2011

A Pilot Study of Small-Scale Variations in Outdoor Benzene Concentrations

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A Pilot Study of Small-Scale Variations in Outdoor Benzene Concentrations

by

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A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Public Health
Department of Environmental and Occupational Health
College of Public Health
University of South Florida

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Date of Approval:
July 13, 2011

Keywords: Radiello RAD130 passive sampler, urban air toxics, air pollution, environmental exposure, health risk estimation

ACKNOWLEDGEMENTS

This material is based upon work supported by the National Science Foundation under Grant No. 0846342. The author would like to thank Haofei Yu, Eric Fridh and Josh Linman for their generous donation of time and assistance in sampler deployment and retrieval. Many thanks to thesis committee member Dr. Mason, and particularly Dr. Jaward for the use of his laboratory instruments and guidance. The author is particularly grateful to Dr. Stuart for her constant support and direction throughout the last two years.

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ABSTRACT

Benzene is an important toxic chemical in urban air and known human carcinogen released substantially by mobile sources. It's important to understand the spatial variation of benzene concentrations in order to understand exposures of susceptible subpopulations such as children and minority groups. Current monitoring networks use large and expensive air samplers that require electricity and restrict the location and number of samplers, not allowing for fine spatial resolution data.

The goals of this study are to develop and evaluate protocols for passive sampling and analysis of ambient benzene concentrations, and conduct a pilot study investigating small-scale variations over an area where children are likely to be exposed. Protocols were developed for the use and analysis of the Radiello RAD130 passive sampler for field sampling over the spatial scale of a city park adjacent to an elementary school. A pilot study was conducted from 4/27/11-5/4/11, where 11 samplers were exposed for a seven day sampling period at the park. After sampler exposure, benzene concentrations were determined through solvent desorption followed by analysis using a Varian gas chromatograph/mass spectrometer. Co-location with the existing regulatory active sampler in the county and of two samplers at the same site was done to evaluate the accuracy and precision of the methods, respectively. Health risk estimates were calculated using risk assessment guidance from the U.S. and California Environmental Protection Agencies.

Concentrations over the park were found to range from 0.23-0.34 $\mu g\ m^{-3}$ with a coefficient of variation of 11%. A relative percent difference of 3% was found between the co-located sampler and the active sampler, and a 14% relative percent difference was found between the two duplicate samplers. The variation in health risk from concentration variation due to sampler placement contributed less to the overall uncertainty in the estimates than the uncertainty built in to the calculation parameters of inhalation unit risk and cancer potency factor, as estimated by the U.S. EPA and California EPA, respectively.

These results suggest that the exposure of an individual at the park would be characterized sufficiently for standard health risk analysis through the use of one sampler. Further research is necessary into using passive samplers over both the same spatial scale in other areas, as well as on a larger scale to determine intra-urban benzene concentration distributions. The protocols developed here will be used in a future planned study of benzene concentration measurements to characterize neighborhood-scale exposures in Hillsborough County.

CHAPTER 1:

INTRODUCTION

Motivation

Benzene is a known human carcinogen with various other health effects, including respiratory and neurological effects. However, there is very little known about these health effects at environmental concentrations. Due to emissions from both mobile sources (traffic) and point sources (such as gas stations), it has been demonstrated that the distribution of benzene concentrations is heterogeneous over space (Health Effects Institute, 2008). In order to study possible associations between health effects and environmental concentrations of benzene it is necessary to know the exposures that specific populations experience. A better understanding of benzene concentration distributions would contribute to the ability of future studies to more accurately assess exposure of subpopulations, such as children or minorities. Neighborhood-scale monitoring data would enhance understanding of environmental equity, i.e. differences in exposure between minority or socioeconomic groups (Wheeler & Ben-Shlomo, 2005). Better data for children's exposures to benzene, such as concentrations experienced over a school ground, would play a part in improving research into the difference in susceptibility between children and adults. With the current use of active samplers to measure ambient concentrations of benzene, it is not possible to have extensive sampling networks capable of this fine spatial resolution. There is a need for research into using

passive samplers to measure ambient concentrations of benzene (Namiesnik et al., 2005). These samplers are less expensive and they do not need a power source to operate, making it possible to attain higher spatial resolution measurements. Previous studies have used these samplers to study variations in benzene concentrations between urban and rural environments, with distance from emission sources, or between indoor and outdoor levels (Fushimi, Kawashima, & Kajihara, 2005; Godoi et al., 2009; Janssen et al., 2001). However, there is a lack of available research into using passive samplers to study the distribution of benzene concentrations over a small area such as a school's grounds.

The specific aims of this thesis work were to: 1) develop protocols for the passive sampling and analysis of benzene in the local environment, 2) evaluate the protocols through a pilot study, and 3) investigate the spatial variation in concentrations of benzene and calculated risk levels for chronic health effects (both cancer and non-cancer) over a small area. These aims are designed to address the gap in our understanding of how benzene exposures vary over small areas, such as parks and school grounds where children are exposed.

The design and evaluation of a passive sampling protocol for benzene will provide guidance for a larger study to be completed over the Hillsborough county area. The pilot study investigating the spatial distribution of benzene concentrations will aid in the development of a highly-spatially-resolved understanding of concentrations necessary for regulatory network design. The subsequent risk assessment calculations using the pilot study data will improve knowledge of exposure differences over a small area and variations in calculated risk associated with sampler placement. This information will provide useful insight for future studies aiming to characterize exposures to benzene as

well as help gauge the distribution and number of passive samplers needed to effectively monitor benzene concentrations where people are.

Background & Literature Review

Benzene is a volatile organic compound (VOC) found in the environment due to emissions from industrial sources, mobile sources (such as car exhaust), burning of coal or oil, cigarette smoke, and natural sources such as volcanoes and forest fires (Agency for Toxic Substances and Disease Registry, 2007). The distribution of environmental benzene concentrations has been shown to vary with different anthropogenic sources. Vehicular emissions of benzene cause concentrations to be approximately doubled in urban environments when compared to rural environments (Health Effects Institute, 2008). Within urban environments, concentrations have also been shown to decrease with distance from roads (Olson et al., 2009), and be higher in street canyons than adjacent parks (Upmanis, Eliasson, & Andersson-Skold, 2001). Although the dominant source of benzene to the environment in urban areas is on-road mobile sources, it is also emitted due to evaporation from gasoline stations and hazardous waste sites (Health Effects Institute, 2008). Measured benzene concentrations in Greece were significantly higher near gas stations than background concentrations in urban, suburban, and rural environments, indicating that this point source may play an important role in local exposures (Karakitsios et al., 2007). Fushimi et al. (2005) found similar results when measuring benzene concentrations in an area surrounding an industrial complex in Japan. The relative contributions from point sources and mobile sources vary in space. In order to understand the distribution of benzene concentrations in an area, further studies

investigating the relative contributions of different sources through spatially-resolved monitoring are necessary.

As a consequence of this distribution of benzene concentrations, exposures of benzene have been shown to vary. Ruchirawat et al. (2007) measured concentrations of benzene in the blood of school children and found significantly higher blood benzene levels in children at urban schools in Bangkok versus children in rural Thai schools. Similar results were found in a study measuring benzene biomarkers of Italian school children (Protano et al., 2010). Karakitsios et al. (2007) estimated a 3%-21% increase in risk of leukemia from living in the vicinity of gas stations. These studies indicate that exposures to benzene vary spatially and that these exposure differences are significant enough to be associated with increased health risks. However, more research into spatial distributions of pollutants and concurrent population exposures is necessary in order to obtain data than can contribute to the understanding of relationships between benzene and its health effects.

Since people generally spend most of their time indoors, another important factor when considering an individual's benzene exposure is indoor benzene concentrations and how these concentrations are related to outdoor sources. Benzene, as well as other VOCs, is generally present at higher concentrations indoors as opposed to outdoors (Massolo et al., 2010). However, multiple studies have found that the ratio of indoor to outdoor concentrations indicates that outdoor sources of benzene, particularly vehicle emissions, are responsible for the majority of indoor benzene concentrations (Kinney et al., 2002; Jia et al., 2008; Massolo et al., 2010). Even though people are mainly exposed to benzene indoors, these studies highlight the importance of monitoring and controlling

outdoor sources of benzene as they are ultimately the driving force behind this exposure. Monitoring to improve knowledge of how benzene varies over space outdoors will be helpful to the understanding of indoor benzene concentrations over the same areas.

Environmental equity is an area of research that investigates the distribution of environmental risk with regards to populations of different race or socioeconomic status. Wheeler and Ben-Shlomo (2005) have observed that in urban areas, households of lower socioeconomic status have been found to be located in areas with poor air quality. In southern California, the structure of the cities and their transportation systems create an environment where a disproportionate amount of minority and low income children live in areas of significantly higher traffic density and these areas have been associated with higher amounts of traffic related pollutants (Houston et al., 2004). Pastor et al. (2002) found that in Los Angeles, minority children were more likely to attend a school with higher health risks regarding outdoor air toxics exposure. Current research is also being completed in the Tampa Bay area concerning environmental equity. Chakraborty (2009) used modeled data for mobile source air toxics from the 1999 National-Scale Air Toxic Assessment (NATA) to estimate the lifetime cancer risk and non-cancer respiratory risk at the census tract level. The author found that census tracts with the highest proportions of black and Hispanic populations are located near roadways and experience higher levels of air toxics. Stuart et al. (2009) found that on the census block group level, areas with higher proportions of black, Hispanic and below-poverty populations were located disproportionately closer to air pollution sources and away from regulatory monitors. Stuart and Zeager (2011) used passive samplers to monitor NO_2 concentrations outside 75 elementary schools in Hillsborough County and found that schools with a higher

enrollment of black, Hispanic, or underprivileged school children were associated with higher NO_2 levels and higher traffic counts on nearby roads. These studies demonstrate not only the spatial variation in air toxics exposure, but also the variation and potential inequity of population exposure to traffic related pollutants on a neighborhood scale. Spatially-resolved monitoring data would enhance research in this field by allowing investigation into more accurate exposure estimations and pollutant related health effects on the neighborhood scale.

The monitoring and regulation of air toxic substances in the environment is important because of their associated human health effects. Benzene is classified as a known human carcinogen (Group A) by the U.S. Environmental Protection Agency (EPA) due to sufficient human epidemiological data and animal studies; health effects associated with benzene are leukemia, damage to the immune system, aplastic anemia, respiratory effects, cardiovascular effects, neurological effects and gastrointestinal effects (Agency for Toxic Substances and Disease Registry, 2007; Bird et al., 2010). Many of these listed health effects were demonstrated in occupational studies with higher airborne concentrations than seen in the environment. However, Whitworth et al. (2008) demonstrated that the census tracts with highest concentrations of benzene and 1,3-butadiene (as modeled using the EPA's Assessment System for Population Exposure Nationwide) were associated with higher incidences of childhood leukemia in southeast Texas. A positive association has also been found between symptoms in asthmatic Hispanic children and 24-hour ambient VOC concentrations in Los Angeles (including benzene) (Delfino et al., 2003). McCarthy et al. (2009) found that when using ambient monitoring data for benzene with EPA chronic dose-response values for carcinogenic

effects, ambient concentrations of benzene result in a greater than 10^{-6} risk level for cancer in areas of the U.S. The previous studies have used modeled data, total VOC concentrations, or low spatial resolution monitoring data to assess exposure levels. There is a lack of ambient concentration data for benzene at a spatial resolution high enough to characterize differences in exposure at the small spatial scale necessary to match human activity patterns and study subgroup health effects and associated risk.

High concentrations of combustion related pollutants (including benzene) have been associated with higher incidences of acute respiratory infections in children (Myers & Maynard, 2005), who are more susceptible to air pollution health effects than adults (Alexis et al., 2004). A study in Thailand found that school children in Bangkok had levels of a benzene metabolite in their urine comparable to adult street vendors, even though street vendors were exposed to higher ambient concentrations of benzene (Ruchirawat et al., 2007). The authors hypothesize that this difference may be due to a higher rate of metabolism of benzene in children than in adults, indicating that children may be more likely to have effects to benzene exposure. The U.S. Environmental Protection Agency (1998) has indicated in their toxicological support documents that benzene carcinogenicity differs in type of leukemia and susceptibility between children and adults; however, not enough data are available to quantify these observed differences in risk assessment calculations. Higher resolution data would contribute additional information for closer examination of potential health effect differences between children and adults from benzene.

In order to characterize the exposures experienced by children, it is beneficial to understand how concentrations of benzene vary over small areas where children spend

time, such as parks and school grounds. Mejía et al. (2011) conducted a literature review of studies pertaining to assessing exposure of children to air pollutants at schools, focusing on the methods used in previous studies. The authors found that most studies used data from remote monitoring stations or dispersion modeling, and many studies that placed monitoring devices on the school grounds did not indicate the location of the samples. The focus of the literature available also appears to be on measuring NO_2, ozone, SO_2 and particulate matter; few studies were available that included measurement of benzene (Mejia et al., 2011). Janssen et al. (2001) measured indoor and outdoor concentrations of traffic-related pollutants, including benzene, at 24 schools located within 400 meters of motorways in the Netherlands. The authors found that outdoor benzene concentrations decrease with distance from the motorway; however, indoor concentrations were observed to be higher than outdoor concentrations. In Brazil, Godoi et al. (2009) measured concentrations of benzene and other pollutants inside classrooms at two schools, and compared the values to an outdoor measurement taken at each school. The authors concluded that the indoor air concentrations could be credited to the outdoor pollution sources, which is in agreement with studies mentioned previously. While these studies give observations concerning benzene concentrations between schools and indoor/outdoor concentrations at a school, there is a lack of monitored data with regard to spatial variation in outdoor benzene concentrations over a small spatial scale over which children may be exposed.

Due to the various health effects discussed previously, benzene is considered a hazardous air pollutant (HAP), or air toxic, by the United States Environmental Protection Agency. In accordance with the Clean Air Act, this class of pollutants is

regulated by the National Emissions Standards for Hazardous Air Pollutants (NESHAPS), which control emissions of HAPs from sources based on the source category (U.S. Environmental Protection Agency, 2010b). The requirements for each source category can force them to implement a certain level of control technology into their process. A more recent rule enacted by the EPA in 2007, the Mobile Source Air Toxics (MSAT) rule, holds fuel refiners responsible for meeting limits concerning the average and maximum volume of benzene present in fuel (Hubbell et al., 2010). While useful in reducing emissions, these techniques do not guarantee an overall concentration of HAPs in air that is protective of human health. In 2009, the U.S. EPA held a workshop to address the status of current methods of estimating economic benefits to human health from reducing HAPs. It is helpful to understand the economic benefits of reducing these concentrations before making changes to regulations. Among other recommendations, the committee found that future research is necessary to evaluate spatial distribution of pollutants in order to assess exposures and health effects of susceptible populations, such as children (Gwinn et al., 2011). Taking this into account, it is important to monitor these compounds at a fine spatial resolution to evaluate the efficacy of the source regulations in protecting human health, and estimate what benefits could come from stricter regulations.

Air toxics are monitored nationally by several networks. These include the National Air Toxics Trends Stations (NATTS), the Urban Air Toxics Monitoring Program (UATMP) and the Photochemical Assessment Monitoring Strategy (PAMS). The former two programs include benzene in their measurements and their data are used to complement one another; the UATMP focuses on air toxics in urban environments and

the goal of the NATTS is to generate long-term data in both urban and regional environments (Eastern Research Group, Inc., 2008). There are 50 UATMP/NATTS monitoring sites across the country, in rural, suburban and urban/city center areas (Eastern Research Group, Inc., 2008). The purpose of the PAMS network is to measure tropospheric ozone and its precursors; benzene is monitored by this network because it undergoes photochemical reactions in the environment which create tropospheric level ozone (U.S. Environmental Protection Agency, 2009b). Severe, serious or extreme non-attainment areas for ozone concentrations are required to have a PAMS network (in order to help them reach their attainment goals), in which at least five monitoring sites are required; this gives a better spatial resolution for the monitoring data from areas of highest concentration to those upwind and downwind than areas with only one monitoring station (U.S. Environmental Protection Agency, 2009b). However, since the PAMS networks are only required during times and in areas of non-attainment, these may not give consistent long-term concentration data. In the Houston area, a study was done to determine the representativeness of the monitoring locations chosen in two census tracts by placing passive samplers at the centroid of each census tract as well as at the current monitoring location (Stock et al., 2005). The authors found that the concentrations observed at the centroids of the census tracts were significantly different than those at the monitoring sites; for benzene, one significantly higher at the centroid and the other significantly lower. This study shows that a monitoring station may not be able to sufficiently represent the concentrations seen over one census tract. There is not an existing network that measures benzene concentration variations at a resolution in which the population exposures have been shown to vary. Without this monitoring data

it is difficult to examine possible associations between adverse health effects at different ambient exposure levels of benzene.

The two main approaches to ambient air monitoring are active and passive sampling. Active sampling requires air to be pumped through the sampling device, which can become rather expensive and require a power source. Passive samplers, which don't require a pump but rather work by diffusion or permeation across a membrane, are a cheaper alternative to active sampling for higher spatial resolution of measurements (Partyka et al., 2007). A disadvantage to passive sampling is that the uptake times for compounds at low concentrations are much longer, so the sampling time must be increased and short-term variations in concentrations cannot be seen (Namiesnik et al., 2005). Active sampling can take measurements much more often in order to see short-term fluctuations in concentration, however due to the expensive nature of these machines and the power requirements it is not typically possible to gain high spatial resolution of pollutant concentrations. Since most current sampling is done with sparsely located active samplers, there is a need for research into methods using passive samplers to determine how pollutant concentrations vary spatially. This will allow investigation of concentration distributions relative to where sensitive populations (such as children) spend their time, and how representative the current levels monitored by active samplers are of population exposures.

In occupational environments, diffusive samplers have been used for about 30 years to measure the higher concentrations of workplace air (Aragon, Atienza, & Climent, 2000). More recently, researchers have been working to validate the use of passive samplers for lower environmental concentrations over longer sampling periods.

Evaluation of passive samplers for use in sampling ambient benzene has been done on many brands, including Radiello (Bruno et al., 2005; Cocheo, Boaretto, & Sacco, 1996; Strandberg et al., 2005; Strandberg et al., 2006), 3M Organic Vapor Monitors (Bergerow et al., 1999; Chung et al., 1999), Perkin-Elmer type (Martin et al., 2003), and SKC-Ultra (Strandberg et al., 2005; Strandberg et al., 2006). Many of the studies cited previously in this literature review have used passive samplers to obtain their measurements. Godoi et al. (2009) used passive samplers to measure concentrations inside school classrooms. Karakitsios et al. (2007) deployed the samplers near gas stations. Stock et al. (2005) placed passive samplers at the centroids of census tracts to compare with the active monitoring sites. Passive sampling has been shown to be a portable and affordable way to measure ambient benzene concentrations, however there is a lack of studies that focus on using passive sampling technology to determine the spatial variation of benzene over a small area. This study is designed to help fill that gap.

CHAPTER 2:

RESEARCH DESIGN AND METHODS

Protocol Development

The first specific aim of this thesis was to develop protocols for the passive sampling and analysis of benzene in the local environment. In order to accomplish the first aim of the project, a sampler and sorbent must be chosen and then a protocol developed for the use of the device in the study conditions. This was completed through a thorough literature review of studies evaluating passive samplers for use in measuring benzene and technical data sheets from the manufacturers' websites.

