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The Mobile Source Effect on Curbside 1,3-Butadiene, Benzene, and Particle-Bound Polycyclic Aromatic Hydrocarbons Assessed at a Tollbooth

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ABSTRACT

On-road mobile sources contribute substantially to ambient air concentrations of the carcinogens 1,3-butadiene, benzene, and polycyclic aromatic hydrocarbons (PAHs). The current study measured benzene and 1,3-butadiene at the Baltimore Harbor Tunnel tollbooth over 3-hr intervals on seven weekdays (n = 56). Particle-bound PAH was measured on a subset of three days. The 3-hr outdoor 1,3-butadiene levels varied according to time of day and traffic volume. The minimum occurred at night (12 a.m.–3 a.m.) with a mean of 2 $\mu g/m^3$ (SD = 1.3, n = 7), while the maximum occurred during the morning rush hour (6 a.m.–9 a.m.) with a mean of 11.9 $\mu g/m^3$ (SD = 4.6, n = 7). The corresponding traffic counts were 1413 (SD = 144) and 16,893 (SD = 692), respectively. During the same intervals, mean benzene concentration varied from 3 $\mu g/m^3$ (SD = 3.1, n = 7) to 22.3 $\mu g/m^3$ (SD = 7.6, n = 7). Median PAH concentrations ranged from 9 to 199 ng/m^3. Using multivariate regression, a significant association ($p < 0.001$) between traffic and curbside concentration was observed. Much of the pollutant variability (1,3-butadiene 62%, benzene 77%, and PAH 85%) was explained by traffic volume, class, and meteorology. Results suggest >2-axle vehicles emit 60, 32, and 9 times more PAH, 1,3-butadiene, and benzene, respectively, than do 2-axle vehicles. This study provides a model for estimating curbside pollution levels associated with traffic that may be relevant to exposures in the urban environment.

IMPLICATIONS

Mobile source emissions present a unique public health threat because of toxic emissions and exposure potential resulting from their proximity and integration into U.S. communities. Urban communities are especially susceptible because of population density and dense commuting traffic. The current study provides a quantitative assessment of the relationship between traffic volume and class and the curbside concentration of key environmental carcinogens. This assessment defines an experimental approach and estimate of the mobile source effect on the curbside pollutant concentration under real-world meteorological conditions. The resulting models may be useful for evaluating ambient exposure, risk, and control strategies.

INTRODUCTION

Benzene, 1,3-butadiene, and polycyclic aromatic hydrocarbons (PAHs) are listed by the U.S. Environmental Protection Agency (EPA) among 31 priority mobile source air toxins.[1] Recently, 1,3-butadiene was reclassified as a "known human carcinogen"[2] based on epidemiologic and mechanistic information. Exposure to 1,3-butadiene is associated with lymphosarcoma[3,4] and leukemia[5–8] in occupationally exposed workers. Benzene also has been long established as a known human carcinogen.[9–11] Exposure to benzene is associated with acute nonlymphocytic leukemia and chronic lymphocytic leukemia.[12–19]

Emissions of chemicals such as 1,3-butadiene, benzene, and PAH into the environment by mobile sources are of great public health concern because of their carcinogenicity and heightened exposure potential that results from their proximity and integration into U.S. society at all levels (urban, suburban, and rural). Several epidemiologic studies have observed higher cancer rates among urban compared with suburban populations.[20–23] Air pollution, including benzene, 1,3-butadiene, and PAHs, is believed to be a contributing risk factor.[20]

The potential for exposure to automobile exhaust containing these carcinogenic chemicals is most pronounced in urban locations where heavily commuted roadways transect densely populated communities. Human exposure to these mobile source emissions can be substantial because of increasing (1) traffic volume and congestion, (2) vehicle miles driven, and (3) numbers of heavier, less efficient sport utility vehicles. Increased emissions may be only partially offset by technological gains in emissions control. Based on modeling results from the Assessment System for Population Exposure Nationwide for 1990, Rosenbaum et al.[24] estimate mobile

sources contribute 63, 59, and 63% to total ambient benzene, 1,3-butadiene, and polycyclic organic matter (POM), respectively. (POM is the more comprehensive family of organics that subsumes the carbon and hydrogen-only containing PAHs.) Taking into account point and area sources in addition to mobile sources, for the 60,803 census blocks in the contiguous United States, Rosenbaum et al. estimate median ambient levels of 1.6, 0.099, and 0.18 $\mu g/m^3$ for the three pollutants, respectively. These modeling results are further substantiated by studies indicating large pollution differences between weekends and weekdays attributable to varying traffic levels. In a series of studies, Vukovich[25] identified 27–42% higher VOC levels in the Northeast and in Texas on weekdays relative to weekends. Ilgen et al.[26] reported geometric mean benzene levels of 3.1 and 1.8 $\mu g/m^3$ in German homes located on high- and low-traffic streets, respectively.

