Potential for City Parks to Reduce Exposure to Hazardous Air Pollutants

Michael Milazzo

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Linsey C. Marr, Chair
Julia M. Gohlke
Gabriel Isaacman-VanWertz

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Academic Abstract

Benzene, toluene, ethylbenzene, and xylenes (BTEX) are hazardous air pollutants commonly found in outdoor air. Several studies have explored the potential of vegetation to mitigate BTEX in outdoor air, but they are limited to a northern temperate climate and present conflicting results. To investigate this issue in a subtropical climate, we deployed passive air samplers for two weeks in parks and nearby residences at four locations: three in an urban area and one in a rural area in Alabama, USA. All BTEX concentrations were below health-based guidelines and were comparable to those found in several other studies in populated settings. Concentrations of TEX, but not benzene, were 3-39% lower in parks than at nearby residences, and the differences were significant. In and around two of the parks, toluene:benzene ratios fell outside the range expected for vehicular emissions ($p<0.01$), suggesting that there are additional, industrial sources of benzene near these two locations. The ratio of m-,p-xylene:ethylbenzene was high at all locations except one residential area, indicating that BTEX were freshly emitted. Concentrations of individual BTEX compounds were highly correlated with each other in most cases, except for locations that may be impacted by nearby industrial sources of benzene. Results of this study suggest that parks can help reduce BTEX exposure by a modest amount, but future research is needed to ascertain this potential through more measurements at higher spatial and temporal resolution and analysis of vegetation for evidence of uptake of BTEX.

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General Audience Abstract

Benzene, toluene, ethylbenzene, and xylenes (BTEX) compose a significant fraction of anthropogenic non-methane organic gases in the atmosphere. These compounds are harmful to human health and are precursors to secondary organic aerosol and ozone. Several chamber studies have demonstrated that plants can reduce exposure to BTEX in indoor environments, but, to the best of our knowledge, no study has identified this effect in ambient air. To investigate this issue, we sampled for two weeks in parks and nearby residences at four locations; three were in the city of Birmingham, Alabama, and one was in the rural city of Camden, Alabama. All BTEX concentrations were below health-based guidelines and were comparable to those found in several other studies in urban and rural settings. TEX levels were lower in parks compared to residential areas, and the difference was significant. BTEX were attributable to vehicular emissions in the Camden site and one Birmingham site. In the other two Birmingham sites, there were likely additional, industrial sources of benzene. Future research should investigate the effect of different types of vegetation between parks and explore seasonal cycles in vegetation.

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Chapter 1. Literature Review

1.1 Background

Outdoor air pollution exposure is estimated to be responsible for 3.7 million premature deaths a year.[1] Volatile organic compounds (VOCs) are an important component of outdoor air pollution, as they have both direct and indirect impacts on health. Benzene, toluene, ethylbenzene, and xylenes (BTEX; Figure 1.1.1) are a set of monocyclic aromatic VOCs that can comprise over 60% of non-methane anthropogenic VOCs detected in ambient air in certain locations[2] and are present in a wide variety of products, most significantly in gasoline, solvents, paints, and varnishes.[3–6] Xylenes consist of three isomers: ortho-xylene, meta-xylene, and para-xylene; they can present challenges in separation and analysis and are therefore often reported as total xylenes. BTEX are listed as hazardous air pollutants under the Clean Air Act Amendments of 1990.[7] Benzene is widely known as a carcinogen[8] and all BTEX compounds have myriad health effects in the cardiovascular, respiratory, and endocrine systems, even at ambient concentrations deemed safe by the U.S. Environmental Protection Agency (EPA).[9]

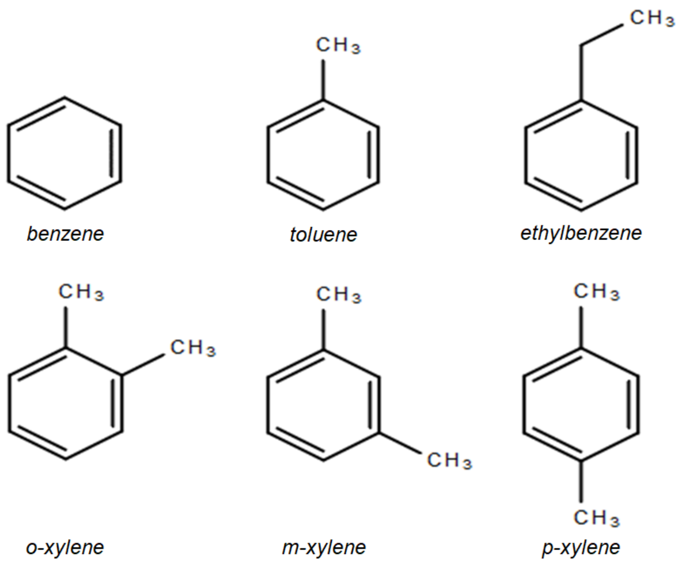

Figure 1.1.1. Structures of BTEX. Molecules drawn using ChemSpider.[10]

Benzene, toluene, and xylenes are primarily produced during the refining of fossil fuels. They are produced from oil in reformates and in pyrolysis gasoline and then extracted from these streams, and they are also found in coal-derived coke oven light oil.[3,4,6] Approximately 90% of ethylbenzene is produced through the alkylation of benzene.[5] After production or isolation, significant fractions of benzene, toluene, and ethylbenzene are used as an intermediate in manufacturing other chemicals.[3–5] Industrial applications of individual BTEX components include use in solvents, diluents, plastics, rubbers, resins, explosives, sealants, and furniture wax.[3–6,8,11–13] Most importantly, however, all BTEX are blended into automotive gasoline either for their anti-knocking properties or to increase its octane rating.[3–6]The predominant source of BTEX in the atmosphere is the combustion of gasoline from onroad vehicles. Evaporative emissions from gasoline storage tanks and industrial solvent use also contribute significantly to ambient BTEX due to their high vapor pressures.[3–6] Natural processes provide minor sources of BTEX. For example, benzene and toluene are emitted in smoke from volcanoes as well as forest fires.[8,11] Toluene, ethylbenzene, and xylenes are found in certain plants; toluene is found in pine trees,[11] while emissions of ethylbenzene and xylenes have been reported from alfalfa and grain silage.[12,13] In ambient measurements, individual BTEX compounds are often strongly correlated with each other, implying a common source.[14–17]

U.S. emissions of BTEX are tracked through the National Emissions Inventory (NEI) by the EPA. The NEI categorizes emissions in four groups: point, nonpoint, nonroad, and onroad.[18] Point sources are predominantly large individual facilities at a specific and fixed location. Nonpoint sources, also known as area sources, are smaller and do not exist at a single location; examples include rail lines and shipping lanes. Nonroad sources are largely engines and equipment that do not access highways, such as engines used in agricultural, recreational, or construction activities. Onroad sources are defined as motorized vehicles that are normally on public roadways. In the NEI, point sources are recorded for each process within a single facility, while nonpoint, nonroad, and onroad sources are reported at the county level.

According to the 2014 NEI, annual emissions of benzene, toluene, ethylbenzenes, and xylenes exceed 157, 436, 73, and 289 kilotons, respectively (Figure 1.1.2).[18] Roughly 45% of toluene, ethylbenzene, and xylene emissions are defined as onroad.[18] Less than 35% of benzene emissions share the same classification; the majority of benzene emissions are nonpoint, meaning that their sources are relatively small and dispersed, such as gas stations and paint shops.[18] Less than 1% of each BTEX compound is emitted from facilities large enough to be classified as point sources.[18] However, fugitive emissions still occur from equipment leaks and can result in higher emissions than those estimated.[5]

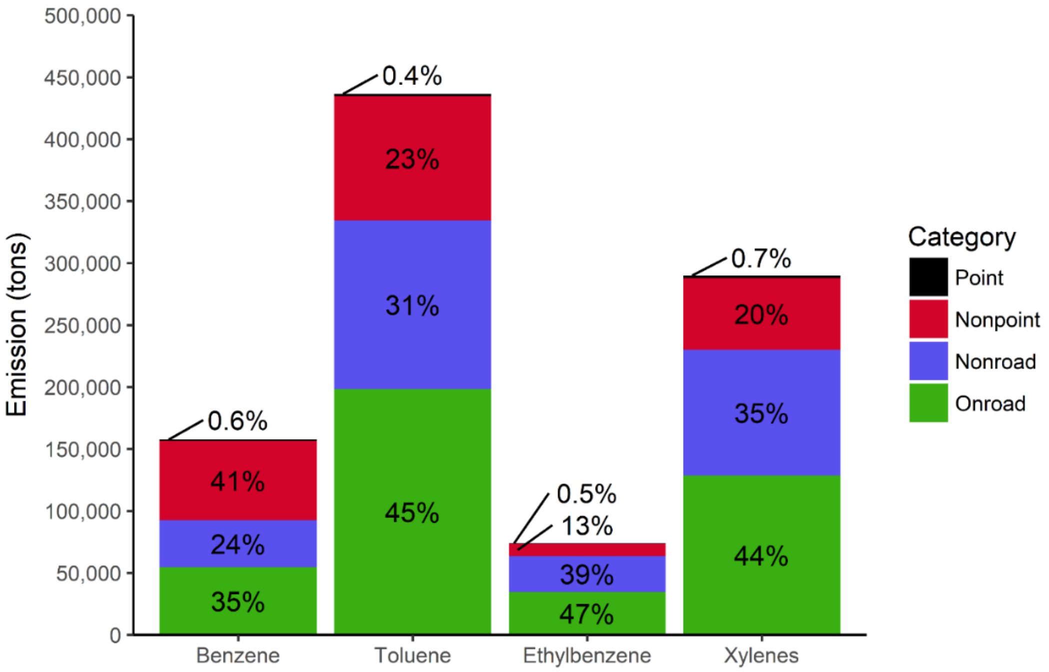

Figure 1.1.2. U.S. BTEX emissions in 2014. Data provided by EPA NEI (2014).[18]

Photochemical reactions are the predominant removal mechanisms for BTEX in the troposphere. Degradation of volatile aromatics is typically initiated through reaction with hydroxyl radicals during the daytime, although they can also react with ozone and nighttime nitrate radicals.[19] Reaction with a hydroxyl radical occurs substantially faster than ozonolysis. With a hydroxyl radical concentration of 10^6 molecules cm^{-3}, the global daytime average,[20] the tropospheric lifetimes of benzene (9.4 days), toluene (1.9 days), ethylbenzene (1.6 days), m-xylene (11.8 hours), p-xylene (19.4 hours), and o-xylene (20.3 hours)[21] are much faster than lifetimes with respect to ozonolysis. Lifetimes of benzene and toluene against reaction with ozone (i.e., ozonolysis) are >4.5 years at an ozone concentration of 7×10^{11} molecules cm^{-3} (28 parts per billion (ppb) at standard temperature and pressure).[19] The radical generated by reaction with the hydroxyl radical principally reacts with O_2, but in rare cases can compete with NO_2 at mixing ratios of 1–5 parts per million (ppm).[19] Depending on NO_x concentrations, BTEX degradation typically yields aromatic aldehydes, benzyl nitrates, unsaturated carbonyls, or phenolic compounds.[19] One important product that is ultimately formed from BTEX oxidation is are ozone.[22] Numerous studies have shown an inverse correlation between BTEX and ozone concentrations.[14,23] Of all BTEX, m-,p-xylene hold the highest ozone formation potential (OFP).[17,24] Toluene and o-xylene have moderate OFP, while benzene and ethylbenzene relatively do not produce much ozone.[17,24,25]

Although chemical reactions are the major pathway for BTEX removal in the troposphere, new questions have emerged regarding removal by vegetation, or phytoremediation. Phytoremediation refers to the remediation of soil, water, and air quality through the implementation of vegetative systems.[26] Phytoremediation is most commonly associated with removal of contaminants from soil and groundwater;[26] however, several studies have demonstrated that it also applies to air. According to one study, U.S. urban parks remove 75 kilotons of air pollution each year, valued at $500 million.[27] However, this claim is largely focused on criteria air pollutants. Uptake of benzene in indoor potted-plants has been shown to occur inside a 0.216 m^3 chamber at a rate of 40–88 mg m^{-3} d^{-1}.[28] Xylenes were shown to be removed in a similar experiment of indoor potted-plants at rated of 47–610 µg h^{-1}.[29] Uptake of both benzene and xylenes were shown to be influenced by plant foliage, plant stems, and the microbial community in the soil, termed the rhizosphere.[29,30] One major question is whether aromatic hydrocarbons are degraded in the plant, or merely sequestered to be later reemitted. It has been shown through isotope analysis that benzene and toluene uptake in spinach leaves leads to degradation or even respiration as $^{14}CO_2$.[31]

While several studies have shown that phytoremediation of BTEX is biologically feasible, there is a significant gap in the literature in terms of testing this hypothesis on ambient BTEX concentrations and their spatial distribution at the local or regional levels. Gas-phase aromatic hydrocarbons can be removed by plants in light and dark conditions. Furthermore, it has been shown that these compounds can be successfully degraded and incorporated into the biomass of the plant. While these studies suggest that BTEX levels may be reduced around large areas of vegetation, it has been shown that evapotranspiration is a significant process for groundwater-based phytoremediation of BTEX,[32] suggesting that the compounds could be emitted into the atmosphere by plants on a site with BTEX-contaminated groundwater. One study[33] identified a reduction of benzene and toluene in parks, but several others[34–36] produced mixed results when aggregating BTEX with other VOCs into a single metric.

Results of previous studies on the potential for vegetation to reduce ambient concentrations of BTEX are inconclusive. Furthermore, these studies were restricted to

Scandinavia, and results may not necessarily apply to other climate and vegetation zones. The research objective of the present study is to determine whether BTEX concentrations are mitigated in parks compared to the surrounding neighborhood in urban settings in the southeastern US. The goal of this research is to determine whether results of laboratory chamber studies translate to the real world and assess the impact of vegetation on ambient BTEX removal.

1.2 BTEX Health Effects

Exposure to BTEX is correlated with a diverse set of health effects. While benzene is a known carcinogen, all BTEX have many noncancerous health effects and are associated with stress on the cardiovascular, respiratory, and endocrine systems. BTEX exposure can be differentiated into acute and chronic; although relatively high and acute exposure generally occurs in occupational settings, acute or chronic exposure at relatively low concentrations can occur anywhere. Ambient (i.e., non-occupational) levels are typically several orders of magnitude lower than occupational levels.