Review of Samplers and Sorbents

There are various types of samplers and sorbents available for measuring ambient benzene concentrations. Types of sorbents for passive sampling include carbon molecular sieves, activated charcoal and graphitized carbon black. Carbon molecular sieves are very hydrophilic and therefore should not be used when sampling in humid areas (such as Florida) (Woolfenden, 2010). Charcoal samplers made by 3M (Organic Vapor Monitor 3500 and 3520) are used to sample organic compounds including benzene (3M Occupational Health and Environmental Safety Divison, 2004). Charcoal sorbent tubes can also be used in tube type samplers, with extraction using the solvent carbon disulfide (CS_2) (Namiesnik et al., 2005). Graphitized carbon black has been found to be the most sensitive type of sorbent for sampling of benzene (Brown & Shirey, 2001),

particularly Carbopack X (Strandberg et al., 2005; Strandberg et al., 2006). Carbopack X requires thermal desorption to remove the analytes for GC/MS analysis as opposed to solvent extraction and this technique allows for higher sensitivity in measurements, letting compound concentrations in the ppb range be detectable (Woolfenden, 2010). Although Carbopack X and thermal desorption allow for more sensitive measurements of benzene, thermal desorption is associated with a higher cost than solvent extraction due to the need for thermal desorption instrumentation. However, if a thermal desorption instrument is not available then benzene may be measured using an activated charcoal sorbent capable of solvent extraction with CS_2 or dichloromethane (Partyka et al., 2007).

Two commonly used types of activated charcoal samplers are the 3M OVM 3500 badge type sampler and the Radiello axial sampler with activated charcoal sorbent. The 3M OVM sampler has a stable uptake rate of approximately 35 ml min^{-1} for a one week sampling time for benzene (Oury et al., 2006), but the limit of detection has been found to be around 0.34-0.4 µg m^{-3} for a seven day sampling period in field studies (Mukerjee et al., 2004; Schneider et al., 2001). The Radiello sampler with activated charcoal has a higher uptake rate of 80 ml min^{-1} for benzene for a 24 hour sampling period (Cocheo et al., 1996), which has also been validated for sampling times of 4-7 days (Allou et al., 2008). The limit of detection (LOD) for the Radiello sampler with activated charcoal for a seven day sampling period for benzene is 0.1 µg m^{-3}, as advertised by Radiello and experimentally determined by Angiuli et al. (2003). In order to detect lower level concentrations of benzene in the environment, the Radiello sampler with activated charcoal (model RAD130) will be used for this protocol development. This allows for

better detection than the OVM sampler and does not necessitate thermal desorption equipment.

Development of Standard Operating Procedures

The first protocol developed for use of the Radiello sampler with activated charcoal (RAD130) is for the preparation and deployment of the sampler for the 7 day sampling period. The protocol is provided as Appendix A. It describes the set-up of the sampler shelter, preparation of the sampler from its component parts, and field deployment and retrieval of the sampling device. The primary documents used in creating this protocol include EPA methods TO-15 and TO-17 (U.S. Environmental Protection Agency, 1999a; U.S. Environmental Protection Agency, 1999b) and the Radiello manual (Fondazione Salvatoremaugeri-IRCCS, 2006).

The Radiello RAD130 sampler consists of a sorbent cartridge stainless steel mesh tube filled with activated charcoal, a white polyethylene diffusive body (1.7 mm thick, average pore size of 25 µm) to hold the cartridge, and a plastic triangular support plate onto which the diffusive body is attached (Fondazione Salvatoremaugeri-IRCCS, 2006). These three components form the sampling device. In the field, a plastic shelter is erected that consists of a roof and two side panels. One open side is attached to a pole or tree, and the front and bottom remain open. The sampling device is clipped on to a hanging device inside the shelter, which protects the Radiello sampler from wind, rain, direct sunlight, and other environmental conditions.

The sampling rate of the Radiello RAD130 sampler varies with temperature but is constant with wind speeds between 0.1-10 m s^{-1} and humidity between 10-90% (Fondazione Salvatoremaugeri-IRCCS, 2006). The temperature adjusted sampling rate

(Q_K) is calculated from the average temperature over the sampling period (K) and the sampling rate at 298 K (Q_{298} = 80 ml min^{-1} for benzene):

$$Q_K = Q_{298}\left(\frac{K}{298}\right)^{1.5} \quad \textbf{Equation 2.1}$$

Hourly weather data collected by the Tampa International Airport during the sampling period is used for determination of the temperature adjusted sampling rate.

The protocol also describes the use of field blanks in order to control for any contamination experienced by the sampling cartridges during transport or set-up. Field blanks are taken at 10% of the sampling sites, or at a minimum two. The field blanks are used to calculate the limit of detection for the sampling method. The limit of detection is defined as three times the standard deviation of the field blank values, where *N* is the number of field blanks, x_i is the concentration of field blank *i*, and $\bar{x}$ is the average of the field blank concentrations:

$$LOD = 3\left(\sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(x_i - \bar{x})^2}\right) \quad \textbf{Equation 2.2}$$

Duplicate samplers are placed at 10% of the sampling sites, or at a minimum one, in order to make calculations of the uncertainties associated with this method. To calculate precision from the duplicate samples, the relative percent difference of the two duplicates at a single site is calculated, where x_1 and x_2 are the concentrations of the duplicate samples and $\bar{x}$ is their average:

$$\%D = \left(\frac{|x_1 - x_2|}{\bar{x}}\right) \cdot 100\% \quad \textbf{Equation 2.3}$$

The second protocol developed is for the extraction of the sampling cartridges and GC/MS analysis of the samples. This protocol is provided as Appendix B. This protocol

was developed using guidance from the Radiello manual (Fondazione Salvatoremaugeri-IRCCS, 2006), US EPA compendium methods TO-15 and TO-17 (U.S. Environmental Protection Agency, 1999a; U.S. Environmental Protection Agency, 1999b), standard methods from the Health and Safety Executive (Health and Safety Executive, 1993), and journal articles describing the use of the Radiello RAD130 sampler (Allou et al., 2008; Angiuli et al., 2003; Cocheo, Boaretto, & Sacco, 1996; Godoi et al., 2009).

After exposure for a seven day sampling period, each cartridge is extracted with 2 ml of carbon disulfide, and a uniform concentration of 2-fluorotoluene is added to each sample as an internal standard. The solutions are analyzed using gas chromatography with mass spectrometry (GC/MS). Benzene standard solutions are created for calibration, at concentrations that encompass the expected sample concentrations. The instrument responses to the samples are compared to the calibration standards and the experimental ambient concentrations of benzene are calculated. In this pilot study, a Varian Saturn 3800-GC, 2000-MS system was used. The column used was a Varian CP-Sil 8 CB capillary column, with dimensions 50 m x 0.25 mm x 0.25 µm. Helium was used as the carrier gas at a flow rate of 1.2 ml min^{-1}. The injector temperature was set to 240°C. The temperature programming started at 35°C for nine minutes, ramped to 60°C at 5°C min^{-1}, and then held at 60°C for 46 minutes, creating a total run time of sixty minutes. This protocol includes the description of laboratory blanks, which are used to control for any contamination introduced during the extraction and laboratory handling of the samples.

To choose an appropriate calibration range for the calibration standards, data from an active sampler run by the Hillsborough County Environmental Protection Commission

were considered. Figure 2.1 shows the distribution of benzene concentrations measured by the EPC's active sampler from 1/1/2008 to 3/27/2010. As the distribution illustrates, the concentrations were generally below 1 µg m^{-3}; however, this active sampler is located in rural Sydney, FL, away from the urban center of Tampa, which may explain the low levels. The Health Effects Institute (2008) completed a literature review of reported concentrations in many settings, and the range of concentrations reported in urban areas was approximately 1-10 µg m^{-3}. To determine an appropriate calibration range for this study, these concentrations were also taken into account. To determine the range of calibration standards needed to encompass the estimated ambient concentrations, Equation 2.4 was used to calculate the mass of benzene that would accumulate on the sampler over a one week exposure time:

$$m_{final} = C_{air} \cdot Q_{298} \cdot t \cdot 10^{-6} \qquad \textbf{Equation 2.4}$$

Where m_{final} is mass of benzene (µg), C_{air} is the ambient concentration of benzene (µg m^{-3}), t is the sampling time (min), and 10^{-6} is a conversion factor from m^3 to ml. To determine the concentration of calibration standards needed, the mass of benzene calculated by Equation 2.4 is divided by a 2 ml extraction volume. This gives a concentration in µg ml^{-1}. The initial concentrations chosen for the calibration standards were (in µg ml^{-1}): 0.15, 0.5, 1.0, 2.5 and 4.0. The calibration curve is shown in Figure 2.2.

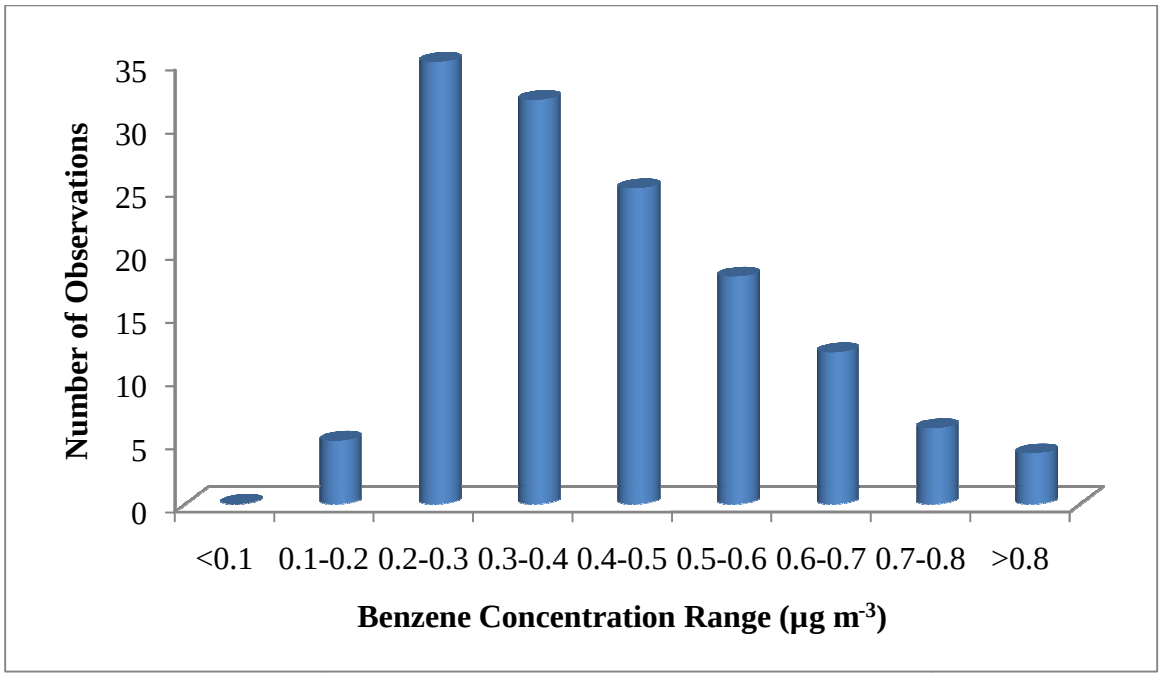

Figure2.1 A frequency distribution of Hillsborough County benzene concentrations. Measurements were taken on 24-hour sampling periods by the Hillsborough County EPC from 1/1/2008-3/27/2010.

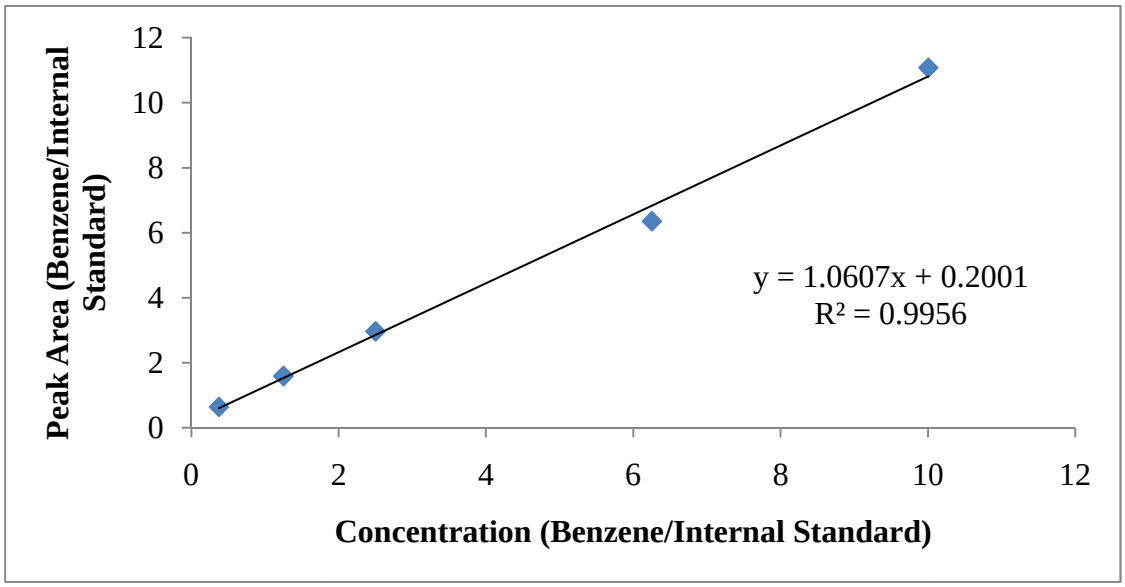

Figure 2.2 The initial calibration curve from March 2011. It was developed using calibration standards ranging from 0.15-4.00 µg ml^{-1}.

The calibration curve shown in Figure 2.2 is used to calculate the concentration of benzene in the unknown samples as:

$$\frac{A_i}{A_{is}} = m\frac{C_i}{C_{is}} + b \qquad \textbf{Equation 2.5}$$

The equation for the calibration line takes the form seen in Equation 2.5, with the slope defined as *m* and the y-intercept as *b*. The area response for benzene is A_i, A_{is} is the area response for 2-fluorotoluene, C_i is the concentration of benzene, and C_{is} is the concentration of 2-fluorotoluene, with concentrations in units of µg ml^{-1}.When an unknown sample is run in the GC/MS, a ratio of the area of the benzene peak to the area of the internal standard peak is obtained. This value is put into Equation 2.5 and the concentration of benzene in the CS_2 solution (C_i) is calculated as:

$$C_i = \frac{C_{is}}{m}\left(\frac{A_i}{A_{is}} - b\right) \qquad \textbf{Equation 2.6}$$

C_{is} is a known value. By multiplying by the total sample volume of 2.08 ml, the mass of benzene desorbed from the sampler (m_{sample}) is calculated in µg. This value is corrected by subtracting the average mass found in the field blanks:

$$m_{final} = m_{sample} - m_{fb,avg} \qquad \textbf{Equation 2.7}$$

The blank-corrected mass (m_{final}) is used to calculate the ambient concentration measured over the 7-day sampling period. The following equation is used:

$$C_{air} = \frac{m_{final}}{Q_K \cdot t} \cdot 10^6 \qquad \textbf{Equation 2.8}$$

Where C_{air} is the ambient benzene concentration in µg m^{-3}, Q_K is the temperature adjusted sampling rate in ml min^{-1}, and *t* is the sampling duration in minutes.

A preliminary sampling run was done with one Radiello sampler in March 2011 in order to test the draft protocols. The calibration data shown in Figure 2.2 were used for quantification, and the measured air concentration for the one week sampling period from 3/4/11-3/11/11 was 0.44 µg m^{-3}. This is similar to previous observations in the Tampa area from the Hillsborough EPC, as seen in Figure 2.1. This preliminary run suggested that concentrations of benzene in the sampling area would be towards the lower range of the calibration standard solutions, and thus the range of solutions for the pilot study was lowered to 0.10-1.75 µg ml^{-1} in order to better characterize lower concentrations. These standard solutions were created before the pilot study and analyzed via GC/MS to ensure the quality assurance criteria were met. The calibration curve developed for quality assurance purposes is shown in Figure 2.3.

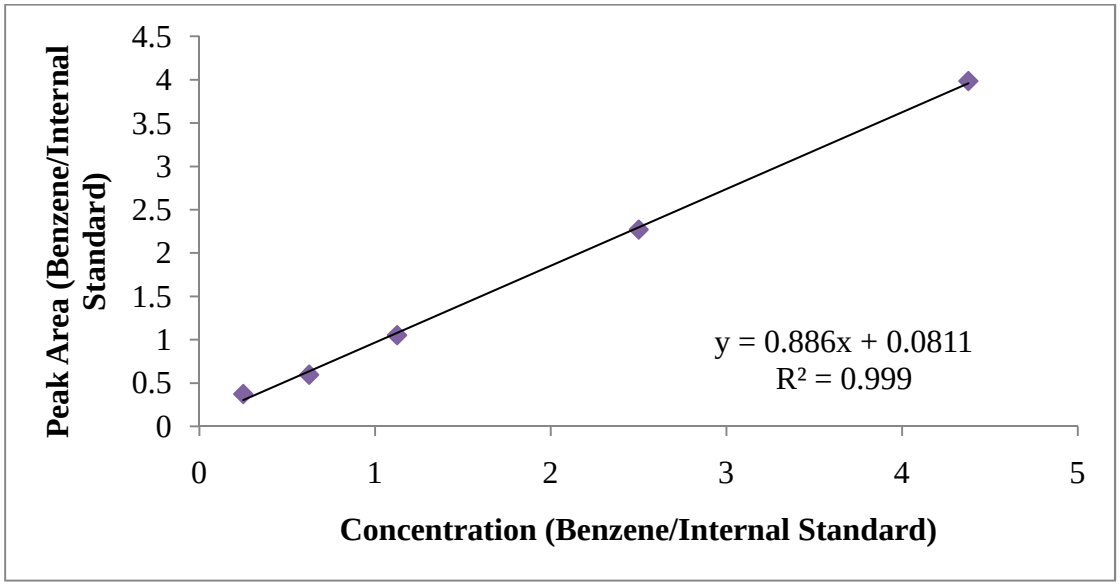

Figure 2.3 Calibration curve generated from standards developed for the pilot study. Concentrations range from 0.10-1.75 µg ml^{-1} benzene.

In addition to the field and laboratory blanks, quality assurance criteria must be met by the calibration standards. These criteria are detailed in the analysis protocol in

Appendix B. In general, the relative response factors (RRFs) of all standards must have a relative standard deviation (RSD) of less than 30% and the relative retention times (RRTs) must be within 0.06 minutes of the mean RRT. The internal standard in all calibration solutions must have an area within 40% of its mean area, and a retention time within 20 seconds of its mean retention time. These criteria must be established upon initial calibration in order to ensure the calibration equation can precisely represent the range of the standards. The protocol also establishes a method to be used for daily calibration checks to ensure the system remains in control; however, for the pilot study daily calibration curves were run during analysis of the unknown samples. A daily control chart was still kept in order to assess the between day confidence in the data. The quality assurance data from the pilot study analyses are provided in Appendix C.

Evaluation of Protocols

The second specific aim is to evaluate these protocols through the co-location of a passive sampler with an existing active sampler during the pilot study. Evaluation of precision is also achieved through the co-location of two passive samplers at the same sampling site during the pilot study. The Radiello RAD130 activated charcoal sampler has already been shown to be effective in previous studies to measure ambient concentrations of benzene over 4-7 day sampling periods (Allou, et al., 2008; Angiuli, et al., 2003). Thus, these co-located observations will allow for evaluation of the standard operating procedures developed through the first specific aim of this project.

There is an active sampler present at the Sydney, Florida monitoring site operated by the Hillsborough County Environmental Protection Commission (EPC). The method used at this air monitoring site to measure benzene is canister sampling over a 24-hour

sampling period (midnight to midnight), every six days. Since the sampling periods of these two methods are different, concentrations are not expected to be directly comparable. However, a comparison of the two concentrations is still important for a qualitative evaluation. The relative percent difference between the EPC data and the Radiello value will be calculated according to Equation 2.3. The sampling period for the pilot study overlapped the final 13 hours of one sampling run and a full day for a second sampling run for the active sampler; 24-hour samples were taken on 4/27/11 and 5/3/11. These two measurements from the active sampler were averaged, and their average was used in the relative percent difference calculation. These measured values, along with the one week measurement, are compared with benzene concentrations from the literature that have been experienced in other urban areas. For example, Janssen et al. (2001) measured weekly average benzene concentrations of 0.3-5.0 $\mu g\ m^{-3}$ outside of schools near motorways, and concentrations in parks in urban areas of Sweden were measured as 2-4 $\mu g\ m^{-3}$ (Upmanis, Eliasson, & Andersson-Skold, 2001).

