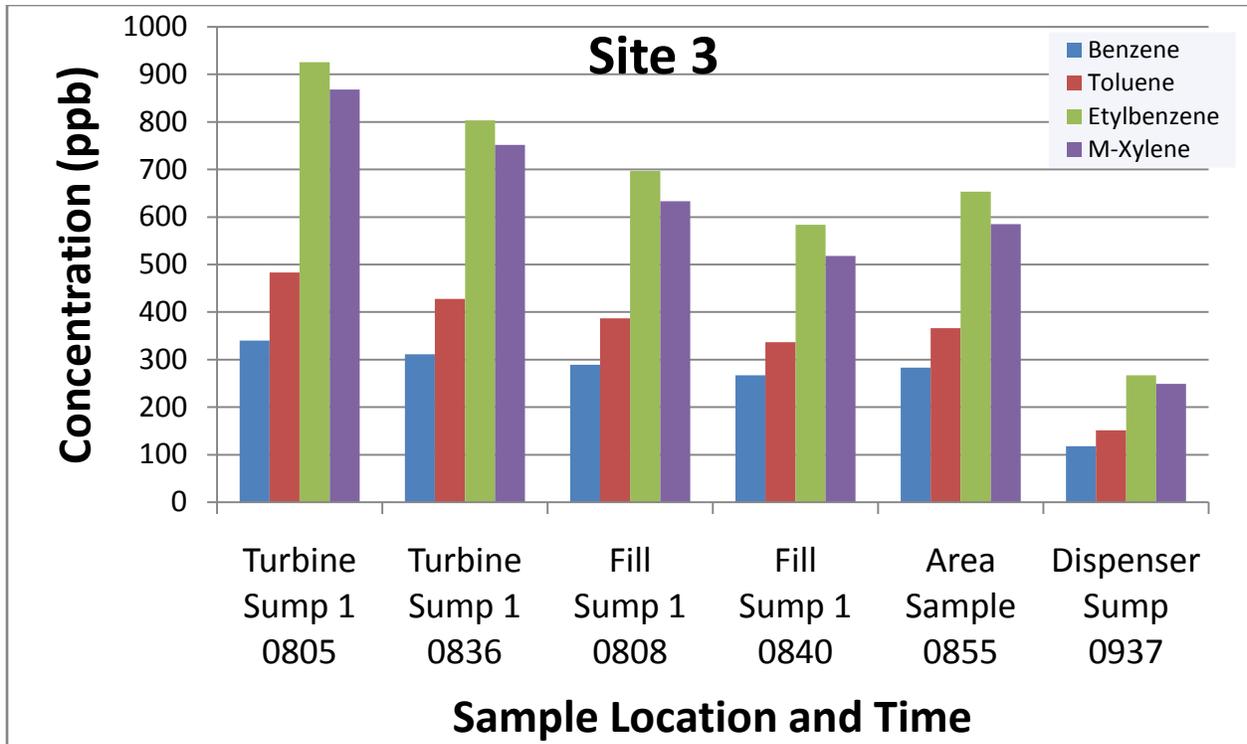


Figure 24. BTEX concentrations collected from site 3 containing unleaded gasoline. Time intervals of 31 minutes. Data is displayed in time sequence order.

There was no statistical differences in concentrations when comparing turbine sumps to fill sumps ($p \geq 0.05$) but were significantly higher to when compared to the dispenser sump ($p \leq 0.05$). As explained previously in the preliminary assessment, turbine sumps contain the distribution piping and pump that transfers gasoline from the tank to the dispenser and thus there is a consistent flow of gasoline through the pipes when fueling gasoline causing elevated VOC concentrations. Also, UST sumps are much larger in depth and diameter compared to dispenser sumps, thus contributing to higher VOC concentrations. These findings are consistent to the findings from the preliminary assessment which supports the hypothesis that turbine sumps emit the highest VOC concentrations due to their constant dispensing operation and relative size.

