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# Spatial Distribution of Nitrogen Oxides, Benzene, Toluene, Ethylbenzene, and Xylenes in Hillsborough County, Florida: An Investigation of Impacts of Urban Forests on Ambient Concentrations of Air Pollutants Associated with Traffic

Jill Sears

University of South Florida, jrsears2@mail.usf.edu

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Spatial Distribution of Nitrogen Oxides, Benzene, Toluene, Ethylbenzene, and Xylenes in  
Hillsborough County, Florida: An Investigation of Impacts of Urban Forests on Ambient  
Concentrations of Air Pollutants Associated with Traffic

by

Jill R. Sears

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of the requirements for the degree of  
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Major Professor: Amy L. Stuart, Ph.D.  
Foday M. Jaward, Ph.D.  
Thomas J. Mason, Ph.D.

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## Abstract

Urban air pollution is responsible for high levels of morbidity and mortality in exposed populations due to its effects on cardiovascular and respiratory function. Transportation-related air pollutants account for the majority of harmful air pollution in urban areas. Forests are known to reduce air pollution through their ability to facilitate dry deposition and atmospheric gas exchange. This work characterizes the interactions between transportation air pollutants and urban forests in Hillsborough County, Florida. A highly spatially resolved passive air sampling campaign was conducted to characterize local concentrations of nitrogen oxides, benzene, toluene, ethylbenzene, and xylenes (BTEX) in Hillsborough County, Florida. Sampling locations included a proportion of densely forested urban areas in order to determine the effects of Hillsborough County's urban forest resources on localized concentrations of selected transportation pollutants. Recommended approaches for the use of urban forests as an effective air pollution mitigation technique in Hillsborough County were generated based on results from the sampling campaign. Results show mean concentrations of 2.1 parts per billion and  $6.5 \mu\text{g}/\text{m}^3$  for nitrogen oxides and total BTEX, respectively. High spatial variability in pollutant concentrations across Hillsborough County was observed, with the coefficient of variation found to be 0.61 for nitrogen oxides and 0.79 for total BTEX. Higher concentrations were observed along interstate highways, in urban areas of the county, and near select point sources in rural areas. Differences in concentrations within forested areas were observed, but were not statistically significant at the 95% confidence level. These results can be used to identify elements of urban design which contribute to differences in concentrations and exposures. This

information can be used to create more sustainable urban designs which promote health and equity of the population.



## **Chapter One:**

### **Introduction**

#### **Motivation**

Urban air pollution contributes to nearly one million premature deaths each year due to increased levels of cardiovascular and respiratory disease in exposed populations (UNEP, 2012; CDC, 2009). High levels of pollutants can prompt acute health effects such as eye and throat irritation, asthma, and bronchitis, while chronic exposure can result in lung damage and certain cancers (EPA, 2010; CDC, 2009). Certain groups are especially susceptible to the adverse health effects of urban air pollution, including the young, elderly, and those with respiratory conditions. Childhood exposure to vehicular and industrial emissions may result in a lifetime of decreased respiratory function (NIEHS, 2012). This mounting evidence linking urban air pollution to population morbidity and mortality has resulted in increasing efforts to identify and reduce emissions from major sources.

Transportation pollutants emitted as combustion products from mobile sources account for the single greatest contributor to urban air pollution in the United States (TCEQ, 2012). These nonpoint transportation sources, including on-road vehicles and nonroad sources such as trains, airplanes, and commercial equipment, are difficult to monitor and control because of their large numbers and constant movement. Gasoline and diesel combustion in vehicles substantially contributes to the emission or formation of four Criteria Pollutants, including ozone, particulate matter, carbon monoxide, and nitrogen oxides (EPA, 2012a). Additionally, many Air Toxics are

emitted by transportation sources, including certain volatile organic compounds known to be carcinogenic, such as benzene (EPA, 2012b; IRIS, 2003; IRIS, 1991). The Clean Air Act allowed for the creation of new vehicle and fuel standards aimed at reducing the amount of harmful emissions from mobile sources (EPA, 2007). These new engine and fuel refining technologies have successfully resulted in cleaner and more efficient motor vehicles. However, as the number of cars and miles travelled continuously increases, urban areas experience very little relief from unsafe pollutant concentrations (FHWA, 2010).

New, comprehensive approaches must now be considered as possible alternatives for reducing urban air pollution. Emissions control technologies do not successfully address the root of the problem—society’s increasing dependency and overuse of personal vehicles (Kahn Ribeiro et al., 2007). Sustainable urban design is one of these comprehensive models aimed at reducing waste, pollution, and energy use by integrating various design concepts into urban landscapes (Jabareen, 2006). This method has been promoted by agencies such as the EU Expert Group of the Urban Environment, Intergovernmental Panel on Climate Change, American Public Transportation Association, and the Earth Institute’s Center for Sustainable Urban Development. Various cities in the United States have adopted sustainable urban design initiatives, including Boston, Minneapolis-St Paul, and Portland (MAPC, 2012; Portland, 2012). There is no blueprint for an urban design which minimizes a population’s exposure to air pollution. Cities must integrate their current infrastructure into their plans for urban redevelopment and growth. Some techniques incorporated into sustainable urban forms that may reduce air pollution include high density developments, enhanced public transportation, increased walkability, and zoning for mixed land-use (Jabareen, 2006). The foundation of sustainable urban design is inclusion of many elements which can be integrated into a community to create a new sustainable paradigm.

Preserving and renewing forest resources inside an urban area has been proposed as a useful technique for increasing the walkability and aesthetics of an area, while providing air quality benefits. Tree leaves can absorb and transform harmful air pollutants, while large canopies provide surface area for pollutants to deposit (Beckett et al., 1998). Forests can also reduce ground-level temperatures through shading and transpiration, resulting in less formation of secondary pollutants (Escobedo, 2010; Nowak et al., 2000). The urban forest in city and suburban areas of Sacramento, California is estimated to take up 789 metric tons of ozone, nitrogen dioxide, particulate matter, and sulfur dioxide each growing season (Scott et al., 1998). Central Beijing's relatively modest forest resources are estimated to remove 1144 metric tons of major air pollutants annually (Yang et al., 2005). Preexisting trees are most effective at air pollutant removal because they tend to have larger canopies with greater surface area for deposition and absorption (Nowak, 1994). This evidence suggests that preservation of forest resources inside urban areas may be a useful technique for reducing concentrations of harmful transportation air pollutants.

The effects of urban forests on levels of many transportation pollutants have not been extensively studied to date. In order to develop a complete toolset for achieving sustainable urban forms, all potential design elements should be evaluated for their efficacy in practice. Current air pollutant concentration data from densely forested urban areas is necessary to identify if actual pollutant reductions result from preserving a city's forest resources. This information will contribute to the development of effective sustainable urban forms which foster a more safe and healthy environment for their inhabitants.

## Background & Literature Review

Previous research regarding the sources and health effects of pollutants of interest will be reviewed to illustrate the significance and appropriateness of the pollutant selection. An overview of chemical and physical interactions between trees and pollutants of interest is provided as support for hypotheses of this study. Current methods and limitations of quantifying an urban forest's ability to remove pollution are described, including results from numerous case studies. This background information provides the foundation for the project's experimental design, and illustrates the need for measurement of ambient pollutant concentrations in order to fully understand how urban forests can be beneficially incorporated into urban designs.

**Transportation Pollutants of Interest.** Combustion processes from mobile sources produce numerous air pollutants which are known to detrimentally impact the health of populations in urban areas. These pollutants are regulated by the Clean Air Act as either Criteria Pollutants or Air Toxics, but continuously prove to be a problem in many cities throughout the United States. In 2010, cities like Los Angeles and Pittsburgh experienced greater than 50 days when air quality was considered unhealthy for sensitive groups, according to the EPA's Air Quality Index ratings for Criteria Pollutants (EPA, 2012c). In 2005, the National-Scale Air Toxics Assessment estimated that mean cancer risks were greater than 100 in a million in cities such as Denver, Detroit, and Portland (EPA, 2012c). Although levels of air pollution are generally decreasing across the country, an estimated 123.4 million people in the United States are still living within areas that exceed National Ambient Air Quality Standards (EPA, 2012c).

Nitrogen oxides (NO<sub>x</sub>) are a category of pollutants that includes NO<sub>2</sub>, a criteria pollutant, and NO. They are closely regulated because of their pervasive nature, smog-forming abilities,

and negative effects on the respiratory systems of exposed populations (EPA, 2012d). Nitric oxide (NO) is formed by the reaction of atmospheric oxygen and nitrogen-containing fuels during the high-temperature combustion present in a vehicle engine (Seinfeld & Pandis, 1998). Rapid oxidation of NO results in the secondary formation of nitrogen dioxide (NO<sub>2</sub>). An estimated 40 to 45% of all nitrogen oxide emissions in the United States can be attributed to transportation sources, with other major contributors being power plants and industry (Seinfeld & Pandis, 1998). Therefore, nitrogen oxides are commonly used as surrogates for representing traffic-related air pollution (HEI, 2010). This study will also monitor concentrations of nitrogen oxides as an indicator of mobile source pollution levels.

In addition to nitrogen oxides, several Air Toxics will be measured in this study. Air toxics are known or suspected to cause cancer or other serious health effects, but are not as prevalent as the Criteria Pollutants (EPA, 2012b). Transportation sources emit a number of air toxics, but this study will focus on aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylenes). These pollutants are emitted directly from mobile sources as a result of fuel combustion processes. Benzene, toluene, ethylbenzene, and xylenes (BTEX) are respiratory irritants and can have neurological effects such as dizziness, fatigue, and nausea. In addition to acute health effects, benzene is a known human carcinogen which has shown increased risk of leukemia (EPA, 2012c).

**Pollutant Removal Pathways.** The developing understanding of the serious health effects associated with urban air pollution has resulted in a search for comprehensive and innovative mitigation strategies. The use of urban forests as an air pollution mitigation technique has been increasingly supported by researchers over the past 15 years. Trees contribute to pollution reduction in two main ways— by providing surface area for dry deposition of

pollutants, and by preventing the formation of secondary pollutants (Beckett et al., 1998; Escobedo, 2010; Nowak et al., 2006; Nowak et al., 2000). Tree canopies intercept particulate and gaseous pollutants, removing them from ambient suspension (Becket et al, 1998). Forests with mature, broad-leaved species are most effective at pollutant removal through dry deposition because their larger surface areas intercept greater amounts of pollution. Once deposited, particulates can adhere to leaf surfaces until washed away by rainfall or dew, or until the leaves fall to the ground. Resuspension of particulates is possible in windy conditions. Gaseous pollutants can be absorbed by leaf stomata, the small pores used for gas exchange in plant photosynthesis, respiration, and transpiration (Nowak et al., 2006). In addition to pollutant interception and absorption, the tree canopy provides shading which lowers ambient temperatures (Escobedo, 2010). Transpiration from leaves also provides temperature benefits which reduce sunlight-driven secondary pollutant formation (Escobedo, 2010; Nowak et al., 2000).

**Pollutant Formation from Biogenic Emissions.** Biogenic emissions of volatile organic compounds (VOC) must also be considered when determining the effects of urban forests on pollutant concentrations. Trees worldwide naturally emit volatile organics at a rate of more than a gigatonne per year (Lelieveld, 2008). Emission type and amount depends upon tree species. Isoprene, emitted by deciduous trees such as sycamore, oak, and willow, accounts for 40% of biogenic VOC emissions (Lelieveld, 2008; Guenther et al., 2006). Coniferous trees like pine, cedar, fir, and spruce emit monoterpenes, including  $\alpha$ -pinene and  $\beta$ -pinene (Varshney, 2007; Lelieveld, 2008). Trees use various VOC emissions as communication, protection, and defense mechanisms (Varshney, 2007). However, these biogenic VOC are subject to atmospheric chemistry once emitted, and can lead to harmful secondary air pollutants. For example, a

hydroxyl radical can oxidize isoprene to formaldehyde in about one hour with sufficient temperatures (Palmer et al., 2003). Biogenic VOC are generally more reactive than anthropogenic VOC, so they can fuel the ozone production cycle more efficiently. Photooxidation of biogenic VOC produces organic peroxy and HO<sub>2</sub> radicals which react with nitric oxide to form nitrogen dioxide. Photolysis of nitrogen dioxide forms ozone and nitric oxide which can be reintroduced into the ozone formation cycle (Atkinson & Arey, 2003). These additional emissions from trees and plants are an important contributor to secondary pollutant formation, and cannot be discounted during source attribution.

**Quantifying Pollutant Removal.** Modeling approaches have been widely utilized by researchers to quantify the air pollutant removal capacity of urban forest resources in a number of cities. These models all incorporate a similar equation to describe the pollutant removal per time period for an area. A simplified version of the equation is shown here (Nowak, 1994):

$$Q = F \times A$$

Where  $Q$  is the mass of pollutant removal per time,  $F$  is the downward pollutant flux, and  $A$  is the total area of canopy cover in the study area. Downward pollutant flux ( $F$ ) is the product of the dry deposition velocity and concentration of a specific air pollutant. Total canopy cover ( $A$ ) can be calculated in various ways including satellite imagery interpretation and field data measurements (Scott et al., 1998; Yang et al., 2005). The U.S. Department of Agriculture's Forest Service has developed a model to help estimate these input variables. The Urban Forest Effects Model (UFORE) uses resistance formulas (Pederson et al., 1995) and regression equations (Nowak, 1996; Nowak & Crane, 2000) to calculate  $F$  and  $A$ . UFORE can be used to estimate removal of the criteria pollutants ozone, sulfur dioxide, nitrogen dioxide, carbon

monoxide, and particulate matter (NRS, 2009). This model does not currently assess the effects of urban forest areas on concentrations of any Air Toxics.

Urban forest air pollutant uptake has been estimated in over fifty North American cities using these types of models. Three of these areas are located in Florida—Jacksonville, Tampa, and Miami. Tampa’s urban forest is estimated to annually remove 156 metric tons of ozone, 123 metric tons of PM<sub>10</sub>, 29 metric tons of nitrogen dioxide, 64 tons of sulfur dioxide, and 13 tons of carbon monoxide (Nowak et al., 2006). This modeling is useful for assessing the pollutant removal capacity of a large city area, but cannot provide information about how trees remove or contribute to pollution within a small area, like a neighborhood or city block. Assessing ambient levels of pollutants at street level is the most reliable way to obtain concentration information for areas which may benefit from increasing tree resources.

Currently, the capacity to measure effects of an area’s urban forest resources is reliant upon modeled data which can determine the total mass of pollutant removed. Whether this mass removal is reflected in localized ambient concentrations has not been extensively studied. Mobile source air toxics are some of the most harmful urban pollutants, yet have been neglected when calculating the potential addition or removal from urban forests. This project is designed to measure the *in situ* effects of urban trees on transportation pollutant concentrations. Nitrogen oxides, benzene, toluene, ethylbenzene, and xylenes have been chosen as pollutants of focus because they provide a mix of well-studied surrogates with less common, but equally harmful urban air pollutants. This study seeks to determine if actual reductions in ambient concentrations can be attributed to air pollutant removal by urban forests. The results of this project will contribute to the understanding of how urban forests can be used as an element in sustainable urban design.



## Objectives

To achieve an accurate representation of transportation pollutant concentrations, this study utilizes a passive ambient air sampling campaign in Hillsborough County, Florida. The study area includes the cities of Tampa, Brandon, Plant City, and the surrounding rural areas. This location was selected because of the heterogeneity of urban and rural areas available for sampling. This work is part of a larger study of the area which includes comparable modeling data. Hillsborough County's urban form includes a dense downtown and large areas of sprawling development which are connected by a network of major interstates and highways. These roads result in great amounts of transportation pollutant emissions by passenger and freight vehicles. Continuous construction and expansion of major roadways also results in nonroad construction equipment emissions. The study has three objectives which are designed to improve understanding of interactions between Hillsborough County's transportation air pollution and urban forests as an element of urban design:

Objective 1: To characterize local concentrations and spatial variations of benzene, toluene, ethylbenzene, xylenes, and nitrogen oxides in Hillsborough County, FL.