To evaluate the precision of these methods, two Radiello samplers were co-located at one sampling site during the sampling period. These samplers were exposed to the same airborne concentrations of benzene, so any differences in their concentrations will be due to uncertainties in the methods. Relative percent difference of the measurements will be used to quantify the repeatability, using Equation 2.3. The U.S. Environmental Protection Agency (1999a) indicates in their compendium method TO-15 that an acceptable level for precision of a method should fall within 25%. The percent difference calculated from the two duplicate samplers in the pilot study will be used to represent error bars when presenting the data, through Equation 2.9:

$$error = \pm(\%D \cdot \bar{x}_i) \qquad \textbf{Equation 2.9}$$

Where $\bar{x}_i$ is the average benzene concentration (after three replicate analyses) of sampling site i. This method will allow for the determination of error due to the sampler and subsequent analysis. Using the standard deviation of replicate GC/MS analyses would only characterize the error from the instrumentation.

Pilot Study

The third specific aim was to investigate the spatial variation in concentrations of benzene over a case study area, such as a school, and determine the resultant variations in risk levels for chronic cancer and non-cancer health effects. This was achieved through a seven day pilot study using the Radiello RAD130 passive sampler.

Sampling Design

The pilot study was carried out from 4/27/11-5/4/11 over Riverhills Park in Temple Terrace, FL. A set of Radiello RAD130 passive samplers was deployed across eleven sampling sites over the grounds of a case study city park containing a playground adjacent to an elementary school. The sampling site selection involved choosing available trees/utility poles in a saturated distribution, approximately equidistant from one another. A satellite image of the sampling locations is shown in Figure 2.4. The samplers were brought back to the laboratory and stored at 4°C until June 2011, when extraction with carbon disulfide and analysis using the GC/MS system was completed. The concentration distributions were mapped using ArcGIS software and visually displayed using the kriging analysis technique, which interpolates from the data points given to create concentration contours over a rectangular area containing the points.

Quantitative analysis of variation in concentration over the sampling area was done through calculation of the coefficient of variation. The coefficient of variation is the ratio of the standard deviation (σ) to the mean (μ) of the observations, and is calculated using the following:

$$CV(\%) = \frac{\sigma}{\mu} \cdot 100\% \qquad \textbf{Equation 2.10}$$

A coefficient of variation of greater than 20% has been used to indicate heterogeneous concentrations over a spatial area for other air pollutants (Blanchard et al., 1999; Wilson et al., 2005).

Figure 2.4 Satellite image of the sampling locations used in the pilot study. The area inside the white box corresponds to the area pictured in Figure 3.2. Source: "Riverhills Park." 28°01'11.93" N and 82°23'09.30" W. Google Earth. April 4, 2010. Accessed: June 10, 2011.

Health Risk Calculations

Since children are a susceptible subpopulation to pollutant health effects, health risk calculations were carried out using parameters that describe a child's risk. Although concentrations at the park may or may not be representative of exposures experienced at the adjacent elementary school, the health risk assessment will assume concentrations measured during the pilot study are experienced by a hypothetical student at the school. The calculated risk estimates will only represent the contribution of risk from benzene exposure at school and are not indicative of cumulative overall lifetime health risk. To calculate the cancer risk from exposure to the measured concentrations, two different methods were used and compared. According to the U.S. EPA, the average exposure concentration for benzene should be calculated from the observed concentrations and then multiplied by the inhalation unit risk (IUR) from the Integrated Risk Information System (IRIS) (U.S. Environmental Protection Agency, 2009c). The following calculations were used to calculate the excess lifetime cancer risk:

$$EC = \frac{C_{air} \cdot ET \cdot EF \cdot ED}{AT} \qquad \textbf{Equation 2.11}$$

$$Excess\ Cancer\ Risk = IUR \cdot EC \qquad \textbf{Equation 2.12}$$

In Equation 2.11 and 2.12, *EC* is the exposure concentration of an individual based on the amount of time spent where the ambient concentration measurement (C_{air}) was taken. Both *EC* and C_{air} have units of $\mu g\ m^{-3}$. The variable *ET* represents exposure time (hours day^{-1}). The exposure time used is 6.5 hours day^{-1}; the school day at the elementary school runs for 6 hours and 20 minutes (Hillsborough County Public Schools, 2011), so 6.5 hours should approximately represent time spent before school after drop-off and

after school before pick-up. *EF* represents the exposure frequency (days $year^{-1}$). The value used here is 180 days, since there are 180 days in the Hillsborough County public school year (Hillsborough County Public Schools, 2010). These calculations also assume an exposure duration (*ED*) of six years, which assumes a child attends the school from kindergarten through 5^{th} grade. The denominator *AT* in Equation 2.11 represents the averaging time. For cancer risk calculations, the averaging time is a 70 year lifetime, in units of hours. The inhalation unit risk (*IUR*) is a range of risk values for a specific compound given by the U.S. EPA in their IRIS database. It represents the increased lifetime risk per $\mu g\ m^{-3}$ of the exposure concentration. For benzene, the range of values for the inhalation unit risk is $2.2x10^{-6}$ to $7.8x10^{-6}$ (U.S. Environmental Protection Agency, 2010a). Although the toxicological support documents in IRIS outline probable differences in susceptibility and resultant cancer type for children and adults from benzene exposure, the authors maintain that there is not enough available data to make modifications to the calculations to account for this (U.S. Environmental Protection Agency, 1998). In order to attempt to represent the susceptibility of children, the upper bound of the *IUR* ($7.8 \cdot 10^{-6}$) was used to assess children's health risk for this pilot study, though the range was also considered in the uncertainty analysis.

Equations 2.11 and 2.12 provide the current method used when carrying out U.S. EPA risk assessments on Superfund sites. However, there are no variables that can be adjusted to examine differences in susceptibility or exposure between children and adults. The California Environmental Protection Agency provides different guidance on how to calculate excess lifetime cancer risk, which includes variables that differentiate adult and child exposure (Hickox & Denton, 2000). In this approach, the dose of benzene received

by inhalation is calculated and then multiplied by a cancer potency factor, which has been developed by the California EPA (Office of Environmental Health Hazard Assessment, 2009). The formula for dose given by Hickox & Denton (2000) is as follows:

$$D = C_{air} \cdot \left[\frac{BR}{BW}\right] \cdot 10^{-6} \cdot A \cdot \frac{EF \cdot ED}{AT} \qquad \textbf{Equation 2.13}$$

$$Excess\ Cancer\ Risk = D \cdot CPF \qquad \textbf{Equation 2.14}$$

The calculated dose (*D*) is the amount of benzene inhaled per kilogram of body weight, per day (mg kg^{-1} day^{-1}). The daily breathing rate (BR) (L day^{-1}) is used, which is divided by the body weight (*BW*) in kg. The daily normalized breathing rate used in this analysis is 0.6 L min^{-1} kg^{-1} for moderate activity of school aged children, or 864 L day^{-1} kg^{-1}, taken from guidance provided by the California EPA (Office of Environmental Health Hazard Assessment, 2004). The term 10^{-6} is a combined conversion factor from µg to mg and L to m^3. The averaging time used in the dose calculation is also 70 years in order to estimate the contribution to lifetime cancer risk, but the units of *AT* in the dose calculation are days instead of hours. The term *A* represents the inhalation absorption factor, which accounts for the proportion of inhaled benzene that is absorbed by the body. The default value for this variable is one, meaning all inhaled benzene is absorbed, unless the cancer potency factor (*CPF*) was developed using a different value. The cancer potency factor is a parameter estimated by the Office of Environmental Health Hazard Assessment (2009) through a review of published studies using both animal and human subjects; the value used is 0.1 (mg kg^{-1} day^{-1})$^{-1}$. It was not developed using an absorption factor, so in this risk assessment the value for *A* will be the default value of one.

To quantify the chronic non-cancer effects from inhalation of benzene, the Hazard Quotient (*HQ*) was calculated using the Reference Concentration (*RfC*) from the IRIS database. The *RfC* given for benzene exposure is the concentration at which humans experience a decreased lymphocyte count (U.S. Environmental Protection Agency, 2010a). The Hazard Quotient is calculated as follows:

$$HQ = \frac{EC}{RfC} \qquad \textbf{Equation 2.15}$$

The exposure concentration (*EC*) used in Equation 2.15 is calculated using the same method as Equation 2.11, except the averaging time is equal to the exposure duration (6 years), in hours. The *RfC* is a value estimated by the U.S. Environmental Protection Agency (2010a) as $3x10^{-2}$ mg m^{-3}, or 30 µg m^{-3}. A value of the *HQ* of greater than one indicates the population is potentially at risk for hematological effects from the observed concentration (U.S. Environmental Protection Agency, 2002). This method once again does not take into account differences between children and adults; however, the authors did not find any significant evidence to suggest that children are more susceptible to the non-cancerous health effects of benzene exposure (U.S. Environmental Protection Agency, 2002).

The calculation of these values will allow investigation of uncertainties in children's health risk calculations associated with high resolution spatial variations over the small sampling area of this city park. For instance, if a sampler were to be placed at one location rather than the other, these results will show if there are any considerable differences associated with the health risk calculations due to sampler placement. To consider the contribution of uncertainty in risk calculations from sampler placement, the percent difference between the minimum and maximum health risk estimates were

calculated for each method. These were compared to the percent difference between average health risk when calculated using minimum and maximum values for the inhalation unit risk and cancer potency factor. This allows for an illustration of the amount of uncertainty contributed by sampler placement compared to the amount of uncertainty contributed by estimation of the cancer potency factor/inhalation unit risk values. This method for comparison places less importance on the accuracy of the variables chosen when calculating the exposure concentration and dose, since the same values are used when estimating the risk at each site. The uncertainty that this analysis is focused on is the contribution from sampler placement.

CHAPTER 3:

RESULTS AND DISCUSSION

Concentrations Observed During Pilot Study

This pilot study was carried out between 4/27/11-5/4/11 over Riverhills Park in Temple Terrace, FL. The average temperature over the sampling period was 79.11 °F, or 299.3 K; the hourly wind speed and humidity fluctuated within their acceptable ranges for constant sampling rate. The temperature adjusted sampling rate for the pilot study was calculated as 80.53 ml min^{-1} using Equation 2.1, which is slightly higher than Q_{298}. Table 3.1 shows a summary of the concentrations found over the study area. The measured concentrations ranged from 0.23-0.34 µg m^{-3}. The mean value observed at these sites was 0.30 µg m^{-3} benzene. This is comparable to previously measured values taken by the Hillsborough County EPC; as seen in Figure 2.1., the mode value of the observations taken between 1/1/2008-3/27/2010 was the range between 0.2-0.3 µg m^{-3} benzene. These results are also comparable to the lower end of outdoor weekly concentrations taken at schools near motorways in the Netherlands, where Janssen et al. (2001) observed concentrations of 0.3-5.0 µg m^{-3}. The results from this pilot study also show concentrations comparable to the low end of the range from observations taken in other urban areas as seen in a review compiled by the Health Effects Institute (2008) of 1-10 µg m^{-3}. They are lower than measurements taken in urban parks in Sweden where concentrations were found to range from 2-4 µg m^{-3} (Upmanis, Eliasson, & Andersson-

Skold, 2001). The low concentrations observed during the pilot study may be due to the location of the pilot study park within a neighborhood without major roadways as an immediate border.

Table 3.1 Data and summary statistics for the pilot study. Concentrations measured from eleven sampling sites over Riverhills Park during the pilot study from 4/27/11-5/4/11. The percent difference was calculated using the minimum and maximum observed concentrations. The limit of detection is calculated using the benzene concentrations from the two field blanks and one laboratory blank.

Site	Concentration Benzene (µg m^{-3})
1	0.33
2	0.33
3	0.34
4	0.28
5	0.31
6	0.27
7	0.29
8	0.29
9	0.26
10	0.23
11	0.31
Mean	0.30
Standard Deviation	0.03
Minimum	0.23
Maximum	0.34
Relative Percent Difference	39%
Coefficient of Variation	11%
Limit of Detection	0.18

Evaluation of Methods through Co-location

Table 3.2 shows the results obtained from the two duplicate samplers as well as their percent difference.

Table 3.2 Precision data from co-location of duplicate samplers. The samplers were both exposed at sampling site number eight during the pilot study. The percent difference was calculated previous to rounding to two significant digits.

	Benzene
Duplicate 1 (µg m^{-3})	0.29
Duplicate 2 (µg m^{-3})	0.34
Relative Percent Difference	14%

The percent difference of these two measurements is 14%. The U.S. EPA guidance for the sampling of VOCs through compendium method TO-15 recommends a percent difference value for duplicate samples within 25% (U.S. Environmental Protection Agency, 1999a). The percent difference of 14% seen in this pilot study fits within the recommended precision guidelines.

Table 3.3 shows measurements taken by the EPC sampler and the results from the passive sampler in the pilot study. The results given by the EPC are unofficial, as they have not completed the entire quality control verification process.

Table 3.3 Accuracy data from co-location with the active sampler. The calculations were done previous to rounding to two significant digits.

	Benzene
Active Sample 4/27/11 (µg m^{-3})	0.24
Active Sample 5/3/11 (µg m^{-3})	0.28
Active Sample Average (µg m^{-3})	0.26
Passive Sample (µg m^{-3})	0.26
Percent Difference	3.0%

The percent difference of 3% is calculated using the passive sample observation and the average of the two active sampler measurements, before rounding. Even though the

sampling times are not the same, this result indicates that the passive sampling methods used for the pilot study give very similar results to currently used active sampling methods. To two significant digits, the concentrations measured by both methods are the same. The value of 3% is also within the precision of the method (14%) as indicated by the duplicate samplers, signifying that the values are effectively equal. This result encourages the use of the methods developed in this thesis for future use in a larger scale passive sampling campaign over Hillsborough County.

Spatial Variation of Concentrations

In order to visually interpret the concentrations of benzene over the sampling area, a kriging interpolation was performed on the data using ArcGIS software. This technique estimates concentration contours from the concentration data points given. The contour map can be seen in Figure 3.1. Figure 3.2 shows the individual measurements taken at each sampling location, in decreasing order. While the magnitude in concentration variation may be small, Figure 3.1 illustrates that the highest concentrations were found in the northwest corner of the sampling area. This part of the park contained the entrance from the street and two parking lots, which may contribute to the higher concentration. This area also is near a playground where children from the elementary school were observed playing during sampler retrieval. The variation over the study area can be characterized by the 39% relative percent difference seen between the highest and lowest concentrations. This variation is larger than the values used to describe the precision (14%) and accuracy (3%) error estimates, indicating an actual difference in measured concentrations.

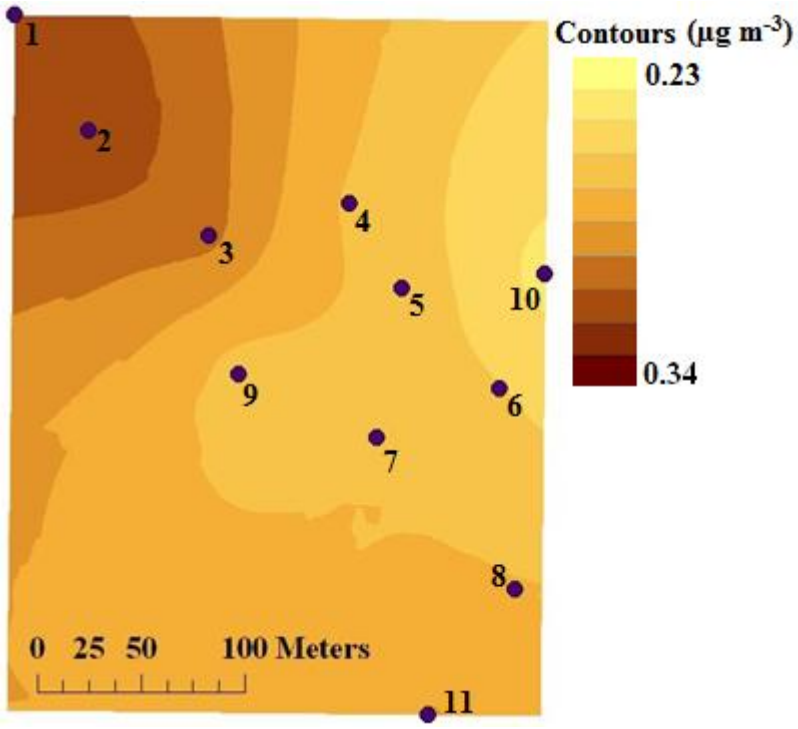

Figure 3.1 Concentration contours over the study area. The map was created using the kriging interpolation technique in ArcGIS software. The area pictured in this image is the area inside the white box in Figure 2.4.

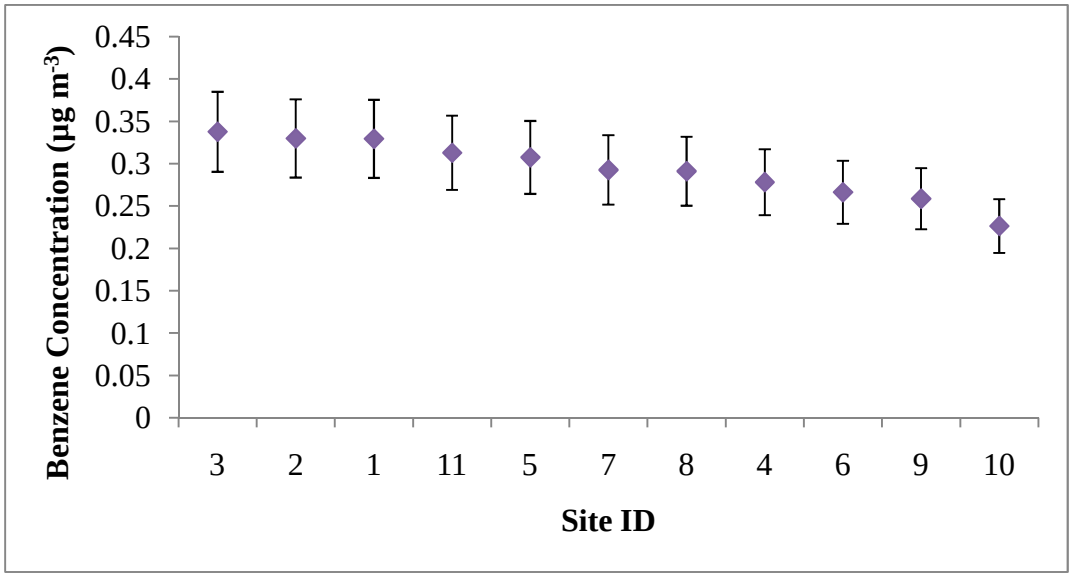

Figure 3.2 Individual measurements taken during the pilot study. The error bars represent an uncertainty of ±14%, which is the percent difference between the duplicate sample measurements. The data is arranged from highest to lowest concentration measured.

Previous studies have used the coefficient of variation to quantify the spatial heterogeneity of air pollutants (Blanchard et al, 1999; Wilson et al., 2005). The authors suggest that a coefficient of variation of greater than 20% indicates that the concentrations of a pollutant are heterogeneous over the sampling area. However, there is no real standard for quantifying spatial heterogeneity. In this study, the coefficient of variation of the samples taken over Riverhills Park is 11%. Although Figure 3.1 shows an uneven concentration distribution over the area of the park, this result implies that the measured concentrations of benzene have little variation and can be considered relatively homogenous. This is better illustrated through Figure 3.2, which shows that all measurements have overlapping error bars.

Health Risk Estimations

Since the low coefficient of variation indicated somewhat homogeneous concentrations over the sampling area, it seems reasonable to assume that these measurements may be representative of levels experienced by children at the adjacent school. The minimum and maximum values for lifetime cancer risk contribution are given in Table 3.4. The hazard quotient was also calculated, which is used to illustrate risk of non-cancer health effects.

Table 3.4 Summary of health risk estimates. Minimum and maximum estimates of health risks were calculated using the highest and lowest observed concentrations from the pilot study. The percent difference is equal to the percent difference between the high and low concentrations, and is the same for all risk estimates.