For turbine sump 1, concentrations decreased by a concentration differences of 29 ppb ± 0.027 (8% decrease) for benzene, 55 ppb ± 0.037 (11% difference) for toluene, 123 ppb ± 0.011 (13%

difference) for ethylbenzene, and $116 \text{ ppb} \pm 0.044$ (13% difference) for *m*-xylene over a 31 minute period. For fill sump 1, over a 32 minute period, concentrations decreased by a concentration differences of $22 \text{ ppb} \pm 0.024$ (8% decrease) for benzene, $60 \text{ ppb} \pm 0.050$ (15% decrease) for toluene, $13 \text{ ppb} \pm 0.054$ (16% decrease) for ethylbenzene and $15 \text{ ppb} \pm 0.062$ for *m*-xylene (18% decrease). Concentrations did not decrease by 50% decrease like site 1 and 2. Benzene concentrations showed a slight decrease over time and a higher decrease for toluene, ethylbenzene and xylene for site 3. This is a contrary to the study's initial hypothesis as benzene has the highest vapor pressure and lowest boiling point from the group making it the most volatile and thus expected to decrease the most in concentration. It is possible that any changes in Benzene concentrations were difficult to detect because of the sensitivity ranges on the PetroPRO. The PetroPRO has detection limit for Benzene of 50 ppb LDL / 100 ppm UDL.

Site 4

For all sumps, before and after, the lowest concentrations were recorded for *m*-xylene and the highest recorded for benzene (Table 21). Benzene concentrations are opposite to the concentrations found at Site 3; they were the lowest at Site 3. This agrees with the study's initial hypothesis as benzene has the highest vapor pressure and lowest boiling point from the group making it the most volatile. For site 4 the highest BTEX concentrations were emitted from the dispenser sumps and lowest from the fill sumps ($p \leq 0.05$). This is also opposite to Site 3, as the highest were emitted from turbine sumps. It is possible that dispenser sumps emitted the highest BTEX concentrations for site 4 due specifically to that sumps cleanliness. Dirtier sumps might contain leaked fuel inside that will cause higher exposed concentrations. Also, temperature can be a factor by increasing evaporation and thus might cause dispensers to emit higher concentrations. In addition, wind movement can also affect concentrations by removing or diluting concentrations in an enclosed space.

Table 21. BTEX Concentrations in ppb for Site 4.

	Fill Sump 1		Turbine Sump 1		Dispenser Sump 1		Dispenser Sump 2	
	Before (0904)	After (0927)	Before (0909)	After (0933)	Before (0915)	After (0941)	Before (0921)	After (0953)
Benzene	111	712	279	730	443	769	592	624
Toluene	81	453	195	463	298	504	379	419
Ethylbenzene	75	447	197	448	289	503	370	413
m-Xylene	68	362	168	353	240	406	303	339

Table 22. Atmospheric Conditions for Site 4.

Sample Location	Sample time	Temperature °C	Wind Speed FPM	Relative Humidity %
		2/1/2017		
Site 4	0904-0954	20.9	168	34.3