*Hypothesis:* Concentrations of all pollutants of interest are expected to be greatest near heavily travelled roadways. Urban areas of the county will have higher and more variable pollutant concentrations than rural areas.

Objective 2: Determine effects of Hillsborough County's urban forest on the localized concentrations of pollutants of interest.

*Hypothesis:* Local concentrations of benzene, toluene, ethylbenzene, xylenes, and nitrogen oxides will be slightly decreased by the presence of urban forests.

Objective 3: Recommend approaches for the use of urban forests as effective air pollution mitigation technique in Hillsborough County.

The successful fulfillment of these objectives will allow for a more complete understanding of spatial variation of pollutant concentrations throughout the county. Additionally, conclusions regarding the effects of trees on localized ambient concentrations can be used to determine the effectiveness of including urban forests in a sustainable urban design.

## **Chapter Two:**

### **Research Design and Methods**

A passive sampling campaign of 100 locations in Hillsborough County provided concentration information which was utilized for mapping concentrations and statistically interpreting the effects of Hillsborough County's urban forest on ambient transportation pollutant concentrations. This data was used to evaluate the benefits of current forest resources in Hillsborough County, as well as aid in the development of a plan for most effectively incorporating trees within existing and future urban designs.

#### **Sampling Campaign Design**

An air sampling campaign measuring benzene, toluene, ethylbenzene, xylenes, and nitrogen oxides was designed in order to accomplish Objectives I and II of this project. It was necessary to consider multiple variables at each sampler location to ensure that results could be effectively interpreted to answer the research questions of the project. These variable attributes, including urban/rural classification, tree cover, population, and distance from other samplers, were used to create a sampling campaign that was suitable for this project's purposes.

A total of 50 sampling areas were used for this campaign. Each of these sampling areas corresponded to a Census Block Group, for which detailed demographic data was available. Census Block Groups were utilized as the unit of analysis in support of the goals of the larger study that this work is a part of. In each of the 50 selected Block Groups, two samplers, known as A and B, were located approximately 300 meters apart, for a total of 100 samples.

Hillsborough County has 920 Block Groups, with 661(72%) located completely within an “Urban” area, as classified by the U.S. Census Bureau (2010). Since air pollution is most variable within urban areas, a similar proportion of Urban Block Groups were sampled for this campaign (Briggs et al., 2000; Vardoulakis et al., 2011). Therefore, 36 Urban Block Groups and 14 Rural Block Groups were chosen as sampling areas to achieve the goal of 100 samples.

In order to understand the effects of urban forests and trees on differences in air pollutant concentrations, 25 of the 50 Block Groups had samplers located in a “Forested” area. These “Forested Block Groups” were proportionally distributed between urban and rural areas, resulting in 18 urban and 7 rural. Since rural areas often have more forested land than urban areas, this proportional distribution ensured that the forested sampling locations were not more likely to be randomly located in rural areas where pollution tends to be less severe. Table 2.1 summarizes the attributes of the sample.

### **Sampling Site Selection**

A multi-step procedure was used to select the 50 Block Groups used in the campaign. Randomization was applied whenever appropriate to minimize confounding effects on pollutant concentrations. Block groups were first divided into Urban and Rural based on their classification from the U.S. Census Bureau in 2010. Certain block groups are partially classified as an urban area or urban cluster by the Census Bureau. Only the block groups completely contained within Hillsborough County’s urban areas and clusters were classified as urban for this project. All other block groups which were partially or completely excluded from the Census Bureau’s “Urban” classification were grouped into the second “Rural” category. These areas may actually be periurban, but the entire group is referred to as rural in accordance with the

Census Bureau's procedures. Urban areas are contiguous areas identified by their dense settlement and population of at least 50,000, while urban clusters are densely settled areas with a population of less than 50,000 but greater than 2,500 (U.S. Census Bureau, 2012). Certain commercial or industrial areas may also be classified as urbanized, even though they contain smaller residential populations.

ArcGIS 10 was used to create maps for urban and rural block groups within Hillsborough County. Thirty-six random points were produced by ArcMap 10 and projected on the urban map. Thiessen polygons were drawn within the urban area from these generator points. The Thiessen polygons range from 1.5-19.5 square miles. Next, 18 of the polygons were randomly selected for the location of a forested sampler. The other 18 polygons have samplers located in a non-forested area. One block group inside each of these 36 polygons was chosen as the sampling area. The specific block groups to be sampled were chosen because they possessed features like good accessibility and availability of mounting structures which made them more suitable for this sampling campaign. This process was repeated for rural areas, using 14 random points and Thiessen polygons, with 7 randomly selected for forested and 7 for non-forested. Rural Thiessen polygons ranged from 15-118 square miles. One block group from each polygon was chosen for sampling, with preference again being given to accessible locations and areas with mounting structures.

For purposes of this study, areas were considered either "Forested" or "Non-Forested" based on land cover data from the Southwest Florida Water Management District (SWFWMD), as well as visual interpretation of Google Earth satellite imagery. SWFWMD uses the Florida Fish and Wildlife's (FWC) Florida Land Use and Cover Classification System (FLUCCS) to interpret color-infrared digital aerial photography at a scale of 1:8,000. This system is very

effective at characterizing tree resources and species when no other land use is present. However, some areas of significant canopy cover can be overlooked using only the Florida Land Use and Cover Classification System. For example, many low-density neighborhoods have a significant proportion of tree canopy cover, but the presence of houses results in a residential classification. This is because the FLUCCS classification system is not designed to characterize the *urban forest* which exists simultaneously with the various commercial, industrial, and residential land uses. An additional classification procedure was developed to supplement the SWFWMD land cover data in order to more accurately define areas of urban forest. Aerial views and satellite imagery from Google Earth were manually viewed to identify areas of significant tree coverage that were not classified as forested land cover by the SWFWMD data set, because an alternate classification was available. The Florida Land Use and Cover Classification System defines an upland forest area as containing 25-100 percent tree canopy closure. The United States Geographic Service's Land Cover Institute (LCI) uses an identical definition. This study will also consider any land area greater than 300m x 300m of 25-100 percent canopy coverage as a forested area. This 900 square meter land area was chosen to ensure that two samplers can be located the required 300 meters apart within a contiguous forested area. Figure 2.1 shows the block groups chosen for the sampling campaign.

**Sampler coverage.** Sampler coverage over urban areas in Hillsborough County was greater, due to the increased variation in ambient pollutant concentrations in these areas. Urban areas had an area-to-sampler ratio of 4 sq. miles per sampler, while rural areas had a ratio of 28 sq. miles per sampler. Urban areas account for less than half of the total land area in Hillsborough County, but made up the majority of sampling locations for this campaign.

## Sampler Selection, Deployment, & Analysis

Passive sampling techniques were utilized in the sampling campaign in order to achieve the desired spatial resolution. Each category of pollutant was analyzed using different laboratory techniques that share similar principles. Pilot studies in Hillsborough County developed protocols for use of passive samplers to measure concentrations of nitrogen dioxide, benzene, and aldehydes (Zeager, 2008; Fridh, 2011; Evans, 2010). This study applied the techniques and procedures established by these pilot studies in the development of a county-wide sampling campaign of 100 locations.

Passive samplers were chosen for this sampling campaign based on cost, ease-of-use, availability, and evidence of measurement precision and accuracy. Samplers were loaded and deployed for seven days at designated locations, then collected and sealed in airtight containers until laboratory analysis. Field blanks were utilized at 10% of sampling locations to correct for possible contamination that may have occurred before or after the sampling period. Two laboratory blanks were analyzed to correct for contamination during extraction and instrument analysis.

Sampling for benzene, toluene, ethylbenzene, and xylenes (BTEX) was performed using *Radiello Passive Diffusive Samplers for VOC/BTEX with CS<sub>2</sub> Desorption*. Radiello diffusive bodies were filled with charcoal adsorbent cartridges that collect pollutants of interest. Carbon disulfide was used to desorb sample and blank cartridges. Gas chromatography with select ion monitoring (SIM) mass spectrometry was subsequently used for separation and analysis of BTEX compounds. Pollutant masses were determined by comparing retention time and peak

area to the standard calibration curve for each compound. Complete sampling and laboratory protocols are included in Appendix A.

Nitrogen oxide sampling was performed using the *Ogawa Sampler for NO and NO<sub>2</sub>*. The reusable Ogawa samplers were loaded with pre-coated collection fiber filters during sampling, then removed and soaked in deionized water for analysis. A color producing reagent powder pillow was added to the sample, which was then shaken and cooled. Light absorbance of the sample was analyzed using a UV-visible spectrophotometer at 545 nm. Pollutant mass was quantified by comparing absorbencies to a daily standard curve. Complete sampling and laboratory protocols are included in Appendix B.

Quality control measures for this study were designed to minimize human procedure and instrumental error. Field blanks were utilized to control for contamination during sampler preparation and transport. A limit of detection was calculated as three times the standard deviation of the field blank samples. Laboratory blanks were also utilized during each sampling period to control for contamination during sample extraction and analysis. Precision of samplers was determined using duplicate samplers at a ten sampling locations. Precision of analytical instruments was determined by comparing replicated sample runs in 10% of samples. Error was calculated using the product of the averaged sample concentration and the percent difference of the duplicate samplers. Daily calibration checks and control charts for analytical instruments were completed to ensure accuracy. Standard operating procedures for quality control measures are located in Appendices A and B. Example calibration results and quality control data are located in Appendix C.



Conversion from mass to concentration was necessary to evaluate the 14-day averaged ambient levels of pollutants of interest. This calculation used a blank-adjusted pollutant mass, sampling rate, temperature, and humidity. The general equation for calculation of ambient concentration is:

$$C_{air} = \frac{m}{Q_K \cdot t}$$

Where  $C_{air}$  is the 14-day ambient pollutant concentration,  $m$  is the blank-adjusted mass,  $Q_K$  is the temperature and humidity adjusted sampling rate, and  $t$  is the sampling time in minutes. See Appendix A and Appendix B for stepwise calculations for each class of pollutant.

## Data Analysis

Various statistical, mapping, and data synthesis techniques were used to analyze concentration data obtained from the sampling campaign. Descriptive statistics were used to characterize pollutant concentrations in Hillsborough County for Objective I. Hypothesis testing was used to determine the effects of urban forest on localized pollutant concentrations. A synthesis of the literature review and Objectives I and II was used to recommend approaches for the use of urban forests as a pollution mitigation technique. These methods are discussed in detail below.

**Objective I data analysis methods.** In order to *characterize the local concentrations of benzene, toluene, ethylbenzene, xylenes, and nitrogen oxides in Hillsborough County*, descriptive statistics and mapping techniques were used. Summary statistics of pollutant concentration data were used to investigate the distribution of the 14 day-averaged pollutant concentrations from the 50 sampled Block Groups. The spatial variability of pollutant concentrations was analyzed using

two different techniques. To visually interpret variation, a map of pollutant concentrations in Hillsborough County was produced for each pollutant using ArcGIS10. To quantify variation, the coefficient of variation was calculated using the ratio of the standard deviation to the mean of the observations for each pollutant.

**Objective II data analysis methods.** In order to *determine the effects of Hillsborough County's urban forest on the localized concentrations of pollutants of interest*, inferential statistical techniques were utilized. An independent two samples *t*-test of unequal variances, also known as Welsh's *t*-test, was used to evaluate whether concentrations of pollutants of interest were significantly different in certain areas. A two-tail test was used to evaluate three null hypotheses:

- 1.)  $H_0$ : Urban, Forested mean = Urban, Non-forested mean
- 2.)  $H_0$ : Rural, Forested mean = Rural, Non-forested mean
- 3.)  $H_0$ : Total Forested mean = Total Non-forested mean

These three tests were repeated for each measured pollutant. Two tailed tests were necessary because of the uncertainty regarding *in situ* effects of urban forests on pollutant concentrations.

**Objective III data analysis methods.** A synthesis of data from the Literature Review and Objectives I and II was used to *recommend approaches for the use of urban forests as effective air pollution mitigation technique in Hillsborough County*. Recommendations took into account the relative reductions and/or increases in ambient concentrations of transportation pollutants. The plan outlines and prioritizes areas in Hillsborough County which may benefit

from increased urban forest resources. A list of species which are most effective at reducing pollutant levels is included. A description of other benefits, including temperature reductions, energy savings, increased walkability, and improved aesthetics was provided for areas which were recommended for urban forest improvement.

Table 2.1 Sampling location attributes

	Urban	Rural	Total
Forested	18	7	25
Not Forested	18	7	25
Total	36	14	50

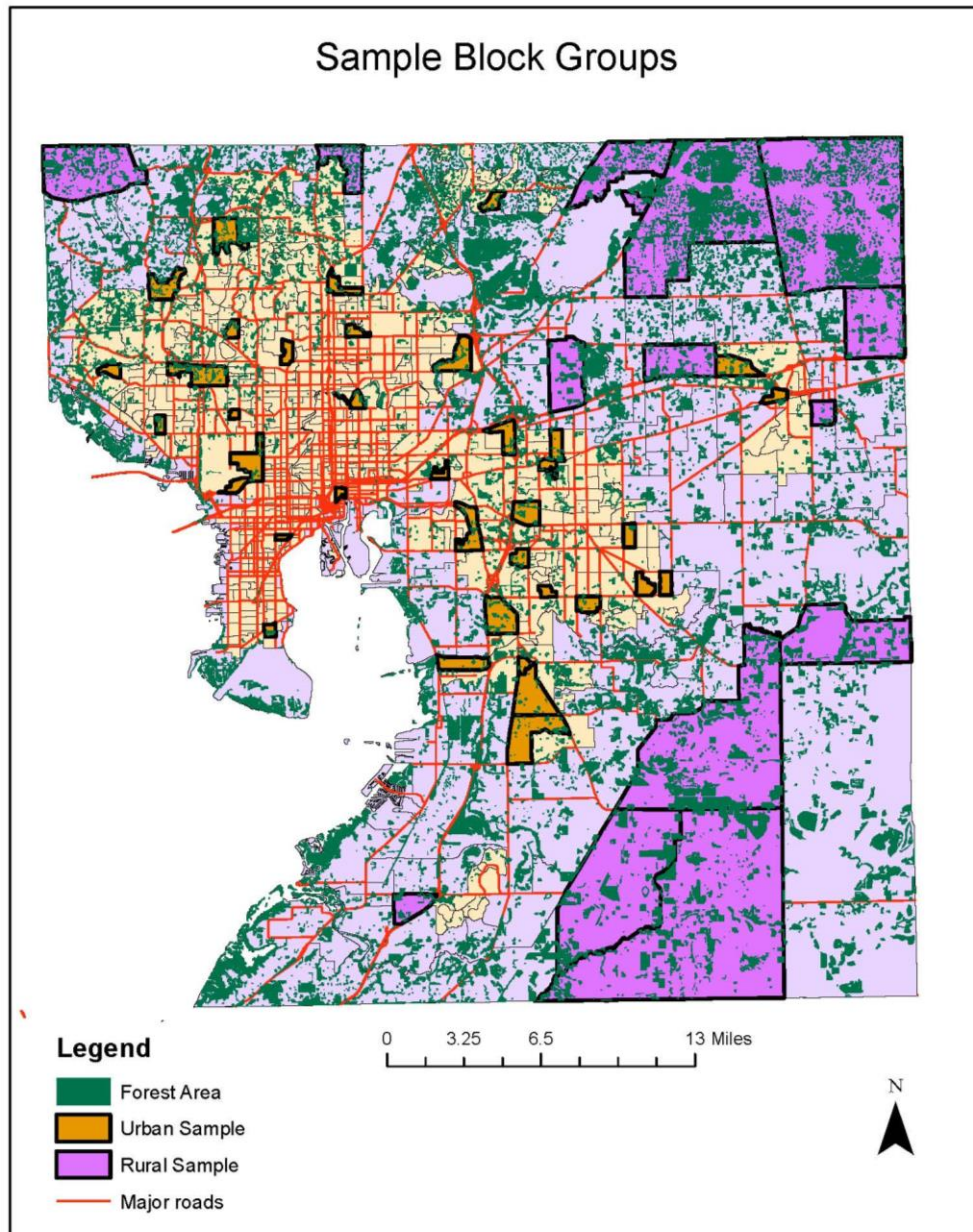


Figure 2.1 The block groups chosen as sampling locations are highlighted in yellow and purple.

