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RESEARCH REPORT

Air Toxics Exposure from Vehicle Emissions at a U.S. Border Crossing: Buffalo Peace Bridge Study

John Spengler, Jamson Lwebuga-Mukasa, Jose Vallarino, Steve Melly, Steve Chillrud, Joel Baker, and Taeko Minegishi



Includes a Commentary by the Institute's Health Review Committee



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ABOUT HEI

The Health Effects Institute is a nonprofit corporation chartered in 1980 as an independent research organization to provide high-quality, impartial, and relevant science on the effects of air pollution on health. To accomplish its mission, the institute

- Identifies the highest-priority areas for health effects research;
- Competitively funds and oversees research projects;
- Provides intensive independent review of HEI-supported studies and related research;
- Integrates HEI's research results with those of other institutions into broader evaluations; and
- Communicates the results of HEI's research and analyses to public and private decision makers.

HEI typically receives half of its core funds from the U.S. Environmental Protection Agency and half from the worldwide motor vehicle industry. Frequently, other public and private organizations in the United States and around the world also support major projects or research programs. HEI has funded more than 280 research projects in North America, Europe, Asia, and Latin America, the results of which have informed decisions regarding carbon monoxide, air toxics, nitrogen oxides, diesel exhaust, ozone, particulate matter, and other pollutants. These results have appeared in the peer-reviewed literature and in more than 200 comprehensive reports published by HEI.

HEI's independent Board of Directors consists of leaders in science and policy who are committed to fostering the public-private partnership that is central to the organization. The Health Research Committee solicits input from HEI sponsors and other stakeholders and works with scientific staff to develop a Five-Year Strategic Plan, select research projects for funding, and oversee their conduct. The Health Review Committee, which has no role in selecting or overseeing studies, works with staff to evaluate and interpret the results of funded studies and related research.

All project results and accompanying comments by the Health Review Committee are widely disseminated through HEI's Web site (*www.healtheffects.org*), printed reports, newsletters and other publications, annual conferences, and presentations to legislative bodies and public agencies.

ABOUT THIS REPORT

Research Report 158, Air Toxics Exposure from Vehicle Emissions at a U.S. Border Crossing: Buffalo Peace Bridge Study, presents a research project funded by the Health Effects Institute and conducted by Dr. John Spengler of the Harvard School of Public Health, Boston, Massachusetts, and his colleagues. This report contains three main sections.

The HEI Statement, prepared by staff at HEI, is a brief, nontechnical summary of the study and its findings; it also briefly describes the Health Review Committee's comments on the study.

The Investigators' Report, prepared by Spengler and colleagues, describes the scientific background, aims, methods, results, and conclusions of the study.

The Commentary is prepared by members of the Health Review Committee with the assistance of HEI staff; it places the study in a broader scientific context, points out its strengths and limitations, and discusses remaining uncertainties and implications of the study's findings for public health and future research.

This report has gone through HEI's rigorous review process. When an HEI-funded study is completed, the investigators submit a draft final report presenting the background and results of the study. This draft report is first examined by outside technical reviewers and a biostatistician. The report and the reviewers' comments are then evaluated by members of the Health Review Committee, an independent panel of distinguished scientists who have no involvement in selecting or overseeing HEI studies. During the review process, the investigators have an opportunity to exchange comments with the Review Committee and, as necessary, to revise their report. The Commentary reflects the information provided in the final version of the report.

HEI's Research Program on Air Toxics Hot Spots

INTRODUCTION

Air toxics comprise a large and diverse group of air pollutants that, with sufficient exposure, are known or suspected to cause adverse effects on human health, including cancer; effects on the development of organs and tissues, and damage to the respiratory, immune, neurologic, and reproductive systems. These compounds are emitted by a variety of indoor and outdoor sources and large numbers of people are exposed to them. Therefore, the compounds are a cause for public health concern, even though the ambient levels are generally low. The low ambient levels are one reason that tools and techniques for assessing specific health effects of air toxics are very limited.

Air toxics are not regulated by the U.S. Environmental Protection Agency (EPA) under the National Ambient Air Quality Standards. However, the EPA is required under the Clean Air Act and its amendments to characterize, prioritize, and address the effects of air toxics on public health and the environment, and it has the statutory authority to control and reduce the release of air toxics. The EPA is also required to regulate or consider regulating air toxics derived, at least in part, from motor vehicles (referred to as mobilesource air toxics [MSATs]) by setting standards for fuels, vehicle emissions, or both. In 2001 the EPA designated 21 high-priority MSATs that needed to be reduced (U.S. EPA 2001a). However, the EPA did not take any specific regulatory action at that time because rules mandating the reduction of sulfur in both gasoline and diesel fuels as a way to decrease particulate matter (PM) in emissions were expected to result in the reduction of several MSATs as well (U.S. EPA 2000, 2001b). Subsequently, the EPA identified eight MSATs that, based on their emissions and reported toxicity, pose the greatest risk to health benzene, 1,3-butadiene, formaldehyde, acrolein,

naphthalene, polycyclic organic matter, diesel PM, and diesel exhaust organic gases — and mandated the reduction of benzene in gasoline and of hydrocarbons (including MSATs) in exhaust (U.S. EPA 2007). In 2007, HEI published a critical review of the literature on exposure to and health effects associated with these highest-priority MSATs (HEI Air Toxics Review Panel 2007).

In trying to understand the potential health effects of exposure to toxic compounds, scientists often turn first to evaluating responses in highly exposed populations, such as occupationally exposed workers. However, workers and their on-the-job exposures are not representative of the general population, and therefore such studies may be somewhat limited in value.

Another strategy is to study populations living in "hot spots" — areas that have high concentrations of these pollutants owing to their proximity to one or more sources. Some hot spots may have sufficiently high pollutant concentrations to make them suitable locations for studies to determine whether there is a link between exposure to air toxics and an adverse health outcome. Such areas offer the potential to conduct health investigations in groups that are more representative of the general population. Before health effects studies can be initiated, however, actual exposures to pollutants including their spatial and temporal distributions — in such hot-spot areas must be characterized.

DESCRIPTION OF THE PROGRAM

In January 2003, HEI issued a Request for Applications (RFA 03-1) entitled "Assessing Exposure to Air Toxics," seeking studies aimed at identifying and characterizing exposure to air toxics from a variety of sources in areas or situations where concentrations were expected to be elevated. The rationale for the RFA was that understanding exposures in hot spots, as well as the sources of these exposures, would improve our ability to select the most appropriate sites, populations, and endpoints for subsequent health studies. HEI was particularly interested in studies that focused on the high-priority MSATs.

Five studies, including the one by Spengler and colleagues described in this report (Research Report 158), were funded under this RFA to represent a diversity of possible hot-spot locations and air toxics. The studies are summarized below.

"Assessing Exposure to Air Toxics," Eric M. Fujita, Desert Research Institute, Reno, Nevada (Principal Investigator)

In this study, presented in HEI Research Report 156 (2011), Fujita and colleagues measured the concentrations of PM and MSATs on major California freeways and compared them with corresponding measurements obtained at fixed monitoring stations. The diurnal and seasonal variations in concentrations of selected pollutants and the contribution of diesel-and gasoline-powered vehicles to selected air toxics and elemental carbon were also determined.

"Measurement and Modeling of Exposure to Air Toxics and Verification by Biomarkers," Roy M. Harrison, University of Birmingham, Birmingham, United Kingdom (Principal Investigator)

In the study described in HEI Research Report 143 (2009), Harrison and colleagues investigated personal exposure to a broad range of air toxics, with the goal of developing detailed personal-exposure models that would take various microenvironments into account. Repeated measurements of exposure to selected air toxics were made for each of 100 healthy nonsmoking adults who resided in urban, suburban, or rural areas of the United Kingdom, among which exposures to traffic were expected to differ; repeated urine samples were also collected for analysis. Harrison and colleagues developed models to predict personal exposure on the basis of microenvironmental concentrations and data from time-activity diaries; they then compared measured personal exposure with modeled estimates of exposure.

