

**Potential for City Parks to Reduce Exposure to BTEX in Air**

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Complete List of Authors:	Milazzo, Michael; Virginia Tech, Civil and Environmental Engineering Gohlke, Julia; Virginia Tech, Population Health Sciences Gallagher, Daniel; Virginia Tech, Civil and Environmental Engineering Scott, Anna; Johns Hopkins University, Earth and Planetary Sciences Zaitchik, Benjamin; Johns Hopkins University, Earth and Planetary Sciences Marr, Linsey; Virginia Tech, Civil and Environmental Engineering

Environmental Significance Statement

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5 Benzene, toluene, ethylbenzene, and xylenes (BTEX) in the atmosphere can be harmful to
6 human health and are precursors to the formation of secondary organic aerosol and ozone.
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8 Vegetation has been shown to reduce concentrations of BTEX in chamber studies, but its
9 potential to affect concentrations in outdoor air is not well known. In this work, BTEX levels
10 were quantified in four urban parks and their surrounding residential areas in Alabama. Levels of
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12 TEX, but not benzene, were 3-39% lower in parks compared to residential areas, and the
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14 difference was significant. This work shows that parks can help reduce exposure to certain air
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16 pollutants by a modest amount.
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Potential for City Parks to Reduce Exposure to BTEX in Air

Michael J. Milazzo,^a Julia M. Gohlke,^b Daniel L. Gallagher,^a Anna A. Scott,^c Benjamin F. Zaitchik,^c Linsey C. Marr^{a,*}

^aDepartment of Civil and Environmental Engineering, Virginia Tech, Blacksburg, Virginia, USA

^bDepartment of Population Health Sciences, Virginia Tech, Blacksburg, Virginia, USA

^cDepartment of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, Maryland, USA

*corresponding author. E-mail: lmarr@vt.edu

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 their results lack consensus. To investigate this subject 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. Site type (park vs. residential) was a significant predictor of TEX concentrations, while distance to the nearest major road was a significant predictor of BTX concentrations. In and around two of the parks, toluene:benzene ratios fell outside the range expected for vehicular emissions ($p < 0.01$), suggesting that there were 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 have been impacted by nearby industrial sources of benzene. Results of this study suggest that parks can help reduce exposure to TEX by a modest amount in some situations.

Key words: parks, VOC, trees, air toxics, ecosystem services

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 some 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, according to the US Environmental Protection Agency's 2014 National Emissions Inventory. For TEX, onroad emissions are the predominant source, whereas for benzene, nonpoint emissions are higher (41%, compared to 35% onroad). In urban environments, concentrations of individual BTEX compounds are often highly correlated with each other,^{8–11} 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 typical of emissions from traffic.^{9,12–14} A m-,p-X:E ratio of approximately 3.6 is expected for fresh emissions, regardless of source,¹⁵ while a lower ratio suggests photochemical aging since m-xylene and p-xylene degrade faster than ethylbenzene.¹⁶

Phytoremediation is the remediation of soil, water, and air quality through the implementation of vegetative systems. In the usual application of phytoremediation for BTEX, plants and trees are used to remediate contaminated groundwater, where the major removal pathway is evapotranspiration.^{17–19} 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 m³ chamber removed benzene from air at a rate of 40–88 mg m⁻³ d⁻¹.²⁰ Sriprapat and Thiravetyan (2013)²¹ 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 m² of plant leaf after 72 hours. In a separate chamber study, household plants exposed to benzene at much lower concentrations of

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3 405–1380 $\mu\text{g m}^{-3}$ removed 48–90% of benzene.²² In an open-top chamber experiment on grass
4 (*Lolium perenne*), exposure to 250 $\mu\text{g m}^{-3}$ of benzene yielded an in-grass concentration of
5 0.55±0.08 ng g^{-1} after 24 hours.²³
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9 Uptake of BTEX by plants depends on several competing factors. Uptake from the air occurs
10 through a plant's leaves, stem, and even rhizosphere. In leaves, the pollutants are absorbed
11 primarily through the stomata-containing abaxial (bottom) side, although adaxial (top)
12 absorption occurs as well.^{21,24} BTEX uptake is also attributable to the plant soil and its microbes,
13 which accounted for 8.1 to 20.4% of uptake of benzene over 24 hours in one study²² and 50.5 to
14 53.0% of uptake of xylenes in another,²⁵ even after the plant was removed.²²
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20 Studies have assessed concentrations of volatile organic compounds (VOCs) in and around city
21 parks, all in a northern temperate climate. Upmanis et al. (2001)²⁶ reported that concentrations of
22 benzene and toluene were at least one-third lower inside parks compared to built-up areas in two
23 Scandinavian cities. Thorsson and Eliasson (2006)²⁷ profiled benzene concentrations inside a
24 large urban park in Sweden and found that the reduction of benzene inside the park was more
25 pronounced in May, when leaves were present, than in February, when leaves were not present.
26 Setälä et al. (2013)²⁸ observed that the total VOC concentration was significantly lower inside vs.
27 outside the tree canopy by 19% in August (i.e., full leaf cover) but not in March (i.e., leaf-free) in
28 two cities in Finland, although the totality of their results suggested that the ability of vegetation
29 to remove air pollutants is minor. In a study in Finland contrasting tree-covered and open areas,
30 Yli-Pelkonen et al. (2017)²⁹ concluded that urban forests did not reduce total anthropogenic VOC
31 levels. Focusing on urban parks in Sweden, Klingberg et al. (2017)³⁰ found that the VOC
32 phenanthrene was not consistently higher or lower before and after leaf emergence. The sum of
33 these results indicate that urban parks play at most a small role in reducing ambient VOC
34 concentrations, and some of the studies attributed part of the effect to greater distance from
35 vehicular sources inside parks.
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48 Studies beyond the northern temperate climate are needed to ascertain the potential of vegetation
49 to reduce ambient BTEX concentrations. The objective of this study is to test the hypothesis that
50 city parks can mitigate BTEX in air and therefore reduce exposure to the compounds. As part of
51 a larger investigation of heat exposure,^{31–34} this study assesses whether parks have a
52 measureable, beneficial effect on ambient BTEX concentrations. The analysis considers
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3 proximity to nearby vehicular and industrial sources. The study took place in Alabama, in the
4 cities of Birmingham and Camden, where air pollution has been identified as a top
5 environmental health priority in the underserved populations of these areas.³¹ An assessment of
6 air toxics in northern Birmingham in 2011–2012 identified BTEX as chemicals of potential
7 concern in this area.³⁵
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11 **Materials and Methods**