Both indoor and outdoor sources factor into human exposure and risk. There are several known indoor sources of benzene and PAHs, such as cleaning products, paints, glues, and tobacco smoke for benzene, and wood burning, cooking, and tobacco smoke for PAHs.[27–30] For 1,3-butadiene, the only known indoor source is tobacco smoke, which can elevate indoor 1,3-butadiene concentrations significantly.[31]

Although there is a growing body of literature identifying a substantial mobile source contribution to ambient pollution, these estimates largely rely on dynamometer emissions testing coupled with estimates of vehicle miles driven. The current study is unique in examining the actual measured association between vehicle volume and class and the resulting curbside ambient pollutant concentration, providing a real-world basis by which to validate models and estimate exposure. The study was conducted at a tollbooth facility where traffic count and type were carefully quantified, providing a basis for a real-world estimate of the mobile source effect on curbside concentration for 1,3-butadiene, benzene, and PAH.

METHODS

Study Site and Sampling

This study was conducted at the Maryland Transportation Authority (MDTA)–operated Baltimore Harbor Tunnel tollbooth facility. This facility has 14 tollbooths evenly divided between northbound and southbound traffic. Sampling was conducted at a single northbound tollbooth (number 3). It was selected because it is open and operator-occupied 24 hr/day. Samplers were placed immediately outside the tollbooth on the south side (vehicles approaching) approximately 3 ft above ground. Sampling was conducted over seven weekdays during the period from June 18 to June 28, 2001.

Three-hour integrated 1,3-butadiene and benzene samples were collected using a Perkin-Elmer STS-25 sequential sampler. Samples were collected sequentially onto stainless-steel Perkin-Elmer Air Toxic Tubes packed with a solid sorbent (Supelco, catalog no. 25051), using an SKC 210 pocket pump (SKC, Inc.) set at a nominal flow rate of 25 mL/min. Pumps were calibrated upon initiation of sampling using a DryCal DC-2 primary standard (BIOS International Corp.). Sample flows were checked after sampling to account for any drift during sampling.

Every 24 hr, the sampled air toxic tubes were removed from the sequential sampler and returned to the laboratory for analysis. Samples were thermally desorbed (Perkin-Elmer ATD-400), separated by gas chromatography (GC), and detected with mass spectrometry (MS) using a Shimadzu GC-17A gas chromatograph and QP-5000 mass spectrometer (Shimadzu Biotech). The conditions used for the ATD-400, GC, and MS were adapted from Kim et al.[32] Chromatographic separation was obtained using Restek Rtx-624 column, 60 m $\times$ 0.25 mm ID with 1.4 μm thickness (Restek Corp., catalog no. 10969).

Calibration standards were prepared at six levels by diluting 2 mg/mL 1,3-butadiene stock solution (Accustandard, catalog no. S-406A-10x) and 2 mg/mL custom VOC mix (Accustandard, catalog no. S-2081-R10–10x) in methanol. One-μL injections were made into clean sampling tubes using a modified GC injector port (50 °C, He flow of 80 mL/min for 10 min). The final amount on sampling tubes ranged from 1 to 25 ng and from 1 to 50 ng for benzene and 1,3-butadiene, respectively.

Particle-bound PAH was measured using an Ecochem PAS 2000 PAH Ambient Analyzer (Ecochem Technologies). This is a direct-reading instrument that measures PAH on particles by photoionization. Particles entering the instrument are irradiated with UV light at 222 nm (6.7 eV). Particles containing PAH with photoelectric threshold less than 6.7 eV will loose an outer-shell electron and become positively charged. The charge particles are collected onto a filter, resulting in an electrical current proportional to the ions collected. Therefore, all particles with a photoelectric threshold less than 6.7 eV will be ionized and measured as PAH.[33] Air is sampled at a flow rate of 2 L/min. The inlet is not configured to provide a size-specific classification; however, electrons emitted from larger particles are more likely to be recaptured. Therefore, ionization and instrument response is most effective for particles containing PAH in the size range $<$1–2 μm in diameter.[34] The Echochem PAS 2000 was placed side-by-side with the STS-25 sequential samplers, and samples were collected continuously for 2 days during the study period. Measurements were logged in 1-min intervals. These data were combined to give 3-hr average

concentrations corresponding to the traffic count intervals.