	Cancer Risk, EPA Method	Cancer Risk, California EPA Method	Hazard Quotient	Percent Difference (%)
Minimum	2.0E-08	8.3E-07	0.0010	39
Maximum	3.0E-08	1.2E-06	0.0015	

The U.S. EPA recommends that when calculating risk assessment estimates, a one in a million level (or 10^{-6}) is an acceptable upper limit of risk for health effects. The overall magnitude of the added health risk is lower than the standard 10^{-6} value at all sites when calculated using the inhalation unit risk. When calculated using the more conservative values for cancer potency factor from the California EPA, the estimates are near this 10^{-6} level, meeting or exceeding it at nine of the eleven sites. These calculations only take into account the risk contribution from exposure to benzene over a 6 year school period and are not indicative of any individual's total risk. To quantify the uncertainty in the health risk estimate due to sampler placement, a percent difference calculation was used. The percent difference between the health risk estimate calculated using the highest observed concentration (site 3) and the lowest (site 10) is 39%. For a comparison of what the magnitude of this uncertainty means, an examination of the uncertainty inherent in the risk estimate calculations was done. Instead of examining the uncertainty in the variables chosen by the researcher (such as the time and body weight estimates that are specific to the particular study), both the EPA and the California EPA provided possible ranges for the values of the inhalation unit risk and the cancer potency

factor. The percent difference was calculated between the high and low reported values for each parameter. As seen in Table 3.5, the uncertainty in the calculations due to the parameters used was 112% and 148%. The uncertainty inherent in the risk calculations is much greater than the uncertainty introduced by sampler placement in this study.

Table 3.5 Uncertainty due to parameters used in health risk calculations. The range of values reported for the inhalation unit risk by the U.S. EPA is shown, as well as the range of values for the cancer potency factor reported by the California EPA. The percent difference of the minimum and maximum values for each parameter is calculated.

	Inhalation Unit Risk Range $(\mu g\ m^{-3})^{-1}$	**Cancer Potency Factor Range** $(mg\ kg^{-1}\ day^{-1})^{-1}$
Minimum	2.20E-06	0.03
Maximum	7.80E-06	0.2
Percent Difference	112%	148%

A study in Pittsburgh looked at the spatial variation in toxic air pollutant concentrations over a larger intra-urban scale in order to investigate environmental equity issues for populations near the heavily industrialized parts of the city. The researchers found that while concentrations of individual pollutants varied between the sites, the additive risk from organic air pollutants (driven mainly by formaldehyde and benzene) ranged from $6.1x10^{-5}$ to $9.5x10^{-5}$ (Logue et al., 2010). This is a relative percent difference of approximately 44%, which is comparable to the relative percent difference of 39% found in this study. The comparison between health risk uncertainty contributions from the sampler placement versus parameter estimates brings up a question about what is spatially resolved "enough" in terms of measuring the variation in benzene, or other air toxics, concentrations. Variation in levels may need to be relatively large (compared to this study) to overcome the uncertainty inherent in the risk assessment

calculations, which implies that there is a limit to what resolution in monitoring data is necessary to determine if levels are protective of human health for regulatory risk purposes. However, monitoring data at a resolution higher than what is necessary to show variation in exposure estimates may aid epidemiological studies in associating health effects of pollutants with exposures at environmental levels. Research in this field may in turn lower the amount of uncertainty in current calculation parameters, allowing more variation to be useful. Future studies should continue to investigate spatial distributions of concentrations and the benefits gained from these data in different types of studies.

CHAPTER 4:

CONCLUSIONS AND IMPLICATIONS

Little is known about the health effects of benzene exposures at environmental levels. The use of active monitors in regulatory monitoring stations contributes to this gap. Due to the expensive nature of the instruments there may only be a handful of sites that monitor air toxic substances in a state. This low spatial resolution in measurement data does not allow for precise characterization of the exposure of an individual or susceptible subpopulation, which hampers epidemiologic studies attempting to find associations between exposure and health effects. Concentration differences of mobile source air pollutants within an urban area due to the distribution of roadways have been found to cause large exposure differences between neighborhoods or schools in an urban area, depending on their location. In order to ensure that the measurements being taken at the regulatory monitoring site are protective of all people living in the area, better spatial resolution of concentration data is necessary. Passive sampling allows for a cost-effective method of gaining high spatial resolution monitoring data to better understand subpopulation exposures.

This study aimed to develop and evaluate methods for the passive sampling and analysis of ambient benzene concentrations in Hillsborough County, as well as conduct a pilot study investigating the spatial variation in benzene concentrations on a highly resolved scale. Methods for the use and GC/MS analysis of the Radiello passive sampler

with activated charcoal sorbent were developed. Co-location with an active sampler run by Hillsborough County resulted in effectively no difference between measurements. A pilot study was performed over a city park adjacent to an elementary school in Temple Terrace, FL. Eleven sampling locations were chosen over the park, and the concentrations were found to range from 0.23-0.34 $\mu g\ m^{-3}$ with a mean of 0.30 $\mu g\ m^{-3}$ and precision of 14%. This range is on the low end of concentrations seen in other urban areas, but comparable to measurements taken by the active sampler in the county. When concentration contours are created using the data points, the concentrations in the northwest corner of the sampling area tend to be higher. This area encompasses the entrance and parking lots for the park, illustrating the potential impact of mobile source emissions from those areas on the park benzene concentrations. However, the coefficient of variation of the measurements was 11%, indicating that the observed variation is small in magnitude.

Risk estimates for cancer and non-cancer health effects were calculated for a child attending the adjacent elementary school. The calculated values for contribution to lifetime cancer risk were below the currently acceptable risk level of 10^{-6} when calculated using the inhalation unit risk, but risk estimates were near to but exceeding the currently recommended value at several sites when the more conservative parameters from the California EPA were used. The hazard quotients calculated were much smaller than the 1.0 limit that indicates possible chronic, non-cancer health risk for regulatory purposes. Only for the calculation using the California EPA method does the uncertainty in risk due to sampler placement lead to different categorization of the result as above or below the standard. This uncertainty could therefore have some significance for regulatory

purposes. However, the uncertainty in risk due to sampler placement over the park was found to contribute substantially less to the overall uncertainty in the calculations than the uncertainty inherent in the parameters used in the calculations given by regulatory agencies.

The successful use of the samplers in the pilot study, and the agreement between the measurements taken by the co-located sampler with the active sampler both suggest that these protocols are applicable for use in measuring ambient benzene concentrations in Hillsborough County. The pilot study results imply that for the area of this park in the pilot study, only one sampler may be necessary to characterize the exposure of an individual while in the park due to uncertainty in health risk estimate calculations. However, since people do not spend all of their time in one location, a larger study is necessary in order to better understand the variation in concentrations on a neighborhood scale. While the concentrations seen in this study did not result in large magnitude or variation in risk levels, these factors still need to be considered in future studies where observed concentrations may be higher or have larger variation. These results will aid in the development of a larger passive sampling campaign to be completed over Hillsborough County.

REFERENCES

3M Occupational Health and Environmental Safety Divison. (2004, May 14). *3M Air Monitoring Systems.* Retrieved June 10, 2010, from 3M: http://multimedia.3m.com/mws/mediawebserver?mwsId=SSSSSu7zK1fslxtUmx_GOxMSev7qe17zHvTSevTSeSSSSSS--

Agency for Toxic Substances and Disease Registry. (2007). *Toxicological Profile for Benzene.* Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA.

Alexis, N., Barnes, C., Bernstein, I. L., Bernstein, J. A., Nel, A., Peden, D., et al. (2004). Health effects of air pollution. *Journal of Allergy and Clinical Immunology, 114* (5), 1116 -1123.

Allou, L., Marchand, C., Mirabel, P., & Le Calve, S. (2008). Aldehydes and BTEX Measurements and Exposures in University Libraries in Strasbourg (France). *Indoor and Built Environment, 17* (2), 138-145.

Angiuli, L., Bruno, P., Caputi, M., Caselli, M., de Gennaro, G., & de Rienzo, M. (2003). Radial Passive Samplers for Air Quality Monitoring in Field Comparison with a BTEX Automatic Analyser Preliminary Results. *Fresenius Environmental Bulletin, 12* (10), 1167-1172.

Aragon, P., Atienza, J., & Climent, M. D. (2000). Analysis of organic compounds in air: A review. *Critical Reviews in Analytical Chemistry, 30*, 121-151.

Bergerow, J., Jermann, E., Keles, T., & Dunemann, L. (1999). Performance of two different types of passive samplers for the GC/ECD-FID determination of environmental VOC levels in air. *Fresenius Journal of Analytical Chemistry, 363*, 399-403.

Bird, M. G., Greim, H., Kaden, D. A., Rice, J. M., & Snyder, R. (2010). BENZENE 2009—Health effects and mechanisms of bone marrow toxicity: Implications for t-AML and the mode of action framework. *Chemico-Biological Interactions, 184*, 3-6.

Blanchard, C. L., Carr, E. L., Collins, J. F., Smith, T. B., Lehrman, D. E., & Michaels, H. M. (1999). Spatial representativeness and scales of transport during the 1995 integrated monitoring study in California's San Joaquin valley. *Atmospheric Environment, 33*, 4775-4786.

Boothe, V. L., & Shendell, D. G. (2008). Potential Health Effects Associated with Residential Proximity to Freeways and Primary Roads: Review of Scientific Literature, 1999-2006. *Journal of Environmental Health, 70* (8), 33-42.

Brown, J., & Shirey, B. (2001). *A Tool for Selecting an Adsorbent for Thermal Desorption Applications.* Retrieved April 2, 2010, from Sigma-Aldrich: http://www.sigmaaldrich.com/etc/medialib/docs/Supelco/General_Information/t402025.Par.0001.File.tmp/t402025.pdf

Bruno, P., Caputi, M., Caselli, M., de Gennaro, G., & de Rienzo, M. (2005). Reliability of a BTEX radial diffusive sampler for thermal desorption: Field measurements. *Atmospheric Environment, 39*, 1347-1355.

Chakraborty, J. (2009). Automobiles, air toxics, and adverse health risks: environmental inequities in Tampa Bay, Florida. *Annals of the Association of American Geographers, 99* (4), 674-697.

Chung, C. W., Morandi, M. T., Stock, T. H., & Afshar, M. (1999). Evaluation of a passive sampler for volatile organic compounds at ppb concentrations, varying temperatures, and humidities with 24-h exposures. 2. Sampler Performance. *Environmental Science and Technology, 33*, 3666-3671.

Cocheo, V., Boaretto, C., & Sacco, P. (1996). High Uptake Rate Radial Diffusive Sampler Suitable for Both Solvent and Thermal Desorption. *American Industrial Hygeine Association Journal, 57*, 897-904.

Delfino, R. J., Gong Jr., H., Linn, W. S., Pellizzari, E. D., & Hu, Y. (2003). Asthma Symptoms in Hispanic Children and Daily Ambient Exposures to Toxic and Criteria Air Pollutants. *Environmental Health Perspectives, 111* (4), 647-656.

Duarte-Davidson, R., Courage, C., Rushton, L., & Levy, L. (2001). Benzene in the environment: an assessment of the potential risks to the health of the population. *Occupational Environmental Medicine, 58*, 2-13.

Eastern Research Group, Inc. (2008). *2007 National Monitoring Programs (UATMP and NATTS).* U.S. Environmental Protection Agency.

Fondazione Salvatoremaugeri-IRCCS. (2006, January). *Radiello.* Retrieved September 13, 2010, from Radiello: http://www.radiello.com/english/Radiello's%20manual%2001-06.pdf

Fushimi, A., Kawashima, H., & Kajihara, H. (2005). Source apportionment based on an atmospheric dispersion model and multiple linear regression analysis. *Atmospheric Environment, 39*, 1323-1334.

Godoi, R. H., Avigo Jr, D., Campos, V. P., Tavares, T. M., de Marchi, M. R., Van Grieken, R., et al. (2009). Indoor air quality assessment of elementary schools in Curitiba, Brazil. *Water, Air, & Soil Pollution, 9*, 171-177.

Gwinn, M. R., Craig, J., Axelrad, D. A., Cook, R., Dockins, C., Fann, N., et al. (2011). Meeting Report: Estimating the Benefits of Reducing Hazardous Air Pollutants—Summary of 2009 Workshop and Future Considerations. *Environmental Health Perspectives, 119* (1), 125-130.

Health and Safety Executive. (1993, March). *Volatile Organic Compounds in Air.* Retrieved June 13, 2010, from Methods for the Determination of Hazardous Substances: http://www.hse.gov.uk/pubns/mdhs/pdfs/mdhs72.pdf

Health Effects Institute. (2008, January 9). *Mobile-Source Air Toxics: A Critical Review of the Literature on Exposure and Health Effects.* Retrieved September 8, 2010, from HEI Publications: http://pubs.healtheffects.org/getfile.php?u=390

Hickox, W. H., & Denton, J. E. (2000, September). *Air Toxics Hot Spots Program Risk Assessment Guidelines: Part IV Technical Support Document for Exposure Assessment and Stochastic Analysis.* Retrieved January 19, 2011, from http://oehha.ca.gov/air/hot_spots/pdf/Stoch4f.pdf

Hillsborough County Public Schools. (2010). *Calendars*. Retrieved June 17, 2011, from Hillsborough County Public Schools: http://www.sdhc.k12.fl.us/info/calendars/2010_11impdates.html

Hillsborough County Public Schools. (2011). *Riverhills Information*. Retrieved June 17, 2011, from Hillsborough County Public Schools: http://www.sdhc.k12.fl.us/schools/school_info.asp?site=3621

Houston, D., Wu, J., Ong, P., & Winer, A. (2004). Structural disparities of urban traffic in southern California: Implications for vehicle-related air pollution exposure in minority and high-poverty neighborhoods. *Journal of Urban Affairs, 26* (5), 565-592.

Hubbell, B. J., Crume, R. V., Evarts, D. M., & Cohen, J. M. (2010). Regulation and progress under the 1990 Clean Air Act Amendments. *Review of Environmental Economics and Policy, 4* (1), 122-138.

Janssen, N. A., van Vliet, P. H., Aarts, F., Harssema, H., & Brunekreef, B. (2001). Assessment of exposure to traffic related air pollution of children attending schools near motorways. *Atmospheric Environment, 35*, 3875-3884.

Jia, C., Batterman, S., & Godwin, C. (2008). VOCs in industrial, urban and suburban neighborhoods, Part 1: Indoor and outdoor concentrations, variation, and risk drivers. *Atmospheric Environment, 42*, 2083-2100.

Karakitsios, S. P., Delis, V. K., Kassomenos, P. A., & Pilidis, G. A. (2007). Contribution to ambient benzene concentrations in the vicinity of petrol stations: Estimation of the associated health risk. *Atmospheric Environment, 41*, 1889-1902.

Keith, L. H., Libby, R. A., Crummett, W., Taylor, J. K., Deegan, J. J., & Wentler, G. (1983). Principles of Environmental Analysis. *Analytical Chemistry, 55*, 2210-2218.

Kinney, P. L., Chillrud, S. N., Ramstrom, S., Ross, J., & Spengler, J. D. (2002). Exposures to multiple air toxics in New York City. *Environmental Health Perspectives, 110* (4), 539-546.

Logue, J. M., Small, M. J., Stern, D., Maranche, J., & Robinson, A. L. (2010). Spatial Variation in Ambient Air Toxics Concentrations and Health Risks between Industrial-Influenced, Urban, and Rural Sites. *Journal of the Air & Waste Management Association, 60*, 271-286.

Martin, N. A., Marlow, D. J., Henderson, M. H., Goody, B. G., & Quincey, P. A. (2003). Studies using the sorbent Carbopack X for measuring environmental benzene with Perkin-Elmer-type pumped and diffusive samplers. *Atmospheric Environment, 37*, 871-879.

Massolo, L., Rehwagen, M., Porta, A., & Ronco, A. (2010). Indoor–outdoor distribution and risk assessment of volatile organic compounds in the atmosphere of industrial and urban areas. *Environmental Toxicology, 25* (4), 339-349.

McCarthy, M. C., O'Brien, T. E., Charrier, J. G., & Hafner, H. R. (2009). Characterization of the Chronic Risk and Hazard of Hazardous Air Pollutants in the United States Using Ambient Monitoring Data. *Environmental Health Perspectives, 117* (5), 790-796.

Mejia, J. F., Choy, S. L., Mengersen, K., & Morawska, L. (2011). Methodology for assessing exposure and impacts of air pollutants in school children: Data collection, analysis and health effects -- A literature review. *Atmostpheric Environment, 45*, 813-823.

Mukerjee, S., Smith, L. A., Norris, G. A., Morandi, M. T., Gonzales, M., Noble, C. A., et al. (2004). Field Method Comparison between Passive Air Samplers and Continuous Monitors for VOCs and NO2 in El Paso, Texas. *Journal of the Air and Waste Management Association, 54*, 307-319.

Myers, I., & Maynard, R. L. (2005). Polluted Air- Outdoors and Indoors. *Occupational Medicine, 55*, 432-438.

Namiesnik, J., Zabiegala, B., Kot-Wasik, A., Partyka, M., & Wasik, A. (2005). Passive sampling and/or extraction techniques in environmental analysis: a review. *Analytical and Bioanalytical Chemistry, 381*, 279-301.

Office of Environmental Health Hazard Assessment. (2009, May). *Air Toxics Hot Spots Risk Assessment Guidelines Part II: Technical Support Document for Cancer Potency Factors- Appendix B: Chemical-specific summaries of the information used to derive unit risk and cancer potency values.* Retrieved January 19, 2011, from California Environmental Protection Agency: http://www.oehha.ca.gov/air/hot_spots/2009/AppendixB.pdf

Office of Environmental Health Hazard Assessment. (2004, February). *Guidance for Assessing Exposures and Health Risks at Existing and Proposed School Sites Pursuant to Health and Safety Code §901(f): Final Report.* Retrieved June 17, 2011, from Office of Environmental Health Hazard Assessment: http://oehha.ca.gov/public_info/public/kids/pdf/SchoolscreenFinal.pdf

Olson, D. A., Hammond, D. M., Seila, R. L., Burke, J. M., & Norris, G. A. (2009). Spatial gradients and source apportionment of volatile organic compounds near roadways. *Atmospheric Environment, 43*, 5647-5653.

Oury, B., Lhuillier, F., Protois, J., & Morele, Y. (2006). Behavior of the GABIE, 3M 3500, PerkinElmer Tenax TA, and RADIELLO145 Diffusive Samplers Exposed Over a Long Time to a Low Concentration of VOCs. *Journal of Occupational and Environmental Hygiene, 3*, 547-557.

Partyka, M., Zabiegala, B., & Namiesnik, J. (2007). Application of Passive Samplers in Monitoring of Organic Constituents of Air. *Critical Reviews in Analytical Chemistry, 37*, 51-78.

Pastor, M. J., Sadd, J. L., & Morello-Frosch, R. (2002). Who's minding the kids? Pollution, public schools, and environmental justice in Los Angeles. *Social Science Quarterly, 83* (1), 263-280.

Popek, E. P. (2003). *Sampling and Analysis of Environmental Chemical Pollutants: A Complete Guide.* San Diego: Elsevier Science.

Protano, C., Guidotti, M., Manini, P., Petyx, M., La Torre, G., & Vitali, M. (2010). Benzene exposure in childhood: Role of living environments and assessment of available tools. *Environment International, 36* (7), 779-787.

Ruchirawat, M., Settachan, D., Navasumrit, P., Tuntawiroon, J., & Autrup, H. (2007). Assessment of potential cancer risk in children exposed to urban air pollution in Bangkok, Thailand. *Toxicology Letters,* 200-209.

Schneider, P., Gebefugi, I., Richter, K., Wolke, G., Schnelle, J., Wichmann, H. E., et al. (2001). Indoor and outdoor BTX levels in German cities. *The Science of the Total Environment, 267,* 41-51.

Stock, T. H., Morandi, M. T., Afshar, M., & Chung, K. C. (2005). Temporal and spatial variation of air toxics in census tracts with high or low density of TRI emissions using passive sampling. *Proceedings of the 98th Annual Conference of the Air & Waste Management Association.* Minneapolis, MN.