According to the National Institute for Occupational Safety and Health (NIOSH),[37–42] the exposure routes for all BTEX include inhalation, ingestion, and skin or eye contact. Benzene, toluene, and xylenes can also enter the body via absorption through the skin. Once in the body, all BTEX impact the eyes, skin, respiratory system, and central nervous systems. In addition, benzene and xylenes exhibit hematotoxicity while toluene and xylenes affect the liver and kidneys. Symptoms of acute exposure to any individual compound of BTEX vary but can include irritation of the exposure area; headache, dizziness, or nausea; dermatitis; or feelings of weakness and exhaustion.

The International Agency for Research on Cancer (IARC) preforms critical reviews of exposure data on chemicals or groups of chemicals, estimates their risk, and classifies them based on their carcinogenicity.[43] The IARC places benzene in Group 1, which states that "there is *sufficient evidence* in humans" for its carcinogenicity.[44] Indeed, leukemia has long been associated with benzene exposure.[45] Conversely, there is inadequate evidence of toluene carcinogenicity in humans. Animal experiments suggest that toluene is not carcinogenic; therefore, toluene is placed in Group 3, which is defined as "*not classifiable as to its carcinogenicity to humans.*"[46] Although ethylbenzene exposure studies have concluded that there is sufficient evidence for carcinogenicity in animal experiments, there is inadequate evidence in humans. The IARC concludes that ethylbenzene is in Group 2B and is "*possibly carcinogenic to humans.*"[47] Finally, there is inadequate evidence in both humans and animals for the carcinogenicity of xylenes, so the IARC concludes that they are "*not classifiable as to their carcinogenicity to humans*" and are in Group 3.[48]

Bolden et al. (2015)[9] provides a comprehensive review of the literature exploring the non-cancer health impacts of ambient levels of BTEX. The mean or median BTEX levels in all studies reviewed were below the EPA inhalation Reference Concentration,[9] defined as the estimate of a daily inhalation exposure "that is likely to be without an appreciable risk of deleterious effects during a lifetime."[49] Benzene exposure was linked to a decrease in term birth weight;[50–52] an increase in eczema;[53,54] decreased white blood cell, hemoglobin, hematocrit, and red blood cell counts in children;[55] increased odds of asthma;[54,56–62] and bronchitis risk.[56,63] Exposure to toluene was associated with term low birth weight;[52] increased odds of atopy;[64] bronchitis and eczema;[63] asthma or asthmatic symptoms in children;[57,62,65] and increased odds of cardiovascular disease in adults.[66] Ethylbenzene exposure correlated with term low birth weight;[52] increased odds of rhinitis[67] and atopy;[64] increased odds of asthma or asthma symptoms;[57,59,61] and increased odds of cardiovascular disease in adults.[66] Exposure to xylenes was linked to with term low birth weight;[52] increased odds of rhinitis (for m-,p-xylene);[67] increased odds of asthma;[59] and increased odds of obstructive bronchitis (for m-,p-xylene).[63]

While each BTEX component has its own health impacts, it is vital to discuss the health effects of the entire mixture. The Agency for Toxic Substances and Disease Registry reviewed physiologically-based pharmacokinetic modelling in addition to experimental exposures for BTEX interactions and concluded that “joint neurotoxic action is expected to be additive at BTEX concentrations below approximately 20 ppm of each component.”[68] In addition, other studies have analyzed the non-cancer health impacts of ambient levels of combined BTEX. Combined exposure to BTEX was correlated with decreased birth weight;[69] decreased biparietal diameter in fetuses;[70] increased odds of physician-diagnosed asthma;[59] and wheezing attacks in non-asthmatic populations.[59]

1.3 Phytoremediation of BTEX

U.S. urban park trees are estimated to remove roughly 75,000 tons of air pollution each year, or about 80 pounds per acre of tree cover, through phytoremediation.[27] Plant uptake of environmental pollutants can occur through its roots, stem, or leaves, although remediation can also occur through microbial degradation of pollutants in the soil surrounding the root system, termed the rhizosphere. Phytoremediation of air has traditionally been assessed with respect to carbon dioxide and the criteria air pollutants of the EPA’s National Ambient Air Quality Standards.[27] However, several studies demonstrate the feasibility of phytoremediation of atmospheric BTEX.

The majority of research on gas-phase phytoremediation of BTEX has focused on improving indoor air quality. Early research showed that given an initial benzene level <1 ppm (compared to urban median mixing ratios of 0.52 to 6.07 ppb),[21] myriad household plants could remove the majority of ambient benzene over 24 hours.[30] Other studies demonstrated the same effect at higher levels of benzene (25–50 ppm)[28] and xylenes (>1 ppm),[29] but the former study noted that benzene uptake by certain plants increased significantly after two to four days of exposure.[28] Sriprapat and Thiravetyan (2013) found similar removal trends when assessing uptake of each individual compound of BTEX at 20 ppm over 120 hours by the houseplant *Zamioculcas zamiifolia*.[71] The authors confirmed earlier findings that the diffusion and partitioning rates of each compound are related to their molecular weight and vapor pressure, respectively.[72]

Uptake of gas-phase BTEX by vegetation can be further differentiated into different rates for specific parts of the plant. Several studies have determined that BTEX can be absorbed by the abaxial side of the leaf (i.e., containing stomata) and less so by nonstomatal pathways (e.g., adaxial side, cuticle wax).[71,31] However, one study demonstrated that a large portion of benzene (45.2–64.6%) could be removed from the air by the plant without foliage.[30] Moreover, many studies have noted that a significant fraction of BTEX removal (8.1–20.4% of benzene in one study[30] and 50.5–53.0% of xylenes in another[29]) can occur with the potting soil itself through microbial degradation in the rhizosphere.

Although gas-phase BTEX can be absorbed by plants through many pathways, aqueous-based phytoremediation of BTEX can have an opposing effect. Uptake of BTEX-contaminated groundwater occurs in the roots at a rate related to the logarithm of their octanol/water partition coefficient.[32,73–75] In the root system, endophytic bacteria can aerobically degrade the compounds.[76,77] Degradation in the root system is dependent on both the endophytic bacteria present[77] and the amount of oxygen present.[76] BTEX can leave the root system and travel through the xylem to the trunk, stem, and leaves of plants.[75] BTEX can then enter the air primarily by evapotranspiration though leaves,[32,75] but can also volatilize through stems, trunks, or branches.[75] However, it has been shown that in groundwater contaminated with chlorinated aromatics, evapotranspiration is decreased due to stresses on the plant caused by the phytotoxicity of the compounds themselves.[78]

Although many studies have shown that translocation of BTEX without transformation between environmental media is a major pathway in phytoremediation, research using carbon-isotope analysis also provides evidence that the compounds are permanently degraded in some cases. One study[32] applied a mass-balance approach to aqueous uptake of benzene, toluene, ethylbenzene, and m-xylene. The authors found oxidation products of these compounds most concentrated in the bottom stem (1.1–8.2%) but also in the roots (0.11–3.0%), upper stem (0.39–1.7%), and leaves (0.09–1.6%).[32] Furthermore, Ugrekhelidze et al. (1997) assessed benzene and toluene transformation in sterile spinach leaves (*Spinacia oleracea*) and found that they were oxidized into low-molecular weight organic acids (65% and 66%, respectively), low-molecular weight amino acids (12% and 17%, respectively), high-molecular weight compounds (18% and 13.5%, respectively), and CO_2 (5% and 3.5%, respectively).[31]

Studies that have assessed plant uptake of volatile organic compounds (VOCs) in ambient air have been limited mainly to Scandinavia. Upmanis et al. (2001)[33] examined concentrations of benzene and toluene in two Scandinavian cities in built-up areas and within parks as a function of distance from adjacent roads. Concentrations of benzene and toluene were at least one-third lower inside parks, and this reduction was achieved within 40 m of the park border. Thorsson and Eliasson (2006)[79] also presented a profile of benzene concentrations inside a large urban park in Sweden as a function of distance to a source. The reduction of benzene was more pronounced in May, when leaves were present, than in February, when leaves were not present, but the researchers attributed reductions to dilution at increased distance from a source. Setälä et al. (2013)[34] measured BTEX concentrations under tree canopies and their adjacent open areas in Finland in August (i.e., full leaf cover) and in March (no leaf cover). However, this study assessed the effect by aggregating all BTEX and several other VOCs into one single total VOC value. The authors found that the total VOC concentration was 19.1% lower in tree canopies in August, and the difference was significant. However, the difference between concentrations inside and outside the tree canopy was not significant in March, suggesting that leaf cover is a significant parameter for BTEX uptake.

Two recent studies of VOCs have found conflicting results. In a study in Finland, Yli-Pelkonen et al. (2017)[35] found that urban forests did not reduce total anthropogenic VOC levels. Klingberg et al. (2017)[36] analyzed the VOC phenanthrene in urban parks in Sweden before and after leaf emergence and noted that some sample sites exhibited higher concentrations before leaf emergence and others after leaf emergence; results were affected by distance to the dominating traffic route. These studies present limited information on BTEX.

1.4 Air Quality in Urban and Rural Alabama

The present study was conducted in conjunction with a larger study of heat exposure in two cities in Alabama.[80–83] Birmingham, which resides in Jefferson County, is the most populous city in Alabama with an estimated population of 212,424 in 2016.[84] The city of Camden in rural Wilcox County had an estimated population of 2,560 in 2016.[84] The EPA assessed the risk of exposure to air toxics in North Birmingham, Alabama from 2011–2012.[85] At all four sites studied, benzene had the highest cancer risk (4×10^{-5}–7×10^{-5}) of all air toxics measured.[85] Furthermore, each component of BTEX was individually identified as a chemical of potential concern at all four sites.[85] Separately, air pollution was recently identified as a top environmental health priority in the underserved populations of both Birmingham and Camden.[80]

BTEX emissions data for Jefferson and Wilcox Counties are presented in Figure 1.4.1 and Figure 1.4.2, as reported in the EPA 2014 NEI.[18] The majority of BTEX emissions in Jefferson County come from onroad (i.e., automotive) sources, and while nonroad and nonpoint sources offer substantial contributions, they are proportionally less than the U.S. averages (Figure 1.1.2). Point sources account for a larger fraction compared to the U.S. averages (Figure 1.1.2) but are still relatively small. Alternatively, BTEX emissions in Wilcox County predominantly come from nonroad emission sources while the contributions from onroad and nonpoint sources are far below U.S. averages (Figure 1.1.2). Point sources in Wilcox County produce a significant fraction of BTEX emissions, but it should be noted that all BTEX point sources in Wilcox County come from just two emitters (compared to 25 in Jefferson County).

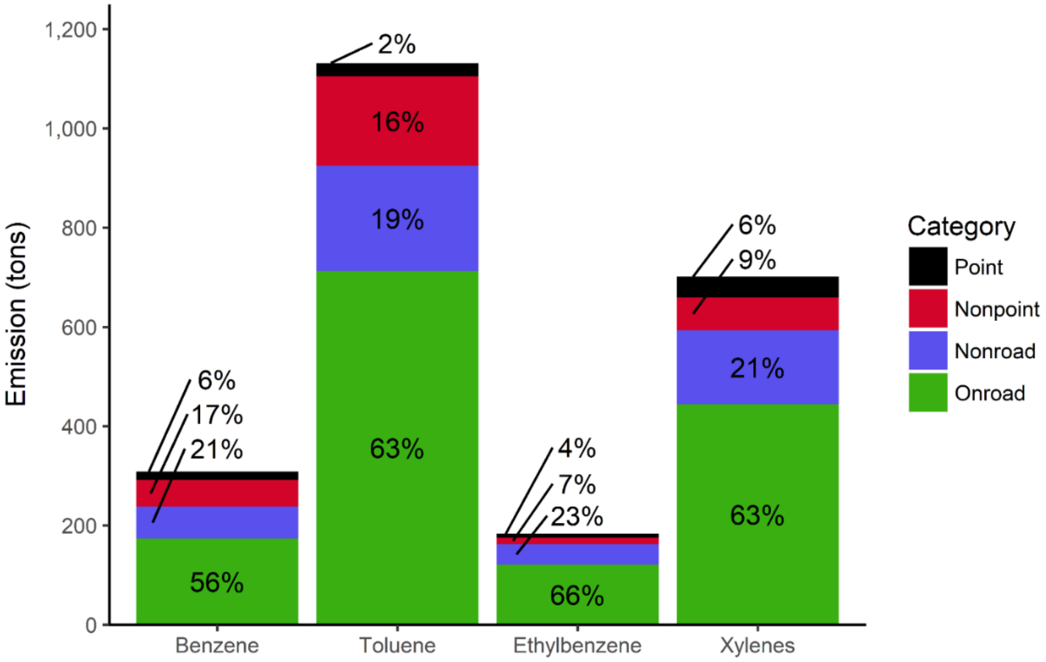

Figure 1.4.1. BTEX emissions in Jefferson County, AL in 2014. Data provided by EPA NEI (2014).[18]

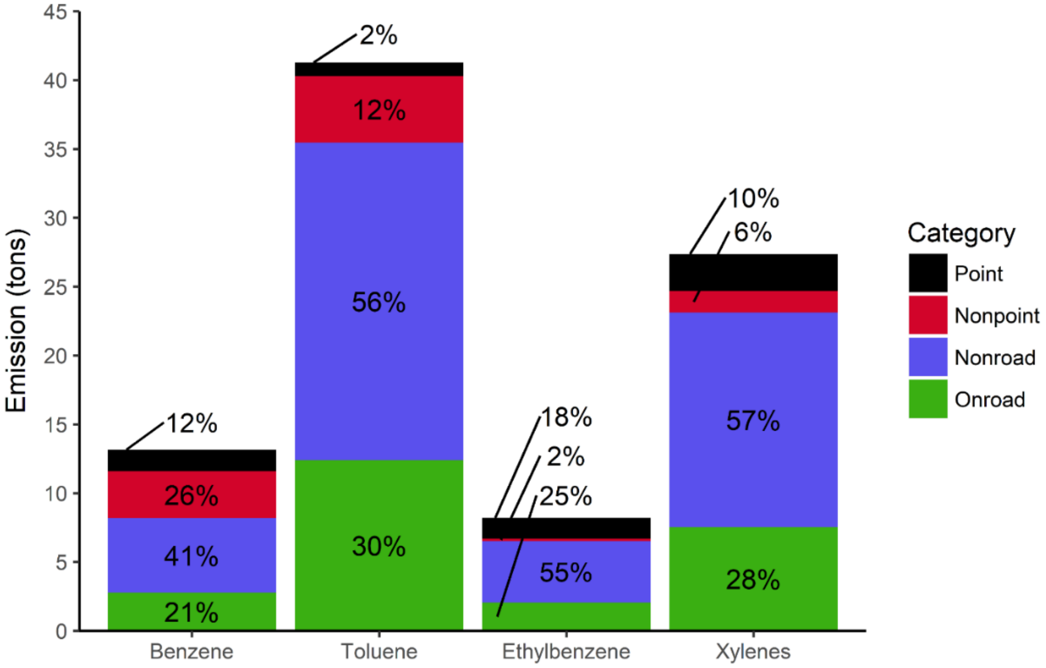

Figure 1.4.2. BTEX emissions in Wilcox County, AL in 2014. Data provided by EPA NEI (2014).[18]

1.5 Research Objectives

The present study is founded on the hypothesis that large areas of vegetation, such as parks, can provide phytoremediation of tropospheric BTEX. The main objective of this study is to determine whether parks have a measureable, beneficial effect on ambient BTEX concentrations. This objective will be achieved by quantifying the change in ambient concentrations inside parks relative to the surrounding residential areas through active and passive sampling methods. The data collected will help identify whether strategies for effectively mitigating tropospheric BTEX should include implementation of vegetative systems. The data will also provide insight into the average levels of summertime BTEX to which local community members are exposed and their associated levels of risk. The specific research objectives are:

1. Collect passive samples at urban and rural sites in Alabama and design analytical methods to calculate BTEX concentrations on passive samplers;
2. Quantify levels of exposure to BTEX and determine their likely sources and photochemical ages;
3. Identify and quantify the effect of phytoremediation of tropospheric BTEX through large areas of vegetation in parks (here, termed the "park effect").