Hourly traffic count data for both northbound and southbound traffic were obtained from the MDTA (Tollbooth Administration at Baltimore Harbor Tunnel), which maintains an hourly record of total vehicle counts passing through each tollbooth, classified by the number of axles on each vehicle. The axle-based classification was compared with the Federal Highway Administration (FHWA) classification system (Table 1).[35] This table indicates that 2-axle vehicles primarily represent passenger cars, minivans, pickups, and single-unit trucks, whereas >2-axle vehicles are primarily buses, large trucks, and trailers.

Meteorological measurements including temperature, relative humidity, rain, wind speed, and direction were made using a Davis meteorological station (Davis Instrument Corp.). The meteorological station was located in East Baltimore approximately 4 mi due north of the toll plaza near the Johns Hopkins Bloomberg School of Public Health. Field (n = 7) and laboratory (n = 10) blanks were included in all sampling and analytical runs. Reported concentrations have been corrected for mean field blank levels. All samples were analyzed on the same day that they were returned from the field. Measurement precision was determined from a single measurement made in triplicate using side-by-side sampling. Recovery was determined by spiking air toxic tubes (n = 7) with 15 ng of 1,3-butadiene and 5 ng of benzene. Tubes were cleaned for reuse by conditioning in the ATD 400 at 350 °C for 15 min. Conditioned tubes were randomly selected and analyzed to verify that there was no carryover of residual analytes from one sample to the other.

Table 1. Comparison of FHWA vehicle class and the number of axle, with examples.

FHWA Vehicle Class	Average No. of Axles per Vehicle	Vehicle Types
1	2	Motorcycles
2	2	Passenger cars
3	2	Pickups, vans, campers, minibus
4	2.2	Buses
5	2	Six-tire, single-unit trucks, including motor homes
6	3	Three-axle single-unit trucks
7	4	Four-axle single-unit trucks on single frame
8	4	Four or fewer axles consisting of two units
9	5	All five axles consisting of two units
10	6	Vehicles with six or more axles with two units
11	5	Five or fewer axles consisting of three units
12	6	All six-axle vehicles with three or more units
13	7	All vehicles with seven or more axles

Data Analysis

The hourly traffic data were summed in a 3-hr interval corresponding to the 3-hr integrated sampling period. A composite traffic volume for a given day was calculated by adding up the vehicle counts for all 14 tollbooths per 3-hr interval. The traffic volume data were grouped into two classes for analysis: 2-axle and >2-axle vehicles. Meteorological data and PAH data were similarly averaged over the same 3-hr sampling interval. All measured concentrations were corrected for recovery and blanks. Multivariate regression model (eq 1) was used to investigate the relationship between curbside pollution levels, traffic volume, and meteorological conditions using Intercooled Stata, version 7 for Windows (Stata Corp.).

$$C_i = \beta_{0i} + \beta_{1i}2\text{-}axle + \beta_{2i} > 2\text{-}axle + \beta_{3i}Temp + \beta_{4i}Wind\ Speed + \varepsilon_t \quad (1)$$

In this model, C_i is the curbside concentration of pollutant i for the 3-hr sampling interval. The regression coefficient β_{1i} represents an average increase in the curbside concentration of pollutant i (ng/m^3) for a unit increase in 2-axle vehicle number, adjusted for the number of >2-axle vehicles, temperature, and wind speed. Similarly, β_{2i} represents an average increase in the curbside concentration of pollutant i (ng/m^3) for a unit increase in >2-axle vehicle number, adjusted for the number of 2-axle vehicles, temperature, and wind speed. These coefficients have units of ng/m^3/vehicle and provide an indication of the mobile source effect on the curbside pollutant concentration. Hereafter, this effect will be referred to as "the mobile source effect." The method detection limit was calculated following the Code of Federal Regulations (40CFR136 Appendix B) as discussed in EPA Compendium Method TO-17.[36] The limit of detection was obtained by multiplying the SD of the seven spiked samples by the Student's t value associated with the 99% confidence interval and 6° of freedom.

RESULTS

The recovery for 1,3-butadiene and benzene (± SD) averaged 85 ± 12% and 97 ± 8%, respectively, for the seven recovery spike samples analyzed. The analysis of a single sample collected in triplicate yielded a coefficient of variation of 2 and 6% for 1,3-butadiene and benzene, respectively. The limit of detection was determined as 0.46 and 0.58 μg/m^3 for the two respective analytes.