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14 *Passive Samplers.* Air samples were collected using diffusion-based organic vapor monitors
15 (OVM; 3500, 3M Occupational Health and Environmental Safety Division, St. Paul, MN)
16 deployed over one-week time periods. The samplers were protected from potential water damage
17 through a rain cover consisting of the top section of a plastic water bottle (Dasani, Atlanta, GA)
18 with the bottom section removed and several holes punched on the sides for ventilation, as
19 shown in Fig. 1S in ESI. An iButton temperature sensor (DS1923, Maxim Integrated Products,
20 Inc., San Jose, CA) was also positioned inside the plastic housing.
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27 *Sample Locations.* Two cities in Alabama were selected for sampling: Birmingham (33.527 °N,
28 86.799 °W; area of 384.8 km²; population of 212,424 in 2016³⁶) in Jefferson County and
29 Camden (31.998 °N, 87.289 °W; area of 10.87 km²; population of 2,560 in 2016³⁶) in rural
30 Wilcox County. They are part of a larger study of heat exposure.^{31–34} Four urban parks in
31 residential areas were selected for sampling on the basis of input from local community
32 members, proximity to large point sources, and accessibility. As shown in Fig. Fig. 1A, North
33 Birmingham Park and Harriman Park are located in the northern part of Birmingham; North
34 Birmingham Park is approximately 2.25 km west-southwest of Harriman Park Park. (“Harriman
35 Park” is the name of the neighborhood that surrounds the park included in this study; the label
36 “park” or “residential” will follow the name of the neighborhood for further clarification.)
37 Woodward Park is located in southwestern Birmingham. As shown in Fig. Fig. 1B, Westgate
38 Park is in Camden and served as a background site; henceforth, this location will be simply
39 referred to as “Camden.”
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50 Characteristics of each park were derived from aerial imagery. North Birmingham Park
51 (approximately 62,700 m²) is primarily covered in grass and has approximately 110 trees. By
52 contrast, the much smaller Harriman Park Park (4,290 m²) has approximately 15 trees. Roughly
53 half of the land defined as Harriman Park Park is grassy while the other half is covered by
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3 pavement or buildings. Woodward Park (43,700 m²) is almost entirely covered in grass and has
4 approximately 100 trees. The park in Camden (28,200 m²) is mostly grassy and has
5 approximately 43 trees. All the parks have some combination of a community center, parking lot,
6 picnic shelter, bathroom, sports courts or fields, swimming pool, and playground.
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11 The sampling locations in Birmingham and Camden were evaluated for potential influence of
12 BTEX sources. Line sources were identified through aerial imagery while the nearest point
13 sources were identified in the EPA's Toxics Release Inventory (TRI); these TRI facilities are
14 mapped in Fig. Fig. 1. North Birmingham Park is bordered by a railroad line along its eastern
15 edge for ~400 m, and the park is ~900 m from an interstate highway at its closest distance.
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17 Furthermore, the TRI shows that North Birmingham Park is 2.4 km northeast of a cast iron pipe
18 manufacturer, 1.5 km southwest of a coke production plant, and 3.9 km southwest of a second
19 coke plant. These facilities emitted thousands of kilograms of BTX in 2016. Harriman Park is 4.5
20 km northeast of the pipe manufacturer, 0.72 km east of the former coke production plant, and 1.8
21 km southwest of the latter coke production plant. The wind roses in Fig. 2S and Fig. 3S in ESI
22 show that the prevailing wind in North Birmingham and Harriman Park varied during the study
23 but was generally northerly. Therefore, these locations were usually downwind of the first coke
24 production plant. The southeastern edge of Woodward Park borders (<100 m) a railroad line, and
25 the park is an approximately 2.4 km upwind of the interstate highway. While Woodward's
26 closest source is an industrial chemical facility 3.5 km north of the park, this facility emitted less
27 than 400 kg of TEX combined in 2016. However, a petroleum-based refined products distributor
28 that is 4.9 km south Woodward emitted hundreds of kilograms of BE and thousands of kilograms
29 of TX in 2016. In Camden, located approximately 180 km southwest, the park is 0.31 km and
30 0.92 km from two state routes. There is one TRI facility (a paper processing plant) in Wilcox
31 County, 16 km west of the Camden park, which was generally downwind during the study, per
32 the wind roses shown in Fig. 4S and Fig. 5S in ESI. Although it did not emit BTEX from 2008 to
33 2016 according to the TRI, the EPA 2014 National Emissions Inventory (NEI) estimated that the
34 paper processing plant emits thousands of kilograms of BTEX per year.³⁷
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51 In each of the four locations, samples were collected at three sites in the park and three sites in
52 the nearby residential area. A "location" describes a park with its surrounding residential area,
53 and a "site" is where a VOC sampler is deployed; each location has multiple sampling sites. Two
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3 community leaders assisted with identification of the residential sampling sites. Criteria for site
4 selection included proximity to the park and major roads, minimal obstruction of the sampler,
5 and consent of residents for researchers to sample on their property. The residential sites near
6 North Birmingham Park were located along its western edge, approximately 14–24 m from the
7 park. Two residential sites near Harriman Park were close to its southern edge while one
8 was significantly further northeast; their distances from the park ranged from 51 to 350 m.
9 Likewise, two residential sites were located near the northwestern edge of Woodward Park while
10 one was situated much further southwest at distances of 17–560 m. All residential sites in
11 Camden were north of the park at distances ranging from 45 to 190 m. All sites were along two-
12 lane streets except the distant Woodward residence, which was located along a busy two-lane
13 road close to an intersection with a three-lane road. Railroad lines were located near residential
14 sites in North Birmingham (120–210 m), Harriman Park (120–480 m), and Woodward (110–170
15 m).