## **Chapter Three:**

### **Results and Discussion**

#### **Objective I: Characterizing Pollutant Concentrations**

A fourteen day passive sampling campaign was conducted in Hillsborough County from July 6-20, 2013. Laboratory analysis of samples was completed July 20-August 15, 2013, according to protocols in Appendix A and B. A total of 99 locations were sampled for NO<sub>x</sub>, NO<sub>2</sub>, and BTEX, with 10 sites receiving duplicate samplers to determine precision. After accounting for losses due to missing or broken samplers, a total of 103 (95 locations plus 8 duplicates) NO<sub>x</sub>-NO<sub>2</sub> samplers and 107 (97 locations plus 10 duplicates) BTEX samplers were analyzed. Results from the laboratory analysis are presented in the following sections.

**Precision of passive samplers and analytical instruments.** Analysis of duplicate samplers provided information needed to determine the precision of the sampling methods used by this study. At each of the ten sites that received duplicate samplers, the relative percent difference was calculated. These percentages were averaged to obtain one percentage which could be used to quantify the error of the sampling method. Table 3.1 presents results from the duplicate analysis.

In addition to duplicate analysis, 10% of samples were analyzed twice, so that instrumental precision could be determined. The percent difference for these replicate analyses are given in Table 3.2. Samples were manually injected and manually integrated, so this value includes both the instrumental error and the operator error.

**Observed concentrations of nitrogen oxides.** Results from the sampling campaign are reported as 14-day averaged pollutant concentrations. The values obtained from the two samplers (A and B) located 300 meters apart at each site were averaged and reported accordingly.  $\text{NO}_x$  and  $\text{NO}_2$  are directly measured by the Ogawa passive sampler device, and NO is calculated by subtracting the concentration of  $\text{NO}_2$  from  $\text{NO}_x$ . Due to sampler variability, this subtraction resulted in a small negative value for NO at certain sites. In this case, a concentration of 0 ppb was reported for NO. Summary statistics for  $\text{NO}_x$ ,  $\text{NO}_2$ , and NO are presented in Table 3.3, and complete results for each site are contained in Appendix D.

Concentrations observed for nitrogen oxides are reported in parts per billion (ppb). The mean concentrations of  $\text{NO}_x$ ,  $\text{NO}_2$ , and NO in Hillsborough County were found to be 2.07 ppb, 1.48 ppb, and 0.59 ppb, respectively. Error was calculated from the average of the ten relative percent difference values for duplicate sampler concentrations, shown in Table 3.1. Since NO was calculated from the  $\text{NO}_x$  and  $\text{NO}_2$  values, and not measured directly, values for error and limit of detection of NO were not included.

The observed concentrations of nitrogen oxides were lower than those from a previous passive sampling campaign measuring  $\text{NO}_2$  (Zeager, 2008), and preliminary samples taken in March 2013. One explanation for this result is the extremely wet weather throughout July, including the 14-day sampling period. According to the National Weather Service, rain fell in the Tampa area on 24 days in July, for a total of 10 inches. These conditions likely facilitated the wet deposition of many pollutants from the atmosphere, including those measured by this study. Higher levels of wet deposition would reduce the ambient concentrations being measured by the passive samplers. Another factor contributing to this difference is the sampling campaign design, which included a proportion of very rural sampling sites. Many of these areas have only

small amounts of traffic emissions, capable of lowering the mean and median of the total sample. Table 3.4 presents separate summary statistics for rural and urban sampling locations. When separating the total sample into rural and urban categories, an apparent difference can be seen in the means of  $\text{NO}_x$  and  $\text{NO}_2$ . The statistical values for the urban category are similar to the values which were expected.

The differences observed between the mean concentrations of the rural and urban samples are presented in Table 3.5 as relative percent difference, calculated as the the difference of the rural and urban mean concentrations divided by the average of those two values. Percent differences of 22%, 49%, and -36% are observed between the urban and rural samples of  $\text{NO}_x$ ,  $\text{NO}_2$ , and  $\text{NO}$ , respectively. The negative percentage calculated for  $\text{NO}$  shows that the mean concentration of  $\text{NO}$  in rural areas was actually greater than in urban areas.

In general, the concentration of  $\text{NO}$  would be expected to be greater inside urban areas because of primary  $\text{NO}$  emissions from vehicles. Rural areas would be more likely to experience higher concentrations of  $\text{NO}_2$  because as plumes travel through the atmosphere the  $\text{NO}$  oxidizes to  $\text{NO}_2$ . An independent two samples  $t$ -test of unequal variances was performed to determine if the differences in rural and urban block group means were significant. Results for this test are shown in Table 3.6.

At the 95% confidence level, the urban mean is greater than the rural mean for  $\text{NO}_2$ . P-values of 0.23 and 0.41 were obtained for  $\text{NO}_x$  and  $\text{NO}$ , so the null hypothesis that the two means are equal could not be rejected. This test lacked power to detect differences because the sample size of rural block groups was only 14. When looking at the concentration data for  $\text{NO}$ , two locations have considerably higher values than the rest of the sample—site 12 and site 3. If

these two locations were treated as outliers and removed from mean calculations, the new mean value would be 0.48 ppb, which is less than the mean of the urban sample.

Site 12, in the southwest corner of the county, was located directly adjacent to a fish farm. When fish food is added to the ponds, excess nitrogen enters the aquatic ecosystem. Fish excrete the nitrogen as ammonia, which will undergo nitrification and form nitrates. Denitrification allows the nitrogen to return to the atmosphere as N<sub>2</sub>, and NO is an intermediate compound in this process. Therefore, the elevated levels of NO observed at site 12 could a result of the excess nitrogen cycle inputs of the nearby fish farm. Site 3 also experienced higher levels of NO compared to the other rural samples. Although this location is in a rural Block Group, the samplers were placed along U.S. Highway 301, a major route for both passenger vehicles and trucks. High levels of NO were expected at this location because of the traffic emissions.

**Observed concentrations of BTEX.** Radiello samplers for VOCs with CS<sub>2</sub> desorption were used to collect ambient BTEX during the 14-day sampling period. These results are reported as a 14-day average concentration in  $\mu\text{g m}^{-3}$ . The Radiello samplers can be used to sample for more than 40 VOCs. This study chose to analyze for benzene, toluene, ethylbenzene, and xylenes because of their presence in transportation pollution and public health importance. A small-scale pilot study of benzene has been performed in the Tampa Bay area using Radiello samplers (Fridh, 2011). High spatial resolution was achieved in this study, but the total area was limited to a local park. This passive sampling campaign was the first of its kind to measure ambient BTEX in a sampling network spanning all of Hillsborough County. Summary statistics for each compound are presented in Table 3.7.



Results from the BTEX analysis show means in the expected range of concentrations for the county. Generally, levels of toluene are expected to be at least twice the benzene concentration. M-xylene and p-xylene were reported together because they have identical retention times in the GC-MS method used for this study. Analysis for benzene and toluene was achieved with relative ease because they have very distinct chromatographic peaks with unique retention times. Ethylbenzene and xylenes were more difficult to integrate because of interferences from other VOCs collected by the Radiello samplers. Integrations for a small proportion of samples were not made for these compounds because incomplete separation of VOCs caused indiscernible chromatograms with high background noise. Due to this, concentrations for ethylbenzene and xylenes may be overestimated because these samples were not included in the analysis.

Similar to nitrogen oxides, BTEX concentrations were observed to be greater in urban areas. Table 3.8 shows summary statistics for rural and urban areas. BTEX is emitted directly from vehicles, so concentrations are expected to be greatest in areas with heavy traffic. The magnitude of difference between rural and urban areas was much greater for BTEX than for nitrogen oxides. In Table 3.6, results from significance testing of mean differences show low probability that these differences are by chance.

**Spatial variation of concentrations within Block Groups.** To quantify the spatial variability within Block Groups, the percent difference of samplers A and B in each of the 50 Block Groups was calculated in Table 3.9. Mean concentrations of nitrogen oxides were less variable than BTEX, with mean relative percent difference values of 38% and 28%, respectively. BTEX variability was larger within Block Groups, with averaged relative percent difference values ranging from 51% for Toluene to 87% for ethylbenzene. The minimum and maximum

values for each pollutant show how large the range of variability is, making it difficult to assign a generalizable amount of variability to Block Groups throughout Hillsborough County.

**Spatial variation of concentrations in Hillsborough County.** The spatial variability of pollutant concentrations was analyzed using mapping techniques and the coefficient of variation. To visually interpret spatial variation, a map of obtained pollutant concentrations in Hillsborough County was produced for each pollutant, using ArcGIS10. Figure 3.1 presents results for  $\text{NO}_x$ ,  $\text{NO}_2$ , and  $\text{NO}$ .

Figures 3.1 and 3.2 illustrate the clear pattern of higher concentrations in Tampa and Brandon, especially along Interstates 75 and 275. To quantify the variation of the sample, the coefficient of variation was calculated using the ratio of the standard deviation to the mean of the observations for each pollutant. Results from this calculation are presented in Table 3.10.

This quantification of the magnitude of standard deviation shows the heterogeneity of the samples taken in Hillsborough County. Previous studies have used a standard of 20% as the lower limit of heterogeneity (Blanchard et al., 1999; Wilson et al., 2005). These values far exceed that standard. From this, it can be concluded that pollutant concentrations in Hillsborough County are not homogeneous.

Results from previous studies of spatial variability of pollutant concentrations support the findings of this work. A study of  $\text{NO}_x$  in 36 European sites showed that 40% of variability was attributed to between site variations, while 60% was within the site. For  $\text{NO}_2$ , 30% of variability was between sites, while 70% was within the site. The within-site variability corresponds to the relative percent difference between the two samplers in each block group used by this study.

Values ranged from approximately 30%-90% for within Block Group relative differences. In

many cases, this is higher than the variability observed between Block Groups. A study by Aguilera et al. (2008) of NO<sub>x</sub>, NO<sub>2</sub>, and BTEX in northeast Spain used measured data to develop a regression model to predict outdoor concentrations. Major predictor variables accounting for 68%, 69%, and 74% for NO<sub>x</sub>, NO<sub>2</sub>, and BTEX, respectively, included variables of source proximity, such as distance from roadways. Results from this study also show that distance from sources, especially traffic sources, contributes to the high spatial variability observed across Hillsborough County.

## **Objective II: Determining Effects of Urban Forests on Pollutant Concentrations**

After characterizing pollutant concentrations for all of Hillsborough County, sampling results were categorized into forested and not forested groups and statistically reviewed to determine if trees may have an effect of ambient concentrations of transportation pollutants. A summary of each category is provided for an overview of the concentration distribution. Hypothesis testing was then performed to determine the significance of any differences observed in ambient concentrations of nitrogen oxides or BTEX.

**Observed concentrations of pollutants in forested areas.** Tables 3.11 and 3.12 present summary statistics for observed pollutant concentrations in the forested sample and not forested sample. The mean concentration and standard deviation for every pollutant of interest, with the exception of NO<sub>2</sub>, was lower for the forested category. All median values were also lower in the forested category. The maximum concentrations observed for every pollutant was located in a non-forested area.

**Significance of urban forest to observed concentrations.** To test whether the differences observed in the previous section were statistically significant, an independent two

samples *t*-test of unequal variances, also known as Welsh's *t*-test, was used to evaluate the forested and not forested samples. A two-tail test was used to evaluate two null hypotheses:

Test 1             $H_0$ : Urban, Forested mean = Urban, Non-forested mean

Test 2             $H_0$ : Total Forested mean = Total Non-forested mean

The rural and urban means were calculated using the average of sites A and B in each Block Group. These tests were repeated for each measured pollutant. Results for each test are shown Table 3.13.

Results from Tests 1 and 2 did not find statistically significant differences in concentration means at the  $\alpha=0.05$  significance level for any of the pollutants of interest. When examining P-values, it is clear that differences in mean nitrogen oxide concentrations based on the presence of trees are not probable. In fact, the probability that there is no difference in mean  $NO_x$  concentrations is 95% for urban areas. Based on this result, it can be inferred that trees in urban areas did not remove nitrogen oxides in amounts large enough to have a distinguishable effect on ambient concentrations using the sampling methods of this study. P-values for  $NO_2$  and NO were similarly high, at 64% and 73%, respectively. The high standard deviation of each sample affected the power of the *t*-tests for significance. Since the concentrations of pollutants throughout Hillsborough County had high spatial variability, a large magnitude of difference would have had to exist in the forested sample for a statistically significant result to be found.

Previous studies have concluded that the spatial heterogeneity of air pollution in cities affects the pollutant removal functionality of an urban forest. Escobedo & Nowak (2009) showed how the amount of pollutant removed is affected by pollution concentration differences in Santiago, Chile. Higher concentrations allow for higher removal rates. Jim & Chen (2008)

obtained similar results in Guangzhou, China. This study identified the two most important factors in pollutant removal as tree cover and pollutant concentration. However, results from this study were not able to show differences in the measured ambient concentrations of areas with urban forests.

## **Limitations**

Sampling methods, equipment precision, and campaign design all contributed to this study's limitations and uncertainty. Passive sampling devices allow for high spatial resolution to be achieved, but temporal resolution is lost because the concentration is averaged over 14 days. Due to this, daily and weekly concentration patterns cannot be characterized with the methods utilized in this study. Limitations due to certain environmental factors also contributed to the uncertainty associated with pollutant measurements. Differences in weather conditions among sampling locations were not accounted for using this sampling method. A 14-day average temperature and humidity value taken from Tampa International Airport was applied to all sites because it was not feasible to obtain individual weather data from each location. Rainfall also varied between sites, potentially altering sampling results if a sampler were to get wet. Although samplers were located under shelters, it is not possible to know which, if any, may have gotten wet.

Uncertainty associated with the precision of the samplers and analytical instruments was also a limitation of this study. Duplicate samplers had a relative percent difference of approximately 15% which is associated with the sampler precision. The relative percent difference was shown to be about 10% for replicate analysis of BTEX, which quantifies the uncertainty associated with the analytical instrument and its operation. Additionally, the

uncertainty of concentrations within Block Groups is a major limitation of this study. A wide range of concentration differences between A and B samplers make it difficult to estimate the variability within any given block group. This also contributed to the reduced power of statistical testing for mean differences because the sample standard deviation was very high.

### **Future Work**

Future studies investigating the interactions of urban forests and trees with air pollution can use this work to guide their study design and selection of analytical techniques. This study used the Census Block Group for a spatial scale because the concentration data was needed for purposes beyond looking at interactions with urban forests. A more appropriate spatial scale could be selected for subsequent studies which incorporates areas with uniform emissions so that lower levels of variability can be achieved. The effect of urban forests on pollutant concentrations may become discernible with a better sampling design. Tests of statistical significance can also be used more effectively when standard deviation of the sample is lower.