Strandberg, B., Sunesson, A.-L., Olsson, K., Levin, J.-O., Ljungqvist, G., Sundgren, M., et al. (2005). Evaluation of two types of diffusive samplers and adsorbents for measuring 1,3-butadiene and benzene in air. *Atmospheric Environment, 39,* 4101-4110.

Strandberg, B., Sunesson, A.-L., Sundgren, M., Levin, J.-O., Sallsten, G., & Barregard, L. (2006). Field evaluation of two diffusive samplers and two adsorbent media to determine 1,3-butadiene and benzene levels in air. *Atmospheric Environment, 40,* 7686-7695.

Stuart, A. L., & Zeager, M. (2011). An inequality study of ambient nitrogen dioxide and traffic levels near elementary schools in the Tampa area. *Journal of Environmental Management, 92* (8), 1923-1930.

Stuart, A. L., Mudhasakul, S., & Sriwatanapongse, W. (2009). The Social Distribution of Neighborhood-Scale Air Pollution and Monitoring Protection. *Journal of the Air & Waste Management Association, 59* (5), 591-602.

U.S. Environmental Protection Agency. (n.d.). *Air Quality System Data Mart.* Retrieved June 22, 2010, from http://www.epa.gov/ttn/airs/aqsdatamart

U.S. Environmental Protection Agency. (2010a, December 20). *Benzene (CASRN 71-43-2).* Retrieved January 6, 2011, from Integrated Risk Information System: http://www.epa.gov/iris/subst/0276.htm

U.S. Environmental Protection Agency. (1998, April). *Carcinogenic Effects of Benzene: An Update.* Retrieved January 6, 2011, from Integrated Risk Information System: http://www.epa.gov/ncea/pdfs/benzenef.pdf

U.S. Environmental Protection Agency. (1999a, January). *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Compendium Method*

TO-15. Retrieved August 13, 2010, from http://www.epa.gov/ttnamti1/files/ambient/airtox/to-15r.pdf

U.S. Environmental Protection Agency. (1999b, January). *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Compendium Method TO-17*. Retrieved August 30, 2010, from U.S. EPA: http://www.epa.gov/ttnamti1/files/ambient/airtox/to-17r.pdf

U.S. Environmental Protection Agency. (2009a, July 7). *Human Health Exposure Assessment*. Retrieved December 16, 2010, from http://www.epa.gov/region8/r8risk/hh_exposure.html

U.S. Environmental Protection Agency. (2009b, June 12). *PAMS- General Information*. Retrieved April 1, 2010, from Photochemical Assessment Monitoring Stations (PAMS): http://www.epa.gov/oar/oaqps/pams/general.html

U.S. Environmental Protection Agency. (2009c, January). *Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part F, Supplemental Guidance for Inhalation Risk Assessment).* Retrieved December 16, 2010, from http://www.epa.gov/oswer/riskassessment/ragsf/pdf/partf_200901_final.pdf

U.S. Environmental Protection Agency. (2010b, January 28). *Rules and Implementation*. Retrieved April 1, 2010, from Technology Transfer Network Air Toxics Website: http://www.epa.gov/ttn/atw/eparules.html

U.S. Environmental Protection Agency. (2002, October). *Toxilogical Review of Benzene (Noncancer Effects).* Retrieved January 6, 2011, from Integrated Risk Information System: http://www.epa.gov/iris/toxreviews/0276tr.pdf#page=124

Upmanis, H., Eliasson, I., & Andersson-Skold, Y. (2001). Case studies of the spatial variation of benzene and toluene concentrations in parks and adjacent built-up areas. *Water, Air and Soil Pollution , 129*, 61-81.

US Environmental Protection Agency. (n.d.). Retrieved June 22, 2010, from Air Quality System Data Mart [internet database] : http://www.epa.gov/ttn/airs/aqsdatamart

Varian, Inc. (2003). *Saturn 2000 GC/MS MS Workstation Operation Manual.* USA: Varian, Inc.

Varian, Inc. (2003). *Saturn MS 2000 Workstation Tutorial Manual.* USA: Varian, Inc.

Wheeler, B. W., & Ben-Shlomo, Y. (2005). Environmental equity, air quality, socioeconomic status, and respiratory health: a linkage analysis of routine data from the Health Survery for England. *Journal of Epidemial Community Health, 59*, 948-954.

Whitworth, K. W., Symanski, E., & Coker, A. L. (2008). Childhood Lymphohematopoietic Cancer Incidence and Hazardous Air Pollutants in Southeast Texas, 1995-2004. *Environmental Health Perspectives, 116* (11), 1576-1580.

Wilson, J. G., Kingham, S., Pearce, J., & Sturman, A. P. (2005). A review of intraurban variations in particulate air pollution: Implications for epidemiological research. *Atmospheric Environment, 39*, 6444-6462.

Woolfenden, E. (2010). Sorbent-based sampling methods for volatile and semi-volatile organic compounds in air. Part 2. Sorbent selection and other aspects of optimizing air monitoring methods. *Journal of Chromatography A, 1217*, 2685-2694.

APPENDICES

APPENDIX A:

SOP: SAMPLER DEPLOYMENT & RETRIEVAL

1. **Purpose and Applicability**

   This standard operating protocol (SOP) is written to create a consistent procedure for the passive sampling of outdoor benzene concentrations using Radiello activated charcoal sampling cartridges for a seven day sampling period. Using these samplers and protocol, spatial variations in concentrations of benzene will be determined and the resultant variations in exposures and health effect risks will be estimated. Problems encountered with this SOP during the pilot study should be noted and fixed, allowing for a more successful application of this SOP during future applications.

2. **Summary of Method**

   In this method, Radiello pre-packed activated charcoal sampler cartridges are used to collect ambient benzene over a seven day sampling period for subsequent analysis to determine ambient concentrations. The sampling cartridges will be placed inside of a Radiello diffusive body, which is then hung on the inside of a protective shelter for the seven day sampling period. At the end of the seven days, the samplers are removed and taken back to the lab for storage and analysis. They are stable for 6 months at 4°C before elution.

3. **Interferences**

   3.1 The sampling rate of the Radiello sampler varies with temperature. This can be expressed through the following equation:

   $$\boldsymbol{Q_k = Q_{298}\left(\frac{K}{298}\right)^{1.5}}$$

   Q_k = The sampling rate at temperature K.

   Q_{298} = The sampling rate for the compound at 298 Kelvin. For benzene, this is 80 ml min^{-1}.

   K = Average temperature during sampling period.

   3.2 The sampling rate is stable within the humidity range of 15-90% and between wind speeds of 0.1-10 m s^{-1}.

   3.3 Hourly weather data (temperature, wind speed, and humidity) measured at the Tampa International Airport should be obtained through the National Weather Service website.

4. Definitions

4.1 Field Blank

A field blank is a sampling cartridge that is brought into the field during sampler deployment, taken out of the plastic bag, and uncapped for 5 seconds at one site. This helps control for any contamination of the cartridges that could have occurred from transport or handling of the device during deployment. The field blank is subsequently analyzed with all of the field samples and laboratory blanks.

5. Equipment and Materials

5.1 Sampling Equipment

5.1.1 Radiello Cartridge Adsorbents- code RAD130 (pack of 20)

- For sampling VOCs/BTEX with CS_2 desorption
- Matrix: stainless steel net (100 mesh, 5.8mm diameter), with activated charcoal (30-50 mesh)
- Dimensions: 60 mm length x 5.8 mm diameter
- Stored in a glass tube with a polypropylene cap
- An adhesive barcode label is included

5.1.2 Radiello Diffusive Body, white- code RAD120 (pack of 20)

- Polyethylene body
- 25 □m average pore size
- Thickness of 1.7 mm with a diffusive path length of 18 mm
- Dimensions: 60 mm length x 16 mm diameter
- Stored in a polypropylene container

5.1.3 Radiello Triangular Support Plate- code RAD121 (pack of 20)

- Made of polycarbonate
- Includes clip for hanging
- Includes transparent adhesive pocket for label

5.1.4 Radiello Outdoor Shelter- code RAD196 (pack of 10, need 2 packs)

- Made of polypropylene
- Can house up to four Radiello samplers
- Each shelter is comprised of three identical panels, two bars for suspending samplers, and two support bars
- Includes two mounting strips per shelter, but extra strips should be brought during field deployment of the samplers in case they are necessary for attachment around larger objects.

5.2 Materials

5.2.1 A VOC-free ballpoint pen is necessary for labeling samplers.

5.2.2 A cooler with ice packs is necessary for the transport of the samplers from the field back to the laboratory.

5.2.3 A step ladder is necessary for reaching the appropriate height when placing the samplers.

5.2.4 A measuring tape and masking tape are necessary for measuring and marking sampler height.

5.2.5 Labels to place on the shelters with contact information in case of questions or concerns.

5.2.6 A laboratory notebook for recording sampler information and observations.

6. Preparation and Assembly of Shelters and Support Plates

6.1 These procedures should be done at least 24 hours prior to the start of the sampling period. The assembly should take place in the laboratory. The assembly instructions are for one shelter and one support plate; repeat as necessary.

6.2 Assembly of Shelters

6.2.1 Choose one of the three identical panels to be the roof. Insert the two bars for suspending samplers into the slots of the roof panel, so that they run along the length of the panel on the inside of the shelter.

Figure A1 Insertion of the suspension bars. Used for suspending the Radiello sampler.

6.2.2 Attach each side panel to the roof panel, putting the hooks from the roof panel into the slots on the side panels. Make sure that the curved ends of all three panels are on the same side of the shelter.

Figure A2 Attachment of the side panels.

6.2.3 Use the two support bars and place them inside the shelter, connecting the two side panels. The support bars should go into the first and third slots on the side panels. Once the support bar is in the slot on each side, turn the support bar ninety degrees until it clicks.

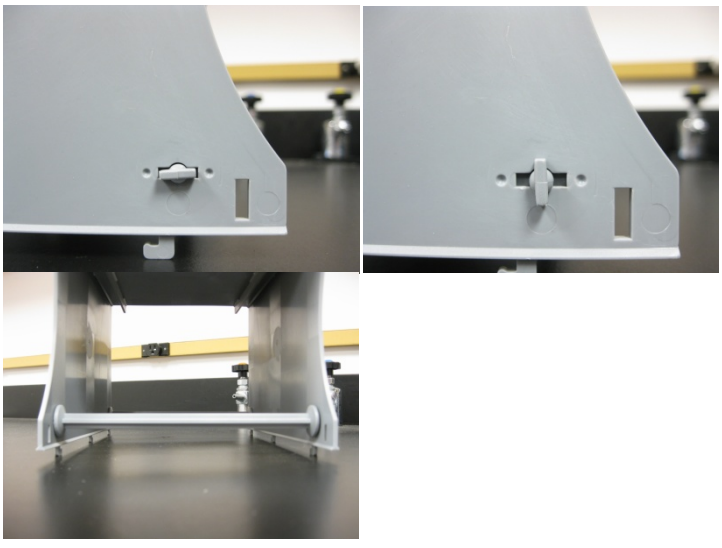

Figure A3 Assembly of the support bars.

6.2.4 Place two mounting strips on the curved end of the shelter, through a hole on each side of the shelter. One strip will be on top and the other will be on the bottom. The square box on one end of the mounting strip should be facing the outside when a circle is made with the strip.

- Do not close the strips; they will be used to mount the shelter in the field.

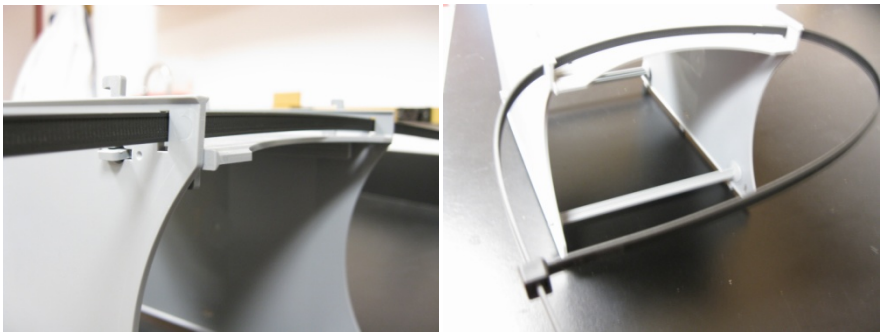

Figure A4 Insertion of the mounting strips.

6.3 Assembly of Support Plates

6.3.1 Insert the strip with the clip into the slot at the top of the triangular support plate. Click the peg into the hole so the strip hangs from the plate. This clip will be used to hang the sampler from the shelter.

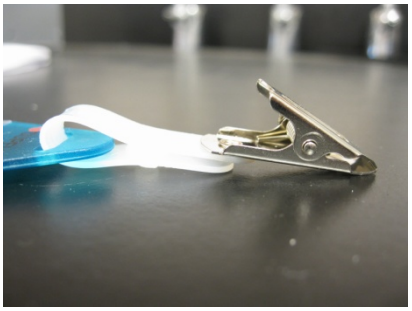

Figure A5 Attachment of the clip to support plate.

6.3.2 Peel off the backing to the transparent pocket that will be used to hold the label. Place the pocket on the support plate near the center, with the opening for the label on the side (to protect the label from rain).

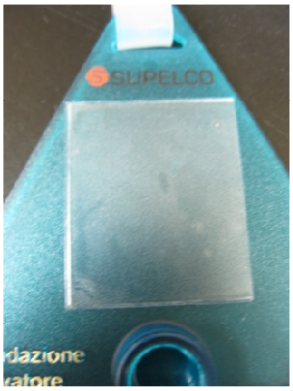

Figure A6 Attachment of transparent pocket to support plate.

7. Deployment and Retrieval of Samplers

7.1 These procedures should take place in the field at the sampling site. The following instructions are for one Radiello sampler; repeat as necessary.

7.2 Deployment of Shelters

7.2.1 Twenty-four hours prior to the sampling period, take the shelter to its sampling location. This will help to judge the safety of the location for the sampler as well as facilitate deployment of the Radiello sampler. The shelter should be attached to a stable object, such as a tree or utility pole.

- At the predetermined location, use the measuring tape and masking tape to mark a height of 3m on the object (tree or pole).
- Place the curved end of the shelter against the tree/pole, and close the mounting strips around the object. Do not close them so tightly that the shelter becomes deformed. If the mounting strips are too short, multiple strips can be attached to one another to form a larger circle.

7.3 Deployment of Samplers

7.3.1 Deployment of the samplers will take place on the first day of the sampling period at least twenty-four hours post shelter deployment.

7.3.2 Standing away from and downwind of the vehicle at the sampling site, open the plastic bag containing the glass tube with sorbent cartridge. Remove the white diffusive body from its polypropylene container, holding it by the blue plastic ends. Do not touch the white diffusive body.

- Close the polypropylene container and keep it for sampler retrieval.

7.3.3 Holding the diffusive body so the cartridge slot is facing upwards, uncap the glass tube containing the sampling cartridge and tip the glass tube so that the cartridge slides into the hole of the diffusive body.

- Make sure that the cartridge does not stick out at all from the top of the diffusive body. If any cartridge sticks out over the rim, tap on the blue plastic of the diffusive body until it falls into its seat inside.
- Store the capped glass tube inside of the plastic bag that it came with. Make a note in the laboratory notebook of the sampler location and code on the plastic bag that corresponds to that sampler.

7.3.4 Continue to hold the diffusive body with the hole upwards, and screw the triangular support plate onto the diffusive body.

7.3.5 Use a VOC-free pen to mark the sampling start time and date on a label. Insert the label into the pocket on the triangular support plate.

- Also mark the starting time and date in a laboratory notebook, in case the environment causes the label to fade. Take notes on any features of the sampling site that may be relevant to benzene concentrations, such as nearby traffic or other sources of air contaminants.

7.3.6 Use the clip on the triangular support plate to hang the diffusive body from a rod on the inside of the roof of the shelter. The diffusive body should be facing the inside of the shelter.

7.4 Field Blank

7.4.1 At a location where a sampler is deployed, take the field blank cartridge out of its plastic bag, uncap the tube and immediately reseal it. Transport the field blank back to the laboratory and store at 4°C until analysis.

- One field blank should be taken in at least 10% of the sampling locations, or two field blanks minimum.

7.5 Replicate Samplers

7.5.1 At 10% of the field sites (or one at a minimum), two samplers should be deployed to the same shelter. These samplers will be exposed to approximately the same air. This will allow for analysis of the precision associated with these passive sampling methods.

7.6 Retrieval of Samplers

7.6.1 Retrieval of the samplers will take place seven days after deployment.

7.6.2 Find the same plastic bag and glass tube that the sampling cartridge originally came in, using the code on the plastic bag. Remove the triangular support plate and sampler from the inside of the shelter.

7.6.3 Unscrew the diffusive body from the support plate, holding the blue plastic of the diffusive body and positioned with the triangular support plate on top. Open the glass tube and slide the sampling cartridge from the diffusive body into the tube. Cap the tube.

7.6.4 Take the label from the inside of the pocket on the triangular support plate and mark the ending date and time with a VOC-free pen. Place the label on the glass tube so that the barcode runs vertically along the tube.

- Place the tube back into its plastic bag and put it into a cooler with icepacks for transport back to the laboratory.

7.6.5 Place the white diffusive body into its polypropylene container and close it.

7.6.6 Remove the shelter and bring all materials back to the laboratory.

7.6.7 Once in the laboratory, remove the plastic bag containing the tube and cartridge from the cooler and store at 4°C until extraction and analysis.

- Cartridges are stable for 6 months before extraction when properly stored.

8. Quality Control

8.1 The field blanks taken according to section 7.4 will help to discern if any benzene became absorbed onto the cartridge during the transport or set-up of the sampling device. Opening the cartridge tube and immediately resealing allows for an approximation of the time it takes to slide the cartridge into the diffusive body.

8.1.1 The limit of detection (LOD) is calculated from the field blanks. The LOD is calculated as three times the standard deviation of the field blank values.

8.1.2 $$LOD = 3\left(\sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(x_i - \bar{x})^2}\right)$$

N = The number of field blanks.

x_i = The concentration of field blank *i*.

$\bar{x}$ = The average of the field blank concentrations.

8.2 Replicate samples will be taken at 10% of the sampling sites, or at a minimum one site, according to section 7.5. These samples will be analyzed in the same manner and they will allow for precision calculations. Since they were exposed to the same airborne concentrations, any differences in the measured concentrations will be due to imprecision in these methods.

8.2.1 To calculate the analytical precision, the relative difference between the two samples is calculated, expressed as a percentage.

8.2.2 $$Precision = \left(\frac{|x_1 - x_2|}{\bar{x}}\right) \times 100\%$$

x_1 = The measured concentration of one of the two tubes taken from the same sampling site.

x_2 = The measured concentration of the second of the two tubes taken from the sampling site.

$\bar{x}$ = The average of x_1 and x_2.

Bibliography

Fondazione Salvatoremaugeri-IRCCS. (2006, January). Volatile Organic Compounds-Chemically Desorbed by CS2. Retrieved September 13, 2010, from Radiello: http://www.radiello.com/immagini/EN/D1_D6_EN_01-06.pdf

Keith, L. H., Crummett, W., Deegan Jr., J., Libby, R. A., Taylor, J. K., & Wentler, G. (1983). Principles of Environmental Analysis. Analytical Chemistry , 55, 2210-2218.

U.S. Environmental Protection Agency. (1999a, January). Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Compendium Method TO-15. Retrieved August 30, 2010, from U.S. EPA: http://www.epa.gov/ttnamti1/files/ambient/airtox/to-15r.pdf

U.S. Environmental Protection Agency. (1999b, January). Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Compendium Method TO-17. Retrieved August 30, 2010, from U.S. EPA: http://www.epa.gov/ttnamti1/files/ambient/airtox/to-17r.pdf

APPENDIX B:

SOP: PREPARATION AND GC/MS ANALYSIS OF SAMPLES

1. Purpose and Applicability

The purpose of this standard operating procedure is to provide guidelines for the analysis of benzene, as collected through the sampling SOP, from the ambient air in Hillsborough County, Florida. The analysis of benzene is carried out through gas chromatography (GC) separation followed by mass spectrometry (MS) analysis. This analysis is based on the United States Environmental Protection Agency (EPA) Compendium Method TO-15, EPA Compendium Method TO-17, and the Health & Safety Executive Methods for the Determination of Hazardous Substances 88.