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27 *Sample Deployment.* Air samplers were deployed at sampling sites for two 7-day periods: July
28 8–15, 2017 (Week 1) and July 15–22, 2017 (Week 2). Three samplers were placed inside each
29 park (total of 12 per week) and three in the residential area surrounding each park (total of 12 per
30 week). The samplers were placed at a mean height of 2.1 ± 0.29 m above the ground, hanging
31 from trees, fences, or porch frames. A map illustrating sampling sites in the parks and residential
32 areas appears in Fig. 6S in ESI.

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38 *Meteorological Conditions.* During the field campaign, the average temperatures at the nearest
39 weather stations available through the National Centers for Environmental Information were
40 26 ± 9.1 °C (mean \pm standard deviation) and 28 ± 9.2 °C during Weeks 1 and 2, respectively, for
41 Birmingham International Airport and 26 ± 9.6 °C and 27 ± 10 °C for Selma 6 SSE, the nearest
42 station to Camden. Precipitation ranged from 3 to 35 mm on three days in Birmingham and from
43 0.5 to 16 mm on five days near Camden during the two-week period. Table 1S in ESI lists daily
44 temperatures and precipitation amounts during the field campaign, while Fig. 2S–5S in ESI
45 present wind roses. Wind direction was variable but generally northerly in Birmingham and
46 southeasterly in Camden.
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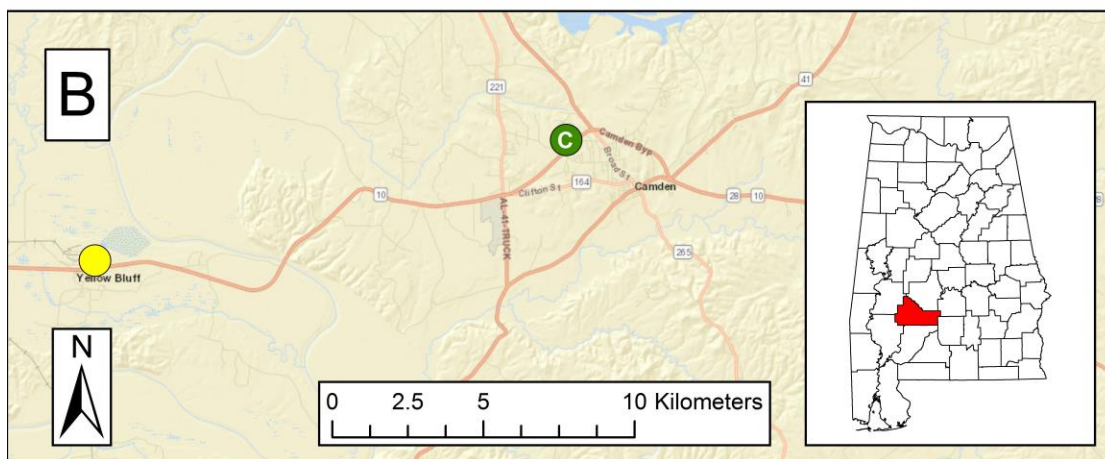
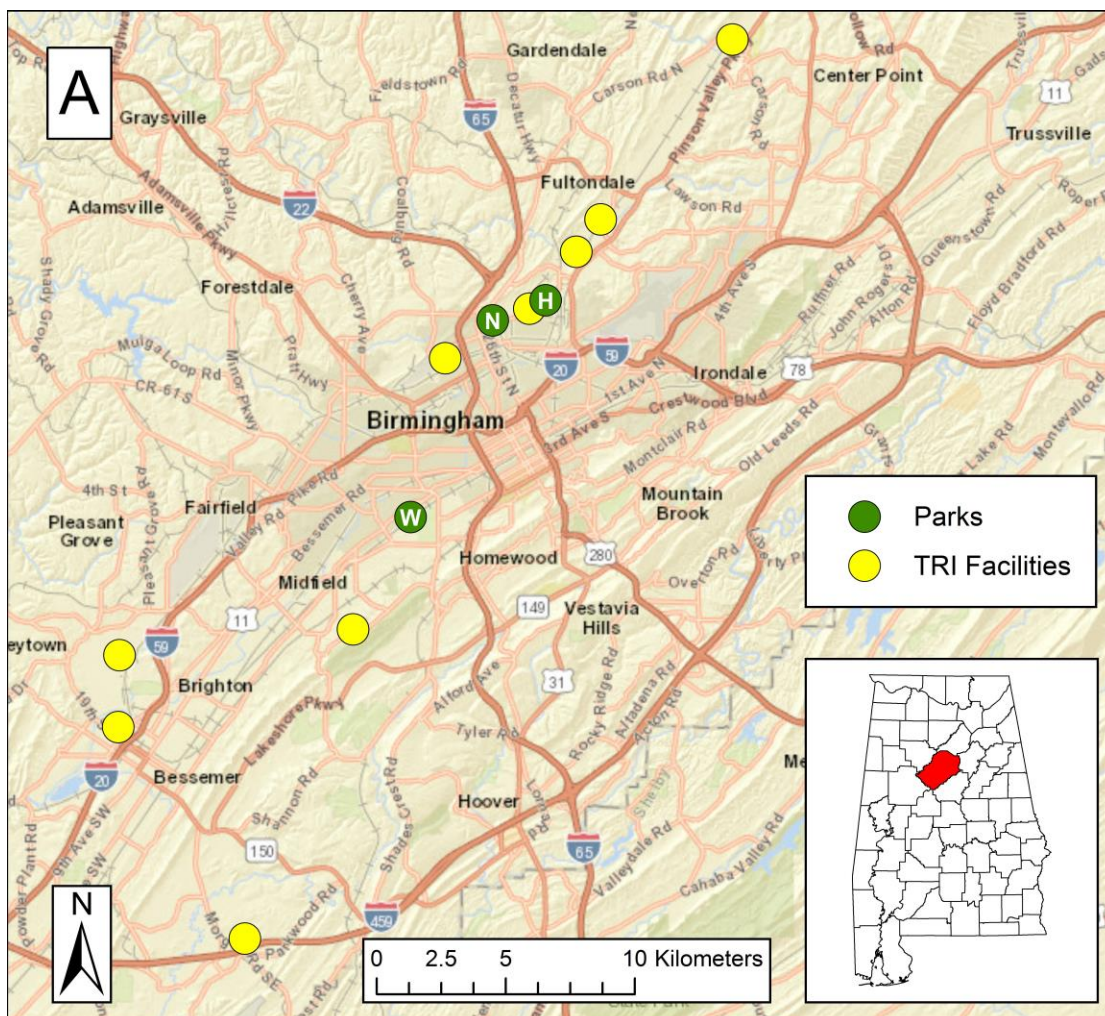