"Assessing Personal Exposure to Air Toxics in Camden, New Jersey," Paul Lioy, Environmental and Occupational Health Sciences Institute, Piscataway, New Jersey (Principal Investigator)

Lioy and colleagues measured ambient and personal exposure concentrations of air toxics and fine PM for 107 nonsmoking participants in two neighborhoods of Camden, New Jersey. One, considered to be a hot spot, had a high density of industrial facilities serviced by truck traffic and nearby busy roads. The other, with no industrial sources but near several highways, was considered an urban reference site. The investigators collected four sets of 24-hour personal air samples from the study subjects — in summer and winter and on weekdays and weekend days — and made simultaneous measurements of ambient pollutant concentrations at a fixed monitoring site in each neighborhood. To characterize finer spatial variability in pollutant levels, air toxics levels were measured at multiple sampling sites in each neighborhood during three sampling periods. The investigators also used modeling to estimate the contribution of ambient sources to personal exposure.

"Air Toxics Hot Spots in Industrial Parks and Traffic," Thomas Smith, Harvard School of Public Health, Boston, Massachusetts (Principal Investigator)

The study by Smith and colleagues measured levels of air toxics and PM in truck cabins and in 15 truck terminals across the United States. The HEI study was added to an ongoing study, funded by the National Cancer Institute, of the relationship between exposure to diesel exhaust and mortality from lung cancer among dockworkers and truck drivers at more than 200 truck terminals in the United States. Smith and colleagues measured pollutants at upwind and downwind locations around the perimeter of each terminal and at loading docks. The degree of variation at different locations and the influence of wind direction were also evaluated with the goal of identifying the potential impact of truck terminals on the surrounding areas. Continuous sampling was performed inside delivery truck cabins during a work shift.

"Air Toxics Exposure from Vehicular Emissions at a U.S. Border Crossing," John Spengler, Harvard School of Public Health, Boston, Massachusetts (Principal Investigator)

The study by Spengler and colleagues, presented in this report, assessed concentrations of MSATs surrounding the plaza adjacent to the Peace Bridge, a major border crossing between the United States and Canada, located in Buffalo, New York, Three fixed monitoring sites were used to compare pollutant concentrations upwind and downwind of the plaza. Meteorologic measurements and hourly counts of trucks and cars crossing the bridge were used to examine the relationship between the concentrations of air toxics and traffic density. To study spatial distributions of pollutants, members of the investigative team used portable instruments and a Global Positioning System to obtain location-specific, timestamped measurements as they walked along four routes in a residential neighborhood near the plaza.

The report on the study of Spengler and colleagues is the third of the five funded under RFA 03-1 to be published. Harrison and colleagues' report was published in 2009 and that by Fujita and colleagues in 2011. The two remaining studies have been completed and are currently at varying stages of the publications process. They are expected to be released in 2011 and early 2012. HEI is committed to continuing research on air toxics — for example, as part of studies to assess the health outcomes of air quality actions or studies to evaluate the effects of new technologies and fuels.

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HEI STATEMENT Synopsis of Research Report 158

Air Toxics Exposure from Vehicle Emissions at a U.S. Border Crossing

BACKGROUND

Motor vehicles and other combustion sources emit many air toxics that are either known or suspected, with sufficient exposure, to cause adverse health effects. Characterization of exposure to air toxics has been challenging, in part, because of the low ambient levels of individual compounds. HEI has had a long-standing commitment to improving methods for measuring selected air toxics and increasing our understanding of exposure and health effects. In 2003 HEI targeted research to identify and characterize so-called hot spots, areas where concentrations of one or more air toxics are expected to be elevated. Dr. John Spengler and colleagues hypothesized that vehicle-related emissions from traffic backed up at the Peace Bridge in Buffalo, New York, one of the nation's busiest border crossings, would result in higher levels of mobile-source air toxics (MSATs) directly downwind. They proposed a study to measure levels of air toxics, including MSATs, upwind and downwind of the plaza adjacent to the Peace Bridge, to examine the relation between traffic at the bridge and pollutant concentrations in ambient air, and to explore geographic patterns of ambient air pollutants in this potential hot spot for mobile-source emissions.

APPROACH

The investigators measured levels of a large number of compounds that might be expected in exhaust from diesel and gasoline vehicles, including volatile organic compounds (VOCs), polycylic aromatic hydrocarbons (PAHs), and nitrogenated PAHs (NPAHs). Their analyses focused on comparing pollutant levels measured at fixed sites on opposite sides of the 17-acre plaza adjacent to the Peace Bridge, which comprised the U.S. Customs Building, a customs inspection and holding area, tollbooths, a duty-free store, the Peace Bridge Authority Administration Building, and parking space. Residential and commercial areas abut the plaza to the east, north, and south, with Lake Erie and the Niagara River to the west.

During pilot studies in July 2004 and January 2005, the investigators sampled air at sites upwind and downwind of the plaza and tested a variety of routes for mobile monitoring in a neighborhood next to the plaza. They collected meteorologic data and bridge traffic counts by vehicle type (cars, trucks, and buses), for all sampling days. Prevailing wind directions were determined from 10 years of weather data from the Buffalo Niagara International Airport, which demonstrated that the wind blows from the west side of the plaza (off Lake Erie) about 45% of the time (lake winds) and from the east on the Buffalo side of the plaza (city winds) about 31% of the time. The investigators established two fixed sampling sites for both continuous monitoring and integrated sampling during the summer 2004 pilot study: one to the southwest of the plaza at the Great Lakes Center (GLC site), which they describe as an upwind site, and the other in front of the Episcopal Church Home (Chapel site) adjacent to the east side of the plaza, which they describe as a downwind site. They also tested routes, equipment, and protocols for mobile monitoring of pollutants around the Peace Bridge plaza area, including the neighborhood of Buffalo directly to the east. The researchers added a third fixed sampling site in this neighborhood (School site) during the winter 2005 pilot study.

After the two pilot studies, Spengler's team conducted two larger-scale sampling campaigns featuring both fixed-site and mobile monitoring components. Samples were collected simultaneously at all three fixed sampling sites for two weeks in July 2005 and two weeks in January 2006. The research team collected integrated samples at

This Statement, prepared by the Health Effects Institute, summarizes a research project funded by HEI and conducted by Dr. John Spengler, of the Department of Environmental Health, Harvard School of Public Health, Boston, Massachusetts, and colleagues. Research Report 158 contains both the detailed Investigators' Report and a Commentary on the study prepared by the Institute's Health Review Committee.

these sites and also from collocated real-time continuous monitors that took measurements every minute.

The mobile monitoring campaign was designed to assess the levels of selected pollutants in the neighborhood adjacent to the Peace Bridge plaza. Staff members wore backpacks containing air monitoring equipment and carried GPS (Global Positioning System) units while walking along one of four designated routes in the neighborhood. Pollutant data and GPS coordinates from the mobile monitoring campaigns were used to create maps showing the spatial distribution of pollutants in the neighborhood east of the Peace Bridge plaza.

RESULTS

Spengler and colleagues discuss most of their results by comparing sites that were predominantly upwind and downwind of the Peace Bridge plaza. By considering both the prevailing wind direction and the wind direction measured during the sampling campaigns, they were able to draw inferences about the likelihood that these measurements were related to the volume and composition of traffic traversing the Peace Bridge plaza. Approximately two thirds of the sampling days were classified as having lake-wind conditions that resulted in the GLC site being directly upwind, the Chapel site being directly downwind, and the School site being less directly downwind of the plaza.

The investigators compiled a wealth of comparative data on several different classes of MSATs — VOCs and carbonyls, elements, PAHs, and NPAHs — and measurements from continuous sampling of particulate matter (PM) $\leq 10 \ \mu m$ and $\leq 2.5 \ \mu m$ in aerodynamic diameter (PM₁₀ and PM_{2.5}, respectively), ultrafine particles (UFPs, defined as particles < 0.1 μm in aerodynamic diameter), particle-bound PAHs (pPAHs), and gaseous pollutants. For PM₁₀ and PM_{2.5}, and for the fraction of elemental carbon (EC) present in the collected PM_{2.5}, the mean daytime levels were highest at the Chapel site (typically downwind of the plaza), and higher at the residential School site than at the upwind GLC site.