Chapter 2, Potential for City Parks to Reduce Exposure to Hazardous Air Pollutants, addresses these research objectives in the format of a manuscript that will be submitted for publication in a peer-reviewed, scientific journal. In this study, passive samplers were deployed in Birmingham, Alabama and Camden, Alabama in July 2017. Sensors measuring temperature and relative humidity were deployed with passive samplers to calculate the appropriate effective sampling rate. BTEX were desorbed chemically from passive samplers and analyzed by GC-MS.

Finally, gas-phase concentrations were calculated and statistical tests were conducted to characterize likely sources and assess the “park effect.”

Chapter 3 concludes this thesis by summarizing the main results of the study as well as suggesting opportunities for future work.

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Chapter 2. Potential for City Parks to Reduce Exposure to Hazardous Air Pollutants

Michael J. Milazzo,[a] Julia M. Gohlke,[b] Dan L. Gallagher,[a] Anna A. Scott,[c] Benjamin F. Zaitchik,[c] Linsey C. Marr[a,*]

[a]Department of Civil and Environmental Engineering, Virginia Tech, Blacksburg, Virginia, USA
[b]Department of Population Health Sciences, Virginia Tech, Blacksburg, Virginia, USA
[c]Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, Maryland, USA

* Corresponding author

E-mail: lmarr@vt.edu

Mailing address:
Virginia Tech
Department of Civil and Environmental Engineering
418 Durham Hall,
Blacksburg, VA 24061
United States

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2.1 Abstract

Benzene, toluene, ethylbenzene, and xylenes (BTEX) are hazardous air pollutants commonly found in outdoor air. Several studies have explored the potential of vegetation to mitigate BTEX in outdoor air, but they are limited to a northern temperate climate and present conflicting results. To investigate this issue in a subtropical climate, we deployed passive air samplers for two weeks in parks and nearby residences at four locations: three in an urban area and one in a rural area in Alabama, USA. All BTEX concentrations were below health-based guidelines and were comparable to those found in several other studies in populated settings. Concentrations of TEX, but not benzene, were 3-39% lower in parks than at nearby residences, and the differences were significant. In and around two of the parks, toluene:benzene ratios fell outside the range expected for vehicular emissions ($p<0.01$), suggesting that there are additional, industrial sources of benzene near these two locations. The ratio of m-,p-xylene:ethylbenzene was high at all locations except one residential area, indicating that BTEX were freshly emitted. Concentrations of individual BTEX compounds were highly correlated with each other in most cases, except for locations that may be impacted by nearby industrial sources of benzene. Results of this study suggest that parks can help reduce BTEX exposure by a modest amount, but future research is needed to ascertain this potential through more measurements at higher spatial and temporal resolution and analysis of vegetation for evidence of uptake of BTEX.

2.2 Environmental Impact Statement

Benzene, toluene, ethylbenzene, and xylenes (BTEX) compose a significant fraction of anthropogenic non-methane organic gases in the atmosphere. BTEX are harmful to human health and are precursors to secondary organic aerosol and ozone. Vegetative systems are known to reduce exposure to BTEX in indoor environments, but their potential to affect outdoor concentrations is not well known. In this work, BTEX levels were quantified in Alabama in four urban parks and in their surrounding residential areas. TEX levels were lower in parks compared to residential areas, and the difference was significant. BTEX were attributable to vehicular emissions in two locations; in two others, there were likely additional, industrial sources of benzene.

2.3 Introduction

The hazardous air pollutants benzene, toluene, ethylbenzene, and ortho-, meta-, and para-xylene (BTEX) can comprise over 60% of anthropogenic non-methane organic compounds in the atmosphere in certain locations.[1] BTEX are present in a wide variety of commercial and industrial products including gasoline, solvents, paints, and varnishes.[2–5] Benzene is a known carcinogen,[6] and all BTEX compounds have noncancerous health effects. Chronic BTEX exposure has been associated with adverse health outcomes in the cardiovascular, respiratory, and endocrine systems, even at levels below the inhalation Reference Concentrations set by the US Environmental Protection Agency (EPA).[7]

In the United States, 35–47% of emissions of each BTEX compound come from onroad sources such as automobiles, compared to 0.4–0.7% from stationary point sources.[8] For TEX, onroad emissions are the predominant source, whereas for benzene, nonpoint emissions are higher (41%, compared to 35% onroad).[8] In urban environments, concentrations of individual BTEX compounds are often highly correlated with each other,[9–12] reflecting a common source of the pollutants. Additionally, analyses of toluene:benzene (T:B) and m-,p-xylene:ethylbenzene (m-,p-X:E) ratios provide information on source type and photochemical age. A T:B ratio of 1.5–3.0 is emblematic of emissions from traffic.[10,13–15] A m-,p-X:E ratio of approximately 3.6 is expected for fresh emissions, regardless of source,[16] while a lower ratio suggests photochemical aging since m-xylene and p-xylene degrade faster than ethylbenzene.[17]

Phytoremediation is the remediation of soil, water, and air quality[18] through the implementation of vegetative systems. In the most typical applications of phytoremediation for BTEX, plants and trees are used to remediate contaminated groundwater, where the major removal pathway is evapotranspiration.[19–21] However, vegetation can also remove BTEX from air. Several studies have assessed the capacity of house plants for uptake and removal of gas-phase BTEX in small chambers. In one study, plants in a 0.216 m^3 chamber removed benzene from air at a rate of 40–88 mg m^{-3} d^{-1}.[22] Sripraprat and Thiravetyan (2013)[23] demonstrated that BTEX at concentrations of ~80 mg m^{-3} (roughly 1000 times higher than typical ambient concentrations) were removed by *Zamioculcas zamiifolia* at rates of 0.075–0.098 µg per m^2 of plant leaf after 72 hours. In a separate chamber study, household plants exposed to benzene at much lower concentrations of 405–1380 µg m^{-3} removed 48–90% of benzene.[24] In an open-top chamber experiment on grass (*Lolium perenne*), exposure to 250 µg m^{-3} of benzene yielded an in-grass concentration of 0.55±0.08 ng g^{-1} after 24 hours.[25]

Uptake of BTEX by plants depends on several competing factors. Uptake from the air occurs through a plant's leaves, stem, and even rhizosphere. In leaves, the pollutants are absorbed primarily through the stomata-containing abaxial (bottom) side, although adaxial (top) absorption occurs as well.[23,26] BTEX uptake is also attributable to the plant soil and its microbes, which accounted for 8.1 to 20.4% of uptake of benzene over 24 hours in one study[24] and 50.5 to 53.0% of uptake of xylenes in another,[27] even after the plant was removed.[24]

Studies that have assessed plant uptake of volatile organic compounds (VOCs) in ambient air have been limited mainly to Scandinavia. Upmanis et al. (2001)[28] examined concentrations of benzene and toluene in two Scandinavian cities in built-up areas and within parks as a function of distance from adjacent roads. Concentrations of benzene and toluene were at least one-third lower inside parks, and this reduction was achieved within 40 m of the park border. Thorsson and Eliasson (2006)[29] also presented a profile of benzene concentrations inside a large urban park in Sweden as a function of distance to a source. The reduction of benzene was more pronounced in May, when leaves were present, than in February, when leaves were not present, but the researchers attributed reductions to dilution at increased distance from a source. Setälä et al. (2013)[30] measured BTEX concentrations under tree canopies and their adjacent open areas in Finland in August (i.e., full leaf cover) and in March (no leaf cover). However, this study assessed the effect by aggregating all BTEX and several other VOCs into one single total VOC value. The authors found that the total VOC concentration was 19.1% lower in tree canopies in August, and the difference was significant. However, the difference between concentrations inside and outside the tree canopy was not significant in March, suggesting that leaf cover is a significant parameter for BTEX uptake.

Two recent studies of VOCs in parks have found conflicting results. In a study in Finland, Yli-Pelkonen et al. (2017)[31] found that urban forests did not reduce total anthropogenic VOC levels. Klingberg et al. (2017)[32] analyzed the VOC phenanthrene in urban parks in Sweden before and after leaf emergence and noted that some sample sites exhibited higher concentrations before leaf emergence and others after leaf emergence; results were affected by distance to the dominating traffic route. These studies present limited information on BTEX.

Studies beyond the northern temperate climate are needed to ascertain the potential of vegetation to reduce ambient BTEX concentrations. The objective of this study is to test the hypothesis that city parks can provide phytoremediation of BTEX in air and therefore reduce exposure to the compounds. As part of a larger investigation of heat exposure,[33–36] this study assesses whether parks have a measureable, beneficial effect on ambient BTEX concentrations. The study took place in Alabama, in the cities of Birmingham and Camden, where air pollution has been identified as a top environmental health priority in the underserved populations of these areas.[33] An assessment of air toxics in northern Birmingham in 2011–2012 identified BTEX as chemicals of potential concern in this area.[37]

2.4 Materials and Methods

Passive Samples. Air samples were collected using diffusion-based organic vapor monitors (3M OVM 3500) deployed over one-week time periods. The samplers were protected from potential water damage through a rain cover consisting of the top section of a plastic water bottle with the bottom section removed and several holes punched on the sides for ventilation, as shown in Figure 2.9.1. An iButton temperature sensor was also positioned inside the plastic housing.

Sample Locations. Two cities in Alabama were selected for sampling: Birmingham (33.527 °N, 86.799 °W; area of 384.8 km^2;[38] population of 212,424 in 2016[39]) in Jefferson County and Camden (31.998 °N, 87.289 °W; area of 10.87 km^2;[38] population of 2,560 in 2016[39]) in rural Wilcox County. They are part of a larger study of heat exposure.[33–36] Four urban parks in residential areas were selected for sampling on the basis of input from local community members, proximity to large point sources, and accessibility. As shown in Figure 2.4.1A, North Birmingham Park and Harriman Park are located in the northern part of Birmingham; North Birmingham Park is approximately 2.25 km west-southwest of Harriman Park Park. (N.B.

"Harriman Park" is the name of the neighborhood that surrounds the park included in this study; the label "park" or "residential" will follow the name of the neighborhood for further clarification.) Woodward Park is located in southwestern Birmingham. As shown in Figure 2.4.1B, Westgate Park is in Camden and served as a background site; henceforth, this location will be simply referred to as "Camden."

Characteristics of each park were derived from aerial imagery.[40] North Birmingham Park (approximately 62,700 m^2) is primarily covered in grass and has approximately 110 trees. By contrast, the much smaller Harriman Park Park (4,290 m^2) has approximately 15 trees. Roughly half of the land defined as Harriman Park Park is grassy while the other half is covered by pavement or buildings. Woodward Park (43,700 m^2) is almost entirely covered in grass and has approximately 100 trees. The park in Camden (28,200 m^2) is mostly grassy and has approximately 43 trees. All the parks have some combination of a community center, parking lot, picnic shelter, bathroom, sports courts or fields, swimming pool, and playground.

The sampling locations in Birmingham and Camden were evaluated for potential influence of BTEX sources. Line sources were identified through aerial imagery while the nearest point sources were identified in the EPA's Toxics Release Inventory (TRI);[41] these TRI facilities are mapped in Figure 2.4.1. In Birmingham, the western edge of North Birmingham Park borders (<100 m) a railroad line, although the park is also close (>920 m) to an interstate highway. Furthermore, the TRI shows that North Birmingham Park is 2.4 km northeast of a cast iron pipe manufacturer, 1.5 km southwest of a coke production plant, and 3.9 km southwest of a second coke plant. These facilities emitted thousands of kilograms of BTX in 2016. Harriman Park is 4.5 km northeast of the pipe manufacturer, 0.72 km east of the former coke production plant, and 1.8 km southwest of the latter coke production plant. The wind roses in Figure 2.9.2

and Figure 2.9.3 show that the prevailing wind in North Birmingham and Harriman Park varied during the study but was generally northerly. Therefore, these locations were usually downwind of the first coke production plant. The southern edge of Woodward Park borders (<100 m) a railroad line, and the park is an approximately 2.4 km upwind of the interstate highway. While Woodward's closest source is an industrial chemical facility 3.5 km north of the park, this facility emitted less than 400 kg of TEX combined in 2016. However, a petroleum-based refined products distributor that is 4.9 km south Woodward emitted hundreds of kilograms of BE and thousands of kilograms of TX in 2016. In Camden, located approximately 180 km southwest, the park is 0.31 km and 0.92 km from two state routes. There is one TRI facility (a paper processing plant) in Wilcox County, 16 km west of the Camden park, which was generally downwind during the study, per the wind roses shown in Figure 2.9.4 and Figure 2.9.5. Although it did not emit BTEX from 2008 to 2016 according to the TRI, the EPA 2014 National Emissions Inventory (NEI) estimated that the paper processing plant emits thousands of kilograms of BTEX per year.[8]

In each of the four locations, samples were collected at three sites in the park and three sites in the nearby residential area. A "location" describes a park with its surrounding residential area, and a "site" is where a VOC sampler is deployed; each location has multiple sampling sites. Two community leaders assisted with identification of the residential sampling sites. Criteria for site selection included proximity to park and major roads, minimal obstruction of sampler, and consent of residents for researchers to sample on their property. The residential sites near North Birmingham Park were located along its western edge, approximately 14–24 m from the park. Two residential sites near Harriman Park Park were close to its southern edge while one was significantly further northeast; their distances from the park ranged from 51 to 350 m. Likewise, two residential sites were located near the northwestern edge of Woodward Park while one was situated much further southwest at distances of 17–560 m. All residential sites in Camden were north of the park at distances ranging from 45 to 190 m. All sites were along two-lane streets except the distant Woodward residence, which was located along a busy two-lane road close to an intersection with a three-lane road. Railroad lines were located near residential sites in North Birmingham (120–210 m), Harriman Park (120–480 m), and Woodward (110–170 m). The nearest intersections were 12 to 230 m from the park and residential sampling sites.