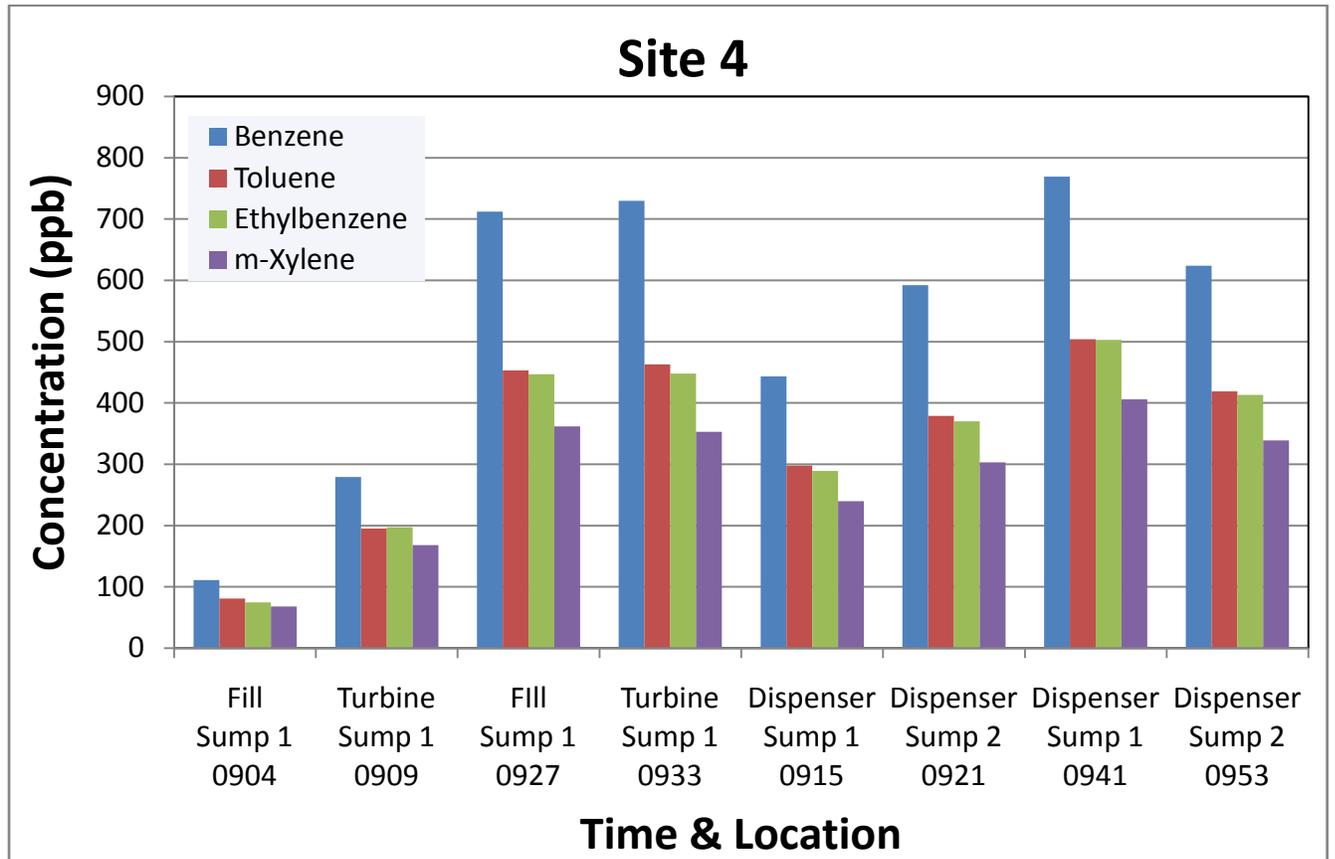


Figure 25. BTEX concentrations collected from site 4 containing unleaded gasoline. Time intervals of 23-32 minutes. Data is displayed in time sequence order.

In comparison to Site 3, all concentrations at Site 4 increased over time. For Fill Sump 1, after 23 minutes, concentrations increased by a concentration differences of 601 ppb \pm 0.57 (541% increase) for benzene, 372 ppb \pm 0.52 (459% increase) for toluene, 372 ppb \pm 0.54 (496% difference) for ethylbenzene, and 294 ppb \pm 0.53 (432% increase) for *m*-xylene. For turbine sump 1, over a 24 minute period, concentrations increased by a concentration differences of 451 ppb \pm 0.30 (161% increase) for benzene, 268 ppb \pm 0.27 (137% increase) for toluene, 251 ppb \pm 0.25 (127% increase) for ethylbenzene and 185 ppb \pm 0.23 for *m*-xylene (110% increase). For dispenser sump 1, over a 26 minute period, concentrations increased by a concentration differences of 326 ppb \pm 0.17 (74% increase) for benzene, 206 ppb \pm 0.16 (69% increase) for toluene, 214ppb \pm 0.17 (74% increase) for ethylbenzene, and 166 ppb \pm 0.16 (69% increase) for *m*-xylene. Final, for dispenser sump 2 after 32 minutes, concentrations increased by a concentration differences of 32 ppb \pm 0.016 (5% increase) for benzene, 40 ppb \pm 0.031 (10% increase) for toluene, 43 ppb \pm 0.034 (11% increase) for ethylbenzene, and 36 ppb \pm 0.034 (12% increase) for *m*-xylene.

Overall, BTEX concentrations for site 4 increased overtime. This is possibly due to higher increasing temperatures resulting in more rapid rates of vaporization. According to the Clausius-Clapeyron equation, vapor pressure and temperature are exponentially related, thus with higher temperature are higher vapor concentrations. This can be hazardous for workers working on USTs during the hot summer days. Because benzene has the lowest boiling point from the group (80°C), results showed the highest concentrations for benzene and the lowest concentration for *m*-xylene with the highest boiling point (136 °C). Concentrations for every compound were proportionally related to their boiling points; lower boiling points results in higher evaporation rates (see Sec 1.2.1.3.). Obtaining more samples from other sites the same day during the assessments would have provided more information regarding the high concentrations emitted from the dispenser sumps and how temperature and wind speed influence concentrations.