The investigators created summary categories for selected VOCs and chlorinated compounds. In weekday 12-hour samples, overall mean and median levels of benzene, toluene, ethylbenzene, and xylenes (BTEX) were highest at the neighborhood School site, followed by the Chapel site, and then the GLC site. Overall mean and median levels of a summary category of five chlorinated compounds were very similar across the three sites. Median daytime benzene and formaldehyde levels were lowest by far at the GLC site. Overall mean and median daytime acetaldehyde levels were highest at the GLC site, nearly as high at the School site, and much lower at the Chapel site. Acetone levels for all daytime samples were slightly elevated at the GLC site.

Spengler's team analyzed fixed-site $PM_{2.5}$ samples for 28 different elements, of which only six calcium, chromium, manganese, iron, copper, and antimony — varied considerably across the three fixed sampling sites. Mean daytime weekday levels of these were, on average, higher at the Chapel site than at the other sites. The authors suggest that the higher concentrations of these elements at the Chapel site were related to emissions from traffic at the Peace Bridge plaza.

The researchers also noted important contrasts in levels of PAHs and NPAHs across the three fixed sampling sites. Concentrations of all but a few of the PAH compounds were higher at the Chapel site when the site was downwind of the city of Buffalo (rather than downwind of the bridge), implying that regional combustion and urban infrastructure contributed more PAHs than the emissions from traffic at the Peace Bridge plaza. Low-molecularweight PAHs, however, were consistently highest at the Chapel and School sites. Comparison of median concentrations of 14 NPAHs at the GLC and Chapel sites under lake-wind conditions showed that some were notably higher at the downwind Chapel site, indicating that traffic at the Peace Bridge plaza was a potential local source for these compounds.

In results from 600 hours of continuous measurement at each of the three fixed sampling sites, mean UFP counts were substantially higher at the Chapel site, followed by the School and GLC sites. The relative differences in UFP counts between the sites were similar in winter and summer, with all three sites recording higher counts in the winter. Concentrations of $PM_{2.5}$ were relatively uniform at the three sites, indicating that $PM_{2.5}$ levels in the study area may be dominated by regional air pollution patterns. For both 10-minute average and 12-hour average concentrations of PAHs in $PM_{2.5}$.

the highest mean concentrations were at the Chapel site, followed by the School and GLC sites. These results indicate an enrichment of PAHs at the Chapel and School sites, since the levels of PAHs in $PM_{2.5}$ varied across the sites while the levels of $PM_{2.5}$ did not.

During the mobile monitoring campaigns, UFP and pPAH levels were measured under different wind conditions at different times of day. Sampling results under city-wind conditions indicated that busy intersections, high-traffic roads, and neighborhood combustion sources are likely to have contributed to the UFP and pPAH levels measured by the mobile monitoring staff. Under lake-wind conditions, mobile monitoring results showed a general increase in concentrations of UFPs and pPAHs with decreasing distance from the Peace Bridge plaza.

The authors performed a source apportionment analysis using principal component analysis to analyze the data for individual elements and positive matrix factorization for the site-specific PAH measurements from the winter 2005, summer 2005, and winter 2006 sampling campaigns. The principal component analysis indicated that measured levels of elements associated with traffic emissions were higher at the Chapel site when it was downwind of the Peace Bridge plaza. Positive matrix factorization analyses, which divided the PAHs into light, medium, and heavy profiles based on their molecular weight, demonstrated relatively higher levels of the light PAHs at the upwind GLC site, higher levels of the medium PAHs at the downwind Chapel and School sites, and relatively uniform distribution of the heavy PAHs at all three sites.

Overall, to assess the plausibility of a relationship between traffic at the Peace Bridge plaza and levels of airborne pollutants at the Chapel and GLC sites on either side of the plaza, Spengler's team compared measurement data obtained with lake winds and with winds blowing over the city of Buffalo toward the lake. Pairing samples by sampling period and calculating the ratio of measured levels at the Chapel site to those at the GLC site, the authors ranked the results in terms of EC reflectance (EC-r). The Chapel-to-GLC ratios for EC-r were highest with lake-wind events, which would enrich levels of EC-r at the downwind Chapel site if they were the result of mobile-source emissions at the plaza. Based on these comparisons and their overall results, the investigators suggest that the traffic at the plaza was a source for the higher levels of compounds measured at the Chapel site.

INTERPRETATION

In its independent review of the study, the HEI Review Committee considered the methods that Spengler and his research team used to measure a large number of pollutants in a variety of ways to be sound and generally well implemented. The sampling campaigns were very well conducted, and the data were of high quality overall. The mobile monitoring scheme using GPS units and real-time measuring equipment carried in backpacks was innovative and successful. However, the investigators' source apportionment analysis was exploratory and inconclusive, owing to the relatively small number of samples available for analysis.

The investigators made some important innovations and contributions to study design for research intended to identify potential hot spots, particularly for emissions from traffic and roadway sources. The study demonstrated that a concentration of mobilesource emissions, combined with relatively consistent meteorologic conditions, could result in an area of elevated pollutant concentrations that shifts with changing wind conditions. Thus the results indicate that wind speed and wind direction should be considered in the selection of sampling sites in any study attempting to characterize measured pollutant levels surrounding a putative hot spot.

Whether a hot spot can be defined as a particular location with elevated concentrations of pollutants arising from a local source, as it is in this study, or whether it should be more broadly defined as an area where levels of pollutants are excessively high in general (compared with a standard level or with levels reported in the literature), is debatable. The Review Committee had two reservations regarding the investigators' conclusion that the study area constituted a hot spot. First, while differences in methods, instruments, and other conditions make it difficult to compare results across studies, the MSAT levels reported in this study were not high relative to levels measured at other U.S. locations. The authors note this in their comparison of the measurements for a variety of elements and compounds with those in the 2006 TEACH (Toxics Exposure Assessment Columbia and Harvard)

studies in New York City and Los Angeles and the 2005 RIOPA (Relationships of Indoor, Outdoor, and Personal Air) study in Houston and Los Angeles. Second, though meteorologic conditions will affect pollutant levels at any location, the Committee noted that the elevated concentrations near the Peace Bridge were particularly dependent on wind direction: the neighborhood to the east did not generally experience higher pollutant levels for the 55% of the time (40% in the summer) when the wind was not blowing from the Peace Bridge plaza.

The Review Committee decided that differences of interpretation in the definition a hot spot should not detract from the research effort by Spengler and his team and their excellent job of characterizing and investigating an area with potentially high emissions of MSATs.

CONCLUSIONS

Although the levels of MSATs in the area near the Peace Bridge in Buffalo may not be high relative to those in other locations in the United States, these data contribute to our understanding of how traffic emissions may result in elevated levels of air toxics in a local area. Spengler and colleagues devised a study design and sampling program for characterizing concentrations of air toxics in an area of potentially high emissions that included some important and innovative features. They selected a good location for a study of traffic-related emissions by targeting a somewhat geographically isolated source of potentially high emissions for intensive sampling and analysis. Finally, their mobile monitoring program for measuring pollutant levels in a local neighborhood is technically sound and economical, and thus will be valuable for studies of fine variations in pollutant concentrations in relatively small geographic areas.

Air Toxics Exposure from Vehicle Emissions at a U.S. Border Crossing: Buffalo Peace Bridge Study

John Spengler, Jamson Lwebuga-Mukasa, Jose Vallarino, Steve Melly, Steve Chillrud, Joel Baker, and Taeko Minegishi

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ABSTRACT

The Peace Bridge in Buffalo, New York, which spans the Niagara River at the east end of Lake Erie, is one of the busiest U.S. border crossings. The Peace Bridge plaza on the U.S. side is a complex of roads, customs inspection areas, passport control areas, and duty-free shops. On average 5000 heavy-duty diesel trucks and 20,000 passenger cars traverse the border daily, making the plaza area a potential "hot spot" for emissions from mobile sources.