2. Summary of Method

Air samples are collected by passive sampling following the sampling SOP. Samplers are stored at 4°C until they are desorbed with low benzene carbon disulfide, and then the solvent and analyte solution is stored at 4°C until analysis. A Varian gas chromatograph (3800-GC) and mass spectrometer (2000-MS) system is used for the analysis, fitted with an autosampler and using helium as the carrier gas. The retention times and peak areas are compared with a standard calibration curve for benzene to quantitatively determine the concentration of the samples.

3. Definitions

3.1 Calibration Standards

Solutions with known concentrations of the analyte of interest (for this method, benzene) that encompass the range of concentrations of the unknown samples. All calibration standards must also have an equal concentration of internal standard.

3.2 Daily Calibration Check

A procedure that must be done once every 24 hours of GC/MS analysis, after the first initial calibration check is completed. The calibration standard used during the daily calibration check must be the same as one of the calibration standards used in the initial calibration check. This procedure makes sure that the linearity and sensitivity of the instrument are within the results demonstrated by the initial calibration check.

3.3 Field Blank

A field blank is a sampling cartridge that is taken into the field with the other sampling devices, opened and immediately resealed. It is subsequently analyzed using the same procedures as the field samples. It helps to distinguish actual concentrations from any contamination that may have occurred during sample preparation and transport. At least two field blanks must be taken, or at 10% of the sampling locations.

3.4 Initial Calibration Check

A procedure that must be run once at the start of the GC/MS analysis of samples, immediately after any cleaning or maintenance is done on the system, or if the daily calibration check does not meet acceptance criteria. This procedure checks for the linearity of the GC/MS response and sensitivity of the instrument.

3.5 Instrument Performance Check

This procedure needs to be completed initially, and once every 24 hours of sample analysis. If any cleaning or maintenance is done on the GC/MS system the instrument performance check should be immediately performed. This performance check is used to ensure that the mass calibration and resolution of the machine are accurate.

3.6 Laboratory Blank

A laboratory blank is a sampling cartridge that was not taken into the field and has not been exposed to the environment. The extraction and analysis procedures are carried out on this cartridge in the same manner as the field samples. This can help reveal any contamination that occurs during the extraction and analysis procedures. Two laboratory blanks are used for each sampling period.

4. Equipment and Materials

4.1 Supplies

4.1.1 All glassware should be cleaned and baked prior to use.

- Calibrated, sterilized micropipettes (0.5 µl-5 ml) (Finnipipette)
- GC 1 ml vials with crimp tops
- 10 sterile, 15 ml brown glass vials with screw top lids
- Two sterile, 100 ml beakers for holding CS_2 and waste
- Syringe and needle for removal of CS_2 from container
  - Stainless steel syringe needle with non-coring point: size 16 gague, 12 inch length
  - Luer lock glass syringe, 20 ml volume
- Fume hood for extraction procedures

4.2 Equipment

4.2.1 Gas Chromatograph (GC) and Mass Spectrometer (MS) System

- Varian CP-3800 Gas Chromatograph
- Varian Saturn 2000 Mass Spectrometer
- Varian CP-8400 Autosampler
- Varian Capillary Column CP-Sil 8 CB 50m x 0.25mm x 0.25µm #CP7453
- Helium Carrier Gas

4.3 Personal Protective Equipment

4.3.1 Personal protective equipment should be worn at all times when inside the laboratory.

- Closed-toed sneakers
- Long sleeved laboratory coat
- Laboratory goggles
- Laboratory specialty PVA (Silver Shield) gloves

5. Reagents and Chemicals

5.1 Chemicals

5.1.1 The chemicals should be stored in accordance with their flammability or toxicity guidelines on their MSDS, or according to storage instructions on the manufacturer's technical data sheet.

- Benzene standard
  - Fluka, Benzene puriss p.a., standard for GC ≥99.9%
  - Stored in the refrigerator at 4°C
- 2-Fluorotoluene internal standard
  - Sigma-Aldrich, ≥99%
  - Stored in the refrigerator at 4°C
- Carbon disulfide
  - Sigma-Aldrich, ReagentPlus, ≥99.9%, low benzene
  - Stored in the refrigerator at 4°C

6. Creating the Standard Solutions

6.1 Creating the Internal Standard Stock Solution

6.1.1 The internal standard to be used is 2-fluorotoluene.

6.1.2 The internal standard should be present at approximately the same concentration as the analyte of interest in the samples.

- The range of concentrations of benzene measured in the Tampa Bay area over the last two years is approximately 0.1-1.0 µg m^{-3} (US Environmental Protection Agency). However, this monitoring station is located in a rural area outside of downtown Tampa. A general range of concentrations of benzene measured in urban areas around the world of 1-10 µg m^{-3} should be considered (Health Effects Institute, 2008).

- If the ambient concentration of benzene sampled is 1.0 µg m^{-3}, then this would lead to a concentration of approximately 0.40 µg ml^{-1} in the extracted solution.
  - $C_{air}\,\frac{\mu g}{m^3} = \frac{m\,\mu g}{Q_K \frac{ml}{min} \cdot t\,min} \times 10^6\,\frac{ml}{m^3}$
  - $m\,\mu g = C_{air}\,\frac{\mu g}{m^3} \times Q_K\,\frac{ml}{min} \times t\,min \times 10^{-6}\,\frac{m^3}{ml}$
  - $m\,\mu g = 1.0\,\frac{\mu g}{m^3} \times 80\,\frac{ml}{min} \times 10080\,min \times 10^{-6}\,\frac{m^3}{ml}$
    $m = 0.8064\,\mu g$
  - Added to 2 ml of CS_2 during the extraction process:
    0.8064 µg/2 ml CS_2 = 0.40 µg ml^{-1}
- The internal standard is originally pure liquid 2-fluorotoluene. A lower concentration stock solution must be created so that a conveniently measurable amount can be added to each solution during extraction.
  - If we want to add 80 µl of internal standard to each tube during extraction, then the final volume of solution in the tube would be 2.08 ml. The final concentration of internal standard should be 0.4 µg ml^{-1}, so the concentration of stock solution can be calculated:

    $$C_{stock} = \frac{C_{final} \times V_{final}}{V_{stock}}$$

    $$C_{stock} = \frac{0.4\frac{\mu g}{ml} \times 2.08ml}{0.08ml}$$

    $$C_{stock} = 10.4\,\frac{\mu g}{ml}$$
- To obtain an initial diluted solution, add 0.05 ml of the pure 2-fluorotoluene to 9.95 ml of CS_2. This creates 10 ml of a 5005 µg ml^{-1} solution.
  - The density of the pure 2-fluorotoluene is 1.001 g ml^{-1} at 25°C.

    $$C_{final} = \frac{C_{initial} \times V_{initial}}{V_{final}}$$

    $$C_{final} = \frac{1.001\frac{g}{ml} \times 0.05ml}{10ml}$$

    $$C_{final} = 5.005 \times 10^{-3}\,\frac{g}{ml} = 5005\,\frac{\mu g}{ml}$$
- To obtain a 25.025 ml solution of CS_2 with 2-fluorotoluene present at a concentration of 10.4 µg ml^{-1}, 52 µl of the initial solution must be added to 24.973 ml of CS_2.

  $$V_{initial} = \frac{C_{final} \times V_{final}}{C_{initial}}$$

$$V_{initial} = \frac{10.4\frac{\mu g}{ml} \times 25.025ml}{5005\frac{\mu g}{ml}}$$

$$V_{initial} = 0.052\ ml$$

- This process must be done under the fume hood, using sterile, calibrated micropipettes and sterile volumetric flasks (or other glassware). The final solution must be stored in a sealed brown glass vial and labeled with the concentration, date, and initials. Store the final solution at 4°C.

6.2 Creating Standard Solutions for Calibration

6.2.1 The standard solutions should encompass the range of concentrations likely to be seen in the samples taken in Hillsborough County.

- Since the concentrations in Hillsborough County are taken in a rural area and actual concentrations in the urban area of the county are unknown, concentrations seen in other urban areas of 1-10 µg m^{-3} should be taken into account when creating calibration standards (Health Effects Institute, 2008).
- Using the calculation given in section 6.1.2, the five calibration standards should range from 0.10-4.0 µg ml^{-1} in order to correspond to the range seen in other areas. A preliminary sampling run was completed with one sampler using this calibration range, and the measured concentration was low, 0.44 µg m^{-3} benzene. A lower calibration range should be used in order to better represent the lower end of the calibration range.
- The calibration standards created here will range from 0.10-1.75 µg ml^{-1}.
- The lower four standard concentrations should be made from serial dilutions of the highest concentration standard.
- All dilutions must be done underneath the fume hood, using sterile, calibrated micropipettes and sterile volumetric flasks (or other glassware).
- The stock solution is benzene, with a density of 0.874 g ml^{-1} at 25°C.
  - This solution must first be diluted so that the very low concentrations of benzene can be attained.
  - To create a diluted working solution, 15 µl of benzene is added to 26.07 ml of CS_2 to create 26.22 ml of a 500 µg ml^{-1} solution of benzene.
  - To reduce the concentration even further, 1 ml of the previously created 500 µg ml^{-1} solution is added to 4 ml of CS_2 to create 5 ml of a 100 µg ml^{-1} solution.

- Using this 100 µg ml^{-1} solution, the first standard solution of 1.82 µg ml^{-1} can be created using a dilution.
  - $V_{original\ standard} = \frac{(V_{new\ standard})(C_{new\ standard})}{(C_{original\ standard})}$
  - Therefore, 167 µl of the 100 µg ml^{-1} solution must be added to 9.008 ml of CS_2 to create 9.175 ml of the 1.82 µg ml^{-1} standard.
- From this first 1.82 µg ml^{-1} standard, 4.848 ml are pipetted into a clean vial, and it is diluted with 3.636 ml of CS_2. This creates a total of 8.485 ml of a 1.04 µg ml^{-1} standard.
  - A final volume of 4.327 ml of the 1.82 µg ml^{-1} standard remains.
- From this second 1.04 µg ml^{-1} standard, 4.157 ml are pipetted into a clean vial, and it is diluted with 5.081 ml of CS_2. This creates a total of 9.238 ml of a 0.47 µg ml^{-1} standard.
  - A final volume of 4.327 ml of the 1.04 µg ml^{-1} standard remains.
- From this third 0.47 µg ml^{-1} standard, 4.911 ml are pipetted into a clean vial, and it is diluted with 3.929 ml of CS_2. This creates a total of 8.840 ml of a 0.26 µg ml^{-1} standard.
  - A final volume of 4.327 ml of the 0.47 µg ml^{-1} standard remains.
- From this fourth 0.26 µg ml^{-1} standard, 4.513 ml are pipetted into a clean vial, and it is diluted with 6.770 ml of CS_2. This creates a total of 11.283 ml of a 0.104 µg ml^{-1} standard. Discard 6.956 ml of this final standard solution so that a final volume of 4.327 ml remains.
  - A final volume of 4.327 ml of the 0.26 µg ml^{-1} standard remains.

6.2.2 Each calibration standard must have the internal standard present at the same concentration. The internal standard stock solution created in section 6.1 should now be added to each calibration standard solution created in section 6.2.1.

- As specified in section 6.1, the final concentration of internal standard in each calibration standard solution should be 0.4 µg ml^{-1}.
- To obtain a concentration of 0.4 µg ml^{-1} 2-fluorotoluene, add 173 µl of internal standard stock solution to every calibration standard for a final total volume of 4.5 ml.

6.2.3 Since the volume has changed now that the internal standard has been added, the new concentration of benzene in the calibration standard must be calculated.

- This can be done using the equation in section 6.2.1.
  - $C_{final\ solution} = \frac{(V_{intial\ solution})(C_{initial\ solution})}{(V_{final\ solution})}$
  - For 4.327 ml of the 1.82 µg ml^{-1} standard with 173 µl of the internal standard stock solution added, the new concentration of the standard will be 1.75 µg ml^{-1}.

- $C_{final\ solution} = \frac{(4.327\ ml)(4.16\ \frac{\mu g}{ml})}{(4.5\ ml)}$
- $C_{final\ solution} = 4.0\ \frac{\mu g}{ml}$

- The final concentrations of the five calibration standards are as follows: 0.10 µg ml^{-1}, 0.25 µg ml^{-1}, 0.45 µg ml^{-1}, 1.00 µg ml^{-1}, 1.75 µg ml^{-1}.

7. GC/MS Setup and Calibration

7.1 Creating the GC/MS Method Program

7.1.1 Create a new method using the "Method Builder" application in the Star Toolbar.

- Choose "Create a new method file" and click ok.
- Choose the appropriate instrument file that contains both the GC and MS.
- Choose "2000 Mass Spec at address 40" as the detector module.
- Choose "Channel 1=MS Data" for the channel to process and also choose both "Standard MS Reports" and "MS Data Handling" for post run processes for the MS detector.
- Click finish, and using the Method Builder window click File and save the method as "RAD130benzene".
- To edit the method, click each item on the left side table.
- To edit the GC parameters, click each of the following items under the "3800 GC Control" tab.
  - "Autosampler": Choose the appropriate model for the autosampler; since the autosampler is model CP-8400, choose "8400".
  - "Injector": Since the injector is installed to the front injector position, choose Front Injector Type "1079". Change the injection temperature to 240°C held for 0.00 min.
  - "Flow/Pressure": Since the injector is in the front position and Electronic Flow Control is set-up, choose Front EFC Type "Type 1 (for 1079/1177 Injectors)". Choose Constant Flow "On", and Column Flow "1.2" ml/min to set the rate of carrier gas through the column.
  - "Column Oven": The first row will contain the first step of the temperature program, so change it to Temp: 35, Hold: 9.00 min. For the second part of the temperature program, set the second row to Temp: 60, Rate: 5.0, Hold: 46.00 min. This will create a total time of 60 minutes.
- To edit the MS parameters, use the folder level "2000 Mass Spec Control".

- Under “MS Acquisition Method”, change the End of Delay (first row)/Start time (second row) to “3.00” min so that the filament and multiplier are turned off until after the solvent peak elutes. The End time in the second row should be “60.00” min, since the entire temperature program runs for 60 minutes. In the second row, Low Mass should be set to 35 and High Mass should be set to 150, in order to scan for all the possible ions from the analytes.

7.2 Instrument Performance Check

7.2.1 The first daily procedure is to perform the Instrument Performance Check to ensure that there are appropriate air/water levels and to verify the mass calibration and electron multiplier tuning.

- Open the System Control window and click on Manual Control.
- First, check the radio frequency (RF) voltage tuning of the ion trap by clicking “Adjustments” and “Adjust RF Tuning”.
  - If necessary, use a screwdriver to adjust the screw labeled “RF Adjustment” inside the MS door until the screen reads “RF Response is within limits”. Click “Done”.
- Next, adjust the calibration gas flow rate by clicking “Adjust Cal Gas”. Turn the valve inside of the MS door clockwise to decrease or counterclockwise to increase the calibration gas until the status is at the “OK” level. Click “Done”.
- Set the GC at 60°C, the high temperature for the method, for the Auto Tune process.
- In the “Manual Control” window, click the “Auto Tune” button and choose “Air/Water Check” to check for leaks in the system, “Electron Multiplier Tune” to auto-set the electron multiplier voltage, and “FC-43 Mass Calibration” to calibrate the mass axis. Click on “Start Auto Tune”.
- If any of the above checks fail, the system must be inspected for possible problems and the samples may not be run until all checks are acceptable.

7.2.2 A daily log of the instrument performance check parameters must be kept.

7.3 Initial Calibration Check

7.3.1 To determine the sensitivity and linearity of the instrument, an initial calibration run must be done before the first batch of samples, but after an instrument performance check.

- The initial calibration check is done using a set of five standard solutions of benzene that incorporate the range of concentrations anticipated from the pilot sampling. The calibration standards are

created using the method outlined in section 6. They should all contain the internal standard, 2-fluorotoluene, at equivalent concentrations. Use the following six concentrations of benzene for the calibration standards, created as discussed in 6.2.3:

- 0.10 µg ml^{-1}
- 0.25 µg ml^{-1}
- 0.45 µg ml^{-1}
- 1.00 µg ml^{-1}
- 1.75 µg ml^{-1}

7.3.2 The procedure for running the GC/MS system to analyze the initial calibration standards is as follows:

- Turn on the Saturn 3800-GC, 2000-MS, and open the helium flow gas.
- Open the "System Control" program on the desktop computer that controls the GC/MS system.
- Run the instrument performance check, as instructed in section 7.2.
- In the MS window "2000.40", click on the "Open Method" icon and open the method "RAD130benzene" as created in section 7.1.1.
- Click on the "Acquisition" button and wait until the screen shows "Ready" and "No Faults".
- Open the GC window "3800.40" and make sure the GC says "Ready".
- Place the calibration standards in the autosampler carousel, noting which sample is in each number slot.
- Open the autosampler window "8400 Sampler" and create a sampler list for the samples in the carousel.
  - Sample Name: The name of the calibration standard in each slot, the concentration of each standard can be used as the name.
  - Sample Type: Specify that it is a calibration standard.
  - Cal Level: For calibration standards, use 1 for the lowest concentration standard and 5 for the highest concentration standard.
  - Inj: Since no replication for calibration standards is necessary, enter 1.
  - Vial: Enter the number position of the standard in the autosampler carousel.
  - Injection Volume: Enter 1.0; the volume of standard that will be injected in microliters.
- Click "Data File…" in the bottom right corner and choose where the results will be saved.
- Check both the GC ("3800.40") and MS ("2000.40") windows to make sure the status is still "Ready".
- Open the "8400 Sampler" window and click "Begin" to start the runs.

- To view the results, right click the tab for your method on the left side of the screen and click “View Chromatograph”, then choose the folder where the results are saved and open the file for the sample to see the chromatogram.

7.3.3 In order to facilitate the analysis of unknown samples, these calibration results should be added to the method created previously. To view a chromatogram from the calibration standards, right click the tab for your method on the left side of the screen and click “View Chromatograph”, then choose the folder where the results are saved and open the file for the 1.75 $\mu g\ ml^{-1}$ standard to see the chromatogram.

- In the open window with the chromatogram, click “Spectrum List” and then “Create New Spectrum List”. Save it in the desired folder and click “Yes” to make it the active spectrum list.
- To build the list automatically, click the “Spectrum List” menu and select “Build the Spectrum List from Active Chromatogram”. A new window will appear that contains a list of the peaks found in the chromatogram. Click “Library Search Spectrum List” and the table will be updated with compound identifying information for each peak. Delete all peak entries except for benzene and 2-fluorotoluene. Click “Update all Searches with Matches” to save these results to the list.
- To edit the method, click on the method button on the side of the workstation and select “View/Edit Method”. Under “MS Data Handling” in the right menu, select the “Calculations” menu. Make sure the following parameters are selected:
  - “Measurement Type”: Area
  - “Calibration Type”: Internal Std
  - “RF to Use”: Nearest Internal Std
  - Check the boxes for “Report Missing Peaks”, “Report Unknown Peaks”, and “Library Search Unknown Peaks”.
- Under “MS Data Handling” in the right menu, select the “Compound Table” menu. A dialog box will pop up to ask to select a file to create the list; select the 1.75 $\mu g\ ml^{-1}$ file used to create the spectrum list earlier. Below the Compound Table, click the button that says “Import Compound List” and select the spectrum list created earlier in this section. Click “Select” and this list will be imported into the Method Builder window.
- In the table, double click on the entry for benzene in the “Compound ID” table. Change the following parameters:
  - Click “Analyte” as Compound Type.
  - Enter the CAS number for benzene without dashes, 71432.

- Click the “Next” button for 2-fluorotoluene and change Compound Type to “Internal Standard” and enter the CAS number, 95523. Click “previous” to return to benzene.