Sample Deployment. Air samplers were deployed at sampling sites for two seven-day periods: July 8–15, 2017 (Week 1) and July 15–22, 2017 (Week 2). Three samplers were placed inside each park (total of 12 per week) and three in the residential area surrounding each park (total of 12 per week). The samplers were placed at a mean height of 2.1±0.29 m above the ground, hanging from trees, fences, or porch frames. A map illustrating sampling sites in the parks and residential areas appears in Figure 2.9.6.

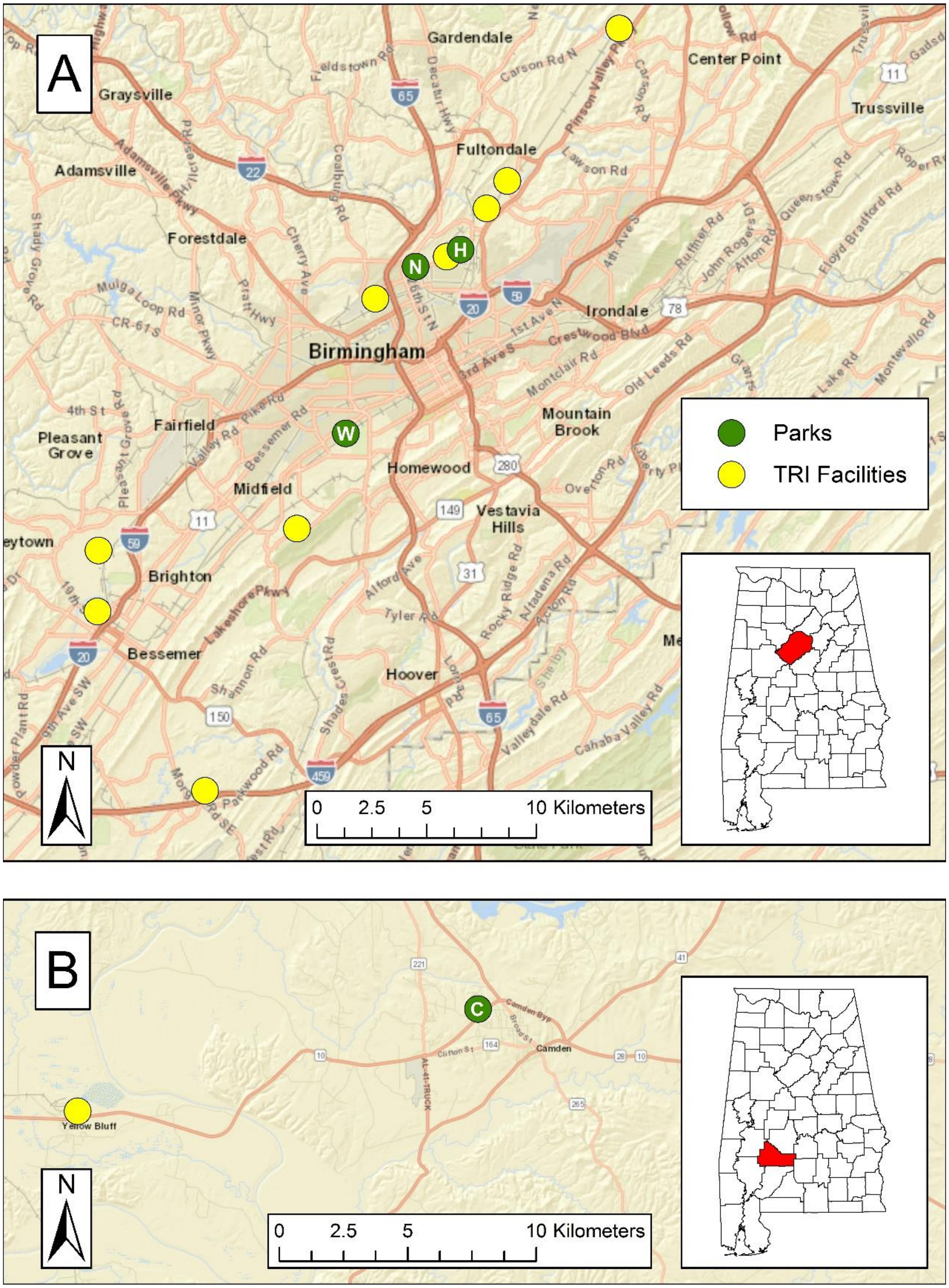

Figure 2.4.1. Parks selected for sampling and point sources of BTEX in 2016 in (A) Birmingham, AL and (B) Camden, AL. Labels denote specific parks, where “N” is North Birmingham, “H” is Harriman Park, “W” is Woodward, and “C” is Camden.

Quality Assurance and Quality Control. A BTEX standard (Restek, 200 µg mL^{-1} in methanol) was diluted in carbon disulfide (Sigma Aldrich ReagentPlus®, low benzene, ≥99.9%) to produce a six-point calibration curve. The method detection limit (MDL) was determined according to EPA-established guidelines;[42] MDL results, reported in full in Table 2.9.2, were all below 31.4 ng mL^{-1}. Benzene and toluene had the highest MDLs while those for ethylbenzene and xylenes were lower by a factor of 5–10. Desorption efficiency (DE) tests were conducted in triplicate at five concentrations according to the NIOSH Manual of Analytical Methods #4000 for toluene.[43] One standard concentration was below the MDL and was therefore discarded, resulting in four usable DE concentrations. All BTEX compounds were recovered at close to 100% efficiency, as shown in Table 2.9.4 and Figure 2.9.7. Overall, toluene had the highest recovery (118±13.5%) while ethylbenzene produced the lowest recovery (96.4±15.2%). At low concentrations, the recovery of benzene and toluene was >100%, probably due to the high MDLs for these compounds, while that of ethylbenzene and xylenes was <100%. Recoveries for all BTEX compounds converged on 100% at higher concentrations. Finally, reagent, method, and trip blanks were analyzed (n=4 each). As shown in Table 2.9.3, no BTEX compounds were detected in any blanks except for toluene in method and trip blanks at levels extremely close to the MDL.

Sample Analysis. Samplers were capped and stored at 4 °C between sampling and analysis. The desorption protocol roughly followed the NIOSH Manual of Analytical Methods #4000 but was altered to maximize desorption efficiency.[43] Briefly, each sampler was disassembled and the adsorbent pad was placed in a 2 mL gas chromatography (GC) amber vial with tweezers. 30 µL of a surrogate standard containing 5 µg mL^{-1} p-bromofluorobenzene (CAS no. 460-00-4) was injected onto the sampler's adsorbent pad, and the sealed vial was left to stand overnight in a fume hood at room temperature. In the morning, carbon disulfide (CAS no. 75-15-0) was added to the vial to bring the total solution volume to 1.5 mL; then, the vial was agitated every 20 minutes for 2 hours. Finally, a 1 mL aliquot of the solution was extracted and placed in a separate 2 mL GC vial for analysis by a gas chromatograph-mass spectrometer (Thermo-Fisher Trace GC, DSQ II).

Gas-Phase Concentration Calculations. Raw data were obtained from the mass spectrometer through peak detection and integration software (Xcalibur version 2.0.7). The mass adsorbed on each sampler was determined by multiplying the reported concentration in the extract by the injection volume (1 µL), multiplying by the solvent dilution factor used in the desorption step, and converting to micrograms. The effective volume of air sampled for each compound was calculated from the sampler deployment time and effective diffusive sampling rate of the compound according to the manufacturer. Effective passive sampling rates at 25 °C for benzene, toluene, ethylbenzenes, and xylenes were 35.5, 31.4, 27.3, and 27.3 mL min^{-1}.[44] The temperatures experienced by the samplers were 28.6±6.6 °C and 29.6±6.6 °C (mean ± standard deviation) during Weeks 1 and 2, respectively, as measured by the collocated iButton temperature monitors. The sample volume was corrected using a multiplicative adjustment factor for temperature. Finally, the mass adsorbed was divided by the effective sample volume to produce weekly average ambient BTEX concentrations.

Statistical Analysis. Statistical analyses were conducted in the R programming language (version 3.4.4). A multiple linear regression was conducted to assess the influence of distinct location, site types, and distance to the nearest major road on BTEX concentrations (lm, stats version 3.4.4). Regression parameters included categorical variables for location (North Birmingham, Harriman Park, and Woodward with Camden serving as the background location for the regression), site type (park or residence), a numerical variable for distance from a road with significant vehicular traffic (greater than approximately 10 cars per minute), and an intercept. Normality was confirmed for most pollutants grouped by location name and site type through Shapiro-Wilk tests (shapiro.test, stats version 3.4.4). Normality was weakly rejected in North Birmingham residential TEX concentrations (p=0.016 or higher for each compound), but for consistency, all data were subjected to the same multiple linear regression. A nonparametric Spearman rank correlation analysis (rcorr, Hmisc version 4.1-1) was also conducted to assess correlation between BTEX concentrations within locations. Finally, two one-sided Student's t-tests (t.test, stats version 3.4.4) with a Bonferroni correction ($\alpha=0.025$) were conducted on T:B ratios to examine whether the ratios were statistically different than the range expected for vehicular emissions. A one-sided t-test was conducted on m-,p-X:E ratios to assess whether they were greater than 3.6. Normality was confirmed through Shapiro-Wilk tests for all T:B and m-,p-X:E ratios except Woodward residential T:B ratios, which weakly rejected normality (p=0.039); therefore, all ratios tests were conducted as parametric t-tests.

2.5 Results

Meteorological Conditions. During the field campaign, the average temperatures at the nearest weather stations available through the National Centers for Environmental Information were 26±9.1 °C (mean ± standard deviation) and 28±9.2 °C during Weeks 1 and 2, respectively, for Birmingham International Airport and 26±9.6 °C and 27±10 °C for Selma 6 SSE (nearest station to the sampling location in Camden).[45] Precipitation ranged from 3 to 35 mm on three days in Birmingham and from 0.5 to 16 mm on five days near Camden during the two-week period. Table 2.9.1 lists daily temperatures and precipitation amounts during the field campaign, while Figure 2.9.2 and Figure 2.9.5 present wind roses. Wind direction was variable but generally northerly in Birmingham and was southeasterly in Camden.

BTEX Concentrations. Week-long BTEX concentrations were stratified by park name and location type (park vs. residential); the original data are presented in Table 2.9.5 while the means and standard deviations are presented by week in Table 2.9.6 and Table 2.9.7. For each sample, the surrogate concentration detected was divided by the expected value and is reported as the surrogate recovery efficiency. Although these recovery efficiencies (60.9±6.91%) are lower than expected, results of the DE analysis indicated that recovery of p-bromofluorobenzene (73.8±9.27%) may not be directly comparable to BTEX recovery (104±14.7% as a whole); therefore, the BTEX results were not adjusted.

BTEX concentrations in and around each park are presented in Figure 2.5.1. Benzene and toluene concentrations were 1.02–2.51 µg m^{-3} in North Birmingham and Harriman Park, and concentrations of ethylbenzene and xylenes were lower. Toluene in Woodward was highest among all the locations and all the compounds (greater than 1.74 µg m^{-3}). In Camden, total mean BTEX concentrations were lower than in the other three locations by a factor of 2.3–2.8, which was expected for a small city away from major highways and several point sources. Concentrations were similar or slightly higher in Week 2, although this difference was only significant for BTEX in the Camden park and ethylbenzene in the Camden residential samples.

For TEX, concentrations were lower in parks than at nearby residences; the average differences were 6.7–19% for toluene, 3.7–39% for ethylbenzene, 4.5–27% for m-,p-xylene, and 5.8–29% for o-xylene. The differences were smallest in Harriman Park for all TEX, while the differences were most pronounced in Camden for EX and Woodward for toluene. Benzene was 20–26% lower in parks in Camden and Woodward but 5.6–7.4% higher in parks in North Birmingham and Harriman Park.