In a series of winter and summer field campaigns, we measured air pollutants, including many compounds considered by the U.S. Environmental Protection Agency (EPA*) as mobile-source air toxics (MSATs), at three fixed sampling sites: on the shore of Lake Erie, approximately 500 m upwind (under predominant wind conditions) of the Peace Bridge plaza; immediately downwind of (adjacent to) the plaza; and 500 m farther downwind, into the community of west Buffalo. Pollutants sampled were particulate matter (PM) \leq 10 μ m (PM₁₀) and \leq 2.5 μ m (PM_{2.5}) in aerodynamic diameter, elemental carbon (EC), 28 elements, 25 volatile

organic compounds (VOCs) including 3 carbonyls, 52 polycyclic aromatic hydrocarbons (PAHs), and 29 nitrogenated polycyclic aromatic hydrocarbons (NPAHs). Spatial patterns of counts of ultrafine particles (UFPs, particles < 0.1 µm in aerodynamic diameter) and of particle-bound PAH (pPAH) concentrations were assessed by mobile monitoring in the neighborhood adjacent to the Peace Bridge plaza using portable instruments and Global Positioning System (GPS) tracking.

The study was designed to assess differences in upwind and downwind concentrations of MSATs, in areas near the Peace Bridge plaza on the U.S. side of the border. The Buffalo Peace Bridge Study featured good access to monitoring locations proximate to the plaza and in the community, which are downwind with the dominant winds from the direction of Lake Erie and southern Ontario. Samples from the lakeside Great Lakes Center (GLC), which is upwind of the plaza with dominant winds, were used to characterize contaminants in regional air masses. On-site meteorologic measurements and hourly truck and car counts were used to assess the role of traffic on UFP counts and pPAH concentrations. The array of parallel and perpendicular residential streets adjacent to the plaza provided a grid on which to plot the spatial patterns of UFP counts and pPAH concentrations to determine the extent to which traffic emissions from the Peace Bridge plaza might extend into the neighboring community.

For lake-wind conditions (southwest to northwest) 12-hour integrated daytime samples showed clear evidence that vehicle-related emissions at the Peace Bridge plaza were responsible for elevated downwind concentrations of $PM_{2.5}$, EC, and benzene, toluene, ethylbenzene, and xylenes (BTEX), as well as 1,3-butadiene and styrene. The chlorinated VOCs and aldehydes were not differentially higher at the downwind site. Several metals (aluminum,

This Investigators' Report is one part of Health Effects Institute Research Report 158, which also includes a Commentary by the Health Review Committee and an HEI Statement about the research project. Correspondence concerning the Investigators' Report may be addressed to Dr. John Spengler, Exposure Epidemiology and Risk Program, Department of Environmental Health, Harvard School of Public Health, P.O. Box 15677, Landmark Center 406 West, Boston, MA 02215.

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 $^{^{\}ast}$ A list of abbreviations and other terms appears at the end of the Investigators' Report.

calcium, iron, copper, and antimony) were two times higher at the site adjacent to the plaza as they were at the upwind GLC site on lake-wind sampling days. Other metals (beryllium, sodium, magnesium, potassium, titanium, manganese, cobalt, strontium, tin, cesium, and lanthanum) showed significant increases downwind as well. Sulfur, arsenic, selenium, and a few other elements appeared to be markers for regional transport as their upwind and downwind concentrations were correlated, with ratios near unity. Using positive matrix factorization (PMF), we identified the sources for PAHs at the three fixed sampling sites as regional, diesel, general vehicle, and asphalt volatilization. Diesel exhaust at the Peace Bridge plaza accounted for approximately 30% of the PAHs. The NPAH sources were identified as nitrate (NO₃) radical reactions, diesel, and mixed sources. Diesel exhaust at the Peace Bridge plaza accounted for 18% of the NPAHs.

Further evidence for the impact of the Peace Bridge plaza on local air quality was found when the differences in 10-minute average UFP counts and pPAH concentrations were calculated between pairs of sites and displayed by wind direction. With winds from approximately 160° through 220°, UFP counts adjacent to the plaza were 10,000 to 20,000 particles/cm³ higher than those upwind of the plaza. A similar pattern was displayed for pPAH concentrations adjacent to the plaza, which were between 10 and 20 ng/m³ higher than those at the upwind GLC site. Regression models showed better correlation with traffic variables for pPAHs than for UFPs. For pPAHs, truck counts and car counts had significant positive correlations, with similar magnitudes for the effects of trucks and cars, despite lower truck counts. Examining all traffic variables, including traffic counts and counts divided by wind speed, the multivariate regression analysis had an adjusted coefficient of determination (R^2) of 0.34 for pPAHs, with all terms significant at P < 0.002.

Study staff members traversed established routes in the neighborhood while carrying instruments to record continuous UFP and pPAH values. They also carried a GPS, which was used to provide location-specific time-stamped data. Analyses using a geographic information system (GIS) demonstrated that emissions at the Peace Bridge plaza, at times, affected ambient air quality over several blocks (a few hundred meters). Under lake-wind conditions, overall spatial patterns in UFP and pPAH levels were similar for summer and winter and for morning and afternoon sampling sessions.

The Buffalo Peace Bridge Study demonstrated that a concentration of motor vehicles resulted in elevated levels of mobile-source-related emissions downwind, to distances of 300 m to 600 m. The study provides a unique data set to assess interrelationships among MSATs and to ascertain the impact of heavy-duty diesel vehicles on air quality.

INTRODUCTION

Section 112(b) of the 1990 Clean Air Act Amendments defines 188 chemicals as hazardous air pollutants (HAPs). A HAP is an air pollutant "to which no ambient air quality standards are applicable and which in the judgment of the administrator [of the EPA] causes, or contributes to air pollution which may reasonably be anticipated to result in an increase in mortality or an increase in serious irreversible, or incapacitating reversible, illness." HAPs are chemicals that can adversely affect human health and the environment. These include, but are not limited to, substances that are known to be, or may reasonably be anticipated to be, carcinogenic, mutagenic, teratogenic, or neurotoxic, that cause reproductive dysfunction, or that are acutely or chronically toxic. An adverse environmental effect is defined as any significant and widespread adverse effect, which may reasonably be anticipated, to wildlife, aquatic life, or other natural resources, including adverse impacts on populations of endangered or threatened species or significant degradation of environmental quality over broad areas. Table 1 lists the 188 compounds specified as HAPs in 1990, as well as asbestos and lead compounds, which were already regulated.

In 1999, the EPA named 33 high-priority air pollutants in its Integrated Urban Air Toxics Strategy: 32 air toxics on the Clean Air Act list of 188 HAPs and diesel PM. In 2002, the EPA reported on its National-Scale Air Toxics Assessment (NATA) for these 33 pollutants based on 1996 emissions (Table 2). The assessment included a national inventory of emissions from outdoor sources, estimated ambient concentrations and population exposures across the contiguous United States, and characterization of potential public health risks due to inhalation of these air toxics, including both cancer and noncancer effects. The goal of the national-scale assessment was to identify those air toxics that are of greatest potential concern in terms of contribution to population risk.

Section 20.2 of the Clean Air Act Amendments sets emissions standards for HAPs from vehicles and fuel additives. In its 2001 Mobile Source Air Toxics rule, the EPA identified 21 MSATs (U.S. EPA 2001). A compound was listed as an MSAT if it was emitted from mobile sources, and if the EPA Integrated Risk Information System (IRIS) either listed the compound as a potential cancer hazard, or provided an inhalation reference concentration or ingestion reference dose for the compound.

Since 2001, the EPA has compiled a master list of more than 1000 compounds from mobile sources including fuel and lubricant additives (U.S. EPA 2006a). Table 3 lists chemical substances from mobile sources that meet the IRIS criteria. Other substances from mobile sources are not included in IRIS but are being assessed on an ongoing basis: for example, cesium, copper, ethanol, platinum, propionaldehyde, and 2,2,4-trimethylpentane. The latter two compounds, while not in IRIS, are HAPs and are thus subject to regulation. The MSAT analytes for the Buffalo Peace Bridge Study are listed together in Table 3. Note, however, that we did not speciate chromium III and chromium VI or identify compounds of beryllium, lead, or silver.

ASSESSING MAJOR SOURCES OF HEALTH RISKS FROM AIR TOXICS

In the NATA based on 1999 emissions, the EPA included national and regional assessments of 177 HAPs and diesel PM (U.S. EPA 2007). The assessment focused exclusively on outdoor exposures and relied extensively on modeled concentrations. Cancer and noncancer health effects were considered for both national-scale and regional-scale analyses that used different population-weighted risk criteria. For cancer, the national criterion was at least 25 million people exposed to risk > 10 in 1 million, and the regional criterion was at least 1 million people exposed to risk > 10 in 1 million, or at least 10,000 people exposed to risk > 100 in 1 million. For noncancer health effects, the national criterion was at least 25 million people with a hazard quotient (level of environmental exposure to the HAP divided by the level at which no adverse effects are expected) > 1.0, and the regional criterion was at least 10,000 people with a hazard quotient > 1. Table 4 lists those ambient HAPs that meet the 1999 NATA criteria for risk to the population, seven of which are considered to have significant contributions from mobile sources (U.S. EPA 2006b).