Results from this study relate to traffic levels, vehicle class, and operating conditions at a specific tollbooth facility. The vehicle operating conditions associated with

the tollbooth are varied, with vehicles decelerating and braking upon approach, idling and traveling slowly to the tollbooth attendant, and then accelerating onto the highway. Total vehicle counts (north- and southbound) per 3-hr interval over the seven-weekday sampling period are shown in Figure 1. The diurnal distribution is bimodal, with modes associated with the morning and evening rush hours, as expected. There is an approximate 8-fold difference between minimum counts occurring during the nighttime hours to the maximum recorded during the rush hour. The total morning rush hour traffic exceeds the midafternoon traffic by a factor of approximately 1.5. However, there is a distinct difference in traffic volume patterns between vehicles with 2 axles relative to vehicles with >2 axles. The morning rush hour is caused by an increase in both 2-axle and >2-axle vehicles, whereas >2-axle vehicle counts remain elevated into the early afternoon hours, while the commuting 2-axle vehicles drop precipitously between the morning and afternoon rush hours. Although the number of >2-axle vehicles continues to increase even after rush hour, the overall traffic count goes down after rush hour because >2-axle vehicles account for only 2–9% of the total vehicle counts. Therefore, the overall decrease in total traffic counts during the afternoon is caused by drastic decreases in commuters on the highways during afternoon hours.

The distributions of 1,3-butadiene and benzene 3-hr integrated outdoor measurements made over the 7-day period are shown in Figures 2 and 3. The concentration profiles of 1,3-butadiene and benzene tracked one another and followed a similar bimodal pattern to the traffic counts, with the lowest levels occurring in the early morning hours and peak levels occurring during morning and afternoon rush hours. The lowest 1,3-butadiene levels (median = 2 $\mu g/m^3$; range = 0.8–4.5 $\mu g/m^3$) were recorded during the interval 12 a.m.–3 a.m., whereas maximum levels (median = 13.5 $\mu g/m^3$; range = 6–19 $\mu g/m^3$) were recorded during the interval 6 a.m.–9 a.m. The corresponding benzene concentrations were 2.7 $\mu g/m^3$ (0.7–9.6 $\mu g/m^3$) and 22.3 $\mu g/m^3$ (12.5–32.5 $\mu g/m^3$), respectively. PAH levels followed a slightly different pattern, with minimum values observed during the evening interval 9 p.m.–12 a.m. (median = 9.3 ng/m^3; interquartile range [IQR] = 10) and maximum levels observed during the 6 a.m.–9 a.m. interval (median = 199 ng/m^3; IQR = 241). IQRs are reported for the PAH measurements because of the large variability in the 1-min measurements.

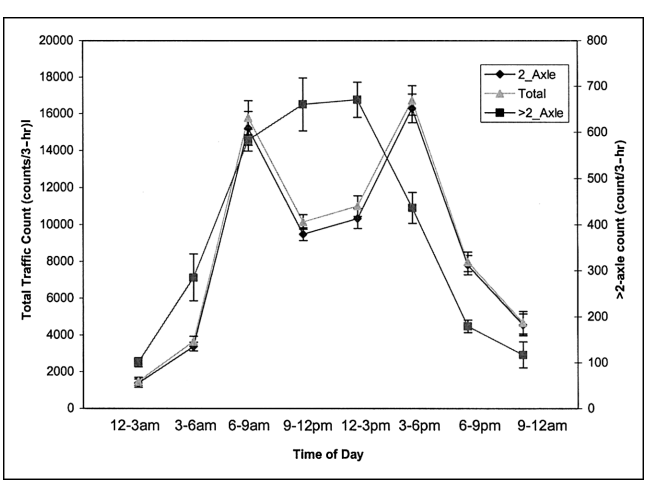

Figure 1. Distribution of 3-hr traffic counts for different vehicle types as a function of time. The mean is plotted with error bars representing the SD.

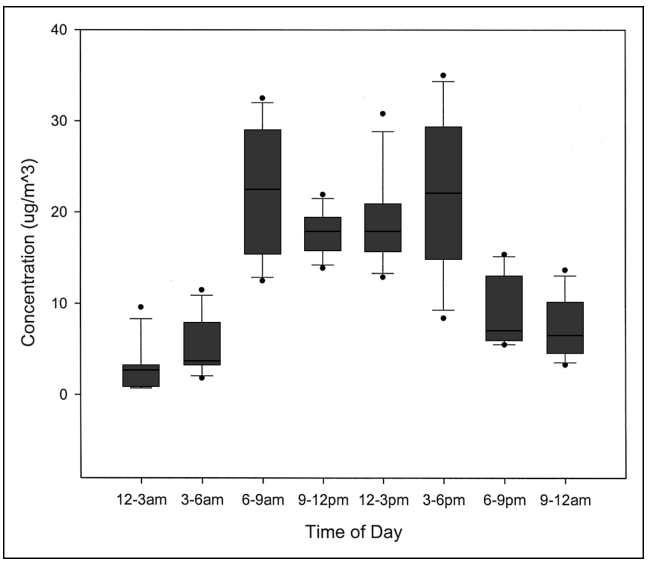

Figure 2. Distribution (n = 7) of outdoor benzene by time of day. The boxes represent 25th and 75th percentiles, whiskers represent 5th and 95th percentiles, and the horizontal bars represent the median value. Individual outliers are represented by the dots.