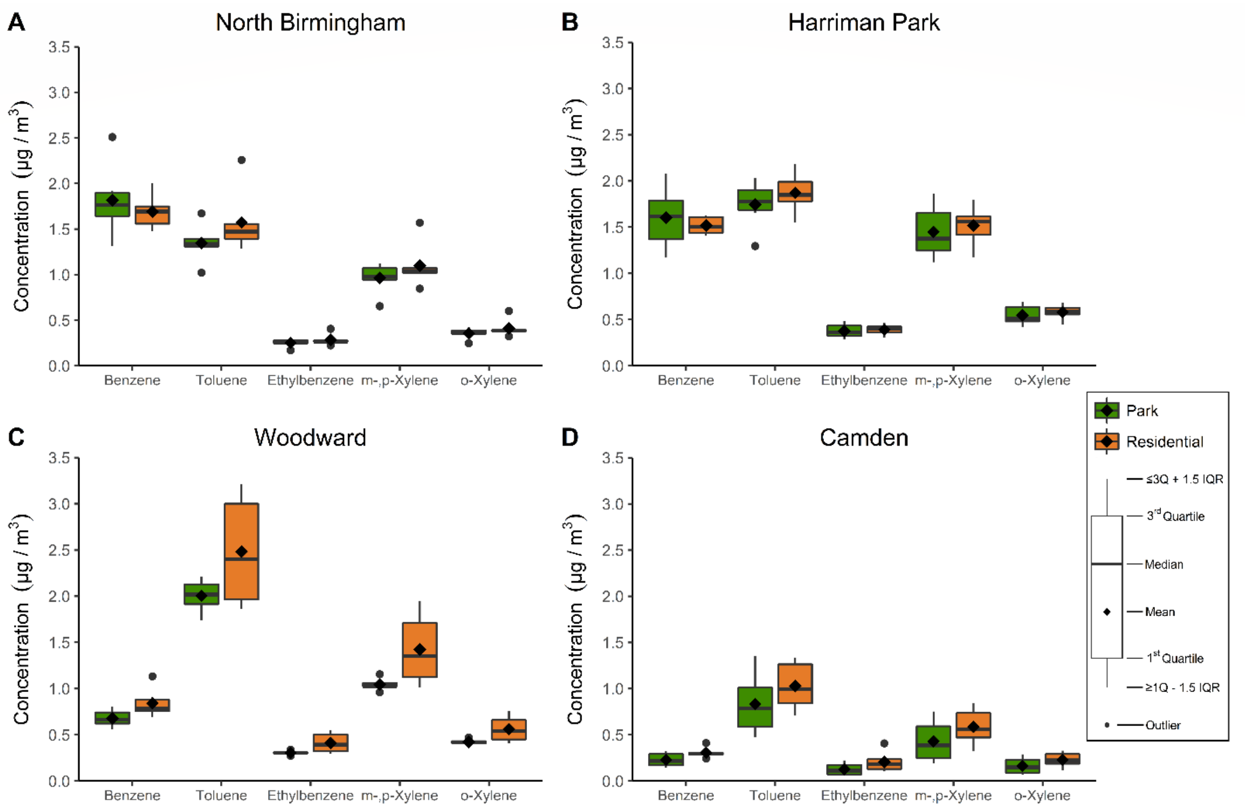

Figure 2.5.1. BTEX concentrations grouped by site type in: (A) North Birmingham, (B) Harriman Park, (C) Woodward, and (D) Camden. Each box represents six data points. Upper whisker is the maximum observation less than 1.5 times the inter-quartile range over the 3rd quartile, while lower whisker is the similar value under the 1st quartile. Outliers are beyond 1.5 times the interquartile range from the 1st and 3rd quartiles.

Park Effect vs. Distance to Major Roads. Due to motor vehicle emissions, concentrations of VOCs are known to decrease with increasing distance from roads.[46] The distance of sampling sites from nearby roads, and thus the impact of vehicle emissions, varied, so a multiple linear regression model was constructed to discern the effect of site type (park vs. residential) from the impact of vehicle emissions. Regression parameter estimates are presented for each BTEX component in Table 2.5.1. Categorical parameters for location were significant ($p<0.0226$), meaning that BTEX concentrations in each of the four locations were different from each other. Furthermore, site type (i.e., “park” or “residential”) was a statistically significant parameter for

TEX ($p<0.002$) but not benzene ($p=0.332$). Parks exhibited 0.0736–0.351 µg m^{-3} lower concentrations of TEX than surrounding residential areas, with the smallest reduction observed for ethylbenzene and the largest observation observed for toluene.

In the multiple linear regressions, distance to the nearest major road was statistically significant for BTX ($p<0.0207$) but not for ethylbenzene ($p=0.0582$). All estimates were negative, and estimates for BTX ranged in magnitude from 0.0005–0.0019 µg m^{-3} m^{-1}, meaning that BTX decreased by 0.0005–0.0019 µg m^{-3} per meter from a major road.

Table 2.5.1. Multiple linear regression estimates and p-values. Estimates are in µg m^{-3} for all parameters except road distance (µg m^{-3} m^{-1} from road).

Compound	Parameter	Type	Estimate	p-value
Benzene	(Intercept)	-	0.622	0.00035
	North Birmingham	Categorical	1.4	$< 2\times10^{-16}$
	Harriman Park	Categorical	1.05	4.10×10^{-10}
	Woodward	Categorical	0.319	0.0059
	Inside Park	Categorical	-0.0615	0.332
	Road Distance	Numerical	-0.0011	0.0207
Toluene	(Intercept)	-	1.68	7.52×10^{-9}
	North Birmingham	Categorical	0.381	0.00587
	Harriman Park	Categorical	0.45	0.0226
	Woodward	Categorical	1	1.75×10^{-7}
	Inside Park	Categorical	-0.351	0.00043
	Road Distance	Numerical	-0.0019	0.0056
Ethylbenzene	(Intercept)	-	0.298	5.00×10^{-6}
	North Birmingham	Categorical	0.0762	0.0218
	Harriman Park	Categorical	0.147	0.00283
	Woodward	Categorical	0.141	0.00083
	Inside Park	Categorical	-0.0736	0.00201
	Road Distance	Numerical	-0.0003	0.0582
m-,p-Xylene	(Intercept)	-	1.05	4.57×10^{-7}
	North Birmingham	Categorical	0.417	0.00013
	Harriman Park	Categorical	0.666	3.34×10^{-5}
	Woodward	Categorical	0.503	0.00016
	Inside Park	Categorical	-0.253	0.0007
	Road Distance	Numerical	-0.0014	0.00784
o-Xylene	(Intercept)	-	0.398	4.16×10^{-7}
	North Birmingham	Categorical	0.148	0.00028
	Harriman Park	Categorical	0.254	2.78×10^{-5}
	Woodward	Categorical	0.214	2.97×10^{-5}
	Inside Park	Categorical	-0.0983	0.0005
	Road Distance	Numerical	-0.0005	0.00993

BTEX Correlations. Correlation and ratio analyses of BTEX concentrations can provide insight into their likely sources and photochemical age. Table 2.5.2 presents the Spearman rank correlation coefficients for BTEX by location for the combined weeks. In all sites, TEX strongly and positively correlated with each other ($p<0.01$). Benzene correlated less with TEX, if at all; in Camden, benzene was moderately correlated with TEX ($p<0.05$). In Woodward, benzene and EX exhibited a moderately positive ($p<0.05$) correlation with each other, but benzene and toluene did not. In North Birmingham, benzene had a moderately positive ($p<0.05$) correlation with o-xylene but no other compound. In Harriman Park, benzene was negatively correlated with TEX, but no correlation was statistically significant.

Table 2.5.2. Spearman rank correlation coefficients between pollutants, within each site.
* denotes significance at $p<0.05$. ** denotes significance at $p<0.01$.
*** denotes significance at $p<0.001$.

Site		Benzene	Toluene	Ethylbenzene	m-,p-Xylene
North Birmingham	Toluene	0.57			
	Ethylbenzene	0.57	0.91^{***}		
	m-,p-Xylene	0.47	0.86^{***}	0.98^{***}	
	o-Xylene	0.69^{*}	0.96^{***}	0.96^{***}	0.92^{***}
Harriman Park	Toluene	-0.09			
	Ethylbenzene	-0.28	0.87^{***}		
	m-,p-Xylene	-0.31	0.87^{***}	0.99^{***}	
	o-Xylene	-0.29	0.90^{***}	0.97^{***}	0.97^{***}
Woodward	Toluene	0.48			
	Ethylbenzene	0.72^{**}	0.83^{***}		
	m-,p-Xylene	0.68^{*}	0.83^{***}	0.99^{***}	
	o-Xylene	0.69^{*}	0.81^{**}	0.97^{***}	0.99^{***}
Camden	Toluene	0.64^{*}			
	Ethylbenzene	0.78^{**}	0.94^{***}		
	m-,p-Xylene	0.78^{**}	0.94^{***}	0.99^{***}	
	o-Xylene	0.78^{**}	0.94^{***}	0.99^{***}	1^{***}

BTEX Ratios. Toluene:benzene (T:B) and m-,p-xylene:ethylbenzene (m-,p-X:E) mass ratios were calculated for each sample; the results were again stratified by location and site type, as shown in Figure 2.5.2 and Table 2.9.8. T:B ratios were exceptionally low in North Birmingham (0.666–1.29) and Harriman Park (0.795–1.56) but moderate in Woodward (2.36–4.03) and Camden (2.48–5.10). No T:B ratios were observed to be statistically greater than 3.0, but T:B ratios in both site types in Harriman Park and North Birmingham were significantly less than 1.5 ($p<0.01$).

In North Birmingham and Harriman Park the range of m-,p-X:E ratios was 3.7–4.0 while Woodward was slightly lower (3.4–3.6). Ratios in Camden were generally lower and more varied, ranging from 2.1 to 3.7; residential m-,p-X:E ratios had a lower mean (3.0) compared to the park ratios (3.4), although this difference was not statistically significant. A one-sided t-test on m-,p-X:E ratios showed that ratios in both site types in North Birmingham and Harriman Park were significantly greater than 3.6 ($p<0.01$) while ratios in Woodward and Camden were not.

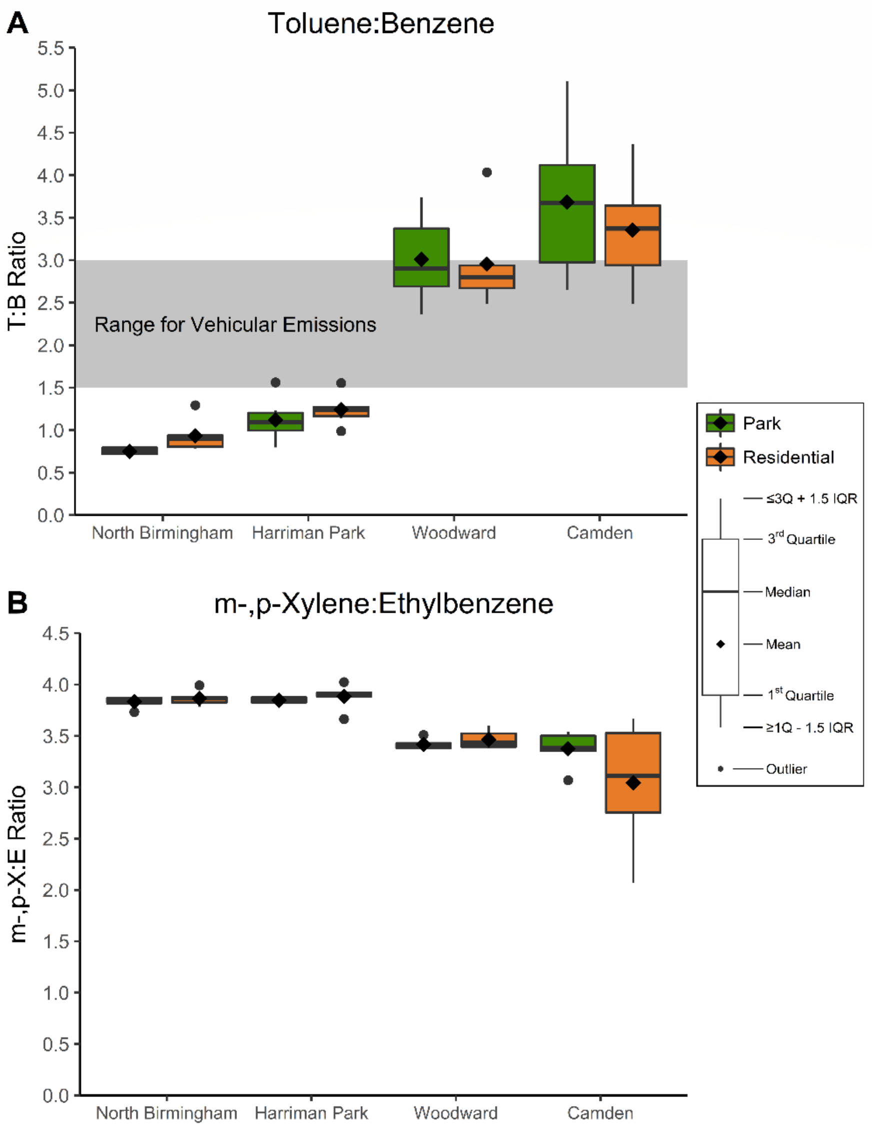

Figure 2.5.2. Measured ratios of (A) toluene:benzene (T:B) ratios and (B) m-,p-xylene:ethylbenzene (m-,p-X:E) by location and site type. Each box represents six data points. Upper whisker is the maximum observation less than 1.5 times the inter-quartile range over the 3rd quartile, while lower whisker is the similar value under the 1st quartile. Outliers are beyond 1.5 times the interquartile range from the 1st and 3rd quartiles.

2.6 Discussion

Comparison to BTEX in Other Studies. Present results were compared to levels found in outdoor air in studies included in a review on BTEX exposure, which suggested that deleterious health effects occur at BTEX levels far below their EPA Reference Concentrations for Inhalation Exposure of 30, 5,000, 1,000, and 100 μg m^{-3}, respectively.[7,47–50] The EPA inhalation Reference Concentration is defined as an estimate "of a daily inhalation exposure of the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime" but only considers noncancerous health effects.[47] The risk for cancerous health effects by exposure to benzene can be assessed through the inhalation unit risk (IUR). The IUR is defined as an increase of a certain amount of risk per concentration unit of carcinogen; for benzene, the IUR ranges from 2.2×10^{-6} to 7.8×10^{-6} per μg m^{-3}.[47] The benzene IUR can be translated to state that 0.13–0.45 μg m^{-3} yields one additional case of cancer per million people. Camden means were within the IUR range while Woodward, Harriman Park, and North Birmingham means were a factor of 2.6, 5.4, and 6.0, respectively, greater than the IUR median value.

In the present study, TEX concentrations at all locations were below the levels found in outdoor air presented in the review[7] and below the lowest effect concentrations provided by Herberth et al. (2014)[51] and Wallner et al. (2012).[52] Benzene concentrations in North Birmingham and Harriman Park were at the lower end of the range of outdoor air levels but above the lowest concentration at which effects have been seen.[7,51] BTEX concentrations in the present study were mostly below annual means measured in similar studies in Naples, Italy[53] and Birmingham, UK,[54] although the latter study reported benzene concentrations similar to those found in North Birmingham and Harriman Park. BTEX concentrations were within the ranges found in Windsor, Ontario,[11] with the exception of concentrations in Camden being generally lower. Compared to the results of a study in Dunkerque, France during the summertime,[55] BTEX levels in North Birmingham, Harriman Park, and Woodward were comparable to those found in urban or industrial settings in France, while levels in Camden were below those documented in a rural setting in France.