Future work should also consider choosing a location known to have high levels of pollutants based on results of this study suggesting that the effects of trees may be most apparent in areas of high concentration. A variable quantifying the amount of tree cover in an urban can also be tested in future multiple regression efforts predicting pollutant concentrations.

Table 3.1 Relative Percent Difference of Duplicate Samplers

Site	NO <sub>x</sub>	NO <sub>2</sub>	Benzene	Toluene	Ethylbenzene	m,p-Xylene	o-Xylene
13 A	21	9	21	22	22	24	21
13 B	13	12	13	13	7	21	14
14 A	18	15	16	10	20	19	7
14 B	12	19	22	19	14	7	26
15 A	11	10	8	16	26	16	11
48 A	--	--	6	7	15	4	14
48 B	8	17	21	15	16	17	18
49 A	--	--	17	12	26	31	22
49 B	14	21	13	15	14	22	13
40 A	18	7	12	9	9	15	20
<b>Average %D</b>	<b>14.4</b>	<b>13.8</b>	<b>14.9</b>	<b>13.8</b>	<b>16.9</b>	<b>17.6</b>	<b>16.6</b>

Table 3.2 Relative Percent Difference of Replicate Analyses

Site	NO <sub>x</sub>	NO <sub>2</sub>	Benzene	Toluene	Ethylbenzene	m,p-Xylene	o-Xylene
1 A	0	0	7	10	13	13	12
10 A	0	0.008	9	5	12	6	5
20 A	0	0	10	8	8	8	3
30 A	0	0	13	15	4	5	18
40 A	0.005	0	9	6	15	11	7
50 A	0	0	3	13	9	9	16
1 B	0	0	8	11	6	9	13
10 B	0.008	0	13	3	8	6	14
20 B	0	0	7	5	12	17	10
30 B	0	0	15	9	13	12	3
40 B	0	0	12	2	10	10	6
50 B	0	0	12	14	11	9	14
<b>Average % D</b>	<b>0.0</b>	<b>0.0</b>	<b>9.8</b>	<b>8.4</b>	<b>10.1</b>	<b>9.6</b>	<b>10.1</b>

Table 3.3 Hillsborough County NO<sub>x</sub>, NO<sub>2</sub>, and NO Summary Statistics

	NO <sub>x</sub>	NO <sub>2</sub>	NO
<b>Count</b>	50	50	50
<b>Mean (ppb)</b>	2.07	1.48	0.59
<b>Median (ppb)</b>	1.64	1.28	0.09
<b>Standard Deviation (ppb)</b>	1.26	0.76	0.82
<b>Minimum (ppb)</b>	0.36	0.36	0.00
<b>Maximum (ppb)</b>	5.54	3.24	3.26
<b>Error (ppb)</b>	±0.30	±0.20	--
<b>Limit of Detection (ppb)</b>	0.16	0.19	--

Table 3.4 Rural and Urban NO<sub>x</sub>, NO<sub>2</sub>, and NO Summary Statistics

	Rural			Urban		
	NO <sub>x</sub>	NO <sub>2</sub>	NO	NO <sub>x</sub>	NO <sub>2</sub>	NO
<b>Count</b>	14	14	14	36	36	36
<b>Mean (ppb)</b>	1.76	1.00	0.75	2.19	1.66	0.52
<b>Median (ppb)</b>	1.51	0.92	0.50	1.80	1.64	0.06
<b>Standard Deviation (ppb)</b>	1.03	0.54	0.89	1.33	0.75	0.79
<b>Minimum (ppb)</b>	0.36	0.36	0.00	0.55	0.53	0.00
<b>Maximum (ppb)</b>	3.58	2.49	2.60	5.54	3.24	3.26

Table 3.5 Relative Percent Difference of Rural and Urban Mean Concentrations

Rural /Urban Percent Difference		
NO <sub>x</sub>	NO <sub>2</sub>	NO
22%	49%	-36%



Table 3.6 Independent Samples *t*-Test Results at 95% Confidence Level

Pollutant	H <sub>0</sub> : Rural mean = Urban mean			Result
	t Critical	t Statistic	P-value	
NO <sub>x</sub>	2.040	-1.213	0.234	Fail to Reject
NO <sub>2</sub>	2.035	-3.447	0.002	<b>Reject</b>
NO	2.074	0.847	0.406	Fail to Reject

Table 3.7 Hillsborough County Ambient BTEX Summary Statistics

	Benzene	Toluene	Ethylbenzene	m,p-Xylene	o-Xylene
Count	49	49	46	47	45
Mean (µg m <sup>-3</sup> )	0.64	2.82	0.70	1.52	0.79
Median (µg m <sup>-3</sup> )	0.53	2.69	0.55	1.08	0.56
Standard Deviation (µg m <sup>-3</sup> )	0.36	1.41	0.62	1.34	0.74
Minimum (µg m <sup>-3</sup> )	0.16	0.35	0.11	0.30	0.15
Maximum (µg m <sup>-3</sup> )	1.90	5.58	3.51	6.51	4.53
Error (µg m <sup>-3</sup> )	±0.10	±0.39	±0.12	±0.27	±0.13
Limit of Detection (µg m <sup>-3</sup> )	0.04	0.31	0.12	0.17	0.14

Table 3.8 Rural and Urban Summary Statistics for BTEX

Rural					
	Benzene	Toluene	Ethylbenzene	m,p-Xylene	o-Xylene
Rural Count	13	13	11	11	10
Mean ( $\mu\text{g m}^{-3}$ )	0.44	1.57	0.51	0.68	0.62
Median ( $\mu\text{g m}^{-3}$ )	0.40	1.46	0.49	0.66	0.56
Standard Deviation ( $\mu\text{g m}^{-3}$ )	0.22	0.74	0.33	0.28	0.26
Minimum ( $\mu\text{g m}^{-3}$ )	0.16	0.48	0.11	0.30	0.25
Maximum ( $\mu\text{g m}^{-3}$ )	0.95	3.39	1.29	1.23	1.26
Urban					
	Benzene	Toluene	Ethylbenzene	m,p-Xylene	o-Xylene
Urban Count	36	36	35	36	35
Mean ( $\mu\text{g m}^{-3}$ )	0.71	3.28	0.75	1.78	0.84
Median ( $\mu\text{g m}^{-3}$ )	0.66	3.42	0.68	1.30	0.56
Standard Deviation ( $\mu\text{g m}^{-3}$ )	0.38	1.32	0.68	1.43	0.83
Minimum ( $\mu\text{g m}^{-3}$ )	0.22	0.35	0.12	0.46	0.15
Maximum ( $\mu\text{g m}^{-3}$ )	1.90	5.58	3.51	6.51	4.53

Table 3.9 Relative Percent Difference within Block Groups

	Relative Percent Difference of A and B Sites						
	NO <sub>x</sub>	NO <sub>2</sub>	Benzene	Toluene	Ethylbenzene	m,p-Xylene	o-Xylene
Mean	38%	28%	65%	51%	87%	68%	64%
Min	2%	<0.01%	3%	4%	2%	1%	6%
Max	141%	100%	181%	138%	170%	162%	170%

Table 3.10 Coefficient of Variation for Pollutants of Interest

<b>Coefficient of Variation</b>	
<b>NO<sub>x</sub></b>	61%
<b>NO<sub>2</sub></b>	51%
<b>NO</b>	138%
<b>Benzene</b>	56%
<b>Toluene</b>	50%
<b>Ethylbenzene</b>	89%
<b>m,p-Xylene</b>	88%
<b>o-Xylene</b>	94%

Table 3.11 Nitrogen Oxide Summary Statistics for Forested and Not Forest Areas

	<b>Forested</b>			<b>Not Forested</b>		
	<b>NO<sub>x</sub></b>	<b>NO<sub>2</sub></b>	<b>NO</b>	<b>NO<sub>x</sub></b>	<b>NO<sub>2</sub></b>	<b>NO</b>
<b>Count</b>	25	25	25	25	25	25
<b>Mean (ppb)</b>	2.06	1.50	0.57	2.07	1.46	0.61
<b>Median (ppb)</b>	1.67	1.28	0.00	1.61	1.29	0.14
<b>Standard Deviation (ppb)</b>	1.24	0.76	0.82	1.31	0.76	0.83
<b>Minimum (ppb)</b>	0.36	0.36	0.00	0.44	0.44	0.00
<b>Maximum (ppb)</b>	4.66	3.17	2.60	5.54	3.24	3.26

Table 3.12 BTEX Summary Statistics for Forested and Not Forested Areas

	Forested				
	Benzene	Toluene	Ethylbenzene	m,p-Xylene	o-Xylene
Count	24	24	21	22	21
Mean ( $\mu\text{g m}^{-3}$ )	0.59	2.69	0.53	1.24	0.65
Median ( $\mu\text{g m}^{-3}$ )	0.52	2.57	0.55	0.92	0.55
Standard Deviation ( $\mu\text{g m}^{-3}$ )	0.25	1.31	0.23	0.74	0.35
Minimum ( $\mu\text{g m}^{-3}$ )	0.22	0.48	0.16	0.46	0.15
Maximum ( $\mu\text{g m}^{-3}$ )	1.11	4.86	0.92	3.60	1.43
	Not Forested				
	Benzene	Toluene	Ethylbenzene	m,p-Xylene	o-Xylene
Count	25	25	25	25	24
Mean ( $\mu\text{g m}^{-3}$ )	0.70	2.95	0.84	1.77	0.92
Median ( $\mu\text{g m}^{-3}$ )	0.58	3.39	0.59	1.13	0.57
Standard Deviation ( $\mu\text{g m}^{-3}$ )	0.45	1.51	0.80	1.67	0.96
Minimum ( $\mu\text{g m}^{-3}$ )	0.16	0.35	0.11	0.30	0.19
Maximum ( $\mu\text{g m}^{-3}$ )	1.90	5.58	3.51	6.51	4.53

Table 3.13 Independent Samples *t*-Test Results at 95% Confidence Level

Test 1: $H_0$ : Urban, Forested mean = Urban, Non-forested mean				
Pollutant	t Critical	t Statistic	P-value	Result
NO <sub>x</sub>	2.035	0.065	0.949	Fail to Reject
NO <sub>2</sub>	2.032	0.475	0.638	Fail to Reject
NO	2.037	-0.343	0.734	Fail to Reject
Benzene	2.064	-0.852	0.402	Fail to Reject
Toluene	2.040	-0.501	0.620	Fail to Reject
Ethylbenzene	2.093	-2.068	0.052	Fail to Reject
m,p-Xylene	2.069	-1.777	0.089	Fail to Reject
o-Xylene	2.086	-1.400	0.177	Fail to Reject
Test 2: $H_0$ : Total Forested mean = Total Non-forested mean				
Pollutant	t Critical	t Statistic	P-value	Result
NO <sub>x</sub>	2.011	-0.018	0.986	Fail to Reject
NO <sub>2</sub>	2.011	0.163	0.871	Fail to Reject
NO	2.011	-0.179	0.859	Fail to Reject
Benzene	2.024	-1.099	0.279	Fail to Reject
Toluene	2.013	-0.639	0.526	Fail to Reject
Ethylbenzene	2.045	-1.848	0.075	Fail to Reject
m,p-Xylene	2.032	-1.432	0.161	Fail to Reject
o-Xylene	2.042	-1.292	0.206	Fail to Reject

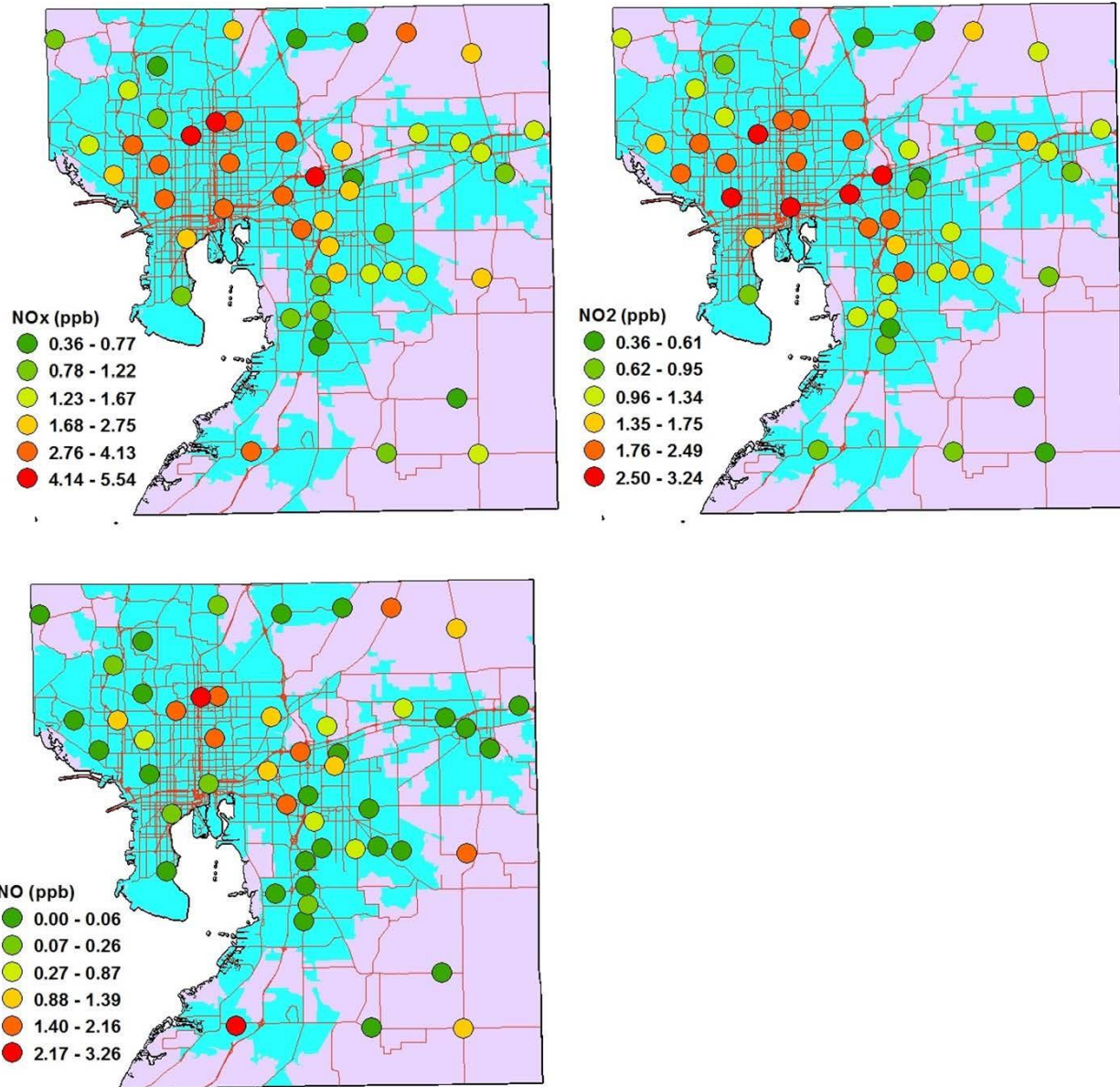


Figure 3.1 Ambient concentrations of NO<sub>x</sub>, NO<sub>2</sub>, and NO obtained during the 14-day sampling period are represented by the colored circles. The purple areas represent rural areas, and the blue areas are urban areas. Major roadways are shown in red.