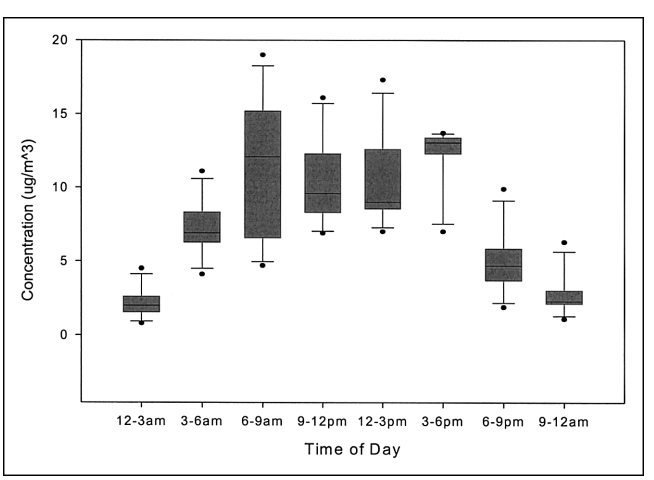

Figure 3. Distribution (n = 7) of outdoor 1,3-butadiene by time of day. The boxes represent 25th and 75th percentiles, whiskers represent 5th and 95th percentiles, and the horizontal bars represent the median value. Individual outliers are represented by the dots.

Meteorological measurements over the 56 3-hr intervals are presented in Table 2. Temperature and humidity ranged from 21.8 to 31.6 °C and from 38.5 to 76%, respectively. Wind speeds ranged from 0.3 to 2.1 m/sec and were in no predominant direction. The association between traffic volume and curbside concentrations of 1,3-butadiene, benzene, and PAH is illustrated by a scatter plot (Figure 4). Simple linear regression of ambient 1,3-butadiene, benzene, and PAH on total traffic volume indicates that 40, 69, and 49% of the pollutant variability is explained by traffic volume.

Table 3 presents a matrix of correlation coefficients for the various pollutant measurements and traffic count and meteorological explanatory variables. As suggested in the concentration profile plots (Figures 2 and 3), 1,3-butadiene and benzene are significantly correlated ($p \leq 0.05$). The meteorological variables humidity and temperature are similarly significantly correlated ($p \leq 0.05$). PAH and 1,3-butadiene showed a stronger correlation with >2-axle vehicles than with 2-axle vehicles, whereas benzene was more strongly correlated with 2-axle vehicles.

The simple linear models were further refined using multivariate analysis that simultaneously took into account vehicle class and meteorological conditions, including temperature, wind speed, and direction. The results of the multivariate analysis are presented in Table 4. In this more complete analysis, traffic volume classified as 2-axle and >2-axle vehicles was significant ($p \leq 0.05$) for both 1,3-butadiene and benzene. In contrast, for PAH, only >2-axle traffic volume was significant. The multivariate models are a significant improvement over the univariate models, as indicated by the increased explained variability in pollutant concentrations: 62, 77, and 85% for 1,3-butadiene, benzene, and PAH, respectively. It is likely that some of the unexplained variability is attributable to spatial differences in wind speed and direction between the toll plaza and the location of the measurements in East Baltimore.

Table 2. Meteorological results (median and range) by sampling interval.

Interval	Temperature (°C)	Relative Humidity (%)	Wind Speed (m/sec)	Dominant Wind Direction
12 a.m.–3 a.m.	23.4 (21.7–26.8)	72.0 (64.2–82.2)	0.3 (0.2–1.2)	NE
3 a.m.–6 a.m.	21.8 (20.2–25.5)	76.0 (70.7–84.7)	0.5 (0.3–1.0)	NNW
6 a.m.–9 a.m.	24.4 (22.7–26.9)	65.5 (60.7–77.0)	0.9 (0.7–1.3)	SE
9 a.m.–12 p.m.	29.3 (26.1–31.3)	45.7 (39.8–56.7)	1.7 (1.1–1.9)	SSE
12 p.m.–3 p.m.	31.6 (27.8–33.5)	38.5 (33.8–53.5)	1.4 (1.2–2.7)	N
3 p.m.–6 p.m.	30.5 (28.3–33.7)	46.3 (41.2–56.8)	2.1 (1.1–3.2)	N
6 p.m.–9 p.m.	27.8 (27.1–31.5)	53.5 (44.2–61.8)	1.9 (0.7–2.8)	E
9 p.m.–12 a.m.	25.5 (22.6–29.1)	58.5 (53.7–80.0)	0.9 (0.1–1.8)	ENE