The Park Effect. The multiple linear regressions showed existence of a park effect in TEX, with lower concentrations in the park compared to the surrounding residential area. To the best of our knowledge, this is the first field study to identify reduced concentrations of individual TEX in parks. This finding builds upon prior studies in Scandinavia, where one identified a reduction in concentrations of benzene and toluene in parks[28] and another identified a reduction of total VOCs in tree canopies.[30] This result is also supported by the results of laboratory chamber experiments that examined uptake of these compounds by plants.[23,24,26,27]

Several factors likely contributed to the reduction of TEX in parks. First, the size of the park and amount of vegetation are likely significant parameters, as the smallest reduction in TEX in parks occurred in the smallest park (Harriman Park). Furthermore, the sampling campaign was conducted in the summer where leaf area is at a maximum, providing the optimal interface for plant uptake. Foliage was determined to have a significant influence on BTEX concentrations in large areas of vegetation in several studies,[29,30] although a recent study determined that foliage was not significant.[31] It was also suggested in an open top chamber experiment that uptake of benzene and toluene at ambient levels may depend on the metabolic activity of the plant.[25] This suggests that the overall plant metabolic activity was high enough to allow for appreciable uptake of TEX. Furthermore, Blume et al. (2002)[56] showed that although surface soil microbial biomass was constant throughout the year, microbial activity increased by up to 83% in summertime temperatures. Finally, the wind speed, as shown in Figure 2.9.2 and Figure 2.9.5, was relatively low and had significant fractions of calm periods recorded, allowing for any uptake by areas of dense vegetation to register as reduced ambient concentrations.

Benzene did not display a park effect, however. Figure 2.5.1 shows that benzene levels were lower in parks in Woodward and Camden but higher in parks in North Birmingham and Harriman Park. These differences negated each other when combining the entire dataset for the multiple linear regression, which prevented the identification of a park effect across all locations. Benzene concentrations may have been higher in the parks in North Birmingham and Harriman Park because these two locations are close (1.5 km and 0.72 km, respectively) to a coke production plant that emitted 32,400 kg of benzene in 2016,[41] and at both locations, the park sites were closer to the coke plant than were the residential sites. Thus, higher concentrations would be expected in the parks if the coke plant is a dominant source of benzene in this area.

Source Characterization. Spearman rank correlations presented in Table 2.5.2 show that the individual BTEX compounds correlated strongly and significantly with each other across several locations in urban environments, even in different cities. Our analysis suggests that all BTEX came from a shared source in Camden and likely Woodward, while all TEX came from a shared source in North Birmingham and Harriman Park. As onroad emissions are the predominant source of TEX and a major source of benzene,[8] it is likely that this shared source was vehicular exhaust. However, there may be a separate source or sources of benzene in North Birmingham and Harriman Park.

Analysis of T:B ratios shows that vehicles were likely the dominant source in Camden and Woodward but not in Harriman Park and North Birmingham. The low T:B ratios at the latter two sites suggest a separate source of benzene near these locations. Indeed, North Birmingham and Harriman Park are situated between a group of point sources that emit large amounts of benzene, while Woodward and Camden are much further from similar facilities. According to the TRI, the two coke production plants near North Birmingham and Harriman Park have T:B ratios in their emissions of 0.582 and 0.492; these values are only slightly lower than the lowest values found in North Birmingham (0.666) and Harriman Park (0.795). Clearly, these industrial sources impacted North Birmingham and Harriman Park.

The m-,p-X:E ratios in North Birmingham and Harriman Park were significantly greater than 3.6, the value expected for fresh emissions, regardless of source.[16] Although the m-,p-X:E ratios in Woodward and the park in Camden were slightly lower, these ratios were also higher than most m-,p-X:E ratios in urban settings as reported by Miller et al. (2012)[11] and Monod et al. (2001).[17] Residential ratios in Camden were comparable to the reported value (median ± 2σ) of urban background sites in the latter review (3.03±0.79 compared to this study's 3.11±1.2).[17] Thus, the high m-,p-X:E ratios across all locations but the Camden residential sites indicate air masses relatively close to emission sources and yet unaffected by photochemical aging. Exceptionally high ratios in North Birmingham and Harriman Park suggest that these sites are particularly close to BTEX sources.

In summary, most BTEX in Woodward and Camden were likely due to traffic emissions because of the strong correlation between species, moderate T:B ratios, and moderate m-,p-X:E ratios. In North Birmingham and Harriman Park, TEX were also likely attributable to traffic emissions due to the strong correlation between species. However, there was likely another source of benzene in these locations, as suggested by the low T:B ratios and high m-,p-X:E ratios. Although BTEX levels were significantly different in each location, the similarity in results for North Birmingham and Harriman Park was likely due to their proximity to both large point sources and to each other.

Community Impacts. Importantly, this study considered input from community members in the placement of organic vapor monitors, which allowed for the integration of community science in determining local exposure to BTEX. Upon analysis of the samples, the results were disseminated to the specific community members that participated in the study, along with BTEX ToxGuides from the Agency for Toxic Substances and Disease Registry.[57–60] An example of the pamphlet shared with participants can be found in Figure 2.9.8. The conveyance of results strengthened the relationship between the present researchers and communities and fostered curiosity in air quality, public health, and the scientific method.

2.7 Conclusions and Future Work

Passive samplers were deployed in city parks and neighboring residential areas in two cities in Alabama for two weeks in July 2017 to evaluate whether parks can mitigate exposure to BTEX in air. The measured BTEX concentrations were within the range of expected values for summertime in urban and rural environments. Levels of each BTEX compound were significantly different between locations, and TEX concentrations in parks were slightly lower and significantly different than in the surrounding residential areas.

High Spearman rank correlation coefficients suggest a common source or source profile for BTEX in Camden and Woodward and for TEX in North Birmingham and Harriman Park. T:B ratios were within the standard range for vehicular emissions in Camden and Woodward but substantially lower in North Birmingham and Harriman Park; in conjunction with the correlation analysis, this suggests that there was a separate, industrial source of benzene nearby. At all sites except residential ones in Camden, the m-,p-X:E ratio was sufficiently high to suggest a sampled air mass with a young photochemical age.

Future work should further explore the effect of phytoremediation on ambient BTEX in both field and laboratory settings. Field campaigns would benefit by increasing spatial (i.e., sampler density) or temporal (i.e., active sampling) resolution to optimize statistical power. Analyzing vegetation for evidence of BTEX uptake would also be informative. A short study could be conducted with active samplers to assess the presence of a diurnal pattern in BTEX uptake. Future studies should also involve a sampling campaign expanded to cover the full year in order to assess seasonal effects, such as loss of deciduous tree leaf cover and change of microbial activity in the rhizosphere. Field studies would also benefit by placing samplers equidistant from roads (both inside and outside of parks) to negate influence from vehicular emissions. In the controlled environment of a laboratory, more rigorous chamber studies are needed in which a group of plants is exposed to ambient BTEX levels. These studies would benefit from additional studies employing a chamber with an open top where a stream with a constant concentration BTEX can diffuse inward, simulating a more realistic environment.

2.8 Acknowledgements

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2.9 Supporting Information

Figure 2.9.1. Picture of deployed passive organic vapor monitor and iButton with plastic housing.

Table 2.9.1. Temperature and precipitation data during the sampling campaign from stations in Birmingham (WBAN ID 13876) and Selma, AL (WBAN ID 63897). Temperature is summarized as mean ± standard deviation and precipitation is total summation. The weather station in Selma, AL is the closest one to the sampling location in Camden, AL. Data acquired from the National Centers for Environmental Information.[45] The transition between Week 1 and Week 2 took place on July 15, 2017.

Sampling Campaign	Date	Birmingham		Selma	
		Temperature [°C]	Precipitation [mm]	Temperature [°C]	Precipitation [mm]
Week 1	July 8, 2017	26 ± 2.3	TRACE	26 ± 2.8	15.7
	July 9, 2017	26 ± 3.7	0	25 ± 3.7	1.8
	July 10, 2017	27 ± 5.1	0	26 ± 3.4	0
	July 11, 2017	25 ± 2.8	35.3	26 ± 3.3	0
	July 12, 2017	27 ± 3.2	0	26 ± 2.9	0
	July 13, 2017	28 ± 2.8	TRACE	27 ± 3.5	0
	July 14, 2017	26 ± 2.7	29	27 ± 3.9	0
------------	July 15, 2017	25 ± 2.2	3	27 ± 3.5	0.5
Week 2	July 16, 2017	25 ± 2.7	11.4	25 ± 2.4	0
	July 17, 2017	27 ± 3.0	0	26 ± 2.6	4.3
	July 18, 2017	27 ± 3.9	0	26 ± 3.7	0
	July 19, 2017	29 ± 3.9	0	27 ± 4.1	0
	July 20, 2017	29 ± 3.3	0	28 ± 4.1	0
	July 21, 2017	30 ± 3.6	0	26 ± 3.9	0.8
	July 22, 2017	29 ± 3.0	0	27 ± 4.4	0

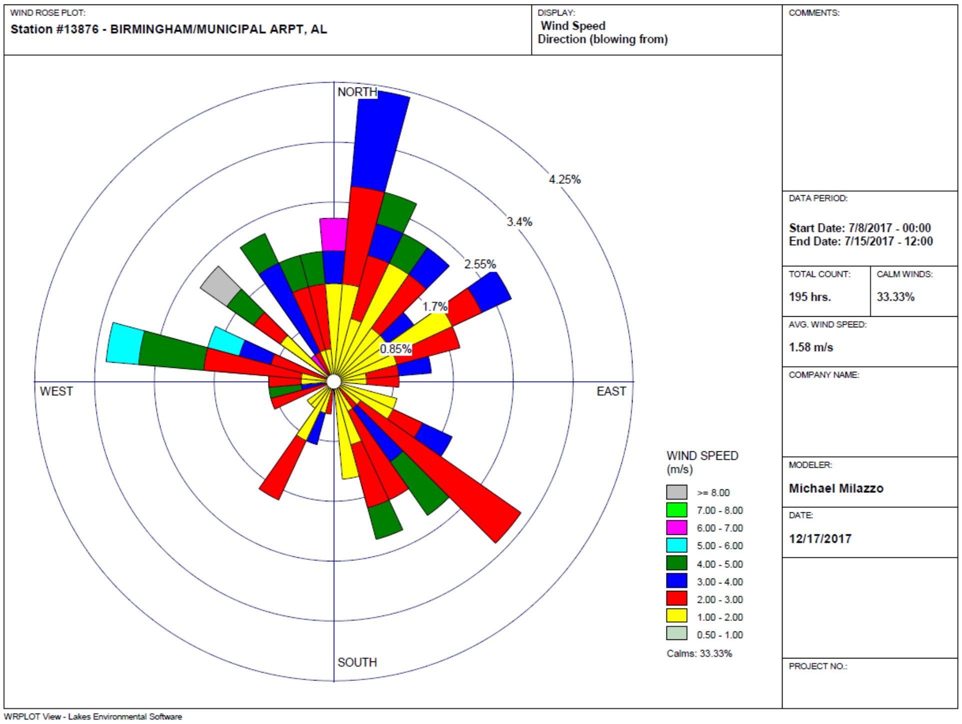


Figure 2.9.2. Wind rose plot[61] during Week 1 from station in Birmingham, AL (WBAN ID 13876). Data acquired from the National Centers for Environmental Information.[45]

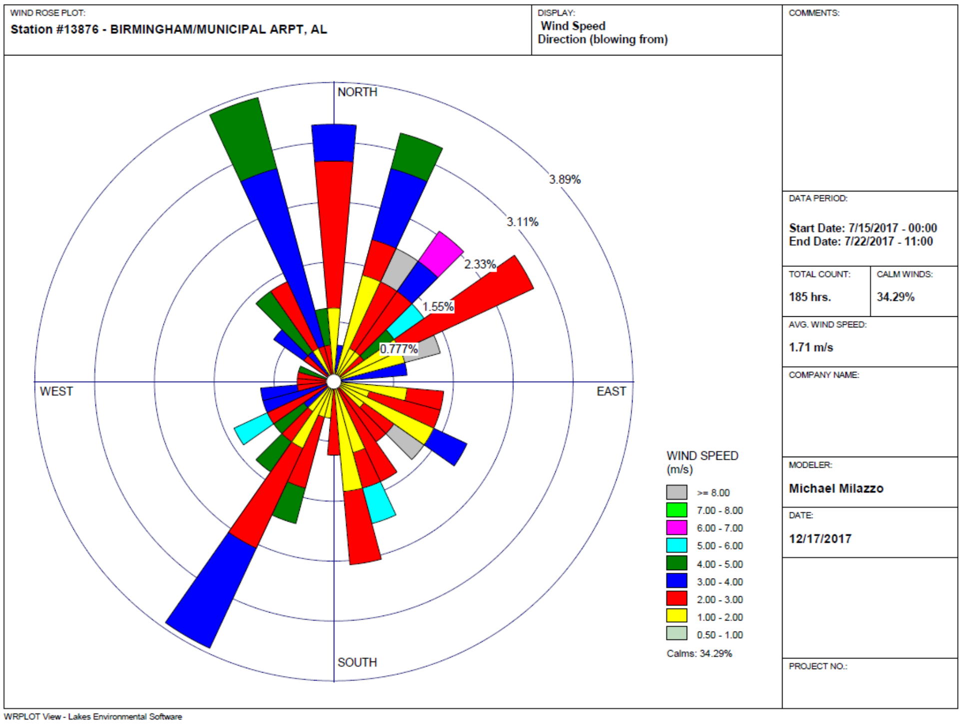


Figure 2.9.3. Wind rose plot[61] during Week 2 from station in Birmingham, AL (WBAN ID 13876). Data acquired from the National Centers for Environmental Information.[45]