Studies like the California Multiple Air Toxics Exposure Study II (MATES-II) have demonstrated the spatial heterogeneity of air pollutants from mobile sources. The Los Angeles freeway studies of Zhu, Zhang, and colleagues demonstrated changing particle dynamics and concentration gradients as airflow crossed and moved downwind of a congested roadway segment (Zhu et al. 2002a, 2004, 2006a, 2006b; Zhang et al. 2004, 2005). A multicity European study used traffic indicators and distance measures to explain differences among sites for compounds related to mobile sources (Brauer et al. 2003). Several studies have now provided land-use and traffic data to relate mobile-source emissions to health (White et al. 2005).

More recently, the EPA has been developing rules to control compounds emitted from mobile sources, either as direct exhaust or as evaporative emissions from fuels (U.S. EPA 2007). Based on the 1999 NATA findings, the EPA estimated the percentages that mobile sources contributed to high-risk compounds in ambient air. Table 5, derived from the 1999 NATA assessment that identified the highrisk compounds found in Table 4, lists the seven high-risk compounds considered to have significant contributions from mobile sources and shows the percentages contributed by all mobile sources and by on-road mobile sources. Although all of the risk from diesel PM and diesel organic gas is attributed to mobile sources, the on-road mobile sources contribute about 38% to the total risk. Both benzene and 1,3-butadiene are from predominantly mobile sources, with more than 40% coming from on-road mobile sources.

ASSESSING POTENTIAL HEALTH RISKS FROM EXPOSURE TO MOBILE-SOURCE POLLUTION

Airports, bus depots, toll plazas, congested segments of roads, and major border crossings, among many other situations, contribute to small-scale variations in exposure from MSATs that are not captured in national or regional assessments of HAP risk. The results of the MATES-II study illustrate this issue (South Coast Air Quality Management District [SCAQMD] 2000). In MATES-II samplers were deployed in a dense array to capture variation in HAP concentrations within selected communities in southern California's Los Angeles Basin. Spatial analysis of MATES-II data showed that concentrations of air toxics were generally higher near their emission sources. Concentrations of MSATs such as benzene and 1,3-butadiene tended to be higher along freeway corridors and junctions. The levels of air toxics and consequently the cancer risks associated with these compounds were found to be highest in central and east-central Los Angeles County, where pollution is dominated by mobile sources.

The number of epidemiologic studies documenting associations between proximity to roadways or traffic exposure and an array of health effects, ranging from diminished quality of life to increased risk of cardiopulmonary mortality, continues to grow (Venn et al. 2000; Shima et al. 2003; Hwang et al. 2005; McConnell et al. 2006). These studies are widely reported for countries that have different mixes of motor vehicles and infrastructure patterns. Japan and European countries have a higher percentage of diesel vehicles than the U.S. and Canada. The proximity of residences to busy roadways also differs among countries, yet

Table 1. List of Hazardous Air	Pollutants as Defined by Section 112(b)	of the 1990 Clean Air Act Amendme	ants ^a
Acetaldehyde Acetamide Acetonitrile	Diazomethane Dibenzofurans 1,2-Dibromo-3-chloropropane	Hydrazine Hydrochloric acid Hydrogen fluoride (Hydrofluoric acid)	1,2-Propylenimine (2-Methyl aziridine) Quinoline Quinone
Acetophenone 2-Acetylaminofluorene	DibutyIphthalate 1,4-Dichlorobenzene(<i>p</i>)	Hydrogen sulfide Hydroquinone	Styrene Styrene oxide
Acrolein Acrylamide	3,3-Dichlorobenzidene Dichloroethyl ether (Bis(2-chloroethvl)ether)	Isophorone Lindane (all isomers)	2,3,7,8-Tetrachlorodibenzo- <i>p</i> -dioxin 1,1,2,2-Tetrachloroethane
Acrylic acid Acrylonitrile Allyl chloride	1,3-Dichloropropene Dichlorvos Diethanolamine	Maleic anhydride Methanol Methoxychlor	Tetrachloroethylene (Perchloroethylene) Titanium tetrachloride Toluene
4-Aminobiphenyl Aniline <i>o</i> -Anisidine	<i>N,N</i> -Dimethylaniline Diethyl sulfate 3,3-Dimethoxybenzidine	Methyl bromide (Bromomethane) Methyl chloride (Chloromethane) Methyl chloroform (1.1.1-Trichloroethane)	2,4-Toluene diamine 2,4-Toluene diisocyanate <i>o</i> -Toluidine
Asbestos Benzene (including benzene from gasoline)	Dimethyl aminoazobenzene 3,3'-Dimethyl benzidine	Methyl hydrazine	Toxaphene (chlorinated camphene) 1,2,4-Trichlorobenzene
Benzidine Benzotrichloride Benzyl chloride Biphenyl Bis(2-ethylhexyl)phthalate (DEHP)	Dimethyl carbamoyl chloride Dimethyl formamide 1,1-Dimethyl hydrazine Dimethyl sulfate Dimethyl sulfate	Methyl iodide (Iodomethane) Methyl isobutyl ketone (Hexone) Methyl isocyanate Methyl methacrylate Methyl <i>tert</i> -butyl ether	1,1,2-Trichloroethane Trichloroethylene 2,4,5-Trichlorophenol 2,4,6-Trichlorophenol Triethylamine
Bis(chloromethyl)ether Bromoform	4,6-Dinitro- <i>o</i> -cresol, and salts 2,4-Dinitrophenol	4,4-Methylene bis(2-chloroaniline) Methylene chloride (Dichloromethane)	Trifluralin 2,2,4-Trimethylpentane
1,3-Butadiene Calcium cyanamide Caprolactam	2,4-Dinitrotoluene 1,4-Dioxane (1,4-Diethyleneoxide) 1,2-Diphenylhydrazine	Methylene diphenyl diisocyanate 4,4-Methylenedianiline Naphthalene	Vinyl acetate Vinyl bromide Vinyl chloride
Captan	Epichlorohydrin (l-Chloro-2,3- epoxypropane)	Nitrobenzene	Vinylidene chloride (1,1-Dichloroethylene)
Carbaryl Carbon disulfide Carbon tetrachloride Carbonyl sulfide Catechol Chloramben	1,2-Epoxybutane Ethyl acrylate Ethyl benzene Ethyl carbamate (Urethane) Ethyl chloride (Chloroethane) Ethylene dibromide (Dibromoethane)	4-Nitrobiphenyl 4-Nitrophenol 2-Nitropropane N-Nitroso-N-methylurea N-Nitrosodimethylamine N-Nitrosomorpholine	Xylenes (isomers and mixture) o-Xylenes m-Xylenes p-Xylenes
Table continues next page			