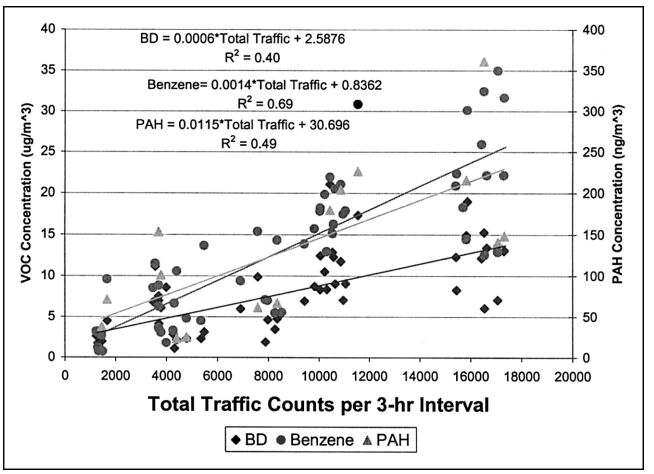

Figure 4. Scatter plot with simple linear regression of 1,3-butadiene, benzene, and PAH vs. total traffic counts per 3-hr interval. PAH concentration in ng/m^3.

The traffic volume regression coefficient is indicative of mobile source effect (ng/m^3/vehicle) based on 3-hr integrated measurements. Accordingly, a unit increase in 2-axle vehicle increases the curbside concentration of 1,3-butadiene, benzene, and PAH by 0.32, 1, and 4.5 ng/m^3, respectively. The >2-axle vehicle mobile source effect of 10.4, 9.5, and 271 ng/m^3/vehicle for 1,3-butadiene, benzene, and PAH exceeds that of 2-axle vehicles by factors of 32, 9, and 60, respectively. However, the difference in mobile source effect is partially offset by the traffic volume in each class, with 2-axle vehicles outnumbering >2-axle vehicles by a factor of 29. Therefore, taking both the mobile source effect and vehicle counts into account, the >2-axle vehicle contribution exceeds that of 2-axle vehicles by factors of 1.1 and 2.1 for 1,3-butadiene and PAH, respectively. For benzene, the inverse is true, with the 2-axle vehicle contribution exceeding the >2-axle vehicle contribution by a factor of 3.2.

DISCUSSION

The current study is designed to inform the source to effect continuum for mobile sources and cancer risk by elucidating the association between traffic volume and curbside levels of mobile source-related air pollution. Benzene, 1,3-butadiene, and PAH are of particular concern as environmental carcinogens. Although emission data are available from dynamometer testing[37] and tunnel tests[38,39] and annual ambient estimates have been modeled,[24,40] the current study represents some of the first time-resolved measurements quantifying the association between outdoor curbside pollutant levels and traffic volume and class. An advantage of the current study approach is that it provides actual in situ measurements that

Table 3. Coefficient of determination (R^2).

	2-Axle	>2-Axle	Temp	Wind Speed	Humidity	1,3-Butadiene	Benzene	PAH
2-Axle	1.0							
>2-Axle	0.5	1.0						
Temp	0.3	0.2	1.0					
Wind Speed	0.3	0.1	0.3	1.0				
Humidity	0.2	0.2	0.7	0.3	1.0			
1,3-Butadiene	0.4	0.5	0.2	0.1	0.2	1.0		
Benzene	0.6	0.5	0.4	0.1	0.3	0.7	1.0	
PAH	0.5	0.8	0.0	0.3	0.0	0.6	0.4	1.0

take into account a host of meteorological factors, including wind speed, temperature, and humidity. Furthermore, because the traffic patterns of 2-axle and >2-axle vehicles differed substantively, it has been possible to resolve their relative contribution to ambient levels.