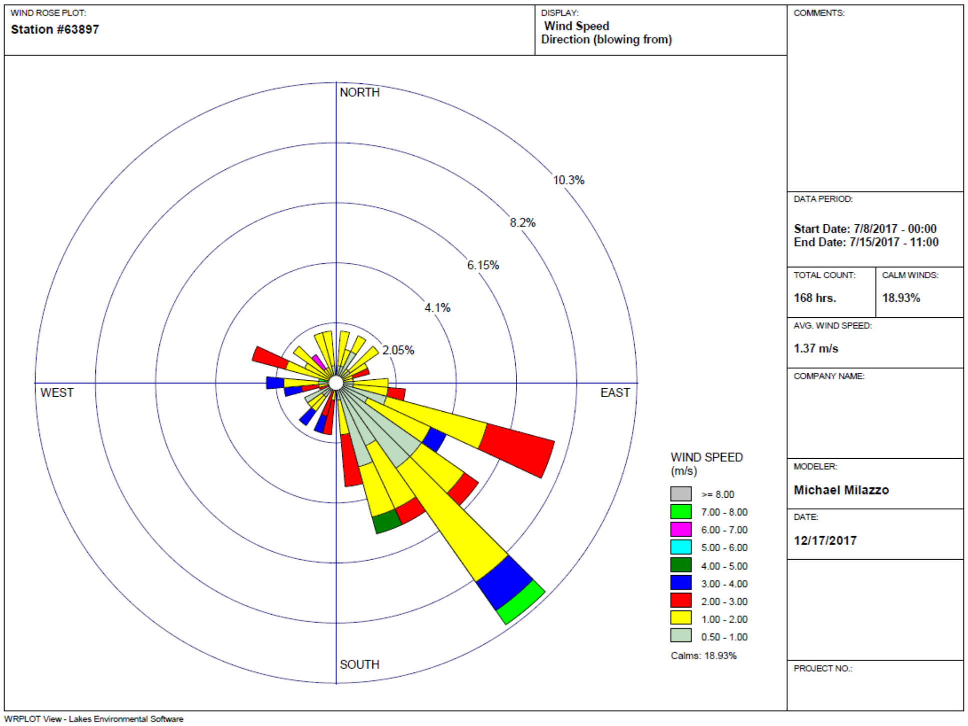


Figure 2.9.4. Wind rose plot[61] during Week 1 from station nearest Camden in Selma, AL (WBAN ID 63897). Data acquired from the National Centers for Environmental Information.[45]

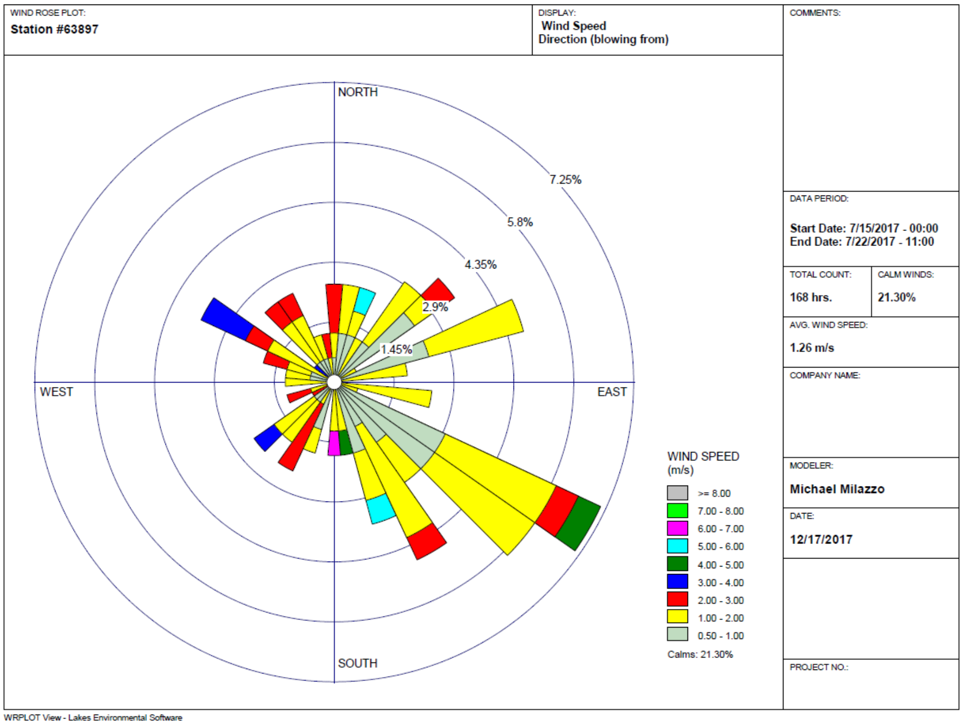


Figure 2.9.5. Wind rose plot[61] during Week 2 from station nearest Camden in Selma, AL (WBAN ID 63897). Data acquired from the National Centers for Environmental Information.[45]

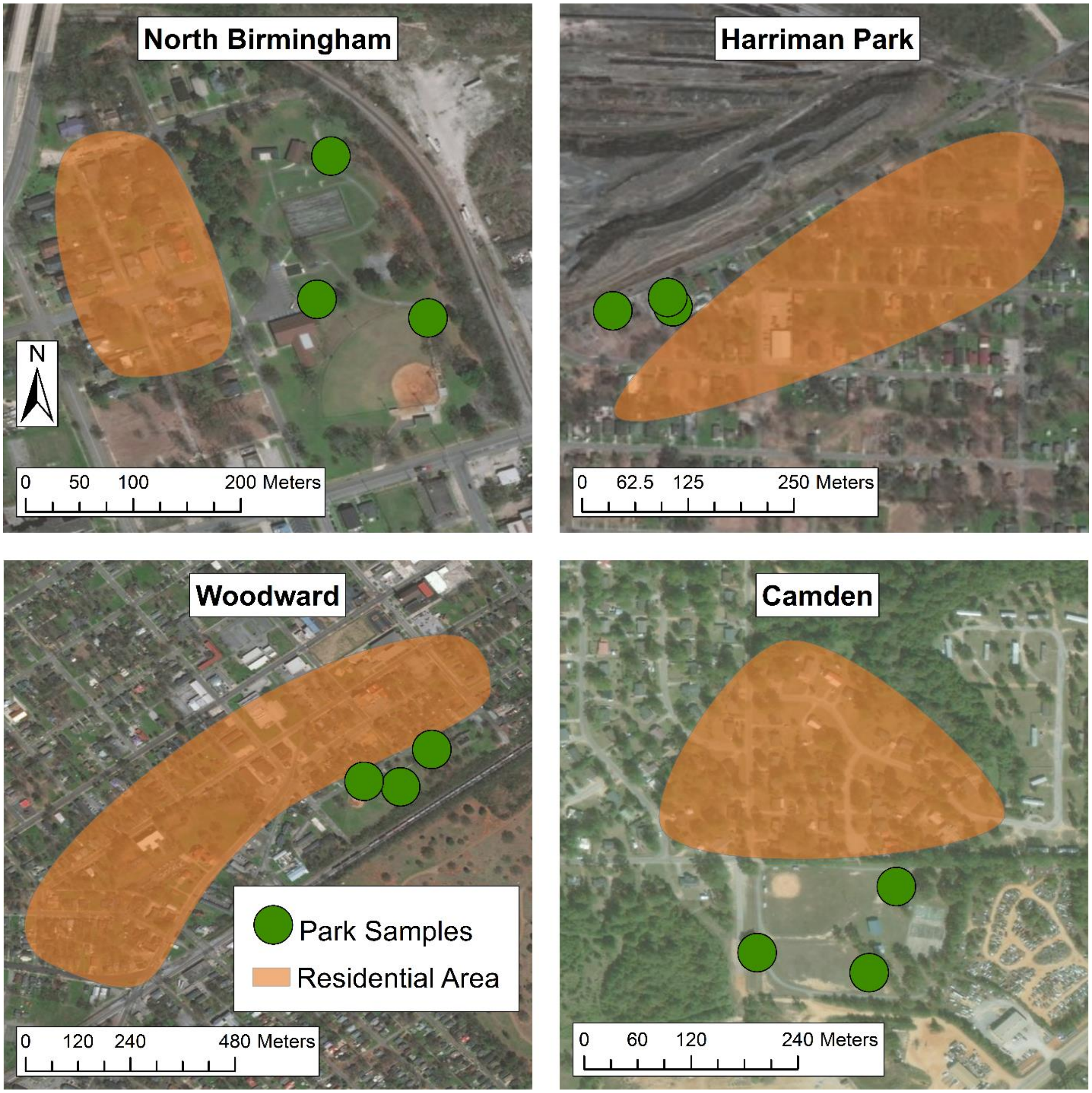


Figure 2.9.6. Sampling locations in (clockwise from top-left): North Birmingham, Harriman Park, Woodward, and Camden.

Table 2.9.2. GC-MS method detection limits for BTEX and surrogate standard [ng mL^{-1}], conducted per EPA Method Detection Limit Procedure.[42]

Benzene	Toluene	Ethylbenzene	m-,p-Xylene	o-Xylene	p-Bromofluorobenzene
31.4	23.9	3.80	5.76	5.67	4.15

Table 2.9.3. Method, trip, and reagent blanks (n=4 each) for BTEX and surrogate standard [ng mL^{-1}]. NF signifies “not found” while * denotes 25% of blanks (1 of 4) were not detected.

Blank type	Benzene	Toluene	Ethylbenzene	m-,p-Xylene	o-Xylene	p-Bromofluorobenzene
Method blanks	NF	25.9 ± 1.6*	NF	NF	NF	56.4 ± 4.1
Trip blanks	NF	29.9 ± 1.3	NF	NF	NF	63.2 ± 2.1
Reagent blanks	NF	NF	NF	NF	NF	NF

Table 2.9.4. BTEX and surrogate standard desorption efficiency recovery [%]

Mass Loaded [ng]	Benzene	Toluene	Ethylbenzene	m-,p-Xylene	o-Xylene	p-Bromofluorobenzene
75	92.6	130	73.2	80.6	81.7	57.1
	122	138	83.9	96.0	92.1	70.0
	133	145	88.6	103	102	72.5
150	108	110	79.1	86.4	86.5	64.1
	117	121	89.2	93.5	94.2	70.8
	106	116	84.1	93.6	91.9	65.7
750	102	111	109	112	105	89.6
	96.3	119	114	117	109	78.4
	89.7	109	105	109	102	74.4
1875	88.3	97.2	100	103	98.8	86.5
	99.2	113	117	118	112	76.5
	93.7	108	113	113	106	80.3

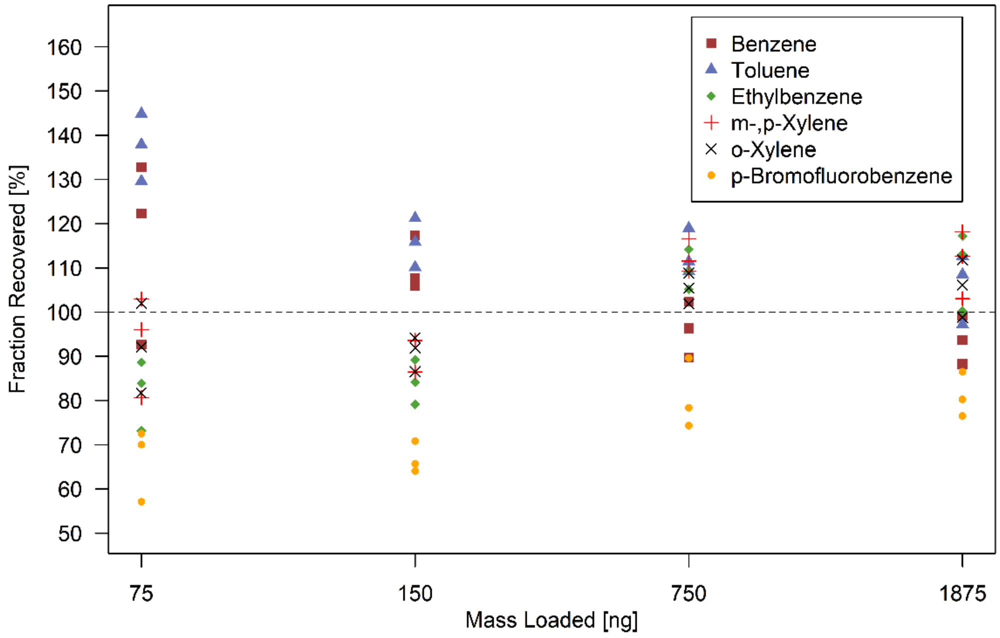


Figure 2.9.7. BTEX and surrogate standard desorption efficiency tests. Dashed line is 100% recovery.

Table 2.9.5. All BTEX concentrations by site and week [µg m^{-3}].

Name	Type	Site	Week	Benzene	Toluene	Ethylbenzene	m-,p-Xylene	o-Xylene	Surrogate recovery efficiency [%]
North Birmingham	Park	A	1	2.51	1.67	0.291	1.13	0.426	71.1
			2	1.83	1.30	0.256	0.989	0.366	56.4
		B	1	1.70	1.36	0.251	0.936	0.353	72.5
			2	1.92	1.41	0.288	1.10	0.394	66.7
		C	1	1.31	1.02	0.170	0.654	0.247	61.0
			2	1.62	1.32	0.251	0.975	0.350	60.6
	Residential	A	1	1.75	1.51	0.266	1.02	0.392	62.4
			2	1.53	1.44	0.279	1.08	0.385	59.4
		B	1	1.64	1.29	0.224	0.846	0.322	58.5
			2	1.47	1.38	0.264	1.05	0.377	67.2
		C	1	2.01	1.57	0.267	1.03	0.395	58.2
			2	1.75	2.26	0.405	1.57	0.600	63.7
Harriman Park	Park	A	1	1.83	1.77	0.357	1.37	0.515	65.5
			2	1.57	1.94	0.459	1.75	0.675	72.4
		B	1	2.08	1.66	0.312	1.21	0.472	68.5
			2	1.17	1.30	0.289	1.12	0.422	65.6
		C	1	1.66	1.79	0.362	1.39	0.504	62.1
			2	1.30	2.03	0.480	1.86	0.694	63.5
	Residential	A	1	1.63	1.86	0.350	1.37	0.548	61.3
			2	1.44	1.76	0.394	1.54	0.577	67.5
		B	1	1.57	1.55	0.303	1.18	0.448	57.1
			2	1.44	1.84	0.405	1.63	0.592	71.1
		C	1	1.62	2.03	0.431	1.58	0.640	60.4
			2	1.41	2.18	0.463	1.80	0.678	81.7
Woodward	Park	A	1	0.608	2.14	0.303	1.03	0.416	60.5
			2	0.558	2.09	0.305	1.03	0.418	58.3
		B	1	0.805	1.90	0.312	1.07	0.437	58.7
			2	0.667	1.95	0.303	1.03	0.407	56.8
		C	1	0.660	1.74	0.274	0.960	0.390	52.9
			2	0.768	2.21	0.339	1.15	0.471	64.5
	Residential	A	1	0.751	1.87	0.293	1.01	0.410	52.7
			2	0.800	2.11	0.330	1.11	0.445	59.7
		B	1	0.693	1.91	0.319	1.15	0.468	47.1
			2	0.906	2.69	0.458	1.55	0.619	69.0
		C	1	0.769	3.10	0.549	1.95	0.755	55.9
			2	1.13	3.21	0.518	1.76	0.674	61.2
Camden	Park	A	1	0.142	0.542	0.065	0.230	0.084	53.1
			2	0.301	1.06	0.186	0.632	0.242	50.5
		B	1	0.170	0.716	0.085	0.300	0.108	54.9
			2	0.265	1.35	0.225	0.753	0.290	54.8
		C	1	0.169	0.472	0.062	0.191	0.073	54.1
			2	0.325	0.861	0.141	0.473	0.189	46.0
	Residential	A	1	0.291	0.830	0.142	0.522	0.219	59.5
			2	0.306	1.34	0.407	0.844	0.329	54.6
		B	1	0.285	0.707	0.108	0.321	0.115	60.6
			2	0.306	1.12	0.223	0.598	0.230	57.9
		C	1	0.244	0.869	0.125	0.454	0.176	57.7
			2	0.412	1.31	0.241	0.783	0.312	66.2

Table 2.9.6. Week 1 BTEX concentrations [μg m^{-3}], grouped by park name and location type.