Comparison to Guidelines and Regulations

Overall, BTEX concentrations were below OSHA's PELs of 1, 5, 10, 100 ppm, respectively, and below OSHA's STELs of 5, 30, 150, and 150 ppm, respectively. In addition BTEX concentrations did not exceed NIOSH STELs of 1, 125, 150, and 150 ppm, respectively. Concentrations did exceed NIOSH RELs of 0.1 ppm (100 ppb) and reached above OSHA's Action Level (AL) at 0.5 ppm (500 ppb) at 769 ppb (0.8 ppm) for benzene. Based on the readings collected, the exposure levels to BTEX were not of immediate concern.

3.1.3 Personal Exposures:

Temperatures and atmospheric pressures were noted during the sampling. All flow rates used to calculate volumes of sampled air are provided in Table 2, Sec 2.3.1.3. Sampling durations varied per site. Samples were coded as follows: 1A front for Site 5, 2A front for Site 6, 1B front for Site 7, and 2B for Site 8. Below are tables with area units for chromatographic BTEX peaks of the personal air samples, concentration of each compound in the personal samples, and the calculated sampling volumes in Tables 23-25.

Table 23. Area Units for Chromatographic BTEX Peaks of the Personal Air Samples

Compounds	Retention Time	4/13/17		4/20/17	
		1B Front (Site 5)	2B Front (Site 6)	1A Front (Site 7)	2A Front (Site 8)
Benzene	11.758+11.898	35,757	ND	3,066	ND
Toluene	16.958	149,487	5,762	39,865	14,256
Ethylbenzene	20.346	24,189	2,229	9,415	7,653
M+P-xylene	20.625	105,990	4,008	26,406	20,033
O-xylene	21.495	33,135	1,368	7,744	7,073
Total =Xylenes	42,120	139,125	5,376	34,150	27,106

ND: Not Detected

Table24. Sampling Volumes for Sites 5-8

Date:	4/13/2017		
	Sampling Time	Flow Rate	= Volume Sampled
Site 5	84 mins	0.198 LPM	0.01663 m ³
Site 6	99 mins	0.201 LPM	0.01990 m ³
Date:	4/13/2017		
Site 7	66 mins	0.200 LPM	0.0132 m ³
Site 8	60 mins	0.190 LPM	0.0114 m ³

Table 25. Concentration of Each Compound in Personal Samples

Compounds	4/13/17		4/20/17	
	1B Front (Site 5) mg/m ³	2B Front (Site 6) mg/m ³	1A Front (Site 7) mg/m ³	2A Front (site 8) mg/m ³
Benzene	0.1302	≤0	0.09606	≤0
Toluene	0.04308	0.03366	0.05151	0.05889
Ethylbenzene	0.06085	0.05031	0.07612	0.08806
Total =Xylenes	0.01068	0.002203	0.005502	0.005753

Site's 5-8

All concentrations were well below all OSHA regulations and below any recommended guideline. It should be noted that samples were analyzed 6 months after initial assessment which might have affected concentrations. Despite the low concentrations, there were still concentration differences between the sites. Benzene had the highest concentrations, except for Sites 6 and 8. This is comparable to Site 4 where benzene also had the highest concentration at higher temperatures. Temperatures for Sites 5-8 were from 19.2 °C to 27.6 °C which are close to Site 4's temperature of 20.9 °C. It is evident that benzene concentrations are highly

exponentially related to temperature because of its high vapor pressure and low boiling point making it highly volatile.

The same occurred for the xylenes. Xylenes had the lowest concentrations at Site 4 at higher temperatures compared to Sites 5-8. Site 8 also had the higher concentrations for toluene, ethylbenzene, and xylenes compared to Sites 5-7. These concentrations were collected for only 66-84 minutes on the observer. Concentrations might have been higher if the personal sampling was done on the worker continuously for a day's exposure. Sampling for times of 60-99 minutes was not representative enough to truly represent a worker's exposure. As previously explained, other factors that could have affected concentrations are wind speed, wind direction, distance to the source of exposure, the relative humidity and cleanliness of the sumps. Wind speeds during the sampling times were higher than at Sites 1-4. Overall, results were inconclusive. Higher concentrations were expected due to continuing exposures at short distances from the source. Strong odors of gasoline fuel were particularly observed during the assessments that could relate to high exposures. The odors also became more intense as temperatures increased throughout the mornings. All data were lower than the 0.1 Cal/OSHA PELs (Table 26).