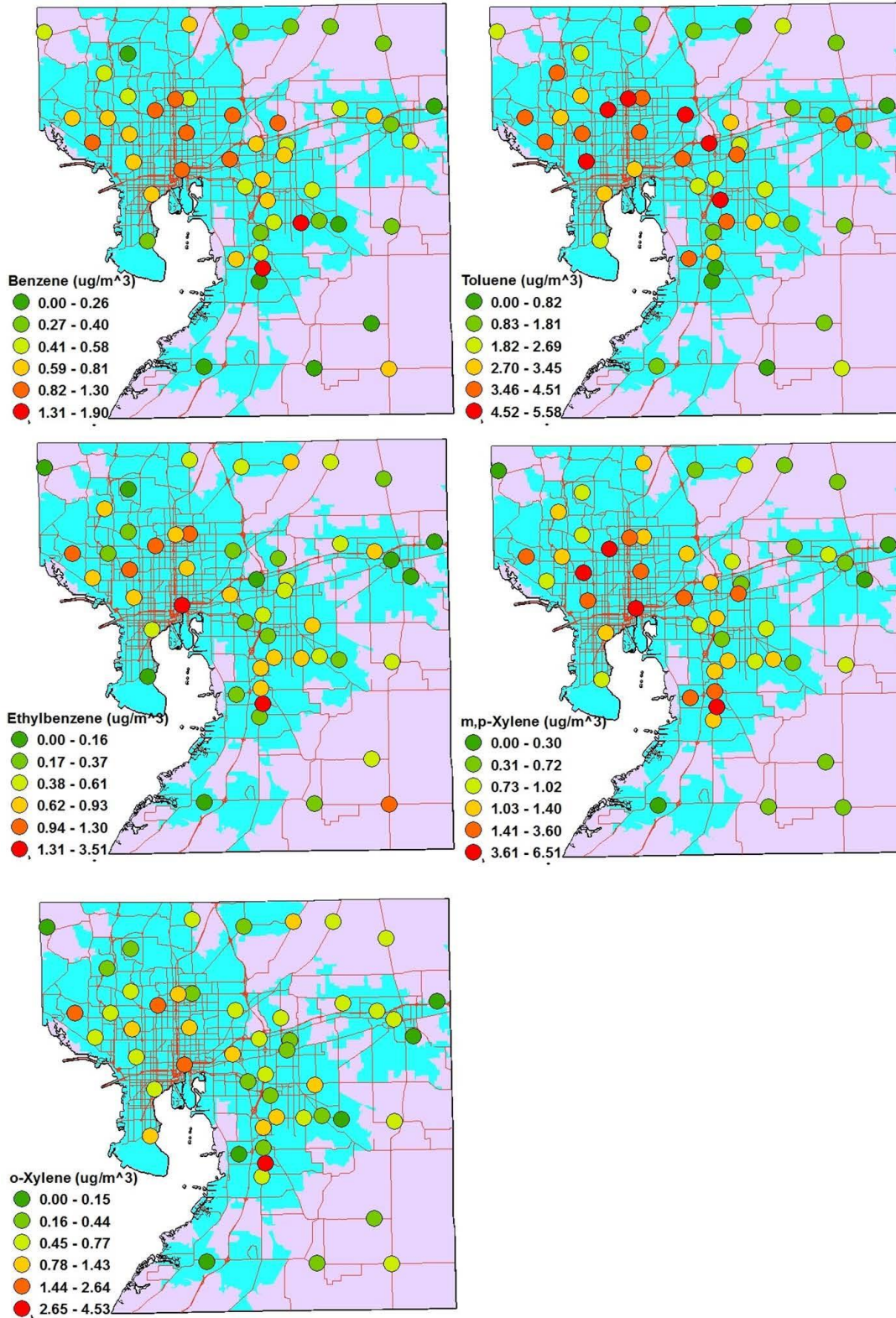


Figure 3.2 Ambient concentrations of BTEX obtained during the 14-day sampling period are represented by the colored circles. The purple areas represent rural areas, and the blue areas are urban areas. Major roadways are shown in red.

## **Chapter Four:**

### **Conclusions and Implications**

#### **Objective III: Recommendations for Using Urban Forests as a Pollution Mitigation**

##### **Strategy**

Despite failing to find statistical significance in mean group differences, findings from this study suggest potential interactions between trees and pollutants, especially for VOC. The mean concentrations of NO<sub>x</sub>, NO, benzene, toluene, ethylbenzene, and xylenes were lower in the forested category. Additionally, the maximum concentration observed for every pollutant of interest was observed in an area classified as not forested. This result suggests that trees may be most usefully incorporated into urban areas of highest pollution, where the atmosphere is more “saturated” with pollutants for deposition or stomatal uptake. In Hillsborough County, areas with highest concentrations were inside the cities of Tampa and Brandon, especially surrounding the Interstate 4 and Interstate 275 corridors.

Trees with larger canopies are more effective at removing pollutants from the atmosphere; therefore, when developing new areas, existing trees should be preserved as much as possible because they are more effective than newly planted trees, which could take years to reach their full removal potential. Evergreen species with broad leaves are most effective at reducing pollution on a year-round basis. Elm trees and birch trees are especially good species to use in an urban setting because of their low biogenic VOC emissions. Hillsborough County should focus their efforts on the most heavily polluted areas in neighborhoods surrounding the

major interstate highways in order to maximize the pollutant removal capacity of any additional trees they plant. When strategically placed, trees can provide additional air benefits from reducing energy consumption in buildings and lowering temperatures to reduce ozone formation.

## **Implications**

This passive sampling campaign utilized low-cost techniques to obtain a high spatial-resolution of transportation pollutant concentrations. Data and results were used for purposes of this study, as well as ongoing studies of localized air pollutant concentrations and urban design in Hillsborough County. The concentration data obtained using these passive sampling methods can also be applied to pollutant modeling efforts in Hillsborough County. This study assessed the amount of variation which exists between certain pollutants at street level. The high levels of variability observed for every pollutant of interest provide evidence that suggests that current monitoring networks with limited spatial resolution may not be adequately characterizing the concentrations that people are actually exposed to. These differences in concentration and among Hillsborough County's block groups which were identified by this study can be evaluated for possible exposure disparities based on socioeconomic factors.

This study also contributes to the advancement of knowledge in urban forest management so that Hillsborough County and other areas can enjoy the health quality and aesthetic benefits of trees throughout their city. Sustainable urban design includes principles of health and equality which this study seeks to evaluate using air pollutant concentration data. By researching and developing urban design methods which promote health and equity, such as urban forest preservation and enhancement inside our cities, more areas can begin to achieve sustainable urban forms.



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## APPENDIX A:

### BTEX Sampling and Laboratory Analysis Protocol

#### Sampling Protocol

##### 1. Purpose and Applicability

This standard operating protocol (SOP) is written to create a consistent procedure for the passive sampling of outdoor BTEX concentrations using Radiello activated charcoal sampling cartridges for a fourteen day sampling period. Using these samplers and protocol, spatial variations in concentrations of BTEX will be determined. This protocol is adapted from a pilot study by Fridh (2011).

##### 2. Summary of Method

In this method, Radiello pre-packed activated charcoal sampler cartridges are used to collect ambient BTEX over a fourteen 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 fourteen day sampling period. At the end of the fourteen 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:

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

$Q_k$  = The sampling rate at temperature K.

$Q_{298}$  = The sampling rate for each compound at 298 Kelvin:

Table A1: BTEX Sampling Rates

Benzene	80 ml min <sup>-1</sup>
Toluene	74 ml min <sup>-1</sup>
Ethylbenzene	68 ml min <sup>-1</sup>
m-xylene	70 ml min <sup>-1</sup>
o-xylene	65 ml min <sup>-1</sup>
p-xylene	70 ml min <sup>-1</sup>

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<sup>-1</sup>.

**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 and retrieval. 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 the field samples and laboratory blanks.

## 5. Equipment and Materials

### 5.1. Sampling Equipment

#### 5.1.1. Radiello Cartridge Adsorbents- code RAD130

- For sampling VOCs/BTEX with CS<sub>2</sub> 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

#### 5.1.2. Radiello Diffusive Body, white- code RAD120

- 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

#### 5.1.3. Radiello Triangular Support Plate- code RAD121

- Made of polycarbonate
- Includes clip for hanging

#### 5.1.4. Radiello Vertical Adapters- code RAD 122

- Made of polycarbonate
- Can substitute for Radiello Triangular Support Plate
- Attached to shelter using Velco

#### 5.1.5. Radiello Outdoor Shelter- code RAD196

- Made of polypropylene
- Can house up to four air samplers
- Each shelter is comprised of three identical panels, two bars for suspending samplers, and two support bars
- Mounted on utility poles using zip tie mounting strips

#### 5.1.6. PVC Outdoor Shelter

- 6-inch polyvinyl chloride end-cap
- Can house two air samplers
- Mounted on utility poles using zip tie mounting strips

### 5.2. Materials

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

5.2.2. A step ladder for reaching the appropriate height when placing the samplers.

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

5.2.4. 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.

**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.

**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.

**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.

### **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.

**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).

## **7. Loading of Samplers**

**7.1.** These procedures should take place just prior to sampler deployment. All samplers and field blanks should be loaded at the same time.

**7.1.1.** 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.

**7.1.2.** Close the polypropylene container and keep it for sampler retrieval.

**7.1.3.** 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.

**7.1.4.** 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.

**7.1.5.** Store the capped glass tube inside of the plastic bag that it came with.

**7.1.6.** Continue to hold the diffusive body with the hole upwards, and screw the triangular support plate or vertical adapter onto the diffusive body.

7.1.7. Place a label with the sampler identification number on the supporting plate or vertical adapter. Return loaded sampler to plastic bag and place an identical label on the bag. Sampler is not ready for deployment.

## **8. Deployment and Retrieval of Samplers**

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

### **8.2. Deployment of Shelters**

8.2.1. 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. Take a GPS record while standing next to each mounted shelter.

- At the predetermined location, use the measuring tape to measure a height of 3m on the object (tree or pole).
- Place the curved end of the Radiello 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.
- For a PVC shelter, hold the shelter against the tree/pole while fastening the mounting strips around both the shelter and the pole. Tighten mounting strips as secure as possible.

### **8.3. Deployment of Samplers**

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

8.3.2. Standing away from and downwind of the vehicle at the sampling site, use the clip on the triangular support plate or Velcro on the vertical adapter to hang the diffusive body from the inside of the shelter. The diffusive body should be facing the inside of the shelter.

- Make a note in the laboratory notebook of sampling start time.
- Take notes on any features of the sampling site that may be relevant to BTEX concentrations, such as nearby traffic or other sources of air contaminants.

### **8.4. Field Blank**

8.4.1. Transport the field blank to sampling locations inside a sealed plastic bag. Return back to the laboratory following deployment and store at 4°C until analysis.

- One field blank should be taken by each team during campaign deployment to account for potentially different exposures.

### **8.5. Replicate Samplers**

8.5.1. At 10% of the field sites, 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.

### **8.6. Retrieval of Samplers**

8.6.1. Retrieval of the samplers will take place fourteen days after deployment.

8.6.2. Find the same plastic bag that the sampler originally came in, using the code on the plastic bag. Remove the triangular support plate or vertical adapter and sampler from the inside of the shelter. Place inside plastic bag and seal. Note the time of retrieval in laboratory notebook.



- 8.6.3.** Remove the shelter and bring all materials back to the laboratory.
- 8.6.4.** Once in the laboratory, 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.
- 8.6.5.** Take the label from the triangular plate or vertical adapter and place 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 refrigerator at 4°C until extraction and analysis.
  - Cartridges are stable for 6 months before extraction when properly stored.

## 9. Quality Control

**9.1.** The field blanks taken according to section 8.4 will help to discern if any BTEX became absorbed onto the cartridge during the transport or set-up of the sampling device.

**9.1.1.** 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.

$$9.1.2. \text{LOD} = 3 \left( \sqrt{\frac{1}{N-1} \sum_{i=1}^N (x_i - \bar{x})^2} \right)$$

N = The number of field blanks.

$x_i$  = The concentration of field blank  $i$ .

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

Example: Benzene

$$\text{LOD} = 3 \times 0.129 \frac{\mu\text{g}}{\text{m}^3} = 0.043 \frac{\mu\text{g}}{\text{m}^3}$$

**9.1.3.** Replicate samples will be taken at 10% of the sampling sites, according to section 8.5. 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.

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

$$9.1.5. \text{Precision} = \left( \frac{|x_1 - x_2|}{\bar{x}} \right) \times 100\%$$

$x_1$  = 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  $x_2$

Example: Benzene, Duplicate Site 1

$$\text{Precision} = \left( \frac{|0.283 \frac{\mu\text{g}}{\text{m}^3} - 0.230 \frac{\mu\text{g}}{\text{m}^3}|}{0.257 \frac{\mu\text{g}}{\text{m}^3}} \right) \times 100\% = 21\%$$

## Laboratory Protocol

### 1. Purpose and Applicability

The purpose of this standard operating procedure is to provide guidelines for the analysis of BTEX, as collected through the sampling SOP, from the ambient air in Hillsborough County,

Florida. The analysis of BTEX 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 gas chromatograph and mass spectrometer system is used for the analysis using helium as the carrier gas. The retention times and peak areas are compared with a standard calibration curve for BTEX to quantitatively determine the concentration of the samples.

## **3. Definitions**

### **3.1. Calibration Standards**

Solutions with known concentrations of the analyte of interest which 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. 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.

### **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  $\mu$ l-5 ml) (Finnipipette)
- 30 sterile, 15 ml brown glass vials with screw top lids
- Two sterile, 100 ml beakers for holding CS<sub>2</sub> and waste
- Stainless steel syringe needle with non-coring point: size 16 gauge, 12 inch length
- Fume hood for extraction procedures

### 4.2. Equipment

4.2.1. Perkin-Elmer Clarus 560 Gas Chromatograph (GC) and Mass Spectrometer (MS) System

- Varian Capillary Column CP-Sil 8 CB 30m x 0.25mm x 0.25 $\mu$ m
- 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.

- 2-Fluorotoluene internal standard
  - Sigma-Aldrich,  $\geq 99\%$
  - Stored in the refrigerator at 4°C
- Carbon disulfide
  - Sigma-Aldrich, ReagentPlus,  $\geq 99.9\%$ , low benzene
  - Stored in the refrigerator at 4°C
- Benzene, Toluene, Ethylbenzene, m-Xylene, p-Xylene, o-Xylene
  - Sigma-Aldrich,  $\geq 99\%$
  - 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 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.
- The concentration of the stock solution can be calculated using the following equation:

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

- To dilute the pure 2-fluorotoluene, add 0.05 ml of 2-fluorotoluene to 9.95 ml of CS<sub>2</sub>. The concentration of this solution is calculated using the density of 2-fluorotoluene (1.001 g ml<sup>-1</sup> at 25°C) and the following equation:

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

- This same equation can be used to find the initial volume of the diluted 2-fluorotoluene solution which is needed to create a final internal stock solution of known volume and concentration.

## 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.

- The range of concentrations of benzene measured in the Tampa Bay area by previous studies is approximately 0.1-1.0 µg m<sup>-3</sup> (US Environmental Protection Agency). A general range of concentrations of benzene measured in urban areas around the world of 1-10 µg m<sup>-3</sup> should be considered (Health Effects Institute, 2008). Similar ranges are recommended for ethylbenzene and xylenes. Concentrations of toluene are expected to be greater than these compounds.
- Five calibration standards corresponding to the selected range should be prepared.
- 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).