Fig. 1. Parks selected for sampling and point sources of BTEX in 2016 in (A) Birmingham, AL and (B) Camden, AL. Labels denote specific parks, where “N” is North Birmingham, “H” is Harriman Park, “W” is Woodward, and “C” is Camden.

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3 *Sample Analysis.* Samplers were capped and stored at 4 °C between sampling and analysis. The
4 desorption protocol roughly followed the NIOSH Manual of Analytical Methods #4000³⁸ but
5 was adjusted to maximize desorption efficiency. Briefly, each sampler was disassembled and the
6 adsorbent pad was placed in a 2 mL gas chromatography (GC) amber vial with tweezers. 30 µL
7 of a surrogate standard containing 5 µg mL⁻¹ p-bromofluorobenzene (CAS no. 460-00-4) was
8 injected onto the sampler's adsorbent pad, and the sealed vial was left to stand overnight in a
9 fume hood at room temperature. In the morning, carbon disulfide (CAS no. 75-15-0) was added
10 to the vial to bring the total solution volume to 1.5 mL; then, the vial was agitated every 20
11 minutes for 2 hours. Finally, a 1 mL aliquot of the solution was extracted and placed in a
12 separate 2 mL GC vial for analysis by a gas chromatograph-mass spectrometer (Thermo-Fisher
13 Trace GC, DSQ II).
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23 *Quality Assurance and Quality Control.* A BTEX standard (Restek, 200 µg mL⁻¹ in methanol)
24 was diluted in carbon disulfide (Sigma Aldrich ReagentPlus®, low benzene, ≥99.9%) to produce
25 a six-point calibration curve. The method detection limit (MDL) was determined according to
26 EPA-established guidelines.³⁹ MDLs, reported in full in Table 2S in ESI, were all below 31.4 ng
27 mL⁻¹ in the extract, corresponding to a gas-phase concentration of 0.132 µg m⁻³ for a 7-day
28 sampling period. Benzene and toluene had the highest MDLs while those for ethylbenzene and
29 xylenes were lower by a factor of 5–10. Desorption efficiency tests were conducted in triplicate
30 at five concentrations according to the NIOSH Manual of Analytical Methods #4000 for toluene.
31 One standard concentration was below the MDL and was therefore discarded, resulting in four
32 usable concentrations. All BTEX compounds were recovered at close to 100% efficiency, as
33 shown in Table 3S and Fig. 7S in ESI. Overall, toluene had the highest recovery (118±13.5%)
34 while ethylbenzene produced the lowest recovery (96.4±15.2%). At low concentrations, the
35 recovery of benzene and toluene was >100%, probably due to the high MDLs for these
36 compounds, while that of ethylbenzene and xylenes was <100%. Recoveries for all BTEX
37 compounds converged on 100% at higher concentrations. Finally, reagent, method, and trip
38 blanks were analyzed (n=4 each). As shown in Table 4S in ESI, no BTEX compounds were
39 detected in any blanks except for toluene in method and trip blanks at levels extremely close to
40 the MDL.
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3 For each sample, the surrogate concentration detected was divided by the expected value and is
4 reported as the surrogate recovery efficiency. Although these recovery efficiencies ($60.9\pm 6.91\%$)
5 are lower than expected, results of the desorption efficiency analysis indicated that recovery of p-
6 bromofluorobenzene ($73.8\pm 9.27\%$) may not be directly comparable to BTEX recovery
7 ($104\pm 14.7\%$ as a whole); therefore, the BTEX results were not adjusted.
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12 A separate experiment, described in detail in ESI, was conducted to determine whether the rain
13 covers used to protect the passive samplers might have affected the measurements. Briefly, four
14 passive samplers, two with rain covers and two without, were deployed outside a residence for
15 one week. Observed concentrations of all compounds were slightly lower with the rain covers, at
16 most by 10%, but the difference in concentration with and without the rain covers was not
17 significant except for m-,p-xylene ($p=0.02$). This was a very limited study that can only rule out
18 a large effect.
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26 *Gas-Phase Concentration Calculations.* Raw data were obtained from the mass spectrometer
27 through peak detection and integration software (Xcalibur version 2.0.7). The mass adsorbed on
28 each sampler was determined by multiplying the reported concentration in the extract by the
29 injection volume ($1\ \mu\text{L}$), multiplying by the solvent dilution factor used in the desorption step,
30 and converting to micrograms. The effective volume of air sampled for each compound was
31 calculated from the sampler deployment time and effective diffusive sampling rate of the
32 compound according to the manufacturer. Effective passive sampling rates at $25\ ^\circ\text{C}$ for benzene,
33 toluene, ethylbenzenes, and xylenes were 35.5 , 31.4 , 27.3 , and $27.3\ \text{mL min}^{-1}$. The temperatures
34 experienced by the samplers were $28.6\pm 6.6\ ^\circ\text{C}$ and $29.6\pm 6.6\ ^\circ\text{C}$ (mean \pm standard deviation)
35 during Weeks 1 and 2, respectively, as measured by the collocated iButton temperature monitors.
36 The sample volume was corrected using a multiplicative adjustment factor for temperature.
37 Finally, the mass adsorbed was divided by the effective sample volume to produce weekly
38 average ambient BTEX concentrations.
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50 *Statistical Analysis.* Statistical analyses were conducted in the R programming language (version
51 3.4.4, R Foundation for Statistical Computing, University of California at Berkeley mirror in the
52 Comprehensive R Archive Network (CRAN), Berkeley, CA). A multiple linear regression was
53 conducted to assess the influence of distinct location, site types, and distance to the nearest major
54 road on BTEX concentrations (lm, stats version 3.4.4). Regression parameters included
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3 categorical variables for location (North Birmingham, Harriman Park, and Woodward with
4 Camden serving as the background location for the regression), site type (park or residence), a
5 numerical variable for distance from a road with substantial vehicular traffic (greater than
6 approximately 10 cars per minute), and an intercept. Normality was confirmed for most
7 pollutants grouped by location name and site type through Shapiro-Wilk tests (shapiro.test, stats
8 version 3.4.4). Normality was weakly rejected in North Birmingham residential TEX
9 concentrations ($p=0.02$ or higher for each compound), but for consistency, all data were
10 subjected to the same multiple linear regression. Although ambient pollutant concentrations are
11 often lognormally distributed, those observed in the current study may be approximately
12 normally distributed because of the small sample size and/or low geometric standard deviation.
13 A nonparametric Spearman rank correlation analysis (rcorr, Hmisc version 4.1-1) was also
14 conducted to assess correlation between BTEX concentrations within locations. Finally, two one-
15 sided Student's t-tests (t.test, stats version 3.4.4) with a Bonferroni correction ($\alpha=0.025$) were
16 conducted on T:B ratios to examine whether the ratios were statistically different than the range
17 expected for vehicular emissions. A one-sided t-test was conducted on m-,p-X:E ratios to assess
18 whether they were greater than 3.6. Normality was confirmed through Shapiro-Wilk tests for all
19 T:B and m-,p-X:E ratios except Woodward residential T:B ratios, which weakly rejected
20 normality ($p=0.04$); therefore, all ratios tests were conducted as parametric t-tests.
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36 **Results**