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Chlordane Chlorine				
Chlorine	Ethylene dichloride (1.2-Dichloroethane)	Parathion	Antin	iony compounds
	Ethylene glycol	Pentachloronit (Ouintobenzer	robenzene Arser ae) inclu	ic compounds (inorganic Iding arsine)
Chloroacetic acid 2-Chloroacetophenone	Ethylene imine (Aziridine) Ethylene oxide	Pentachlorophe Phenol	anol Beryl Cadm	ium compounds ium compounds
Chlorobenzene Chlorobenzilate	Ethylene thiourea Ethylidene dichloride (1.1-Dichloroethane)	<i>p</i> -Phenylenedi Phosgene	amine Chror Cobal Coke	iium compounds t compounds oven emissions
Chloroform Chloromethyl methyl ether Chloroprene	Formaldehyde Heptachlor Hexachlorobenzene	Phosphine Phosphorus Phthalic anhyd	Cyani Glycc Tide Lead	de compounds ^b l ethers ^c compounds
Cresols/Cresylic acid (isome and mixture)	rs Hexachlorobutadiene	Polychlorinate (Aroclors)	ł biphenyls Mang	anese compounds
<i>o</i> -Cresol <i>m</i> -Cresol <i>p</i> -Cresol	Hexachlorocyclopentadier Hexachloroethane Hexamethylene-1,6-diisoc;	 μe 1,3-Propane su β-Propiolacton yanate Propionaldehy 	ltone Merci e Fine i de Nicke	rry compounds nineral fibers ^d l compounds
Cumene Dichlorodiphenyl- dichloroethylene (DDE)	Hexamethylphosphoramid Hexane	le Propoxur (Bayg Propylene dich (1,2-Dichlorof	gon) Polyc loride Radic oropane)	ylic organic matter ^e nuclides (including radon) ^f
2,4-Dichlorophenoxyacetic acid, salts and esters		Propylene oxid	e Selen	ium compounds
¹ For all listings in the table that cont named chemical (e.g., antimony, ar 2 Y'CN where X = H' or any other or	ain the word "compounds" and for glyc senic) as part of that chemical's infrast www.where.a formal dissociation may o	col ethers, unless otherwise specified ructure. cour For example, KCN or Ca(CN).	l, the listing is defined as including	any unique chemical substance that contains the
^c Includes more and diethers of ethy yield glycol ethers with the structu d Includes mineral fiber amissions fr	ylene glycol, diethylene glycol, and tri re: R(OCH2_CH), OH. Polymers are exc	ethylene glycol $R(OCH_2CH_2)^{-1}OR^{-1/2}$. Iuded from the glycol category.	here <i>n</i> = 1, 2, or 3, R = alkyl or aryl	groups, R' = R, H, or groups that, when removed, dismoter 1 nm or less
e Includes organic compounds with 1	more than one benzene ring, and which	h have a boiling point greater than o	r equal to 100°C.	
^f A type of atom that spontaneously ⁱ	undergoes radioactive decay.			
Table 2. Air Pollutants in th	ie 1996 National-Scale Air Tox	cics Risk Assessment		
Acetaldehyde Acrolein Acrylonitrile	Cadmium compounds Carbon tetrachloride Chloroform	Ethylene dibromide Ethylene dichloride Ethylene oxide	Manganese compound Mercury compounds Methylene chloride	s Propylene dichloride Quinoline 1,1,2,2-Tetrachloroethane
Arsenic compounds Benzene Beryllium compounds 1,3-Butadiene	Chromium compounds Coke oven emissions 1,3-Dichloropropene Diesel PM	Formaldehyde Hexachlorobenzene Hydrazine Lead compounds	Nickel compounds Perchloroethylene Polychlorinated biphe Polycyclic organic ma	Trichloroethylene Vinyl chloride ayls ter

Analyzed in This Study		
Acenaphthene	Cadmium	Manganese
Acetaldehyde	Carbon tetrachloride	Methyl <i>tert</i> -butyl ether (MTBE)
Acetone	Chloroform	2-Methylnaphthalene
Acrolein (2-propenal)	Chromium III	Naphthalene
Anthracene	Chromium VI	Nickel
Antimony	Chrysene	Pyrene
Arsenic, inorganic	Dibenz[<i>a</i> , <i>h</i>]anthracene	Selenium and compounds
Benz[<i>a</i>]anthracene	Ethylbenzene	Silver
Benzene	Fluoranthene	Strontium
Benzo[<i>a</i>]pyrene	Fluorene	Styrene
Benzo[b]fluoranthene	Formaldehyde	Toluene
Benzo[k]fluoranthene	n-Hexane	1,1,1-Trichloroethane
Beryllium and compounds	Indeno[1,2,3- <i>c,d</i>]pyrene	Vanadium
1,3-Butadiene	Lead and compounds (inorganic)	Xylenes
		Zinc and compounds
Not Analyzed in This Study		
Acetophenone	1,2-Dibromoethane	2-Methylphenol
Ammonia	Dibutyl phthalate	4-Methylphenol
Barium and compounds	1,2-Dichlorobenzene	Molybdenum
Benzaldehyde	2,4-Dinitrophenol	Nitrate
Benzoic acid	Dichloromethane	N-Nitrosodiethylamine
1,1-Biphenyl	Diesel PM and diesel exhaust organic	N-Nitrosodimethylamine
	gases	
Boron (boron and borates only)	Diethyl phthalate	<i>N</i> -Nitroso-di- <i>n</i> -butylamine
Bromomethane	Ethylene glycol monobutyl ether	<i>N</i> -Nitroso-di- <i>n</i> -propylamine
Butyl benzyl phthalate	Furfural	N-Nitrosopyrrolidine
Carbon disulfide	Hexachlorodibenzo- <i>p</i> -dioxin, mixture	Pentachlorophenol
Chlorine	Hydrogen cyanide	Phenol
Chlorobenzene	Hydrogen sulfide	Phosphorus
	Maragon sumus	
	Methodal	rnmalic annyoride
Curlehevene	Methyl oblogida	1,1,1,2-10TAIIUOFO0TAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
Cyclonexane	Methyl chioride Mathyl athyl katona	Trichleroflycromethero
	Methyl enyl Keloffe	memoromoromemane
Ditz-emymexynphinalate	wennyi isobutyi ketone	

Table 3. Chemical Substances Emitted by Mobile Sources That Are Listed in IRIS^{a,b}

^a Chemical substances listed in IRIS as known, probable, or possible human carcinogens and/or pollutants for which the EPA has calculated a reference concentration or reference dose. 2,2,4-Trimethylpentane, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, 2,4-dinitrophenol polycyclic organic matter, and priopionaldehyde are compounds emitted by mobile sources and are listed in Clean Air Act Amendments section 112(b) but are not listed in IRIS.

^b Bold indicates chemical substances that are also listed in Section 112(b) of the Clean Air Act Amendments.

there is a general consistency within the literature on the health effects of traffic-related pollution.

A few years ago Spengler and Samet convened a multidisciplinary workshop to discuss the evidence for trafficrelated effects on health and to identify the challenging issues still unresolved (White et al. 2005). The following points were made in the summary of the workshop (White et al. 2005) and are included here as a condensed appraisal of the difficulty with exposure assessment:

• Studies from throughout the world have reported increased risk of respiratory symptoms and asthma with proximity to or increased concentrations of traffic-related pollution (Murakami et al. 1990; Braun-Fahrlander et al. 1992; Nitta et al. 1993; Oosterlee et al.

Cancer	Risk ^a	Noncancer Risk			
This Study	Others ^b	This Study	Others ^b		
National Criteria ^c					
Benzene		Acrolein			
Regional Criteria ^d					
Arsenic compounds 1,3-Butadiene Cadmium compounds Carbon tetrachloride Chromium VI Naphthalene	Benzidine Coke oven emissions Ethylene oxide Hydrazine Perchloroethylene 2,4-Toluene diisocyanate	Antimony Arsenic compounds 1,3-Butadiene Cadmium compounds Chromium VI Formaldehyde	Chlorine Diesel PM Hexamethylene 1-6-diisocyanate Hydrazine Hydrochloric acid Maleic anhydride		
Polycyclic organic matter Manganese compounds Nickel compounds	Triethylamine				

Table 4. Pollutants That Meet Criteria for Cancer and Noncancer Risk in 1999 NATA (U.S. EPA 2006b)

^a Though diesel PM does not meet the criteria for cancer risk, the 1999 NATA concluded that it was one of the pollutants that posed the greatest relative cancer risk.

^b "Others" are pollutants that were not analyzed in the Peace Bridge Study.

^c The national criterion for cancer risk is at least 25 million people exposed to risk > 10 in 1 million; for noncancer risk, at least 25 million people exposed to a hazard quotient > 1.

 $^{\rm d}$ The regional criterion for cancer risk is at least 1 million people exposed to risk > 10 in 1 million or at least 10,000 people exposed to risk > 100 in 1 million; for noncancer risk, at least 10,000 people exposed to a hazard quotient > 1.