**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.

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

## 7. GC/MS Setup and Calibration

### 7.1. Creating the GC/MS Method Program

**7.1.1.** Create a new method for the GC/MS using the following parameters:

- Injection temperature: 240°C held for 0.00 min.
- Rate of carrier gas: Constant Flow and Column Flow at 1.1 ml/min
- Temperature program: Initial Temperature of 35°C for 5.4 minutes, ramped to 125°C at 5°C min<sup>-1</sup>, ramp to 175°C at 15°C min<sup>-1</sup>
- Solvent delay: End of Delay at 2.70 min so that the filament and multiplier are turned off until after the solvent peak elutes.

### 7.2. Instrument Performance Check

- 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.

- Set GC at 175°C, the high temperature for the method, for the auto tune process
- Run instrument Auto Tune to check for system leaks, set the electron multiplier voltage, and calibrate the mass axis.
- If any of the 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 BTEX 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.

7.3.2. Analyze initial calibration standards using GC/MS system. An injection volume of 1 microliter will be used.

7.3.3. Obtain chromatograph of calibration standard results. Create a calibration curve by manually choosing area to integrate for each of the BTEX compounds and the internal standard.

7.3.4. A recalculation list should be created for all calibration standards. This is done using a quality control table of relative response factors for each BTEX compound versus the internal standard, relative retention time for each BTEX analyte in each calibration standard, area response, and retention time for the internal standard in each calibration standard.

7.3.5. Quality values for each of these parameters are calculated by finding the maximum absolute differences of each calibration standard with the mean of all calibration standards. In order to pass the initial calibration check, quality values must be met.

### 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<sup>-1</sup> BTEX initial calibration standard solution using the method and procedure given in section 8.3
- Calculate the relative response factor for each analyte.
- 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 analyte in the daily calibration standard.

$\overline{RRF}_i$  = Mean RRF of benzene in the most recent initial calibration.

Example: Day 1, Benzene

$$\%D = \frac{14.70 - 11.87}{11.87} \times 100\% = 24\%$$

- The %D for each analyte must be within  $\pm 30\%$  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.

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

## 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<sub>2</sub> into the glass vial containing the RAD130 cartridge.
- Add 100 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<sub>2</sub> 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

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

8.3.2. The analysis is performed under the following conditions and specifications:

- *Column:* CP-Sil 8 CB; 5% Phenyl 95% Dimethylpolysiloxane (30m x 0.25mm x 0.25µm)

- *Carrier Gas:* Helium
- *Flow Rate:* 1.1 ml min<sup>-1</sup>
- *Temperature Programming:* Initial Temperature of 35°C for 5.4 minutes, ramped to 125°C at 5°C min<sup>-1</sup>, ramp to 175°C at 15°C min<sup>-1</sup>
- *Injection Volume:* 1 µl
- Table A2: SIM Programming

Analyte	m/z	RT (min)
2-Fluorotoluene	109	5.90-6.18
Benzene	78, 77	2.70-3.02
Toluene	91,92	5.21-5.57
Ethylbenzene	91,106	9.05-9.34
m,p-Xylene	91,106	9.35-9.72
o-Xylene	91,106	10.28-10.60

- 8.3.3.** 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 s and all field blank samples.
  - Field samples of unknown concentration for analysis.
  - Remaining laboratory blank.
- 8.3.4.** The procedure for running the GC/MS system to analyze each batch of samples consists of the following:
- Run the instrument performance check.
  - Select appropriate analysis method which was previously created.
  - Ensure that the GC/MS system is ready, and inject sample with clean syringe to begin analysis
    - Syringe should be washed three times before and three times after each injection using carbon disulfide.
  - View results by viewing the chromatograph for each sample.
  - Be sure to save results for each sample

#### 8.4. Chromatograph Results Analysis

**8.4.1.** For each analysis sample, process the chromatograph results using the calibration curve previously made from the calibration data.

- Retention time, area, and concentration of each BTEX compound and 2-fluorotoluene should be obtained for every analysis sample

**8.4.2.** The results from the previous section contain the concentration of BTEX compounds in each of the analysis samples, in units of µg ml<sup>-1</sup>. To determine the mass of BTEX compounds recovered from each cartridge, this number must be multiplied by the total volume of CS<sub>2</sub> added during elution.

$$m(\mu g) = C_{sample} \left( \frac{\mu g}{ml} \right) \times V_{total} (ml)$$

- Use the above equation to calculate the mass of each BTEX compound collected from each cartridge.
- Example: Benzene, Site 1, Sample A

$$m(\mu g) = 0.271 \frac{\mu g}{ml} \times 2.1 ml = 0.57 \mu g$$

**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 each BTEX compound.

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

$$m_{final} = 0.57\mu g - 0.017\mu g = 0.55\mu g$$

**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 (given previously), 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<sup>-1</sup> and within the humidity range of 15-90%.

**8.4.5.** Calculate the ambient concentration of BTEX compound observed at each sampling location using the following equation:

$$C_{air} \frac{\mu g}{m^3} = \frac{m (\mu g)}{Q_k \left( \frac{ml}{min} \right) \cdot t (min)} \times 10^6 \frac{ml}{m^3}$$

- Where  $C_{air}$  is the ambient concentration of each BTEX compound, m is the final mass of each BTEX compound 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.
- Example: Benzene, Site 1, Sample A

$$C_{air} \frac{\mu g}{m^3} = \frac{0.55 \mu g}{80.52 \frac{ml}{min} \cdot 20104 min} \times 10^6 \frac{ml}{m^3} = 0.34 \frac{\mu g}{m^3}$$

## 9. Quality Control

### 9.1. Standard Operating Procedures

These standard operating procedures for the GC/MS analysis of BTEX 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 BTEX analytes 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 control 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.

$$LOD = 3 \cdot \sqrt{\frac{1}{N-1} \sum_{i=1}^n (X_{fb,i} - \bar{X}_{fb})^2}$$

- Where  $X_{fb}$  is the concentration of each BTEX compound 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 10% of samples.

- 9.7.1.** The percent difference (%D) will be calculated as a measurement of the precision for the samplers. The measurements for each of the duplicate samplers will be used to calculate the %D for the duplicate samplers.

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

- 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 sets of duplicate samplers will be used to represent the uncertainty of the measurements taken during the sampling period.

$$error = \pm(\%D \cdot \bar{x}_i)$$

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

Example: Benzene

$$error = \pm \left( \%14.9 \cdot 0.64 \frac{\mu g}{m^3} \right) = \pm \%10$$

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## APPENDIX B:

### NO<sub>x</sub>-NO<sub>2</sub> Sampling & Laboratory Analysis Protocol

#### Sampling Protocol

##### 1. Purpose and Applicability

This standard operating protocol (SOP) is written to create a consistent procedure for the passive sampling of outdoor NO<sub>x</sub>-NO<sub>2</sub> concentrations using Ogawa Passive Samplers for a fourteen day sampling period. Using these samplers and protocol, spatial variations in concentrations of nitrogen oxides will be determined. This protocol is adapted from a pilot study by Zeager (2008).

##### 2. Summary of Method

The Ogawa passive sampler device will be deployed under protective shelters in the vicinity of 100 randomly chosen locations in Hillsborough County neighborhoods to measure NO<sub>x</sub> levels as a surrogate for traffic related air pollution and to determine small scale spatial variation of NO<sub>x</sub>.

##### 3. Interferences

###### 3.1. Temperature & Relative Humidity

Concentration varies with temperature and relative humidity. A Concentration Conversion Coefficient, determined as a function of average temperature and relative humidity, is applied in calculations. Ogawa Sampling Protocols for NO<sub>x</sub> and NO<sub>2</sub> provide tables of coefficient values.

##### 4. Definitions

###### 4.1. Calibration Standards

Solutions with known concentrations of the analyte of interest which encompass the range of concentrations of the unknown samples.

###### 4.2. Field Blank

A field blank is a sampling cartridge that is taken into the field with the other sampling devices. 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.

###### 4.3. 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.

##### 5. Equipment and Materials

###### 5.1. Sampling Equipment

###### 5.1.1. Ogawa Passive Sampler body

- 5.1.2. Ogawa Passive Sampler base pad
- 5.1.3. Ogawa Passive Sampler retainer rings
- 5.1.4. Ogawa Passive Sampler stainless steel screen
- 5.1.5. Ogawa Passive Sampler end cap
- 5.1.6. Ogawa pre-coated collection filter
- 5.1.7. Radiello Outdoor Shelter/PVC Shelter
  - See Appendix A for Preparation and Assembly of Shelters

## 5.2. Materials

- 5.2.1. Plastic bags
- 5.2.2. Non-sterile gloves
- 5.2.3. Airtight containers

## 6. Sampler Preparation

6.1. All sampler components (body, base pad, retainer ring, stainless steel screen, and end cap) are washed three times with 18 MΩ Milli-Q deionized water, thoroughly dried under a lab hood, and stored in plastic airtight storage containers until ready for use.

6.1.1. The sampler body has two chambers and can be used to measure two samples simultaneously.

6.2. One day prior to deployment, using non-sterile gloves the samplers are assembled and loaded with the Ogawa pre-coated collection filter.

6.3. Assembled samplers are individually sealed in a plastic bag, and placed in the airtight plastic brown containers.

6.3.1. The loaded samplers that are sealed in the bag inside the airtight container have a lifetime of sixty days.

## 7. Deployment and Retrieval of Samplers

### 7.1. Deployment of Samplers

7.1.1. Loaded samplers and field blanks that have been previously stored in the airtight containers are transported by car to the predetermined destinations where shelters have already been placed.

7.1.2. Once at the destination, the airtight container is uncapped, the sampler is removed from the plastic bag. The sampler is then fastened vertically to the shelter by clip or Velcro.

7.1.3. The time of placement and any relevant information about the surroundings are recorded in laboratory notebook. Each sampler is deployed in the same manner.

7.1.4. During transport, the field blank is not removed from the container and is returned to the lab once all samplers have been placed. The field blank will remain in the sealed container until all samplers have been retrieved two weeks later, at which time analysis is performed on samples and blanks.

### 7.2. Retrieval of Samplers

7.2.1. Two weeks after deployment, samplers are retrieved at approximately the same time and in the same order as they were deployed.

7.2.2. A loaded field blank is transported in a plastic bag within an airtight container during the retrieval of the samplers.

7.2.3. Upon reaching the sampler destination, the sampler is unfastened from the shelter, sealed into the plastic bag, and returned to the airtight container.

7.2.4. Time of retrieval is recorded in the laboratory notebook.

7.2.5. Once all samplers are collected, the samples stored in the airtight containers are returned to the lab for analysis.

- Exposed samples that are sealed in the plastic bag within the airtight container have a lifetime of fourteen to twenty-one days.

## **Laboratory Protocol**

### **1. Purpose and Applicability**

This protocol describes the laboratory method for analyzing ambient air samples obtained with Ogawa passive sampling devices loaded with coated collection fiber filters.

### **2. Summary of Method**

Following a 14-day exposure, the samples are returned to the lab sealed in plastic bags within airtight containers. They are analyzed for NO<sub>x</sub> and NO<sub>2</sub>, then concentration in air is determined. The Method is derived from the NO, NO<sub>2</sub>, and NO<sub>x</sub> Ogawa Passive Sampling Protocol and the HACH Diazotization Method 8507 using Nitrogen, Nitrite, LR, NitriVer® 3 reagent Powder Pillows. Using this method, exposed samples, field blanks, and lab blanks will be analyzed. Field blanks are passive samplers loaded with collection filters, sealed in plastic bag and airtight containers. They are transported in the same manner as the samplers, but are not removed from the containers. Lab blanks are collection filters that are removed directly from the original container. Field and lab blanks are tested according to the protocol in the same manner as exposed samples.

### **3. Definitions**

#### **3.1. Standard Blank**

0.0 ug/ml nitrite solution

#### **3.2. Lab Blank**

Fiber filter from vial that is subjected to same testing procedure as exposed samples

### **4. Equipment and Materials**

#### **4.1. Supplies**

##### **4.1.1. Ogawa Sampling devices**

- Body, base pad, retainer ring, screen, end cap (x2)
- NO<sub>x</sub> precoated sampling pads
- NO<sub>2</sub> precoated sampling pads

##### **4.1.2. All glassware should be baked prior to use**

- 25 ml Glass Flasks (one used for each sample)
- 15 ml Glass Test Tubes (6)
- 100 ml Glass Flasks (7)
- Pipetters and 0-5ml pipette tip (Fisher brand)
- Parafilm to cover glassware
- Cuvettes for spectrophotometer

#### **4.2. Equipment**

##### **4.2.1. Visible Spectrophotometer**

#### **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
- Nitrile gloves

## 5. Reagents and Chemicals

### 5.1. Chemicals

#### 5.1.1. Nitrite Standard Solution 250ug/ml as NO<sub>2</sub>-N (HACH Company)

- Storage – refrigerator at 5 degrees C
- Components – Chloroform, ACS; Sodium Nitrite; Demineralized Water
- Storage – refrigerator at 5 degrees C

#### 5.1.2. NitriVer 3 Nitrite Color Producing Reagent Powder Pillows (HACH Company)

- Storage – refrigerator at 5 degrees C.
- Components – Chromotropic Acid, Disodium salt; Sodium Sulfanilate; Potassium Pyrosulfate; Potassium Phosphate, Monobasic; 1,2-cyclohexanediaminetetraacetic Acid Trisodium Salt.

#### 5.1.3. Deionized Water

- Deionized water in this method means water that meets ASTM Type I specifications. This is equal to 18.2 MΩ Milli-Q water by Millipore Corporation.

## 6. Procedures

Prior to samplers being deployed, standard solutions of known nitrite concentrations are analyzed and results compared for quality control. A standard curve is prepared and slope calculated using the known standard nitrite solution. This is done prior to the start of sample analysis and at the beginning of analysis of each new sample batch (each day). The samples are then analyzed following the Ogawa and HACH protocols as detailed below. A calibration standard solution of known concentration (0.6 ug/ml SPEX CentriPrep – Fisher Scientific nitrite solution) is analyzed after every 10 samples and compared to previous results for quality control. The slope of the standard curve that is determined each day is used in the calculation of exposed sample NO<sub>2</sub> and NO<sub>x</sub> concentrations for that day's batch of samples.

### 6.1. Preparing Standard Solution

#### 6.1.1. HACH Standard Nitrite Solution (250ug/ml = 1mg/4ml):

- Take 4.0 ml of standard solution, place in a 100ml glass flask and dilute with deionized water to make 100ml. This will equal a concentration of 1.0 mg/ 100 ml = .01 mg/ml = 10 ug/ml
- Then take 0, 2, 4, 6, 8, and 10 ml samples and dilute each with enough deionized water to make total of 100 ml.
- Continue following steps of section 6.1.2 outlined above for Fischer solution.
- Between steps, cover glass containers with parafilm to minimize contamination.
- Compare and record the absorbance of the two standard solution concentrations for quality control. Calculate the slope of each standard according to the “Preparing a Standard Curve” section. The calculated slopes should be within 5% of each other. If this is not the case, consider repeating the steps above or purchasing new reagents. This step is performed prior to exposed sample analysis and after the purchase of new reagents to be used in the protocol. Reagents should be discarded when the expiration date is reached.