37 *BTEX Concentrations.* BTEX concentrations in and around each park are presented in Fig. Fig.
38 2. Week-long BTEX concentrations were stratified by park name and location type (park vs.
39 residential); the original data are presented in Table 6S in ESI while the means and standard
40 deviations are presented by week in Table 7S and Table 8S in ESI. Benzene and toluene
41 concentrations were $1.02\text{--}2.51\ \mu\text{g m}^{-3}$ in North Birmingham and Harriman Park, and
42 concentrations of ethylbenzene and xylenes were lower. Toluene in Woodward was highest
43 among all the locations and all the compounds. In Camden, BTEX concentrations were lower
44 than in the other three locations by a factor of 2.3–2.8, which was expected for a small city
45 farther from major highways and point sources. Concentrations were similar or slightly higher in
46 Week 2, although this difference was only significant for BTEX in the Camden park and
47 ethylbenzene in the Camden residential samples.
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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.

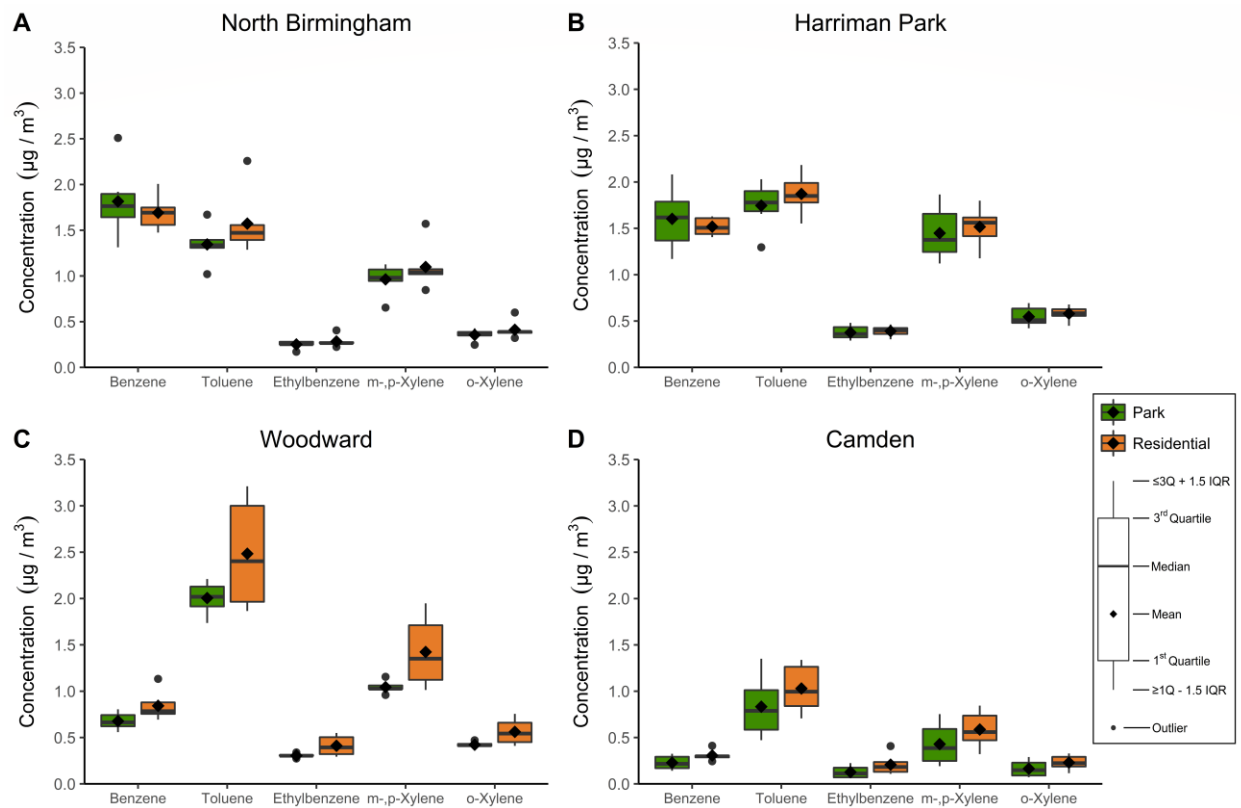


Fig. 2. BTEX concentrations grouped by site type in: (A) North Birmingham, (B) Harriman Park, (C) Woodward, and (D) Camden. Each box represents six data points. Upper whisker is the maximum observation less than 1.5 times the inter-quartile range over the 3rd quartile, while lower whisker is the similar 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.⁴⁰ 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

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3 impact of vehicle emissions. Regression parameter estimates are presented for each BTEX
4 compound in Table 1. Categorical parameters for location were significant ($p < 0.02$), meaning
5 that BTEX concentrations in each of the four locations were different from each other.
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8 Furthermore, site type was a statistically significant parameter for TEX ($p < 0.002$) but not
9 benzene ($p = 0.33$). Parks exhibited $0.0736\text{--}0.351\ \mu\text{g m}^{-3}$ lower concentrations of TEX than
10 surrounding residential areas, with the smallest reduction observed for ethylbenzene and the
11 largest observation observed for toluene.
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16 In the multiple linear regressions, distance to the nearest major road was statistically significant