Table 26. BTEX Concentrations for Personal Samples

	Site 5 (ppb)	Site 6 (ppb)	Site 7 (ppb)	Site 8 (ppb)
Benzene	40.8	≤0	30.1	≤0
Toluene	11.4	8.9	13.7	15.6
Ethylbenzene	14.0	11.6	17.5	20.3
Total Xylene (All isomers)	2.5	0.5	1.3	1.3

Table 27. Atmospheric Conditions for Sites 5 & 6.

Sample Location	Sample time	Temperature °C	Wind Speed FPM	Relative Humidity %
04/13/2017				
Site 5	0946-1105	19.2	405	51.5
Site6	1258-0237	24.6	510	50.2
04/20/2017				
Site 7	0757-0903	25.2	1927	26.3
Site 8	1044-1144	27.6	2226	24.5

3.3 Recommendations

A list of recommendations has been created to assist workers in reducing exposures during inspections. The recommendations are not intended to replace any health and safety training, the use of PPE or the need for further assessments. Below is the list of recommendations that workers can adopt for safer work practices:

1. Keep safe distances (2-3 ft.) from the sumps to avoid direct exposures as obtained with direct reading devices.
2. Stay upwind from the sumps when looking over a sump to prevent downwind exposures.
3. Avoid standing between sumps as concentrations can increase due to the concentration distances from the surrounding sumps.
4. Minimize the time at sites, especially at high temperatures that will increase vaporization of gasoline.
5. Allow time before entering after the cover is lifted so that trapped vapors can escape and thus reduce concentrations.
6. If strong gasoline odors occur, move away!
7. Allow enough sufficient time between inspection days and times to prevent continuous exposures.
8. Minimize outside activities that can lead to further exposures. Outside activities contributing to total BTEX exposures, like bicycling in traffic, can add to a worker's total exposure.

4.0 LIMITATIONS:

Although the research reached its aims, there were some unavoidable limitations. First, because of time limits and inspector schedule availability, this research only conducted exposure assessments on two sites per each phase. Therefore, to generalize the results to other inspectors and UST sites, the study should have assessed more UST locations and more inspectors, possibly from different offices. Second, inspections times varied per site, thus time averages to complete an inspection changed based on the inspector and sites. This can lead to an under or overexposure. All inspectors work at different work places and thus exposures vary. Including more inspectors in the study may provide a more representative generalized exposure and may have differentiated between those that work at fast and slow pace.

Thirdly, sampling was done on the observer and not on the inspector. Thus exposures might differ. Even though this study aimed to closely match exposures, there were some differences in times spent at specific sumps. Also, it was difficult to match exact exposures because of time restraints and trying not to disrupt the workflow. Fourth, personal sampling was not done for full length of inspection due to max volume restrictions for the sorbent tube. All sorbent tubes have a set max volume of air absorption that can be collected before reaching breakthrough and a minimum volume of air needed to detect air contaminants. In this study, setting up a new second sorbent tube will not have allowed enough volume to be collected. Fifth, the ppbRAE was not able to detect concentration readings above 200,000 ppb (200 ppm). Based on the high VOC readings, it is assumed that VOC concentrations would have well reached above the highest recorded readings of 200,000 ppb.

Sixth, cleanliness of sites varied and as a result VOC concentrations levels fluctuated based on the site and thus might under and over-represent a worker's true exposure. For better representation, a week's exposure should be assessed and more sites and workers should also be included. Seventh, charcoal tubes from the personal sampling phase were not analyzed within 30 days from the initial time of sampling as recommended by NIOSH method 1501. Charcoal tubes were stored in a refrigerator at 5 °C and were analyzed approximately 6 months

later. This can affect the retention of the captured analytes on the charcoal and thus lower the concentration results. Lastly, direct reading devices were not recalibrated after sampling due to time constraints. Calibrating equipment before and after provides data to detect any inaccuracies or imprecisions in concentration readings.

5.0 SUGGESTIONS FOR FUTURE WORK

More data for BTEX exposures will provide a better assessment of risk. In this study, only 2 sites were evaluated. This only allowed a comparison between two sites. Each site varies in cleanliness and the time and effort a business puts into maintaining and keeping clean its facility. Inspectors can witness a site that is adequate and another site that is poorly maintained. Even the same site can have variable maintenance. This introduces variation on exposures, as a well maintained site might expose workers to fewer and less toxic vapors and a poorly maintained site to more. Thus exposure can vary on a day-to-day basis per worker. This study examined both, types of sites. Weekly exposures may better quantify worker average exposures. This approach can particularly be helpful since the number of sites can vary from 2-3 per day and 3-5 times a week.