- Click on the “Calculations” tab at the top of the window. Change the following parameters:
  - For “# Calibration Levels” choose 5, since there are five calibration standards.
  - Choose linear for the “Curve Fit Type” and ignore for “Origin Point”, so the calibration will be a line that is not forced to go through the origin.
  - Enter the concentrations of the calibration standards in the “Cali Level Amounts” boxes, placing the lowest concentration (0.10) in the number one box and going in order so the highest concentration (1.75) is in the number five box. For “Results Units” enter “ug/ml”.
  - Click “Next” to see the information for 2-fluorotoluene. The concentration of the internal standard is the same in all of the samples, so for the “Cali Level Amounts” enter 0.4 in all five of the boxes. Click previous to return to benzene.
- Save the changes to the method and exit the Method Builder.

7.3.4 Next, a Recalculation List needs to be created that will contain all of the data files for establishing the calibration curve and later analysis files. To create this, click the “Automation File Editor” button on the workstation toolbar. Under the File menu, choose “New” and then “Recalc List”. Create a name for the list and save in the desired folder.

- In the first row, select “New Calib Block” in the Sample Type field in order to start a new calibration block.
- In the second row, select the “Data File” box and click “Add” and browse for the result file for the first calibration sample of 0.10 ug ml^{-1}. Select “Calibration” in the “Sample Type” field and enter the “Cal. Level” as 1 since this concentration was set as the first calibration level in the method.
- Repeat the above steps in rows 3-5, selecting the file for each calibration standard in order of increasing concentration.
- Save the list and exit the Automation File Editor.
- To view the calibration curve results, click the “Results” button in the MS Data Review toolbar. To manually choose the area to be integrated, click on the peak name in the top table. The integration area will be shown in the bottom of the window. Click on the white arrows pointing to either end of the integration area and drag to the appropriate

points, if necessary. Repeat for both the benzene and the internal standard peak in each file. Save the results.

7.3.5 The calibration curve can be viewed by clicking on the "Maximize/Restore Calibration Curves" button in the bottom left corner of the window. The %RSD, coefficient of determination, and equation of the line of best fit are calculated and shown above the graph.

7.3.6 For each calibration standard, several calculations should be made.

- Create a table of the following form:

Table B1 Sample quality control table. Used to establish the quality assurance guidelines for the initial calibration check.

Calibration Standard Number	**RRF_i**	**RRT_i**	**$A_{is,i}$**	**$RT_{is,i}$**
1				
2				
3				
4				
5				
Mean	$\overline{RRF}$	$\overline{RRT}$	$\bar{A}_{is}$	$\overline{RT}_{is}$
Standard Deviation	SD_{RRF}			
Quality Value	%RSD	$max\|[RRT_i - \overline{RRT}]\|$	$max\left\|\left[\frac{A_{is,i}-\overline{A_{is}}}{\overline{A_{is}}}\right] \times 100\right\|$	$max\left\|[RT_{is,i} - \overline{RT_{is}}]\right\|$
Criteria	≤ 30%	≤ 0.06 minutes	≤ 40%	≤ 20 seconds

- The RRF_i is the relative response factor of benzene versus the internal standard. For each standard, it is calculated as:

$$RRF_i = \frac{A_i C_{is,i}}{A_{is,i} C_i}$$

  - A_i = Area of the primary ion for benzene, count.
  - $A_{is,i}$ = Area of the primary ion for the internal standard, count.
  - $C_{is,i}$ = Concentration of the internal standard spiking mixture, ppbv.
  - C_i = Concentration of benzene in the calibration standard, ppbv.
- The RRT_i is the relative retention time for benzene (RRT) for each calibration standard. It can be calculated as:

$$RRT_i = \frac{RT_i}{RT_{is,i}}$$

- RT_i = Retention time of benzene.
- $RT_{is,i}$ = Retention time of the internal standard in the calibration standard i.

- Next, calculate the mean of each column in the table, i.e. calculate $\overline{RRF}$, $\overline{RRT}$, $\bar{A}_{is}$, $\overline{RT_{is}}$, and insert the values in the table as shown. The mean of any variable x can be calculated as:
  - $\bar{x} = \sum_{i=1}^{n} \frac{x_i}{n}$
- Calculate the standard deviation (SD_{RRF}) and the percent relative standard deviation (%RSD) for the relative response factor of benzene using the $\overline{RRF}$. They can be calculated as follows:

$$SD_{RRF} = \sqrt{\frac{1}{N-1}\sum_{i=1}^{n}(RRF_i - \overline{RRF})^2}$$

$$\%RSD = \frac{SD_{RRF}}{\overline{RRF}} \times 100$$

  - Insert these values into the table, as shown. The %RSD is the quality value for the RRF column.
- Calculate the quality value for the RRT column. For this column, the quality value is the maximum absolute difference between RRT_i and $\overline{RRT}$, i.e.:
  $max|[RRT_i - \overline{RRT}]|$
  - Insert this value into the table, as shown.
- Calculate the quality value for the A_{is} column. For the area response of the internal standard, the quality value is the maximum absolute percentage difference between $A_{is,i}$ and $\bar{A}_{is}$, i.e.:
  $$max\left|\left[\frac{A_{is,i} - \overline{A_{is}}}{\overline{A_{is}}}\right] \times 100\right|$$
  - Insert this value into the table, as shown.
- Calculate the quality value for the retention time ($RT_{is,i}$) column. The quality value for this column is the maximum absolute difference between $RT_{is,i}$ and $\overline{RT_{is}}$, i.e.:
  $max\left|[RT_{is,i} - \overline{RT_{is}}]\right|$
  - Insert this value into the table, as shown.
- The quality values calculated above must fall within the following ranges in order to pass the initial calibration check.

- The %RSD and RRF for benzene at each standard concentration must be less than 30%, with at most two exceptions that do not exceed 40%.
- The RRT for benzene at each calibration standard concentration must be within 0.06 minutes of the $\overline{RRT}$ for benzene.
- The area response ($A_{is,i}$) of each internal standard must be within 40% of the mean area response ($\bar{A}_{is}$).
- The retention time shift of the internal standard over the calibration range must be within 20 seconds of the mean retention time for the internal standard.

▪ If the above criteria are not met, inspect the GC/MS system for any problems or maintenance that may be necessary. Rerun the initial calibration standards.

7.4 Daily Calibration Check

7.4.1 After the first initial calibration check, a daily calibration check needs to be run once every 24 hours when analyzing samples.

▪ The daily calibration check is run once every 24 hour period, after an instrument performance check but prior to analyzing samples.

▪ Run the 0.45 ml^{-1} benzene initial calibration standard solution using the method and procedure given in section 7.3.2.

▪ Calculate the relative response factor for benzene, as in section 7.3.3.

▪ Calculate the percent difference (%D) of the daily RRF from the ($\overline{RRF}$) that was calculated in the most recent initial calibration.

$$\%D = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

- RRF_c = RRF of benzene in the daily calibration standard.
- $\overline{RRF_i}$ = Mean RRF of benzene in the most recent initial calibration.

▪ The value calculated above must fall within the following ranges in order to pass the daily calibration check.

- The %D for benzene must be within ±30% in order to proceed with sample analysis.

▪ If the daily calibration check does not meet the above criteria, the system must be inspected for any problems or maintenance that may be needed. After any maintenance on the machine, the initial calibration check must be run again.

▪ If there are a small number of samples to be analyzed spanning only a few days time, a daily calibration curve may be developed each day using the initial calibration check parameters. In order to assess between day confidence, the daily calibration check criteria should still be met.

7.4.2 A control chart of %D values from the daily calibration checks must be maintained.

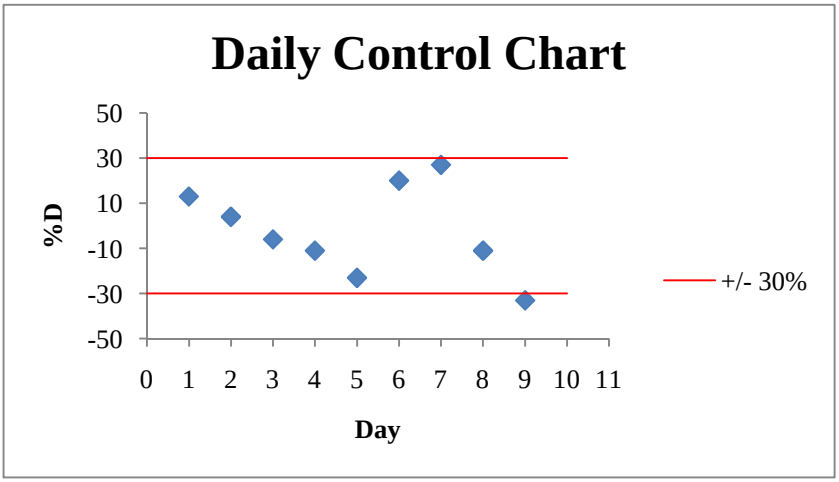

Figure B1 Sample daily control chart. Used to ensure the daily calibration checks meet quality assurance criteria.

8. Sample Analysis

8.1 Sample Preparation

8.1.1 The sampling cartridges should be removed from the field and stored in their respective glass tubes at 4°C before desorption.

8.1.2 The field blank cartridges should be stored in their glass tubes at 4°C. They will be extracted and analyzed with the other samples.

8.1.3 Laboratory blanks will be extracted in the same way as the field samples. Two laboratory blanks will be extracted and analyzed for every sampling deployment.

8.1.4 The cartridges should be extracted within six months from when the sampling period ended.

8.2 Sample Extraction

8.2.1 The cartridges to be extracted are described in section 8.1; they include all field samples, the field blanks and laboratory blanks.

8.2.2 The following steps should be taken underneath a fume hood, with proper personal protective equipment, due to health effects associated with carbon disulfide.

- Pipette 2 ml of CS_2 into the glass vial containing the RAD130 cartridge.
- Add 0.80 µl of the 2-fluorotoluene internal standard stock solution, as created in section 6.1.
- Recap the glass vial securely, and gently shake the tube, allowing the sorbent cartridge to act as an internal stirrer.

- Allow the cartridge to sit in the solution for 30 minutes, agitating occasionally.
- After 30 minutes, transfer 1 ml of the solution into a clean, labeled 1 ml GC vial.
- Seal the GC vial using an aluminum crimp top with septum. Discard the cartridge and store the remaining solution in the capped glass tube. Both of these containers must be stored at 4°C until analysis.

8.2.3 These solutions are stable at 4°C until analysis, but the CS_2 is capable of evaporating through the plastic cap of the cartridge tube. Since an internal standard has been added, the only concern with the evaporation is the loss of solution.

8.3 GC/MS Analysis of Samples

8.3.4 Prior to sample analysis, an instrument performance check should be performed as well as the appropriate initial/daily calibration, in accordance with section 7.

8.3.5 The analysis is performed under the following conditions and specifications:

- *Column:* CP-Sil 8 CB; 5% Phenyl 95% Dimethylpolysiloxane (50m x 0.25mm x 0.25µm)
- *Carrier Gas:* Helium
- *Flow Rate:* 1.2 ml min^{-1}
- *Temperature Programming*: Initial Temperature of 35°C for 5 minutes, ramped to 60°C at 5°C min^{-1}, hold for 46 minutes
- *Injection Volume***:** 1 µl

8.3.6 The sequence of analysis for each group of samples should consist of:

- The initial or daily calibration check, in accordance with section 7.
- One laboratory blank and two field blank samples.
  - Must be analyzed for every group of 20 samples.
  - Must be analyzed in triplicate.
- Field samples of unknown concentration for analysis.
  - Must be analyzed in triplicate. This is done by using the autosampler sampling list, as described in section 8.3.4.
- Remaining laboratory blank.

8.3.7 The procedure for running the GC/MS system to analyze each batch of samples consists of the following:

- Turn on the Saturn 3800-GC, 2000-MS, and open the helium flow gas.
- Open the “System Control” program on the desktop computer that controls the GC/MS system.
- Run the instrument performance check, as instructed in section 8.2.

- In the MS window “2000.40”, click on the “Open Method” icon and open the method “RAD130benzene” as created in section 7.1.1.
- Click on the “Acquisition” button and wait until the screen shows “Ready” and “No Faults”.
- Open the GC window “3800.40” and make sure the GC says “Ready”.
- Place the samples in the autosampler carousel, noting which sample is in each number slot.
- Open the autosampler window “8400 Sampler” and create a sampler list for the samples in the carousel.
  - Sample Name: Enter the name of the sample.
  - Sample Type: Specify that these are analysis samples.
  - Cal Level: These are not calibration standards, so this can be left blank.
  - Inj: Enter how many times the sample should be injected (replicated); this is 3 for unknown samples and blanks.
  - Vial: Enter the position of the sample in the autosampler carousel.
  - Injection Volume: Enter 1.0; the amount of sample to be injected in microliters.
- Click “Data File…” in the bottom right corner and choose where the results will be saved.
- Check both the GC (“3800.40”) and MS (“2000.40”) windows to make sure the status is still “Ready”.
- Open the “8400 Sampler” window and click “Begin” to start the runs.
- To view the results, right click the tab for your method on the left side of the screen and click “View Chromatograph”, then choose the folder where the results are saved and open the file for the sample to see the chromatograph.

8.4 Chromatograph Results Analysis

8.4.1 In the MS Data Review window, select the chromatograph of the first analysis sample as the active file.

- Click the “Process Data” box in the menu toolbar. Make sure that the boxes for “Make Reports” and “Preview Reports” are checked. Click “Process”. This will calculate the concentration of the analysis sample (in $\mu g\ ml^{-1}$) based on the previously run calibration data.
- Choose “Print” → “Summary Reports” → “Printed” to view the print preview screen for the analysis. The retention time, area, and concentration of benzene and 2-fluorotoluene are shown in the report. Save this data for further calculations.
- Repeat these steps for each of the analysis samples run in section 8.3.

8.4.2 The results from the previous section contain the concentration of benzene in each of the analysis samples, in units of µg ml^{-1}. To determine the mass of benzene recovered from each cartridge, this number must be multiplied by the total volume of CS_2 added during elution.

- $\mathrm{m}\ (\mu g) = \mathrm{C_{sample}}\left(\frac{\mu g}{ml}\right) \times \mathrm{V_{total}}\ (ml)$
- $\mathrm{m}\ (\mu g) = \mathrm{C_{sample}}\left(\frac{\mu g}{ml}\right) \times 2.08\ ml$
- Use the above equation to calculate the mass of benzene collected from each cartridge.

8.4.3 Calculate the average mass found in the field blank samples. Subtract this mass from the mass found in each exposed cartridge. This new mass is the value that will be used to calculate the ambient concentration of benzene.

- $m_{final} = m_{sample} - m_{blank,avg}$

8.4.4 The sampling rate, Q, is dependent on the average temperature during the sampling period. Using the hourly temperature data from the Tampa International Airport collected during the sampling period, calculate the average temperature. Use the following equation to determine the sampling rate:

- $Q_k = Q_{298}\left(\frac{K}{298}\right)^{1.5}$

  Where Q_k is the sampling rate at average temperature K, Q_{298} is the sampling rate for the compound at 298 K (for benzene, this is 80 ml min^{-1}), and K is the average temperature during the sampling period.
- Hourly wind speed and humidity data should also be collected from the Tampa International Airport. This calculated sampling rate has been demonstrated to be stable for wind speeds of 0.1-10 m s^{-1} and within the humidity range of 15-90%.

8.4.5 Calculate the ambient concentration of benzene observed at each sampling location using the following equation:

- $\mathrm{C_{air}}\ \frac{\mu g}{m^3} = \frac{\mathrm{m}\ \mu g}{\mathrm{Q_k}\frac{ml}{min}\cdot \mathrm{t}\ min} \times 10^6\ \frac{ml}{m^3}$

  Where C_{air} is the ambient concentration of benzene, m is the final mass of benzene calculated in section 8.4.3, Q_k is the sampling rate as calculated in section 8.4.3, and t is the sampling time for the sample in minutes.

9. Quality Control

9.1 Standard Operating Procedures

These standard operating procedures for the GC/MS analysis of benzene from Radiello RAD130 samplers have been created for guidance in the laboratory.

The SOP should be followed and understood in order to minimize human procedure error.

9.2 GC/MS System Performance

The instrument performance check is done in order to make sure the GC/MS system is in good working order. The RF voltage for the ion trap is checked and calibrated, as well as the level of the calibration gas. The Auto Tune procedure checks the air and water levels to ensure that there are no leaks in the system. It also performs mass calibration and tuning of the electron multiplier.

9.3 Sensitivity

The sensitivity of the instrument towards the target analyte is determined through the initial calibration check. A table of area response for both benzene and 2-fluorotoluene is created, with the corresponding concentrations and retention times. The relative retention time, the mean area response and the retention time shift for the compounds in the table must fall in the guidelines set by section 7.3.3. If the criteria are not met, the GC/MS system must be inspected for any problems or routine maintenance that may be needed.

9.4 Control Chart

To ensure that the system stays in control, a daily calibration check is run once every 24 hour period during analysis. The percent difference (%D) between the relative response factor of the daily calibration standard and the mean relative response factor from the initial calibration is calculated. These %D values are recorded in a chart (as seen in section 7.4.2) and kept as a log to ensure the method is in control and the samples analyzed are valid. If the criteria are not met, the GC/MS system must be inspected for any problems or routine maintenance that may be needed.

9.5 Blanks

Two different types of cartridge blanks are extracted and analyzed in this procedure: laboratory blanks and field blanks. Laboratory blanks control for any contamination that may have been introduced during the extraction and analysis process of the samples. Field blanks controls for any contamination that may have been introduced during the transport and handling of the sampling devices.

9.6 Limit of Detection

The limit of detection for the method is determined by using the measurements of the field blanks. The limit of detection is calculated as three times the standard deviation of the field blank samples.

$$LOD = 3 \cdot \sqrt{\frac{1}{N-1}\sum_{i=1}^{n}\left(X_{fb,i} - \overline{X_{fb}}\right)^2}$$

Where X_{fb} is the concentration of benzene in the field blank.

9.7 Precision

The precision of the samplers will be assessed by duplicate samplers exposed at the same sampling site. The precision of the GC/MS analysis will be achieved through replicate analysis (three injections) of each sample.

9.7.1 The percent difference (%D) will be calculated as a measurement of the precision for the samplers. The average value of the three replicate analyses for each of the duplicate samplers will be used to calculate the %D for the duplicate samplers.

$$\%D = \frac{|x_1 - x_2|}{\bar{x}} \cdot 100$$

Where x_1 and x_2 are the measurements to be compared, and $\bar{x}$ is their average.

9.7.2 The percent difference between the two duplicate samplers will be used to represent the uncertainty of the measurements taken during the sampling period.

$$error = \pm(\%D \cdot \bar{x_\iota})$$

- The variable $\bar{x_\iota}$ represents the average concentration of three replicate analyses of the sample taken at one sampling site.

Bibliography

Allou, L., Marchand, C., Mirabel, P., & Le Calve, S. (2008). Aldehydes and BTEX Measurements and Exposures in University Libraries in Strasbourg (France). *Indoor and Built Environment, 17 (2),* 138-145.

Angiuli, L., Bruno, P., Caputi, M., Caselli, M., de Gennaro, G., & de Rienzo, M. (2003). Radial Passive Samplers for Air Quality Monitoring in Field Comparison with a BTEX Automatic Analyser Preliminary Results. *Fresenius Environmental Bulletin, 12 (10),* 1167-1172.

Cocheo, V., Boaretto, C., & Sacco, P. (1996). High Uptake Rate Radial Diffusive Sampler Suitable for Both Solvent and Thermal Desorption. *American Industrial Hygeine Association Journal, 57,* 897-904.

Fondazione Salvatoremaugeri-IRCCS. (2006, January). Volatile Organic Compounds-Chemically Desorbed by CS2. Retrieved September 13, 2010, from Radiello: http://www.radiello.com/immagini/EN/D1_D6_EN_01-06.pdf

Godoi, R. H., Avigo Jr, D., Campos, V. P., Tavares, T. M., de Marchi, M. R., Van Grieken, R., et al. (2009). Indoor air quality assessment of elementary schools in Curitiba, Brazil. *Water, Air, & Soil Pollution , 9*, 171-177.