17 for BTX ($p < 0.02$) but not for ethylbenzene ($p = 0.06$). All estimates were negative and estimates
18 for BTX implied that their concentrations decreased by $0.0005\text{--}0.0019\ \mu\text{g m}^{-3}$ per meter from a
19 major road.
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23 *BTEX Correlations.* Correlation and ratio analyses of BTEX concentrations can provide insight
24 into their likely sources and photochemical age. Table 2 presents the Spearman rank correlation
25 coefficients for BTEX by location for the combined weeks. At all sites, TEX concentrations
26 strongly and positively correlated with each other ($p < 0.01$). Benzene correlated less with TEX, if
27 at all; in Camden, benzene was moderately correlated with TEX ($p < 0.05$). In Woodward,
28 benzene and EX exhibited a moderately positive ($p < 0.05$) correlation with each other, but
29 benzene and toluene did not. In North Birmingham, benzene had a moderately positive ($p < 0.05$)
30 correlation with o-xylene but no other compound. In Harriman Park, benzene was negatively
31 correlated with TEX, but no correlation was statistically significant.
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39 *BTEX Ratios.* Toluene:benzene (T:B) and m-,p-xylene:ethylbenzene (m-,p-X:E) mass ratios were
40 calculated for each sample; the results were again stratified by location and site type, as shown in
41 Fig. Fig. 3 and Table 9S in ESI. T:B ratios were exceptionally low in North Birmingham (0.666–
42 1.29) and Harriman Park (0.795–1.56) but moderate in Woodward (2.36–4.03) and Camden
43 (2.48–5.10). No T:B ratios were observed to be statistically greater than 3.0, but T:B ratios in
44 both site types in Harriman Park and North Birmingham were significantly less than 1.5
45 ($p < 0.01$).
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Table 1. Multiple linear regression estimates and p-values. Estimates are in $\mu\text{g m}^{-3}$ for all parameters except road distance ($\mu\text{g m}^{-3} \text{ m}^{-1}$ from road).

Compound	Parameter	Type	Estimate	p-value
Benzene	(Intercept)	-	0.622	0.00035
	North Birmingham	Categorical	1.4	$< 2 \times 10^{-16}$
	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

Table 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 $p < 0.001$.

Location		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***

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.