Although the observed tollbooth 1,3-butadiene and benzene concentrations (means ranging from 2 to 11.9 and from 3 to 22.3 $\mu g/m^3$, respectively) are considerably higher than what has been observed even for urban environments, findings from this study may have particular relevance for urban communities built in close proximity to high-traffic arterials as exist in Baltimore. In comparison, the most recent data from the California Air Resource Board[41] indicate annual median 1,3-butadiene levels of 0.60 $\mu g/m^3$ (0.18–2.06) and 0.13 $\mu g/m^3$ (0.04–0.84) for urban and suburban locations, respectively. The corresponding annual median (range) benzene levels are 3.5 $\mu g/m^3$ (1.27–9.54) and 0.95 $\mu g/m^3$ (0.32–4.13). The annual average (range) urban and suburban 1,3-butadiene levels reported for Maryland in 1999 were 0.35 $\mu g/m^3$ (0.07–1.23) and 0.04 $\mu g/m^3$ (0–0.15), respectively. The corresponding values for benzene were 2.2 $\mu g/m^3$ (0.8–5.8) and 0.7 $\mu g/m^3$ (0.3–1.5), respectively.[42] Similar model-based estimates are given by Rosenbaum et al.[24] for all U.S. census tracts showing median annual average benzene and 1,3-butadiene levels of 1.6 and 0.18 $\mu g/m^3$, respectively. Therefore, the high-end tollbooth 1,3-butadiene and benzene levels typically exceed average urban ambient levels by approximately an order of magnitude and by 20–30-fold for the two pollutants, respectively. The observed higher tollbooth levels are caused by the proximity and intensity of the source (i.e., ~70,000 vehicles/day) and provide a valuable laboratory for examining the real-world impact of mobile sources on air quality.

The differences between particle-bound PAH levels previously measured in the urban environment relative to the current tollbooth study are less dramatic than for 1,3-butadiene and benzene. The lowest and highest median concentrations of 9.3 ng/m^3 (IQR = 10.7) and 199.3 ng/m^3 (IQR = 241.3) were observed during 9 p.m.–12 a.m. and 6 a.m.–9 a.m. intervals, respectively. Indoor median concentrations measured in homes without smokers in the Boston region using an Ecochem PAS monitor ranged from 8 to 19 to 31 ng/m^3 at suburban, semiurban, and urban locations, respectively.[43] In the same city during the summer of 1998, Dunbar et al.[44] reported median curbside concentrations over five days that ranged from 10 to 20 ng/m^3 (assuming 1 $fA/ng/m^3$). Based on integrated sampling and laboratory analysis methods, Naumova et al. [45] report outdoor median particle-phase ΣPAH levels ranging from 1 to 4 ng/m^3 for homes in Los Angeles, Houston, and Elizabeth.

Traffic volume was found to be a strong determinant for curbside concentrations of 1,3-butadiene, benzene, and PAH, explaining 62, 77, and 85%, respectively, of the air pollution levels, indicating that of the three pollutants, PAH is most strongly associated with traffic. The observed R^2 for 1,3-butadiene and benzene are consistent with EPA estimates of 56 and 60% of total 1,3-butadiene and benzene emissions attributable to on-road mobile sources.[46] In a recent study where the same model EcoChem instrument was used at a busy Boston intersection, Dunbar et al.[44] attributed 46% of the total particle-bound

Table 4. Multivariate analysis incorporating different VOCs and vehicle types.

Response Vehicle	Covariates	Reg. Coeff.	R^2	*P* value
Outdoor 1,3-butadiene *(n = 56)*	Model		0.62	<0.001
	2-axle	0.00032		0.02
	>2-axle	0.01039		<0.01
	Wind speed	−1.25576		0.08
	Temp	0.24694		0.1
	Intercept	−3.97692		0.27
Outdoor benzene *(n = 56)*	Model		0.77	<0.001
	2-axle	0.00103		<0.01
	>2-axle	0.0095		0.01
	Wind speed	−3.43332		<0.01
	Temp	0.88081		<0.01
	Intercept	−18.8696		<0.01
Outdoor PAH *(n = 14)*	Model		0.85	<0.001
	2-axle	0.00451		0.21
	>2-axle	0.27109		0.02
	Wind speed	40.2166		0.04
	Temp	−14.0235		0.48
	Intercept	370.826		0.04

PAH mass to primary motor vehicle emissions. Of this, 65% of the PAH mass was attributable to buses and trucks and 35% was attributable to cars. Although the basis for vehicle classification differs, these results are comparable to the simple linear regression results that showed 2-axle and >2-axle vehicles explaining 47 and 75% of the particle-bound PAH concentration variability.

Based on 3-hr integrated measurements, the coefficient given by the regression of traffic count on curbside ambient concentration provides an estimate of the mobile source effect on curbside concentration relevant to the location and meteorology of sampling. The magnitude of the source effect varied by pollutant and vehicle class. The highest mobile source effect was 0.2711 ng/m^3/vehicle for particle-bound PAH from >2-axle vehicles. This exceeded the 2-axle mobile source effect of 0.0045 ng/m^3/vehicle by a factor of 60. These results compare with Dunbar et al., [44] who attributed 65% of the total PAH mass to buses and trucks that comprised 6% of the total traffic volume, suggesting a 29-fold difference in mobile source effect between passenger vehicles and trucks and buses. Additional corroboration for high particulate matter emission of diesel vehicles relative to gasoline vehicles is given by Durbin et al.,[47] indicating diesel light-duty vehicles emit 1–2 orders of magnitude more particulate matter relative to gasoline vehicles.