Health & Safety Executive. (1997, December). Methods of the Determination of Hazardous Substances 88: Volatile Organic Compounds in Air. Retrieved August 30, 2010, from Health & Safety Executive: http://www.hse.gov.uk/pubns/mdhs/pdfs/mdhs88.pdf

Health Effects Institute. (2008, January 9). Mobile-Source Air Toxics: A Critical Review of the Literature on Exposure and Health Effects. Retrieved September 8, 2010, from HEI Publications: http://pubs.healtheffects.org/getfile.php?u=390

Jaward, F. (2010). Environmental Analytical Lab Brief Standard Operating Prodecure for GC/MS. Tampa.

Keith, L. H., Crummett, W., Deegan Jr., J., Libby, R. A., Taylor, J. K., & Wentler, G. (1983). Principles of Environmental Analysis. *Analytical Chemistry , 55*, 2210-2218.

Popek, E. P. (2003). Sampling and Analysis of Environmental Chemical Pollutants: A Complete Guide. San Diego: Elsevier Science.

U.S. Environmental Protection Agency. (n.d.). Air Quality System Data Mart. Retrieved June 22, 2010, from http://www.epa.gov/ttn/airs/aqsdatamart

U.S. Environmental Protection Agency. (1999a, January). Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Compendium Method TO-15. Retrieved August 30, 2010, from U.S. EPA: http://www.epa.gov/ttnamti1/files/ambient/airtox/to-15r.pdf

U.S. Environmental Protection Agency. (1999b, January). Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Compendium Method TO-17. Retrieved August 30, 2010, from U.S. EPA: http://www.epa.gov/ttnamti1/files/ambient/airtox/to-17r.pdf

Varian, Inc. (2003). Saturn 2000 GC/MS MS Workstation Operation Manual. USA: Varian, Inc.

Varian, Inc. (2003). Saturn MS 2000 Workstation Tutorial Manual. USA: Varian, Inc.

APPENDIX C:

QUALITY ASSURANCE DATA

In Appendix B, guidelines for quality assurance regarding GC/MS performance are outlined. Since this pilot study contained a relatively small number of samples, a full batch of calibration standards were run on each day of analysis, immediately preceding the samples. Three days were needed to analyze all samples, therefore three sets of calibration standards were run and checked against the criteria outlined for the initial calibration check in Appendix B. The data obtained met all criteria and are as follows.

Table C1 Quality assurance data obtained on 6/13/2011.

Calibration Standard Number	**RRF_i**	**RRT_i**	**$A_{is,i}$**	**$RT_{is,i}$**
1	1.4752	0.5409	30013	12.322
2	0.8924	0.5531	37970	12.426
3	0.9742	0.5427	25266	12.341
4	0.8917	0.5459	27519	12.368
5	0.9650	0.5459	25284	12.369
Mean	1.0397	0.5457	29210.4	12.3652
Standard Deviation	0.2465			
Quality Value	23.7116	0.0074	13.0942	0.0608
Criteria	≤ 30%	≤ 0.06 minutes	≤ 40%	≤ 0.33 minutes
Criteria Met?	yes	yes	yes	yes

Table C2 Quality assurance data obtained on 6/14/2011.

Calibration Standard Number	**RRF_i**	**RRT_i**	**$A_{is,i}$**	**$RT_{is,i}$**
1	1.4567	0.5486	23373	12.399
2	1.0153	0.5520	23819	12.418
3	0.9957	0.5506	21396	12.417
4	0.8384	0.5515	25937	12.411
5	0.8966	0.5504	20573	12.401
Mean	1.0406	0.5506	23019.6	12.4092
Standard Deviation	0.2436			
Quality Value	23.4144	0.0020	7.0726	0.0102
Criteria	≤ 30%	≤ 0.06 minutes	≤ 40%	≤ 0.33 minutes
Criteria Met?	yes	yes	yes	yes

Table C3 Quality assurance data obtained on 6/15/2011.

Calibration Standard Number	**RRF_i**	**RRT_i**	**$A_{is,i}$**	**$RT_{is,i}$**
1	1.5658	0.5505	18760	12.406
2	1.0331	0.5517	19451	12.408
3	1.0095	0.5522	18066	12.415
4	0.8739	0.5498	24276	12.393
5	1.0855	0.5517	16275	12.427
Mean	1.1136	0.5512	19365.6	12.4098
Standard Deviation	0.2646			
Quality Value	23.7623	0.0014	10.3189	0.0172
Criteria	≤ 30%	≤ 0.06 minutes	≤ 40%	≤ 0.33 minutes
Criteria Met?	yes	yes	yes	yes

In order to assess the between-day confidence through quality control, a daily calibration check was done using the 0.45 µg m^{-3} standard. The relative response factor (RRF) of this standard each day was compared to the mean relative response factor of the day one calibration data. The percent difference of the daily RRF from the mean RRF was calculated. A system in control gives a percent difference within 30%.

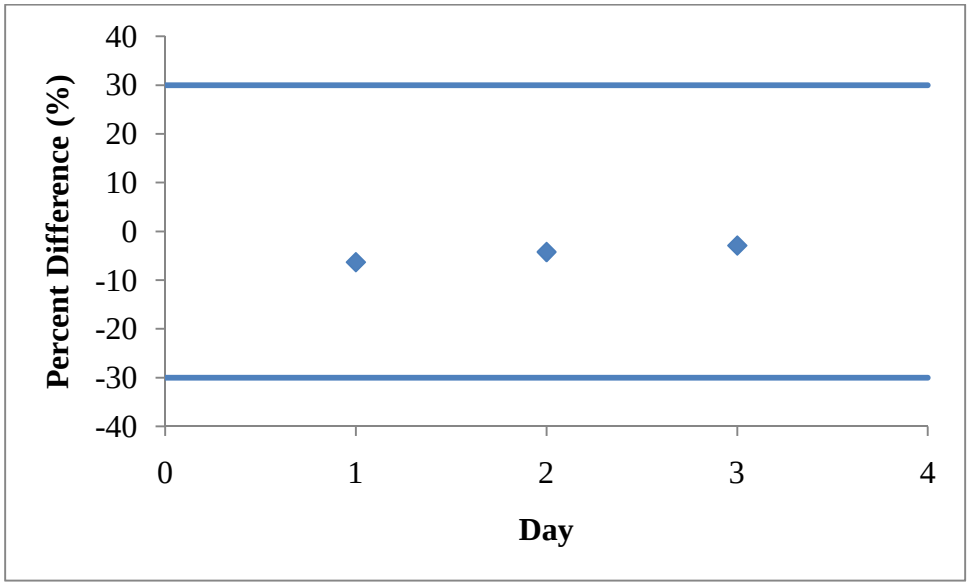

Figure C1 Daily control chart. The mid-level calibration standard was used as the daily control check.

APPDENIX D:

CHROMATOGRAMS FROM SAMPLE ANALYSIS

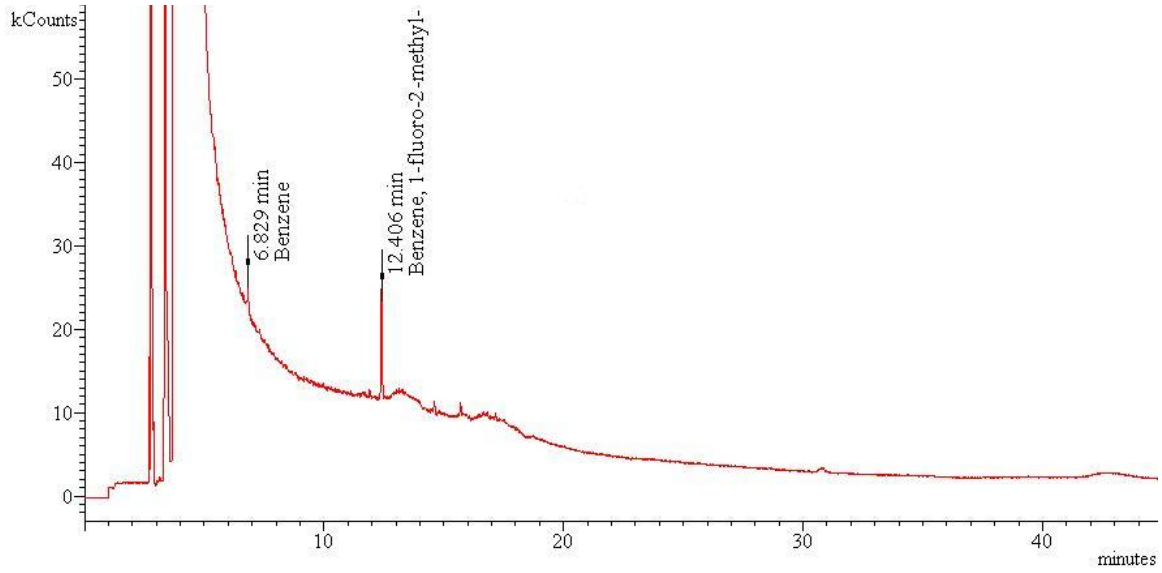

Figure D1 Chromatogram of the 0.1 µg ml^{-1} calibration standard.

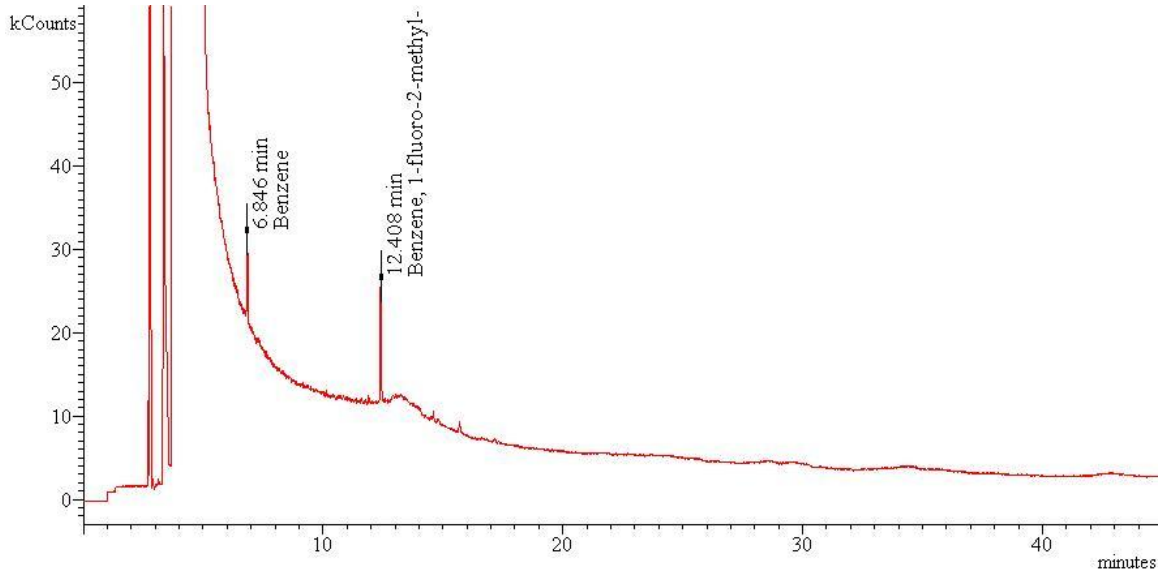

Figure D2 Chromatogram of the 0.25 µg ml^{-1} calibration standard.

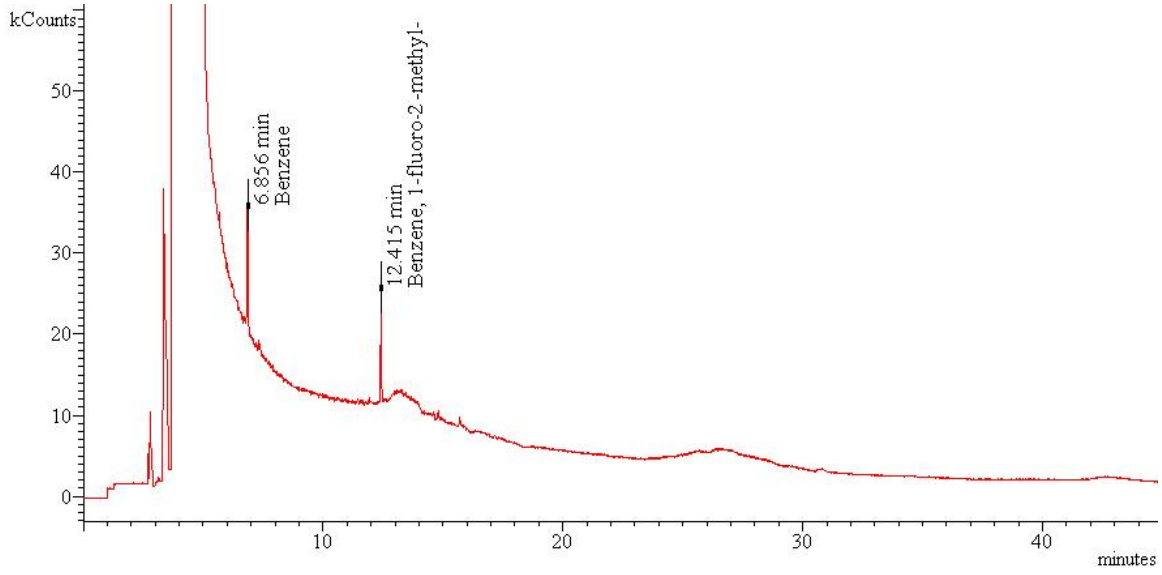

Figure D3 Chromatogram of the 0.45 µg ml^{-1} calibration standard.

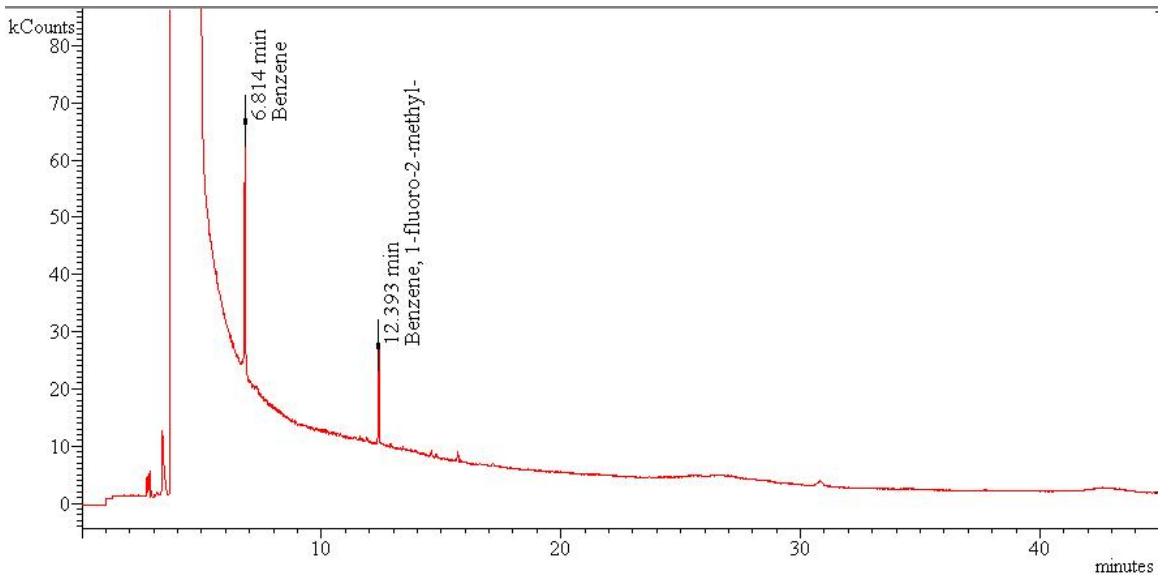

Figure D4 Chromatogram of the 1.0 µg ml^{-1} calibration standard.

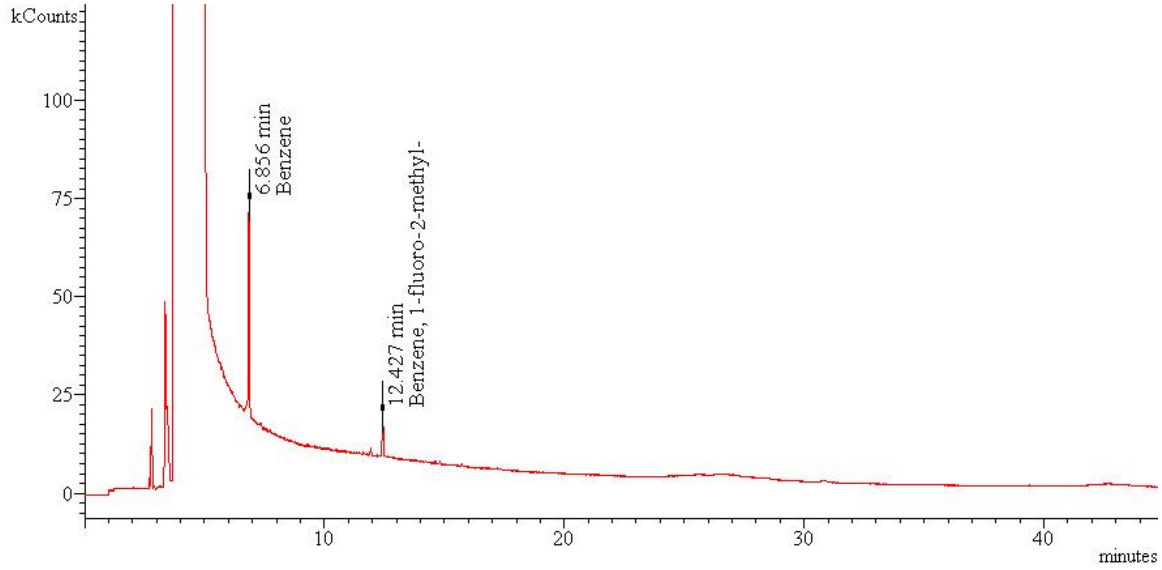

Figure D5 Chromatogram of the 1.75 µg ml^{-1} calibration standard.

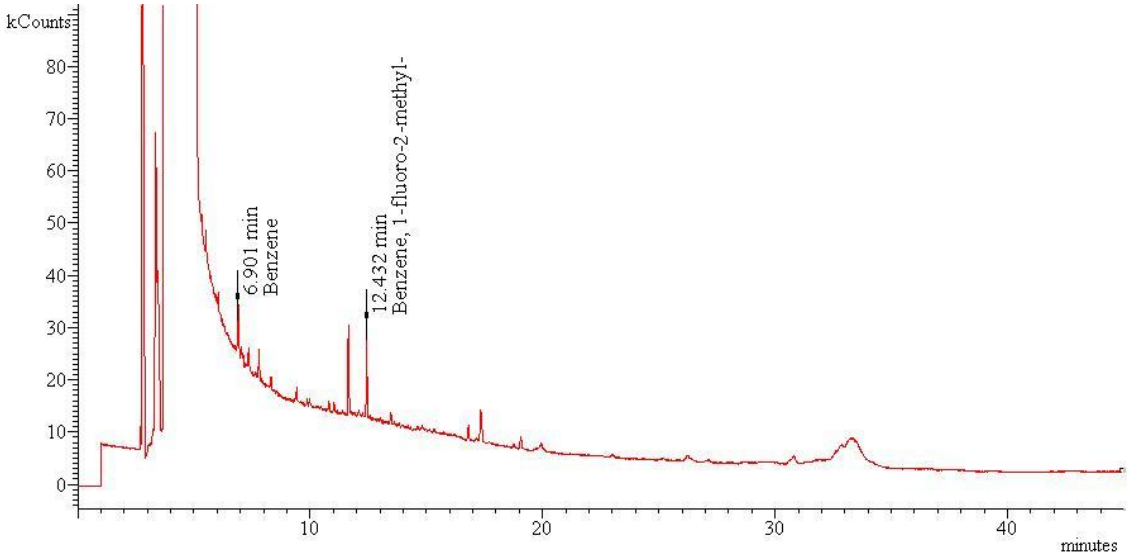

Figure D6 Sample chromatogram of an unknown sample. This chromatogram is from sampling site 5.