For this study, the photoionization detector (PID) and the portable GC-PID for BTEX provided data on the overall VOC and BTEX concentrations for grab air samples. Gasoline is made up thousands of chemicals. A portable GC-MS can be used to identify other specific chemicals found in gasoline that can be toxic to human health. This study also only measured the exposures for inspectors. Future studies should look at the exposures of contractors. Contractors are hired to perform maintenance and repairs. Based on observations, contractors are more directly exposed since they are required to work directly on mechanical equipment and at times they are required to drain gasoline from the sumps. Their exposure durations can range from 4-6 hr per site and 8-12hr per day, 5-6 days a week. In contrast, exposures to inspectors are much shorter. Inspectors are also involved in the removal process of USTs. Previous studies (Sec. 1.2.5.) have reported exposures during UST removals for contractors involved in the cleaning process of USTs and for workers working in proximity. These studies do not represent exposures for inspectors as their job tasks differ from contractors and other employers. Inspectors are involved in overseeing the process that can lead to different exposures.

Lastly, assessing exposures during high temperature days can provide better worst-case exposure data. As the data show in this study, concentrations increased over time with higher temperatures. Higher temperatures result in more rapid rates of vaporization because the vapor pressure increases with temperature is exponential. This can be hazardous for workers working on USTs during hot summer days. The data for this were collected between January and April, during the winter and the beginning of spring.

6.0 CONCLUSIONS

In general, total VOC levels were much higher concentrations when compared to the BTEX readings. The highest concentration observed for total VOCs was 200,000 ppb (200 ppm) and the lowest 147 ppb (0.1 ppm) during the preliminary assessment. Gasoline is made up of hundreds of chemicals and thus it releases high levels of VOC's. For the secondary assessment, BTEX concentrations were below OSHA's PELs of 1, 5, 10, 100 ppm, respectively, and below OSHA's STELs of 5, 30, 150, and 150 ppm, respectively. BTEX concentrations did not exceed NIOSH STELs of 1, 125, 150, and 150 ppm, respectively. Concentrations did exceed NIOSH RELs of 0.1 ppm (100 ppb) and reached above OSHA's Action Level (AL) at 0.5 ppm (500 ppb) for benzene at Site 3. Since both total VOC measurements and personal samples were not done simultaneously any real relationship is speculative.

Personal samples results were basically inconclusive because the samples were not analyzed until 6 months after sampling even though the capped samples were stored at 4 °C on the same day of sampling and remained at that temperature until desorption. This may have led decreased concentrations through evaporation. Also, exposure assessment was not done for a total 8-hour exposure as required to compare with Cal/OSHA regulations and NIOSH guidelines. Similar concentrations were found for benzene and xylene (benzene being the highest concentration and xylenes being the lowest) as Site 4. All data were lower than 0.1 Cal/OSHA PELs, with the highest concentrations being 40.8 ppb for Site 5 and the lowest at 0.5 ppb for Site 6.

Inspectors spent about 1-2 hours per site and completed about 2-3 sites per day. Direct exposures when inspecting the sumps were very short, of duration of about one to two minutes. During those short periods of exposure, inspectors were exposed to high levels of total VOCs. From personal observations, some inspectors began their inspection immediately after opening the sumps and thus were exposed to higher concentrations of vapors. Many inspectors tried to meet a designated time schedule for each site before the next one. Also, based on personal assessment of work practices, some inspectors were more cautious than others when working around USTs and were more aware of the hazards and thus minimized

their exposure times. Others not so aware or careful can be exposed more directly and for longer times.

Environmental factors can also affect a worker's exposure, such as wind direction, wind speed, temperature, humidity (dew point), and closeness to the opening. In this study, concentrations decreased over time with cooler temperatures and increased with warmer temperatures. Because exposure concentrations are exponentially related to temperature (Sec. 1.2.1.3), working in high temperatures can be more hazardous for UST workers. Also, turbine sumps emitted the highest concentrations for Sites 1-3 and Dispenser sumps for Site 4. Overall, based on the readings collected and personal samples results, the exposure levels to BTEX appear not of immediate concern. It is still highly recommended for inspectors to take preventative measures to reduce exposures as provided under the Recommendations section.