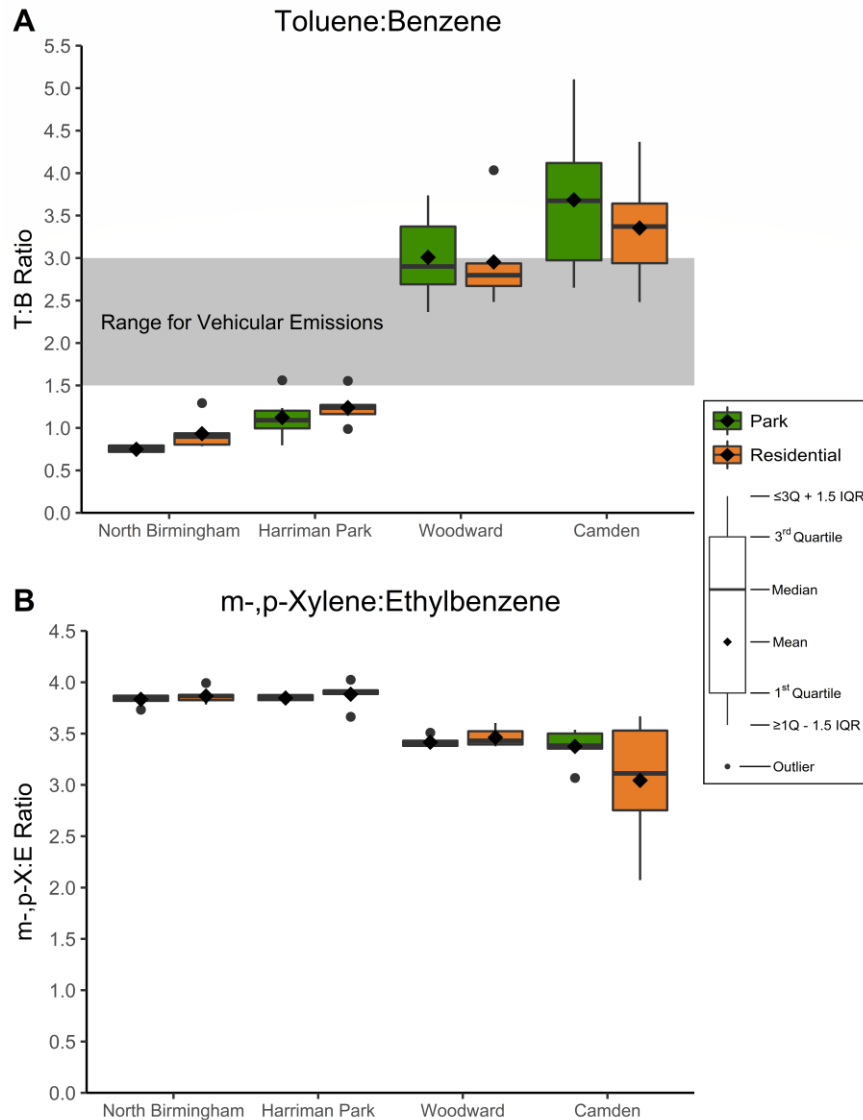


Fig. 3. (A) Toluene:benzene (T:B) ratios by location and site type. (B) m-,p-xylene:ethylbenzene (m-,p-X:E) ratios by park name and location. Each box represents six data points. Upper whisker is the maximum observation less than 1.5 times the inter-quartile range over the 3rd quartile, while lower whisker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

Discussion

Comparison to BTEX in Other Studies. In the present study, TEX concentrations were below the levels found in outdoor air presented in a review of ambient BTEX⁷ and below the lowest effect concentrations presented by Herberth et al. (2014)⁴¹ and Wallner et al. (2012).⁴² Benzene concentrations in North Birmingham and Harriman Park were at the lower end of the range described in the review⁷ and above the lowest concentration at which health effects have been

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3 observed.^{7,41} BTEX concentrations in the present study were mostly below annual means
4 measured in similar studies in Naples, Italy⁴³ and Birmingham, UK,⁴⁴ although the latter study
5 reported benzene concentrations similar to those found in North Birmingham and Harriman Park.
6 BTEX concentrations were within the ranges found in Windsor, Ontario,¹⁰ with the exception of
7 concentrations in Camden being generally lower. Compared to the results of a study in
8 Dunkerque, France during the summertime,⁴⁵ BTEX levels in North Birmingham, Harriman
9 Park, and Woodward were comparable to those found in urban or industrial settings in France,
10 while levels in Camden were below those documented in a rural setting in France.

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13 *Park Effect.* Regression analysis showed the existence of a park effect in TEX, with lower
14 concentrations in the park compared to the surrounding residential area, even when accounting
15 for distance to the nearest major roads. This finding builds upon prior studies in Scandinavia,
16 where one identified a reduction in concentrations of benzene and toluene in parks²⁶ and another
17 identified a reduction of total VOCs in tree canopies.²⁸ This result is also supported by the results
18 of laboratory chamber experiments that examined uptake of these compounds by plants.^{21,22,24,25}

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21 Several factors likely contributed to the reduction of TEX in parks. First, the size of the park and
22 amount of vegetation are likely significant parameters, as the smallest difference in TEX in parks
23 was found in the smallest park (Harriman Park). Furthermore, the sampling campaign was
24 conducted in the summer when leaf area is at a maximum, providing the optimal interface for
25 plant uptake. Foliage was determined to have a significant influence on BTEX concentrations in
26 large areas of vegetation in several studies,^{27,28} although a recent study determined that foliage
27 was not significant.²⁹ BTEX can be taken up by soil and its microbes,^{22,25} and Blume et al.
28 (2002)⁴⁶ showed that microbial activity increased by up to 83% in summertime temperatures.
29 Finally, the wind speed, as shown in Fig. 2S–5S in ESI, was relatively low and had significant
30 fractions of calm periods recorded, allowing for any uptake by areas of dense vegetation to
31 register as reduced ambient concentrations.