1996; van Vliet et al. 1997; Ciccone et al. 1998; Kramer et al. 2000; Venn et al. 2000; Gehring et al. 2002; Brauer et al. 2003; Garshick et al. 2003; Nicolai et al. 2003), and some studies have identified an increased risk of cardiopulmonary and stroke mortality (Hoek et al. 2002; Maheswaran and Elliott 2003). Some evidence also suggests that traffic density and proximity may affect prenatal health (Wilhelm and Ritz 2003; Yang et al. 2003). However, evidence for other outcomes, such as hospitalization and medication use for asthma and risk of a varietv of cancers, has been mixed (Edwards et al. 1994; Duhme et al. 1996; Livingstone et al. 1996; Feychting et al. 1998; English et al. 1999; Harrison et al. 1999; Wilkinson et al. 1999; Morris et al. 2000; Nyberg et al. 2000; Pearson et al. 2000; Buckeridge et al. 2002; Lin et al. 2002; Nafstad et al. 2003; Shima et al. 2003; Reynolds et al. 2004; Zmirou et al. 2004; Gordian et al. 2006). The specific components of the pollution mixture contributing to the adverse health effects, however, are uncertain.

 The primary emissions from mobile sources include nitrogen oxides (NO_x), carbon monoxide (CO), and hydrocarbons. Operating engines generally emit exhaust particles as submicrometer-size aerosols (< 1 µm) (Morawska et al. 1998; Ristovski et al. 1998). The pollutants decrease in concentration as they are dispersed in air, and their size distribution shifts, with increasing domination of larger particles at greater distances from roadways. This dynamic process occurs rapidly (Hitchins et al. 2000; Zhu et al. 2002b; Zhang et al. 2004), and it can be influenced by temperature and meteorologic conditions. In addition, types of vehicles, driving behaviors, and vehicle speeds can all affect the characteristics of local pollution from mobile sources (National Research Council 2000).

- Other potentially hazardous vehicle-related combustion products are VOCs, carbonyls, and semivolatile organic compounds such as PAHs and NPAHs (U.S. EPA 2002). The stress of traffic noise may also contribute to adverse health responses.
- Another source of air pollution is the resuspension of "road dust" caused by traffic. These predominantly coarse particles can contain a complex mixture of earth-crustal material, asphalt, metals, latex tire fragments, debris from the wearing of vehicle parts, and motor oil (Rogge et al. 1993b; Abu-Allaban et al. 2003; Riediker et al. 2004).

While the scientific literature associates vehicle emissions with adverse health outcomes, several unanswered questions about exposure remain. The Buffalo Peace Bridge Study was a detailed examination of air pollution near a site of dense vehicle emissions. The selected analytes covered a broad list of elements, VOCs, PAHs, and NPAHs, including most MSATs. The sampling strategy was

	Percentage Contribution				
Pollutant	All Mobile Sources	On-Road Mobile Sources			
Benzene	68	49			
1,3-Butadiene	58	41			
Formaldehyde	47	27			
Acrolein	25	14			
Polycyclic organic matter ^b	6	3			
Naphthalene	27	21			
Diesel PM and diesel exhaust organic gases	100	38			

Table 5. Contributions of Mobile Sources to 1999 NATAHigh-Risk Pollutants (U.S. EPA 2006b)^a

^a All compounds, except for diesel PM and diesel exhaust organic gases, were part of the suite of compounds analyzed in the Peace Bridge Study.

^b This polycyclic organic matter inventory includes the following 15 compounds, all of which were analyzed in this study: benzo[b]fluoranthene, benz[a]anthracene, indeno[1,2,3-c,d]pyrene, benzo[k]fluoranthene, chrysene, benzo[a]pyrene, dibenz(a,h)anthracene, anthracene, pyrene, benzo(g,h,i)perylene, fluoranthene, acenaphthylene, phenanthrene, fluorene, and acenaphthene.

designed to differentiate mobile-source emissions emanating from the Peace Bridge plaza from the regional air mass, thus identifying and characterizing the complexity of vehicle-related emissions.

PEACE BRIDGE BORDER CROSSING AS A POTENTIAL HOT SPOT FOR MOBILE-SOURCE POLLUTION

International border crossings between the U.S. and its neighbors channel large volumes of vehicles, particularly diesel trucks. The Peace Bridge crossing at Buffalo ranked third among U.S. land ports in terms of handling commercial trade between North American Free Trade Agreement (NAFTA) partners in 2000, behind Detroit, Michigan, and Laredo, Texas (U.S. Department of Transportation 2001). Roughly 5000 diesel trucks and 20,000 passenger cars traverse this border daily (Peace Bridge Authority 2005). The heavy traffic, with vehicles idling and accelerating as they stop for toll collection, passport control, and customs inspection, results in a high concentration of vehicle emissions. A segment of Interstate 190 (the Niagara section of the New York Thruway) that passes through the Peace Bridge border area also contributes to the traffic pollution.

Before 2005, all the tollbooths, customs areas, the Peace Bridge Authority Administration Building, and a duty-free shop were located in the Peace Bridge plaza on the U.S. side of the border, adjacent to west Buffalo neighborhoods. In early 2005 toll collection was relocated to the Canadian side, and the tollbooths on the American side were demolished during June and July 2005. Passport control and customs inspection remained on the U.S. side. The old duty-free shop was demolished and replaced by a larger one, located at the intersection of two streets on the edge of the Peace Bridge plaza.

The EPA defines a hot spot for emissions from mobile sources as a local area where air quality is of concern owing to spatially dense emissions patterns. A variety of situations can create hot spots. Typically, one associates them with infrastructure such as truck stops and tollbooths. Some areas might become mobile-source hot spots on a regular basis, such as converging roads during traffic rush hours; others might become hot spots irregularly, such as when there is an accident, or nearby construction, or during an entertainment event. Hot spots need not be associated with high-volume traffic. Slowly moving vehicles accelerating up inclines can increase emissions densities, as engines in high torque require fuel-rich conditions, increasing emissions of some contaminants.

The Peace Bridge plaza can be considered a mobilesource hot spot on several accounts. Cars and trucks converge there, and the passport controls, customs inspection, overnight rest areas for truck drivers, and duty-free shopping all are associated with increased idle time for trucks. The ramp to the bridge rises abruptly from the plaza directly in front of a residential neighborhood, and vehicles must accelerate on this slope as they leave the U.S. On occasion when congestion builds because of vehicle volume or increased security, traffic is directed onto Busti Avenue, an adjacent neighborhood road.

Whether the high prevalence of asthma reported in the west Buffalo community, which abuts the Peace Bridge plaza, is in any way related to local traffic congestion is unknown. Clustering of cases of chronic respiratory illnesses in the community has raised concern that trafficrelated pollution may be contributing to the disease prevalence and morbidity. Nearly 20% of school-age children in the west Buffalo neighborhood have been reported to suffer from asthma (Lwebuga-Mukasa and Dunn-Georgiou 2000). This is substantially higher than the 5.8% asthma prevalence rate estimated for the entire country (Eder et al. 2006) and is 2.75 times what has been found in the other Buffalo communities (Lwebuga-Mukasa et al. 2005). In case-control studies of asthma and nonrespiratory illness such as acute gastroenteritis in Buffalo, asthma cases were clustered close to the Peace Bridge plaza, and the risk for asthma decreased the farther an individual resided from the plaza (Oyana and Lwebuga-Mukasa 2004; Oyana et al. 2004). The high rates of respiratory disease prevalence were not fully explained by personal, household, or socioeconomic factors (Lwebuga-Mukasa et al. 2004, 2005). In multivariate regression analysis of risk factors, residence in the west Buffalo neighborhood was an independent risk factor for asthma diagnosis (Lwebuga-Mukasa et al. 2004). Furthermore, this area was shown to be downwind of putative sources of traffic-related pollution emanating from truck traffic (Lwebuga-Mukasa et al. 2005).

This border crossing between the U.S. and Canada will continue to be an important corridor for the NAFTA partners, as well as for U.S. and Canadian citizens, as it provides access to the shortest routes between New York, New England, and Detroit. By 2021 it is predicted that truck crossings will increase from the current 1.5 million to more than 4 million per year (Peace Bridge Authority 2000). Since September 11, 2001, increased security has increased waiting times at the border crossing, especially for trucks (Tan 2003). There is a high volume of traffic, in particular diesel trucks, converging on or departing from the Peace Bridge plaza and surrounding roads, and the long idling time at the crossing for these trucks creates an area of vehicle-dominated pollution that leads to higher exposures to air pollutants in the nearby west Buffalo community. The Buffalo Peace Bridge Study was designed to quantify the spatial and temporal effects of Peace Bridge traffic on air pollution.