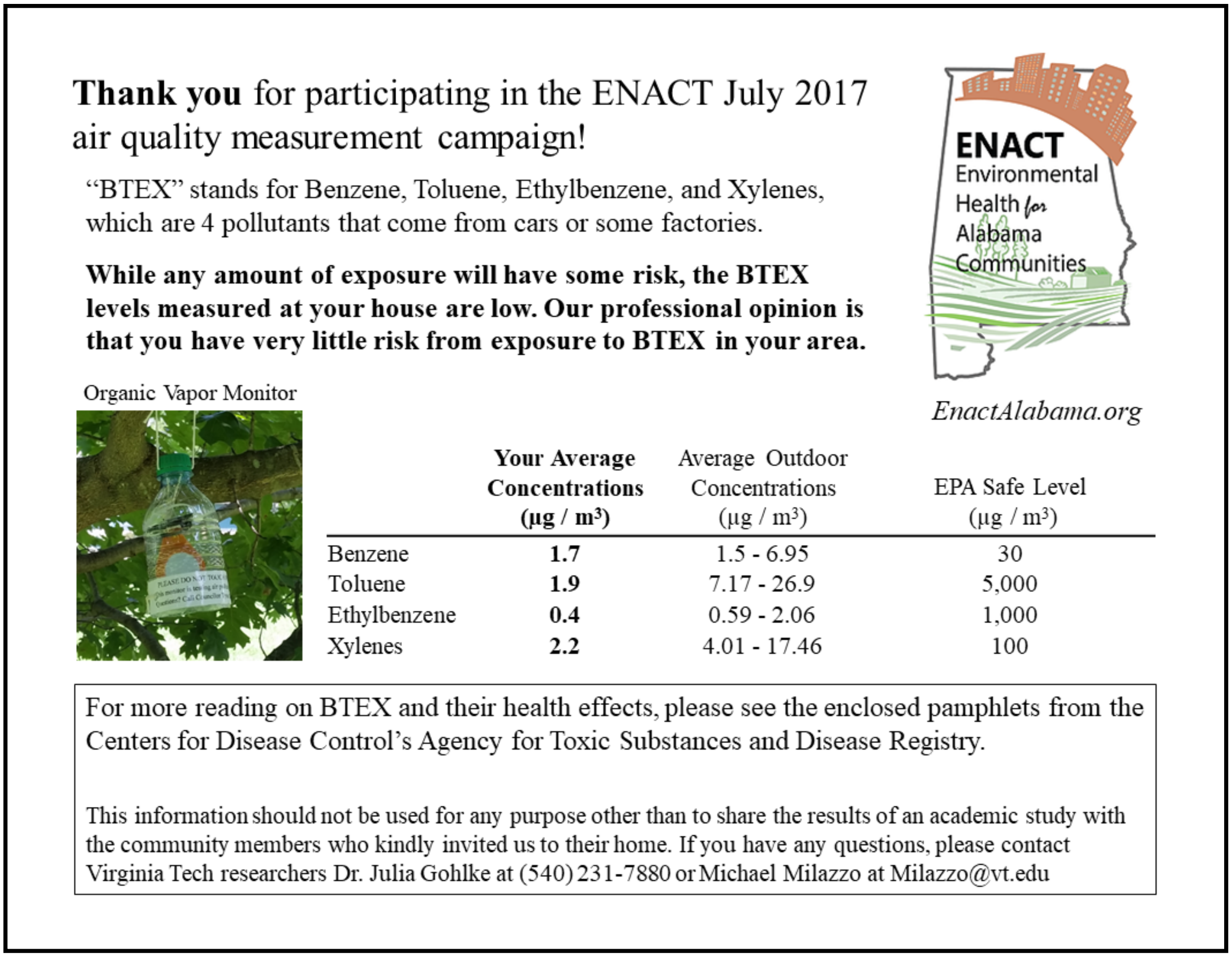
Name	Type	Benzene	Toluene	Ethylbenzene	m-,p-Xylene	o-Xylene	Surrogate recovery efficiency [%]
North Birmingham	Park	1.84 ± 0.610	1.35 ± 0.325	0.237 ± 0.0614	0.905 ± 0.238	0.342 ± 0.0900	68.2 ± 6.24
	Residential	1.80 ± 0.189	1.46 ± 0.150	0.252 ± 0.0248	0.963 ± 0.102	0.370 ± 0.0415	59.7 ± 2.37
Harriman Park	Park	1.86 ± 0.211	1.74 ± 0.0715	0.344 ± 0.0274	1.32 ± 0.0992	0.497 ± 0.0223	65.4 ± 3.21
	Residential	1.61 ± 0.0310	1.82 ± 0.243	0.362 ± 0.0650	1.38 ± 0.202	0.546 ± 0.0958	59.6 ± 2.22
Woodward	Park	0.691 ± 0.102	1.93 ± 0.204	0.296 ± 0.0201	1.02 ± 0.0566	0.414 ± 0.0235	57.4 ± 3.95
	Residential	0.738 ± 0.0395	2.29 ± 0.701	0.387 ± 0.141	1.37 ± 0.505	0.544 ± 0.185	51.9 ± 4.41
Camden	Park	0.160 ± 0.0161	0.576 ± 0.126	0.0707 ± 0.0124	0.240 ± 0.0556	0.0884 ± 0.0179	54.1 ± 0.905
	Residential	0.273 ± 0.0252	0.802 ± 0.0847	0.125 ± 0.0170	0.432 ± 0.102	0.170 ± 0.0524	59.3 ± 1.46

Table 2.9.7. Week 2 BTEX concentrations [μg m^{-3}], grouped by park name and location type.

Name	Type	Benzene	Toluene	Ethylbenzene	m-,p-Xylene	o-Xylene	Surrogate recovery efficiency [%]
North Birmingham	Park	1.79 ± 0.153	1.34 ± 0.0560	0.265 ± 0.0201	1.02 ± 0.0674	0.370 ± 0.0226	61.3 ± 5.16
	Residential	1.58 ± 0.143	1.69 ± 0.492	0.316 ± 0.0776	1.23 ± 0.291	0.454 ± 0.127	63.5 ± 3.92
Harriman Park	Park	1.35 ± 0.206	1.76 ± 0.401	0.409 ± 0.105	1.58 ± 0.400	0.597 ± 0.152	67.2 ± 4.68
	Residential	1.43 ± 0.0199	1.93 ± 0.225	0.420 ± 0.0369	1.66 ± 0.130	0.616 ± 0.0547	73.4 ± 7.34
Woodward	Park	0.665 ± 0.105	2.08 ± 0.130	0.316 ± 0.0201	1.07 ± 0.0737	0.432 ± 0.0342	59.8 ± 4.10
	Residential	0.946 ± 0.170	2.67 ± 0.548	0.436 ± 0.0962	1.48 ± 0.331	0.579 ± 0.119	63.3 ± 5.02
Camden	Park	0.297 ± 0.0304	1.09 ± 0.246	0.184 ± 0.0418	0.620 ± 0.140	0.240 ± 0.0503	50.4 ± 4.39
	Residential	0.341 ± 0.0609	1.26 ± 0.118	0.290 ± 0.102	0.742 ± 0.128	0.290 ± 0.0529	59.6 ± 5.95

Table 2.9.8. Toluene:benzene (T:B) and m-,p-xylene:ethylbenzene (m-p-X:E) mass ratios (mean ± standard deviation).

		Week 1		Week 2	
Name	Type	T:B	m-,p-X:E	T:B	m-,p-X:E
North Birmingham	Park	0.747 ± 0.0710	3.81 ± 0.0719	0.753 ± 0.0516	3.85 ± 0.0375
	Residential	0.810 ± 0.0443	3.82 ± 0.0367	1.06 ± 0.206	3.92 ± 0.0671
Harriman Park	Park	0.946 ± 0.141	3.84 ± 0.0179	1.30 ± 0.235	3.86 ± 0.0438
	Residential	1.13 ± 0.133	3.82 ± 0.140	1.35 ± 0.178	3.94 ± 0.0713
Woodward	Park	2.84 ± 0.606	3.44 ± 0.0628	3.18 ± 0.484	3.39 ± 0.0176
	Residential	3.09 ± 0.827	3.54 ± 0.0735	2.82 ± 0.165	3.39 ± 0.0132
Camden	Park	3.61 ± 0.737	3.38 ± 0.269	3.76 ± 1.24	3.37 ± 0.0313
	Residential	2.97 ± 0.546	3.42 ± 0.391	3.74 ± 0.595	2.67 ± 0.591



Thank you for participating in the ENACT July 2017 air quality measurement campaign!

ENACT
Environmental
Health for
Alabama
Communities

EnactAlabama.org

"BTEX" stands for Benzene, Toluene, Ethylbenzene, and Xylenes, which are 4 pollutants that come from cars or some factories.

While any amount of exposure will have some risk, the BTEX levels measured at your house are low. Our professional opinion is that you have very little risk from exposure to BTEX in your area.

Organic Vapor Monitor

	Your Average Concentrations (μg / m^3)	Average Outdoor Concentrations (μg / m^3)	EPA Safe Level (μg / m^3)
Benzene	**1.7**	1.5 - 6.95	30
Toluene	**1.9**	7.17 - 26.9	5,000
Ethylbenzene	**0.4**	0.59 - 2.06	1,000
Xylenes	**2.2**	4.01 - 17.46	100

For more reading on BTEX and their health effects, please see the enclosed pamphlets from the Centers for Disease Control's Agency for Toxic Substances and Disease Registry.

This information should not be used for any purpose other than to share the results of an academic study with the community members who kindly invited us to their home. If you have any questions, please contact Virginia Tech researchers Dr. Julia Gohlke at (540) 231-7880 or Michael Milazzo at Milazzo@vt.edu

Figure 2.9.8. Example pamphlet distributed to community members who allowed deployment of passive samplers on their property. "Your Average Concentrations" are the values for the two weeks combined; the example data presented are from Harriman Park, Type Park, Site A. "Average Outdoor Concentrations" are ranges of the studies assessed in Bolden et al. 2015.[7] "EPA Safe Level" are inhalation Reference Concentrations.[47–50]

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Chapter 3. Conclusions

3.1 Conclusions

Passive samplers were deployed in two cities in Alabama to determine whether city parks can mitigate BTEX concentrations and help reduce exposure of local residents to these hazardous air pollutants. Samplers were located inside four parks and in their surrounding residential neighborhoods to identify the existence or absence of a measureable park effect. The measured BTEX concentrations were within the range of expected values for summertime in urban and rural environments. Levels of each BTEX compound were significantly different between locations, and TEX concentrations were slightly lower in parks and significantly different than in the surrounding residential areas. This effect could arise from several factors, including type of vegetation, calm meteorological conditions, and increased summertime leaf area and metabolic rates. Levels of BTX also decreased with increasing distance from a major road, and the rate of decrease was significant.

In Woodward and Camden locations, the toluene:benzene ratios indicated that BTEX most likely originated from vehicular sources, while North Birmingham and Harriman Park had low ratios that suggested a significant industrial source or sources of benzene. These findings were corroborated by a Spearman rank analysis which showed correlation among BTEX at all sites except for benzene in North Birmingham and Harriman Park.

This study identifies the effects of air-phase phytoremediation of TEX in a field campaign in a subtropical environment. This finding builds on prior studies in Scandinavia which identified this effect for benzene and toluene but also presented conflicting results for total VOCs. This study also builds on current research which has established plant uptake and degradation of gaseous BTEX at concentrations comparable to indoor settings through chamber studies; these include small closed chambers with houseplants as well as large open-top chambers. This experiment confirmed existing desorption and analysis methods while optimizing procedures for the specific experimental apparatus employed and compounds of interest.

Importantly, this study considered input from community members in the placement of organic vapor monitors, which allowed for the integration of community science in determining local exposure to BTEX. Upon analysis of the samples, the results were disseminated to the specific community members that participated in the study. The conveyance of results strengthened the relationship between the present researchers and communities and fostered curiosity in air quality, public health, and the scientific method.

3.2 Recommendations for Future Work

Future work on phytoremediation of hazardous air pollutants should explore the research question in both laboratory and field settings. Laboratory experiments should consider large chambers with a diverse set of vegetation enclosed in order to determine the net effect of several plant species with potentially compounding impacts on pollutant uptake. Experiments should also be conducted in laboratory chambers at pollutant concentrations observed in ambient settings so that the impact of the pollutant’s diffusive gradient can be properly quantified. Field campaigns should concentrate samplers in one park in order to produce high spatial density of pollutant concentrations that may present valuable quantitative (i.e., statistical) and qualitative (e.g., heat map) information. Field studies would also benefit by placing samplers equidistant from roads (both inside and outside of parks) to negate influence from vehicular emissions. Extended field campaigns would prove beneficial as they would produce temporal data on a weekly or monthly scale that would provide insight into the seasonality of air-phase phytoremediation. Finally, all field campaigns should include a rigorous ecological audit of the local vegetation both inside and surrounding the area of interest.