8.0 APPENDICES

Health and Safety Code 25285.

25285. Permit; Term; Inspection; Fee and Surcharge (a) Except as provided in Section 25285.1, a permit to operate issued by the local agency pursuant to Section 25284 shall be effective for five years. This subdivision does not apply to unified program facility permits. (b) A local agency shall not issue or renew a permit to operate an underground storage tank if the local agency inspects the tank and determines that the tank does not comply with this chapter. (c) Except as provided in Section 25404.5, a local agency shall not issue or renew a permit to operate an underground storage tank to any person who has not paid the fee and surcharge required by Section 25287.

A. Generating a 10L Gas Bag for Benzene at 1.0ppm.

1. $1.0 \text{ ppm} = (1 \text{ mg/m}^3) (24.45)/78.11 \text{ g/mol}$ (Converting 1.0 ppm to mg/m^3)

2. $3.19 \text{ mg/m}^3 \rightarrow 3.19 \text{ mg}/1000 \text{ L}$

1000L in 1.0 L?

0.00319 mg per 1.0 L

$0.00319 \text{ mg} \times 10 \text{ L} = 0.0319 \text{ mg}$

} weight in 10 L gas bag

3. 876 mg per mL?

876 per 1000 μL

$876/1000 \mu\text{L} = 0.876 \text{ mg in } 1.0 \mu\text{L}$

4. $0.0319 \text{ mg} / 0.876 \text{ mg} = 0.04 \mu\text{L}$ (0.04 μL per 1.0 ppm (100x dilute))

$8\text{L}/10\text{L} = 0.8 \text{ L}$

$4 \mu\text{L} \times 0.8 = 3.2 \mu\text{L in } 100 \text{ ppm}$

B. Calculating GC-MS corrected areas to concentrations in ppm.

$Y=31,487x - 32,413$ (linear equation for benzene)

$35,757=31,487x - 32,413$ (linear equation for sample 1B)

$68,170=31,487x$

$X=2.16 \mu\text{g} = 0.00216 \text{ mg}$

$12\text{L (volume of air)}/1000 = 0.012 \text{ m}^3$

Air concentration

$0.00216 \text{ mg} / 0.012 \text{ m}^3 = 0.18 \text{ mg}/\text{m}^3$

$0.18 \text{ mg}/\text{m}^3 \longrightarrow \underline{0.056 \text{ ppm}}$ (Final concentration in ppm)

C. Calculations for Internal Standards

A. $100 \text{ ppm} \rightarrow 434.24 \text{ mg}/\text{m}^3$ (ppm to mg/m^3 converted using ACGIH equation)

B. $\frac{434.23 \text{ mg}/\text{m}^3 / \text{m}^3 (1000 \text{ L})}{12 \text{ L (highest flow rate during sampling)}} = 0.0361858333 \text{ mg} = 36.1 \mu\text{g}$

C. $\frac{434.12 \times 12 \text{ L}}{1000} = 5.21076 \text{ mg} = 5210.76 \mu\text{g}$

D. $860 \text{ kg}/\text{m}^3$ (density)– $1000 \mu\text{L}$

$5.21076 \text{ mg} - X \mu\text{L}$

E. $\frac{5.21076 \text{ mg} \times 1000 \mu\text{L}}{860 \text{ mg}} = 6.05 \mu\text{L}$

6 μL of xylene per 1.0 mL of concentrate

D. Calculating the P-Values Using a Student T-Test

$$(0.332296)^2 \qquad (0.188537)^2 \text{ (Standard Deviations)}$$

$$0.1104206316/n=65 \qquad 0.0355462004/n=64$$

$$=0.0016987789 \qquad =0.0005554094$$

$$0.0016987789 + 0.0005554094 = 0.0022541883$$

$$= \sqrt{0.0022541883}$$

$$= 0.0474782929$$

$$\begin{array}{l} \bar{X}_1 \text{ -- } \bar{X}_2 \\ \downarrow \qquad \searrow \\ 4.389226 \text{ -- } 2.922548 = 1.466678 \text{ (Means)} \end{array}$$

$$1.466678 / 0.047482929 = 30.8885 \text{ (T-value)}$$

$$DF=65+64-2$$

$$= 129-2$$

$$= 127$$

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