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34 Benzene did not display a park effect, however. Fig. Fig. 2 shows that benzene levels were lower
35 in parks in Woodward and Camden but higher in parks in North Birmingham and Harriman Park.
36 These differences negated each other when combining the entire dataset for the multiple linear
37 regression, which prevented the identification of a park effect for benzene across all locations.
38 Benzene concentrations may have been higher in the parks in North Birmingham and Harriman
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3 Park because these two locations are close (1.5 km and 0.72 km, respectively) to a coke
4 production plant that emitted 32,400 kg of benzene in 2016 according to the TRI, and at both
5 locations, the park sites were closer to the coke plant than were the residential sites. Thus, higher
6 concentrations would be expected in the parks if the coke plant is a dominant source of benzene
7 in this area.
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12 *Source Characterization.* Spearman rank correlations presented in Table 2 show that the
13 individual BTEX compounds correlated strongly and significantly with each other across several
14 locations in urban environments, even in different cities. Our analysis suggests that all BTEX
15 came from a shared source in Camden and likely Woodward, while all TEX came from a shared
16 source in North Birmingham and Harriman Park. As onroad emissions are the predominant
17 source of TEX and a major source of benzene,³⁷ it is likely that this shared source was vehicular
18 exhaust. However, there may be a separate source or sources of benzene in North Birmingham
19 and Harriman Park. In hindsight, traffic counts on nearby roads would have been useful to
20 collect during the field campaign and would have strengthened the characterization of sources
21 and analysis of the park effect.
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30 T:B ratios indicate that vehicles were likely the dominant source in Camden and Woodward but
31 not in Harriman Park and North Birmingham. The low T:B ratios at the latter two sites suggest a
32 separate source of benzene near these locations. Indeed, North Birmingham and Harriman Park
33 are situated between a group of point sources that emit large amounts of benzene, while
34 Woodward and Camden are much further from similar facilities. According to the TRI, the two
35 coke production plants near North Birmingham and Harriman Park have T:B ratios in their
36 emissions of 0.582 and 0.492; these values are only slightly lower than the lowest values found
37 in North Birmingham (0.666) and Harriman Park (0.795). Clearly, these industrial sources
38 impacted North Birmingham and Harriman Park. A prior study in Alabama found a small but
39 significant association between preterm birth and residential proximity to coke and steel plants.⁴⁷
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48 The m-,p-X:E ratios in North Birmingham and Harriman Park were significantly greater than
49 3.6, the value expected for fresh emissions, regardless of source.¹⁵ Although the m-,p-X:E ratios
50 in Woodward and the park in Camden were slightly lower, these ratios were also higher than
51 most m-,p-X:E ratios in urban settings as reported by Miller et al. (2012)¹⁰ and Monod et al.
52 (2001).¹⁶ Residential ratios in Camden were comparable to the reported value (median $\pm 2\sigma$) of
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3 urban background sites (3.03 ± 0.79 compared to this study's 3.11 ± 1.2).¹⁶ Thus, the high m-,p-
4 X:E ratios across all locations but the Camden residential sites indicate air masses relatively
5 close to emission sources and yet unaffected by photochemical aging. Exceptionally high ratios
6 in North Birmingham and Harriman Park suggest that these sites were particularly close to
7 BTEX sources.
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12 In summary, most BTEX in Woodward and Camden were likely due to traffic emissions because
13 of the strong correlation between species, moderate T:B ratios, and moderate m-,p-X:E ratios. In
14 North Birmingham and Harriman Park, TEX were also likely attributable to traffic emissions due
15 to the strong correlation between species. However, there was likely another source of benzene
16 in these locations, as suggested by the low T:B ratios and high m-,p-X:E ratios. Although BTEX
17 levels were significantly different in each location, the similarity in results for North
18 Birmingham and Harriman Park was likely due to their proximity to both large point sources and
19 to each other.
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27 *Community Impacts.* Importantly, this study considered input from community members in the
28 placement of organic vapor monitors, which allowed for the integration of community science in
29 determining local exposure to BTEX. Upon analysis of the samples, the results were
30 disseminated to the specific community members that participated in the study, along with
31 BTEX ToxGuides from the Agency for Toxic Substances and Disease Registry. An example of
32 the pamphlet shared with participants can be found in Fig. 8S in ESI. The conveyance of results
33 strengthened the relationship between the present researchers and communities and fostered
34 curiosity in air quality, public health, and the scientific method.
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41 **Conclusions and Future Work**

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43 Passive samplers were deployed in city parks and neighboring residential areas in two cities in
44 Alabama for two weeks in July 2017 to evaluate whether parks can mitigate exposure to BTEX
45 in air. The measured BTEX concentrations were within the range of expected values for
46 summertime in urban and rural environments. Levels of each BTEX compound were
47 significantly different between locations, and TEX concentrations in parks were 3–39% lower
48 than in the surrounding residential areas. Site type (park vs. residential) was a significant
49 predictor of TEX concentrations, while distance to the nearest major road was a significant
50 predictor of BTX concentrations.
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3 High Spearman rank correlation coefficients suggest a common source or source profile for
4 BTEX in Camden and Woodward and for TEX in North Birmingham and Harriman Park. T:B
5 ratios were within the standard range for vehicular emissions in Camden and Woodward but
6 substantially lower in North Birmingham and Harriman Park; in conjunction with the correlation
7 analysis, this suggests that there was a separate, industrial source of benzene nearby. At all sites
8 except residential ones in Camden, the m-,p-X:E ratio was sufficiently high to suggest a sampled
9 air mass with a young photochemical age.

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16 Future work should further explore the effect of phytoremediation on BTEX in ambient air in
17 both field and laboratory settings. Field campaigns would benefit by increasing spatial (i.e.,
18 sampler density) and/or temporal (i.e., active sampling) resolution to improve statistical power.
19 Analyzing vegetation for evidence of BTEX uptake would also be informative. A short study
20 could be conducted with active samplers to assess the presence of a diurnal pattern in BTEX
21 uptake. Future studies should also involve a sampling campaign over the full year in order to
22 assess seasonal effects, such as loss of deciduous tree leaf cover and change of microbial activity
23 in the rhizosphere. Field studies would also benefit by placing samplers equidistant from roads
24 (both inside and outside of parks) to attempt to equalize the influence from vehicular emissions.
25 Finally, future studies should also include estimates of traffic density for nearby roads.

36 **Conflicts of Interest**

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38 There are no conflicts to declare.
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43 **Acknowledgments**

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50 Smiley for her assistance in method development and sampler analysis.
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5 Concentrations of selected organic compounds in the atmosphere were lower in parks compared to
6 nearby residential areas.
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