#### 6.1.2. Of the two reagents that are compared, one is used throughout the remainder of the analysis.

## 6.2. Preparing a Standard Curve

- 6.2.1.** A standard curve is prepared and slope calculated using the known standard nitrite solution. This is done prior to the start of sample analysis and at the beginning of analysis of each new sample batch (each day). This procedure will establish the slope of the standard curve. Results of the standard solutions made in the comparison step will be used to prepare the initial standard curve. This step is repeated prior to each new batch (daily) of exposed samples to be analyzed.
- 6.2.2.** Refer to Table 1 on the following page. The first two columns refer to values related to the concentration of the standard NO<sub>2</sub> solution. The next three columns refer to values related to the absorbance. The last column refers to the calculation of the Slope of the standard curve. Begin at the top left and proceed by filling in values in the different cells. Those cells which have been “*grayed out*” do not require a numerical value. The value in the bottom right cell signifies a completed computation procedure.
- 6.2.3.** Prepare six standard samples. Make sure that the standard samples are of 0, 0.2, 0.4, 0.6, 0.8 and 1.0 µg/ml NO<sub>2</sub> solutions.
- 6.2.4.** Enter absorbance into Table 1. Complete the table as follows.
- The first column requires the concentration of the standard sample (x). Enter the values if they do not exist on the table.
  - The second column requires the calculation of x<sup>2</sup>. Enter the values if they do not exist on the table.
  - Compute  $\Sigma x^2$  (sum of all x<sup>2</sup>) and enter the value in cell (8).
  - Use your colorimeter or spectrometer to measure the absorbance (y) of each sample. Enter the standard absorbance values in cell (2) through (7).
  - Cell (2) represents the blank absorbance y<sub>0</sub> (i.e. absorbance when the concentration is 0.0 µg/ml). Using this value calculate (y - y<sub>0</sub>) and enter the net absorbance A for the various standard samples.
  - The next row represents the product between the concentration and the absorbance. Fill in the values of x (y - y<sub>0</sub>).
  - Compute  $\Sigma x (y - y_0)$  and enter the sum in cell (9).
  - Compute the Slope by calculating  $\Sigma x (y - y_0) / \Sigma x^2$  (cell (9) divided by (8) and enter the value in cell G).



Table B1: Preparing the Standard Curve

Concentration of Standard NO <sub>2</sub> Solution (µg/ml)		Absorbance			Slope
x (1)	x <sup>2</sup> (1) * (1)	y	y - y <sub>0</sub>	x (y - y <sub>0</sub> )	$\frac{\sum x(y - y_0)}{\sum x^2}$
			A	(1)*A	(9) / (8)
0	0	(2)			
0.1	0.01	(3)	(3) - (2)		
0.2	0.04	(4)	(4) - (2)		
0.4	0.16	(5)	(5) - (2)		
0.6	0.36	(6)	(6) - (2)		
0.8	0.64	(7)	(7) - (2)		
	$\sum x^2$ (8) 2.2			$\sum x(y - y_0)$ (9)	(9) / (8) G

### 6.3. Analyzing Exposed Samples

#### 6.3.1. Each exposed sample is analyzed separately.

- At the start of each day, with the spectrophotometer empty and set to a wavelength of 545nm, press read and absorbance will be displayed on screen. Zero the machine.
- Prepare a standard curve as described above. Repeat this step each day prior to exposed sample batch to be analyzed.
- Compare the slope of the standard curve to the slope of the previous day's standard curve. If there is a greater than 5% difference in the slope of the curve, then reanalyze the standards. If there is still a greater than 5% difference, new solutions may need to be purchased.
- With the nitrite solution of known concentration, run one calibration standard of 0.6 ug/ml after each analysis of 10 exposed samples and compare the absorbance of the previous calibration standard. If there is a greater than 5% difference, repeat standard curve and recalculate slope.
- With non-sterile gloved hands, remove exposed passive sampler from airtight container and sealed plastic bag.
- Disassemble passive sampler and remove filter and the two adjacent stainless screens with forceps and place all three into the 25ml glass flask that contains the 10ml deionized water. Use separate flask for each exposed sample.
- Seal flask with parafilm and shake immediately. Over the next 30 minutes, shake flask occasionally.
- At the end of the 30 minutes, place flasks in refrigerator and cool to 2-6°C (approx. 20 minutes).
- After cooled, remove from refrigerator, add the color producing reagent powder pillow, shake gently for 5 minutes until powder is dissolved and return to refrigerator for an additional 30 minutes.
- When the 30 minutes has elapsed, remove flask from refrigerator and allow sample to equilibrate to room temperature (approximately 20 minutes).

- Pour solution into a cuvette to demarcation line, insert cuvette into spectrophotometer set at wavelength of 545nm, read absorbance, and record result.
- 6.3.2.** Analyze the field blanks in the same manner as the exposed samples. Analyze one laboratory blank at the start of analysis and one at the end.

## 7. Calculations

**7.1.** After the Slope for the standard curve has been prepared and the absorbance has been measured for all blanks and exposed samples, calculate the collected weight (mass) in ng for each of the blanks and the NO<sub>x</sub> and NO<sub>2</sub> concentrations for each of the exposed sample that have been collected. Use the Slope from the standard curve to calculate NO<sub>x</sub> and NO<sub>2</sub> concentrations of blanks and exposed.

### 7.1.1. NO<sub>2</sub> Concentration Calculation

- Refer to Table 7.1 on the following page. Repeat calculation for each exposed sample, each field blank and laboratory blank.
- Enter the location (descriptive term) for each site.
- Enter the exposure time in minutes associated with each sample site. Enter values in row (3).
- From a local or national weather service, enter the average temperature and average relative humidity for the time period that exposed samples were deployed. Use Table 4 on page 18-19 of the Ogawa protocol to determine  $\alpha$ NO<sub>2</sub> based on temperature and relative humidity.
- Measure the absorbance associated with a blank sample (0 µg/ml). Enter the values in row (1).
- Using spectrometer measure the absorbance for the sample associated with each site. Enter the values in row (4).
- Calculate the absorbance for each sample. Enter the values in row (5) by taking the difference between rows (4) and (1).
- Calculate the solution concentration in row (6). This is done by taking the absorbance in row (5) and dividing it by G – the Slope of the standard curve. Note, G was computed previously using Table 6.1.
- Calculate the collected weight in ng and enter the value in row (7). This value is obtained by taking a product of the solution concentration (6) and the abstract amount (10 ml) and a factor of 1000 (for converting from PPM to PPB).
- Calculate the adjusted weight by subtracting the blank weight average (BWA1) from the collected weight and enter in row (8).
  - Note: For each blank, follow steps above. Then average the weight of all the blanks (field and lab).
- Calculate the concentration in rows (9). This value is obtained by multiplying the concentration conversion coefficient by the adjusted collected weight (8) and dividing by the exposure time (3).

- This step is performed for the exposed samples only. At 20°C and 70% relative humidity  $\alpha_{NO_2} = 57$  and  $\alpha_{NO} = 60$ . These concentration conversion coefficients vary with temperature and relative humidity, and can be identified in Ogawa sampler protocols.

#### 7.1.2. NO<sub>x</sub> Weight Calculation

- Using spectrometer measure the absorbance for the sample associated with each corresponding site. Enter the values in row (10).
- Measure the absorbance associated with a blank sample (0 µg/ml). Enter the values in row (2).
- Calculate the absorbance for each sample. Enter the values in row (11) by taking the difference between rows (10) and (2).
- Calculate the solution concentration in row (12). This is done by taking the absorbance in row (11) and dividing it by G – the Slope of the standard curve. Note, G was computed previously using Table 6.1.
- Calculate the collected weight in ng and enter the value in row (13). This value is obtained by taking a product of the solution concentration (12) and the abstract amount (10 ml) and a factor of 1000 (for converting from PPM to PPB).
- Calculate the adjusted weight by subtracting the blank weight average (BWA2) from the collected weight (13) and enter in row (14).
- Note: For each blank, follow steps above. Then average the weight of all the blanks (field and lab).

#### 7.1.3. NO Concentration Calculation

- Calculate the collected NO weight in ng and enter the value in row (16). This value is obtained by taking a difference of the NO<sub>x</sub> weight (8) and the NO<sub>2</sub> weight (14).
- Next calculate the concentration in row (17). This value is obtained by multiplying the concentration conversion coefficient  $\alpha_{NO}$  by the collected weight (16) and dividing by the exposure time (3). At 20°C and 70% relative humidity  $\alpha_{NO} = 60$ .
- This step is performed for the exposed samples only. At 20°C and 70% relative humidity  $\alpha_{NO_2} = 57$  and  $\alpha_{NO} = 60$ . These concentration conversion coefficients vary with temperature and relative humidity, and can be identified in Ogawa sampler protocols.

#### 7.1.4. NO<sub>x</sub> Concentration Calculation

- Calculate the concentration of NO<sub>x</sub> in row 15. This value is obtained by adding concentrations of NO<sub>2</sub> (9) and NO (17).

Table B2: Calculation of Concentration Data

Compound	Blank Sample (0.0 ug/ml) Absorbance	Blank Absorbance (Field and Lab)			Blank Weight Average	Slope of Standard Curve	T°C	R H	Concentration Conversion Coefficient	
		B1	B2	B3					$\alpha\text{NO}_2$	$\alpha\text{NO}$
NO <sub>2</sub>	(1)				(BWA1)	(G)				
NO <sub>x</sub>	(2)				(BWA2)					

	Specification		Samples			
	Sample #		1	2	3	4
	Sample Location					
	Sampling Time (min) (3)	= (3)				
NO <sub>2</sub>	Sample Absorbance (4)	= (4)				
	Absorbance (5)	= (4) - (1)				
	Solution Concentration (ug/ml) (6)	= (5) / G				
	Collected Weight (ng) (7)	= (6) x 10 x 1000				
	Collected Weight – BWA1 (8)	= (7) - BWA1				
	Concentration (ppb) (9)	$\alpha\text{NO}_2 \times (8) / (3)$				
NO <sub>x</sub>	Sample Absorbance (10)	= (10)				
	Absorbance (11)	= (10) - (2)				
	Solution Concentration (ug/ml) (12)	= (11) / G				
	Collected Weight (ng) (13)	= (12) x 10 x 1000				
	Collected Weight – BWA2 (14)	= (13) - BWA2				
	Concentration (ppb) (15)	= (9) + (17)				
NO	Collected Weight (ng) (16)	= (8) - (14)				
	Concentration (ppb) (17)	$\alpha\text{NO}_x (16) / (3)$				

## **8. Quality Control**

### **8.1. Standard Solutions**

**8.1.1.** At the beginning of each new batch analysis (each new day), a standard curve is prepared and the slope is calculated. Concentrations are compared to previous results. This step is described above in the section entitled, Preparing a Standard Curve. If greater than 5% difference is found when compared to the previous day's slope, repeat the preparation of the standard curve and slope calculation.

### **8.2. Calibration Standards**

**8.2.1.** As outlined in the section entitled Analyzing Exposed Samples, a calibration standard is run after every 10 exposed samples analyzed (i.e. one known concentration of a standard solution is analyzed and compared to previous results). If greater than 5% difference is found when compared to the previous calibration standard absorbance, repeat preparation of the standard curve.

### **8.3. Field & Laboratory Blanks**

**8.3.1.** As outlined in the section entitled Analyzing Exposed Samples, field blanks are analyzed using the same procedure as exposed samples. Calculations are carried out to determine collected mass in ng for the blank.

**8.3.2.** As outlined in the section entitled Analyzing Exposed Samples, one laboratory blank is analyzed prior to analysis of each new batch (each new day) of exposed samples.

**8.3.3.** The average weight (mass) of all the blanks (field and lab) is subtracted from the sample mass in order to determine the actual mass of pollutant that the sample filter collected.

**8.3.4.** The standard deviation is calculated for the field and lab blanks. Three times the standard deviation is determined to be the minimum detection limit. All exposed sample masses are compared to the minimum detection limit to determine if data collected is usable.

## **Bibliography**

Ogawa & Co., Inc. (2006). NO, NO<sub>2</sub>, NO<sub>x</sub> and SO<sub>2</sub> Sampling Protocol Using The Ogawa Sampler V6.06. USA: Ogawa & Co., Inc..

## APPENDIX C:

### Calibration & Quality Control Data

Examples of calibration curves and quality control charts are provided in this appendix.