For 1,3-butadiene and benzene, the current study suggests that >2-axle vehicles have mobile source effects that are 32 and 9 times greater than 2-axle vehicles, respectively. This difference is consistent in direction but higher than the 3- to 4-fold difference in hydrocarbon emissions suggested by EPA[40] for light-duty gasoline powered vehicles (approximately 0.6 g/mi for 1991–1997 vehicles with 50,000 mi) relative to heavy-duty diesel-powered vehicles (2.1 g/mi for 1991–1997 vehicles with 50,000 mi).

The observed difference in mobile source effect by number of vehicle axles is likely attributable to a combination of fuel type and consumption; that is, larger vehicles with >2 axles are likely to burn more fuel per mile and are more likely to have diesel engines. From the current study design, it is not possible to disentangle these two possible contributing effects. However, based on the Federal Highway Administration's (FHA) database of vehicle miles traveled,[35] it is possible to estimate fuel consumption by vehicle type. To compare the vehicle classification from the current study (i.e., by number of axles) to FHA's classification, it is necessary to assign the FHA classification to categories by axle: 2-axle vehicles = motorcycle, light-duty gas, and light-duty diesel; >2-axle vehicles = heavy-duty gas and heavy-duty diesel. Assuming this classification and based on the FHA database for the surrounding vicinity (Baltimore City, Baltimore County, and Anne Arundel County),[48] 99.7% of the gasoline is consumed by 2-axle vehicles whereas 72.2% of diesel fuel is consumed by >2-axle vehicles. These data indicate that although the 2-axle vehicle class is nearly all gasoline-powered, the >2-axle vehicle class is comprised of a mixture of diesel and gas, although predominantly diesel. Therefore, these data provide some substantiation that a difference between the vehicle axle categories considered in this study is caused by type of fuel.

The regression coefficients for wind speed and temperature were significant in explaining pollutant variability; however, a different effect was observed for the gas-phase VOCs relative to particle-bound PAHs. For 1,3-butadiene and benzene, an inverse association was observed, such that increasing wind speed was associated with decreased pollutant levels. This effect is likely caused by horizontal mixing with relatively less polluted regional air. In contrast, for particle-bound PAH, a direct association was observed with wind speed. The reason for this direct association is unclear. However, it may be because of the instrument's inlet configuration and collection bias caused by size. Because PAH adsorption and the instrument's response are both particle size-dependent,[34,49] it follows that alteration of the particle collection efficiency by size will alter the PAH concentration measurement. The observed effect is consistent with a bias of greater efficiency in sampling small particles with increased wind speed. Alternatively, this effect could result from resuspension of surface-deposited particle-bound PAH. It is unlikely that the observed effect was caused by some regional industrial source because no association was observed with wind direction.

CONCLUSIONS

The current study provides unique time-resolved measurements of traffic counts and vehicle class combined with the curbside concentrations of three key mobile source-related environmental carcinogens, that is, benzene, 1,3-butadiene, and particle-bound PAH. An examination of the variability in the source term relative to the resulting pollutant levels using multivariate regression analysis yielded a statistically significant association ($p < 0.001$), providing an empirical model for estimating pollutant levels from traffic volume and class taking into account wind speed and temperature. Because the traffic volume profile between 2-axle and >2-axle vehicles differed, it was possible to tease out a mobile source effect term (ng/m^3/vehicle) for these two classes. For all three pollutants, the mobile source effect of >2-axle vehicles exceeded that of 2-axle vehicles by as much as a factor of 60 for particle-bound PAH to factors of 9 and 32 for benzene and 1,3-butadiene, respectively. However, because 2-axle vehicles outnumber >2-axle vehicles by

29-fold, the overall contribution of 2-axle and >2-axle vehicles to total pollutant levels are within a factor of 1–3.

The current study's findings are based on measurements from a single location and season; therefore, generalization is limited. However, the high pollutant concentrations measured in close proximity to and during times of high traffic may be relevant to the exposure potential along commuting arterials that transect some urban communities. In cities such as Baltimore, the housing stock has been constructed in very close proximity (i.e., 6–10 ft) to these same heavily trafficked roadways. Exposures can be further exacerbated by the custom of stoop sitting and socializing typical in urban communities. Depending on time-activity patterns of urban residents (e.g., frequency, duration, and time of day at home), their exposure may be underestimated relative to estimates given by ambient central-site monitoring[41,42] or modeling.[24] Building on this study and to examine the relevance of extrapolating from the current study to the urban environment, additional studies are being conducted to assess traffic volume/class and indoor and outdoor pollution data on a busy urban arterial.

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