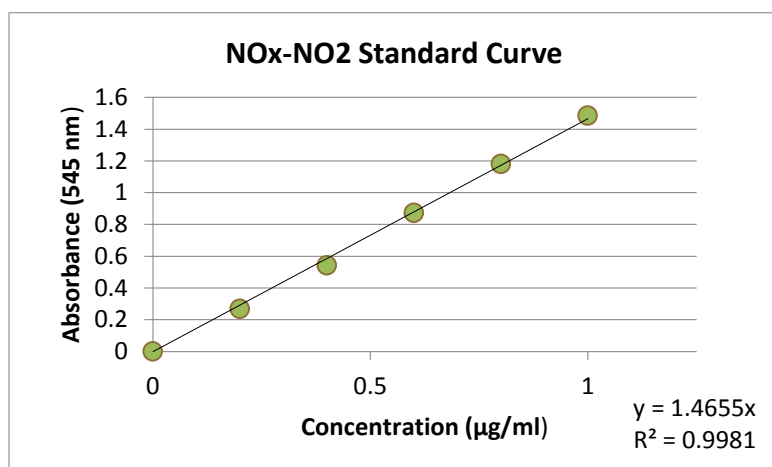


Figure C1: Example of NO<sub>x</sub>-NO<sub>2</sub> Calibration Curve: 7/25/2013

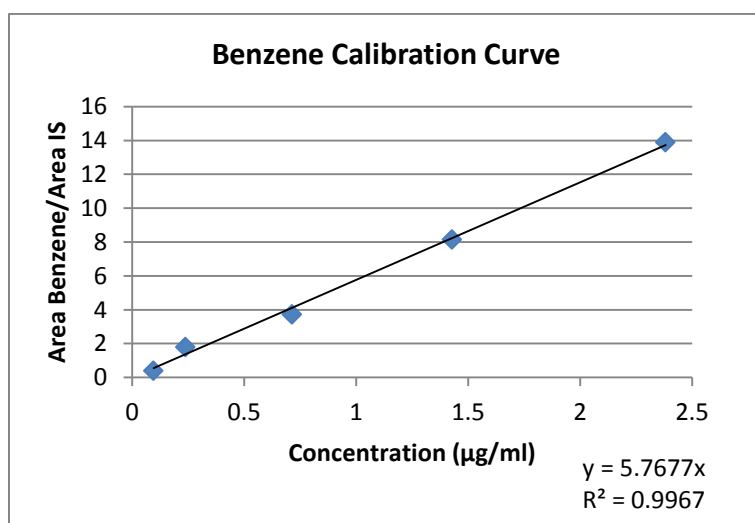


Figure C2: Example of Benzene Calibration Curve: 8/1/2013

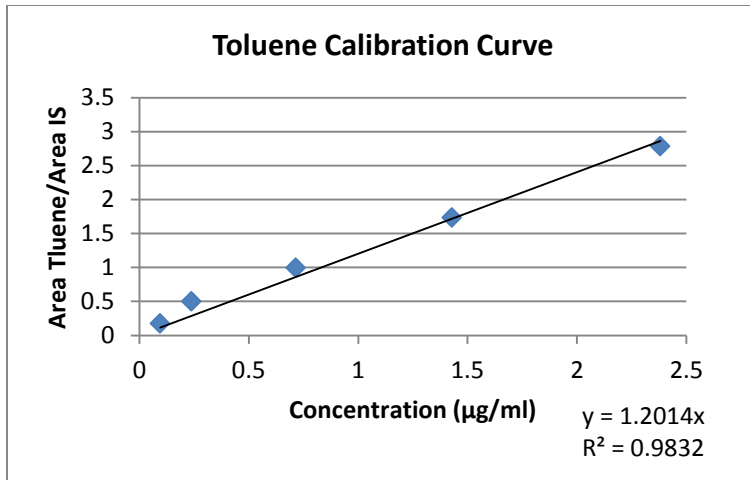


Figure C3: Example of Toluene Calibration Curve: 8/1/2013

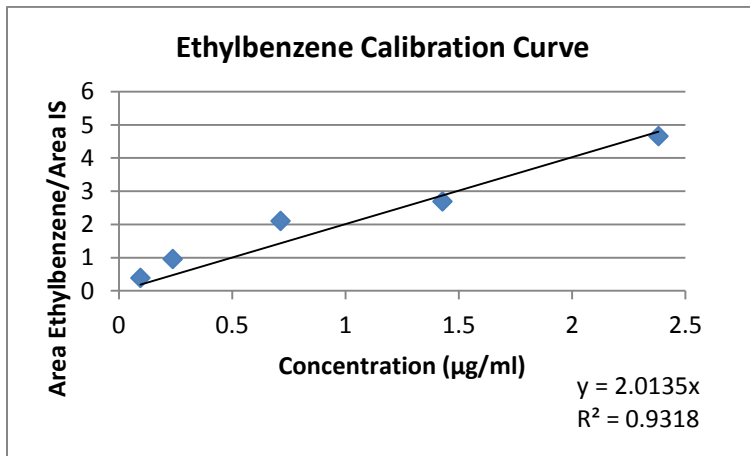


Figure C4: Example of Ethylbenzene Calibration Curve: 8/1/2013

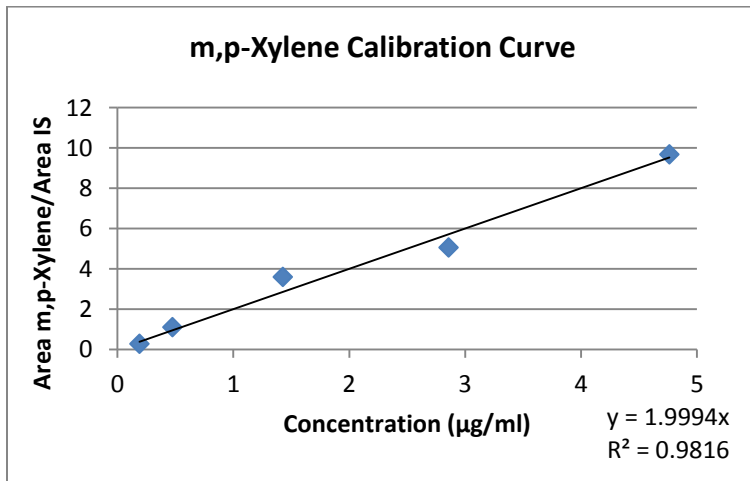


Figure C5: Example of m,p-Xylene Calibration Curve: 8/1/2013

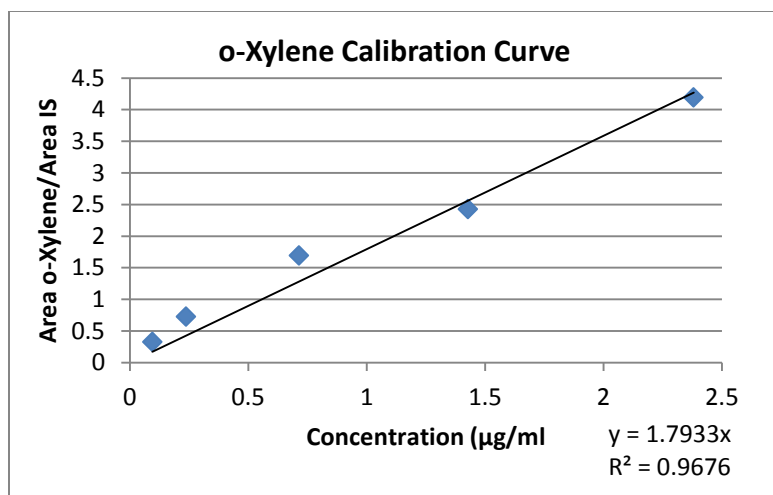


Figure C6: Example of o-Xylene Calibration Curve: 8/1/2013

Table C1: Example of GC-MS Quality Control Chart: Benzene 8/1/2013

Calibration Standard Number	RRF <sub>i</sub>	RRT <sub>i</sub>	A <sub>is,i</sub>	RT <sub>is,i</sub>
1	8.4718	0.4735	11.476	5.992
2	15.7702	0.4734	8.76	6.001
3	10.9170	0.4719	13.942	5.989
4	11.9698	0.4710	19.153	6.021
5	12.2571	0.4826	10.607	5.866
Mean	11.8772	0.4745	12.7876	5.9738
Standard Deviation	2.6376			
Quality Value	22.21	0.0081	23.52	0.1078
Criteria	≤ 30%	≤ 0.06 minutes	≤ 40%	≤ 0.33 minutes
Criteria Met?	yes	yes	yes	yes



**APPENDIX D:**  
**Pollutant Concentrations**

Table D1: Pollutant Concentrations

Site	Sample	NOX	NO <sub>2</sub>	NO	Benzene	Toluene	Ethylbenzene	m+p-Xylene	o-Xylene
1	A	0.627	0.627	0.000	0.342	1.176	0.507	0.594	0.362
	B	0.465	0.465	0.000	0.266	1.840			
2	A	0.268	0.268	0.000	0.584	0.474	0.805	0.859	1.261
	B	0.447	0.447	0.000	0.092	1.163			
3	A	3.464	1.323	2.141	0.322	2.921	0.609	0.557	0.591
	B	3.686	1.503	2.183	0.488	1.293			0.527
4	A	2.539	1.145	1.394	0.498	1.870	0.201	0.211	0.355
	B				0.257	0.719	0.205	0.711	0.771
5	A	1.933	0.661	1.272	0.295	1.249	0.406	0.693	0.807
	B	1.150	0.786	0.363	0.676	1.680	0.703	0.313	0.275
6	A	1.609	1.609	0.000	0.311	1.876	0.676	0.786	0.543
	B	1.734	1.734	0.000	1.293	1.645			
7	A	1.376	1.376	0.000					
	B	1.305	1.305	0.000					
8	A	0.948	0.948	0.000	0.456	1.512			
	B								
9	A	1.377	1.377	0.000					
	B	1.198	1.198	0.000	0.372	3.696	0.120	0.577	0.556
10	A	0.747	0.625	0.121	0.351	2.631	0.350	0.737	0.377

Site	Sample	NOX	NO <sub>2</sub> (ppb)	NO	Benzene	Toluene	Ethylbenzene ( $\mu\text{g m}^{-3}$ )	m+p- Xylene	o- Xylene
11	B	0.590	0.590	0.000	0.708	1.985	0.632	0.522	0.192
	A	0.875	0.875	0.000	0.894	3.596			0.293
12	B	3.097	0.858	2.240	0.617	5.428	0.432	2.050	0.310
	A	0.983	0.357	0.626	0.263	2.069			
13	B	5.652	1.072	4.580	0.256	0.376			
	A	0.697	0.697	0.000	0.283	0.799	0.193	0.632	0.275
14	B	1.073	1.073	0.000	0.159	0.171			0.228
	A	1.835	0.643	1.191	1.300	2.774			
15	B	1.119	0.250	0.868	0.063	1.805	1.293	0.690	0.697
	A	0.454	0.454	0.000	0.224	1.572	0.075	0.114	0.213
16	B	0.436	0.436	0.000	0.089	0.591	0.908	0.534	0.638
	A	0.867	0.744	0.123	0.268	1.098	0.243	1.098	0.533
17	B	0.672	0.672	0.000	0.175	0.341			
	A	0.526	0.526	0.000	0.710	0.353			
18	B	0.752	0.527	0.226	3.095		3.510	6.480	4.526
	A	1.089	1.089	0.000					
19	B	1.130	1.089	0.041	0.642	4.266	0.362	3.571	
	A	1.180	1.180	0.000	0.262	1.907	0.219	0.626	0.191
20	B	1.144	1.144	0.000	0.795	4.986	1.642	4.927	
	A	0.817	0.817	0.000					
21	B	1.380	1.380	0.000	0.397	1.806	0.787	1.268	0.975
	A	2.614	2.614	0.000	0.708	5.106	1.362	2.293	1.402
22	B	1.307	1.307	0.000	0.446	2.925	0.333	0.301	0.391
	A	1.577	1.170	0.407	0.518	3.065	0.933	0.965	0.618
	B	1.539	0.990	0.549	2.671				

Site	Sample	NOX	NO <sub>2</sub> (ppb)	NO	Benzene	Toluene	Ethylbenzene (µg m <sup>-3</sup> )	m+p- Xylene	o- Xylene
	B	1.458	1.458	0.000	0.154	1.954		0.973	
24	A	1.638	1.638	0.000	0.158	1.101			
	B	0.918	0.918	0.000	0.352	1.353	0.359	0.432	0.152
25	A	3.140	1.331	1.808	0.099	1.564	0.587	0.738	0.716
	B	1.789	0.468	1.321	0.513	1.011			
26	A	1.278	1.278	0.000	0.323	3.608	1.133	0.671	0.572
	B	0.954	0.954	0.000	0.552	1.718	0.233	0.824	1.548
27	A	1.727	1.727	0.000	0.805	4.377	0.764	0.696	0.545
	B	2.122	2.122	0.000	1.036	4.538		0.959	
28	A	1.511	1.511	0.000	0.493	3.460	0.360	1.311	0.667
	B	1.458	1.458	0.000	0.770	3.997	2.043	2.879	3.126
29	A	4.832	2.250	2.582	0.804	3.867	0.220	1.188	0.854
	B	2.160	2.160	0.000	0.547	2.068	0.293	1.429	0.691
30	A	1.244	1.244	0.000	0.691				
	B	0.883	0.883	0.000	0.299	1.955	0.106	0.269	
31	A	3.875	2.307	1.568	0.428	3.732	1.144	1.351	0.276
	B	4.377	2.361	2.016	0.563				
32	A	3.584	1.874	1.710	1.115	5.022	1.064	3.280	1.460
	B	7.488	2.685	4.803	1.155	6.145	0.745	1.899	0.783
33	A	5.528	2.271	3.257	1.246	5.350	1.319	8.434	1.886
	B	3.502	2.993	0.509	1.346	4.878	1.276	1.545	1.400
34	A	3.933	3.404	0.529	0.491	2.323	0.459	1.145	
	B	1.567	1.567	0.000	0.788	0.588		1.263	0.532
35	A	0.793	0.793	0.000	0.252				

Site	Sample	NOX	NO <sub>2</sub> (ppb)	NO	Benzene	Toluene	Ethylbenzene (µg m <sup>-3</sup> )	m+p- Xylene	o- Xylene
36	B	0.721	0.721	0.000	0.189	2.227	0.126	0.787	0.410
	A	1.298	1.298	0.000	0.151	2.337	0.229	0.526	0.066
37	B	1.637	1.352	0.285	0.859	5.975	1.337	2.024	0.818
	A	1.080	1.080	0.000	0.567	3.753	0.415	1.255	0.460
38	B	1.367	1.367	0.000	0.436	2.683	0.109	0.607	0.673
	A	2.576	2.373	0.203	0.590	3.396	1.345	3.894	1.246
39	B	3.576	2.032	1.544	0.781	5.405	0.710	4.278	0.935
	A	3.128	3.128	0.000	0.262	2.949		2.580	
40	B	3.217	3.217	0.000	1.350	6.378	0.709	1.647	0.591
	A	1.860	1.443	0.417	0.565	2.384	0.634	1.717	0.640
41	B	2.058	2.058	0.000	0.880	3.546	0.403	0.641	0.428
	A	1.003	1.003	0.000	0.559	2.978		1.051	0.930
42	B	0.792	0.792	0.000	0.089	1.440		0.512	
	A	3.458	3.219	0.238	1.036	3.211	4.605	8.268	2.353
43	B	3.255	3.255	0.000	1.098	3.594	0.881	1.805	2.924
	A	4.491	2.585	1.907	0.659	2.855	0.845	2.038	1.661
44	B	2.919	2.919	0.000	1.564	4.767	0.993	1.991	1.208
	A	3.982	3.365	0.617	0.755	4.582		2.332	
45	B	5.338	2.712	2.626	0.789	5.134	0.159	0.248	0.498
	A	2.110	1.533	0.577	0.811	3.385	0.323	0.989	0.226
46	B	1.721	0.846	0.876	1.095				1.104
	A	5.122	2.153	2.969	1.316	4.590	0.878	2.926	0.874
47	B	2.672	2.154	0.518	0.687	3.670	0.647	0.972	1.153
	A	2.000	2.000	0.000	1.556	5.254	0.181	1.125	0.255
	B	3.944	2.055	1.890	0.752	5.069	0.558	1.132	0.884

Site	Sample	NOX	NO <sub>2</sub> (ppb)	NO	Benzene	Toluene	Ethylbenzene (µg m <sup>-3</sup> )	m+p- Xylene	o- Xylene
	B	2.149	1.512	0.638	0.869	6.114	0.097	0.433	0.105
49	A	5.293	2.660	2.634	0.622	2.127	0.055	0.800	0.278
	B	2.289	1.713	0.576	0.386	2.814	0.411	0.866	0.242
50	A	1.932	1.932	0.000	0.591	2.344	0.280	1.490	0.320
	B	2.023	2.023	0.000	0.859	3.042	0.822	1.260	0.636

## APPENDIX E:

### Sampler Locations

Table E1: Sampler Locations

Site	Latitude	Longitude	Urban/Rural	Forested/Not
1	28.13982	-82.3539	Urban	Not
2	28.14534	-82.2823	Rural	Forested
3	28.14457	-82.2246	Rural	Forested
4	28.12198	-82.1469	Rural	Not
5	28.03967	-82.2119	Rural	Forested
6	28.02897	-82.1623	Urban	Forested
7	28.04057	-82.0744	Rural	Forested
8	27.99625	-82.1098	Rural	Forested
9	28.01745	-82.1377	Urban	Not
10	27.99303	-82.29	Urban	Forested
11	27.98017	-82.294	Urban	Forested
12	27.70965	-82.4147	Rural	Forested
13	27.70572	-82.2545	Rural	Forested
14	27.70359	-82.1462	Rural	Not
15	27.76217	-82.1703	Rural	Not
16	27.81842	-82.333	Urban	Not
17	27.83527	-82.327	Urban	Not
18	27.84729	-82.3657	Urban	Forested
19	27.85541	-82.3302	Urban	Not
20	27.88134	-82.3303	Urban	Forested
21	27.89445	-82.3099	Urban	Not
22	27.89284	-82.271	Urban	Not
23	27.89523	-82.2443	Urban	Not
24	27.89022	-82.2157	Urban	Forested
25	27.88659	-82.1392	Rural	Not
26	27.93518	-82.2534	Urban	Forested
27	27.99997	-82.5728	Urban	Forested
28	28.03175	-82.6017	Urban	Not
29	28.0305	-82.55	Urban	Forested
30	28.14232	-82.6409	Rural	Not
31	28.05501	-82.4307	Urban	Not
32	28.0539	-82.4514	Urban	Not

Site	Latitude	Longitude	Urban/Rural	Forested/Not
33	28.04012	-82.4806	Urban	Not
34	28.14976	-82.4295	Rural	Not
35	28.11268	-82.5196	Urban	Not
36	28.08817	-82.5544	Urban	Not
37	28.05796	-82.5203	Urban	Forested
38	28.0101	-82.5192	Urban	Not
39	27.97421	-82.5129	Urban	Forested
40	27.93272	-82.4876	Urban	Forested
41	27.87239	-82.4942	Urban	Forested
42	27.96314	-82.4432	Urban	Not
43	27.97619	-82.3731	Urban	Forested
44	27.99546	-82.3343	Urban	Forested
45	28.02162	-82.3021	Rural	Not
46	28.01067	-82.4352	Urban	Forested
47	28.03252	-82.3684	Urban	Not
48	27.92263	-82.3188	Urban	Not
49	27.94062	-82.3517	Urban	Forested
50	27.94947	-82.326	Urban	Forested