SPECIFIC AIMS

This study was designed to support the overall goal of HEI's air toxics program: to provide information that will reduce uncertainties in evaluating the human health risks associated with exposure to air toxics. Of particular concern has been the difficulty of measuring exposure to and effects of important air toxics at low levels of exposure. Request for Applications (RFA) 03-01 specifically requested studies conducted at hot spots, such as hot spots dominated by mobile sources of air pollution. The Peace Bridge plaza fits this description, as a major border crossing immediately adjacent to a residential neighborhood, where vehicle congestion could potentially elevate exposures to air toxics. The RFA requested that researchers compare exposure assessment methods using modeling based on emissions information (the method employed in NATA) with methods using area monitors. Most emissions inventories and modeling analyses are of annualized duration, and thus may not adequately reflect exposure events of short duration. In addition, the RFA asked for characterization of the variation in exposures over time and space, as well as identification and characterization of major area sources and mobile sources of air toxics contributing to suspected hot spots.

The overall hypothesis of the Buffalo Peace Bridge Study is that the intensity of vehicle-related emissions in the vicinity of the Peace Bridge plaza on the west side of Buffalo results in a differential exposure to MSATs, PM, and PAHs, and an increase in exposure to UFPs. This report describes a study carried out by the Harvard School of Public Health (HSPH) and associates from other institutions to assess air pollution in the environment near the Peace Bridge plaza.

This study provides extensive field evidence of the impact of a highly trafficked area (the Peace Bridge plaza) on the potential for exposures to mobile-source pollutants in a nearby community. A wide range of pollutants, including UFPs and organic and inorganic air toxics, were sampled at different fixed sites upwind and downwind of the Peace Bridge plaza. Fixed-site monitoring and mobile monitoring were used to measure many MSATs and other contaminants at different distances from the Peace Bridge plaza. These measurements were used to characterize upwind and downwind air pollution in an effort to quantify gradients in air toxics and other pollutants across the Peace Bridge plaza and into the residential community. In addition, meteorologic data from a tower located at the GLC site, 0.5 km west of the Peace Bridge plaza, were used in the estimates of source contributions. For source estimates, we used hourly traffic counts of cars and trucks crossing the bridge that were provided by the Peace Bridge Authority. Fixed-site and mobile monitoring campaigns were conducted over 2-week periods in both summer and winter to meet the principal objective of this study, which was to characterize the spatial and temporal patterns of MSATs and other traffic-related pollution across an area 1 km by 1.5 km encompassing the U.S. border crossing, a potential hot spot. The analytes included the 12 compounds or classes of compounds identified as of interest in the RFA: acetaldehyde, acrolein, benzene, 1,3-butadiene, ethylbenzene, formaldehyde, n-hexane, MTBE, naphthalene, toluene, styrene, and xylene. Diesel exhaust organics and polycyclic organic matter were addressed by measuring particle-phase and gas-phase PAHs, and speciating the samples to look for 52 PAHs and 32 NPAHs. Dioxin and furan compounds were not included in the study design.

To examine the hypothesis that traffic congestion at the Peace Bridge elevates levels of MSATs locally, this study was designed to:

- Characterize the ambient levels of air contaminants including MSATs across a series of days to obtain upwind and downwind concentrations in the vicinity of the Peace Bridge plaza.
- 2. Examine the relation between traffic at the Peace Bridge and pollutant concentrations in ambient air.
- 3. Explore geographic patterns of ambient air pollutants.

Field campaigns were staged to obtain samples under different meteorologic conditions during summer and winter. Integrated measurements, obtained for individual weekdays (12 hours), weekends (48 hours), five weekdays (60 hours), and five weeknights (60 hours), were necessary to detect many of the MSATs. Continuous measurements were made to examine the effects of shorter-term variations in traffic and weather. A mobile monitoring system that provided continuous measurements and GPS locations was used to map spatial patterns of UFPs and pPAHs across a series of cases.

METHODS

STUDY DESIGN

The Peace Bridge plaza is on the west side of Buffalo (42° 54'16.80" N, 78° 53'57.00" W). Lake Erie is to the southwest, and the Niagara River starts only a few hundred meters south of the Peace Bridge plaza. The U.S. side of the plaza is approximately 17 acres in size, and until mid 2005 comprised the U.S. Customs Building, a customs inspection holding area, tollbooths, a duty-free store, parking, and the Peace Bridge Authority Administration Building.

Figure 1 shows the configuration of the Peace Bridge plaza and the surrounding area. The northern end of the

plaza connects to the Peace Bridge, where traffic crosses over the Niagara River into Canada by a three-lane inclined road. Interstate 190 is to the west of the plaza. To the east of the plaza, there is a residential neighborhood known as Buffalo's west side. A few private homes, a chapel, and a nursing home are the most proximate structures along the east side of Busti Avenue adjacent to the plaza. Extending into the neighborhood east of the plaza there are singleand two-family homes and commercial stores, shops, service stations, auto repair shops, and other community buildings. To the south of the plaza is a city park with access by feeder roads from Porter Avenue.

The Peace Bridge plaza was selected for study as a mobile-source hot spot for several reasons. The Peace Bridge Authority provides hourly traffic counts for all trucks and passenger vehicles transiting the border. There are no major industrial sources of air pollution between the Peace Bridge plaza and the neighboring residential community. Community relationships developed by our colleagues at the University at Buffalo, the State University of New York, helped in the establishment of three secure fixed sites for sampling. Air flows predominantly from the southwest and the west across the plaza to the neighboring community. As shown in the 1992 wind rose pattern (Figure 2) from the Buffalo Niagara International Airport (15 km east-northeast of the Peace Bridge plaza), the most frequent wind direction is from the lake and river side of



Figure 1. The study area comprised the Peace Bridge plaza and the three fixed sampling sites (GLC, Chapel, and School), as well as Bird Island Pier and the neighborhood of west Buffalo (boxed), where routes for mobile monitoring were located.



Figure 2. Wind rose showing 1992 annual average wind speed and direction for Buffalo, from the Buffalo Niagara International Airport (15 km east-northeast of the Peace Bridge plaza). Source: Buffalo Airport Scram Surface Met Data 1992 (available from *www.webmet.com*; accessed October 27, 2010).

the plaza (45% of the time), with winds blowing from the city side only 31% of the time. During the summer months, winds at the Peace Bridge plaza are from the lake quadrant 60% of the time.

Study Location and Sampling Sites

In the summer of 2004 (June 20–26), we conducted a pilot study to test the sampling equipment and study design. During this period, two fixed sites for continuous and integrated sampling were established. One was the GLC site, where we could obtain upwind measurements when the breezes were from the southwest quadrant. The other site was in front of the Episcopal Church Home (Chapel site) immediately adjacent to the original outbound tollbooths. These sites were retained for subsequent monitoring campaigns. We evaluated several mobile monitoring schemes to determine the spatial variability of pollutants across and within the community adjacent to the Peace Bridge plaza.

A second pilot study was conducted in winter 2005 (January 9-18). At this time we added a third location for fixedsite sampling at the West Side Community Center and School (School site), which was used through the remaining campaigns. During the winter 2005 pilot study, a sampling scheme was established to characterize MSATs and spatial patterns of UFPs and PAHs around the plaza. The fixed-site schedule of sampling for 12 hours on weekdays (from 7:00 AM to 7:00 PM) was established. Data and analysis in this report include the samples from the winter 2005 pilot study, along with those from the two subsequent field campaigns in summer 2005 and winter 2006. During the two pilot studies we were still experimenting with routes, schedules, and equipment for mobile monitoring, so this report presents only the mobile monitoring data collected during the summer 2005 and winter 2006 campaigns.

Before the summer 2005 campaign, the Peace Bridge Authority relocated toll collection to the Canadian side of the bridge and expanded the tollbooths. The old tollbooths on the U.S. side were being demolished during the summer 2005 campaign. A new and enlarged duty-free shopping mall had already replaced the older duty-free shop. Cars and trucks frequently stopped or idled in an area on the east side of the plaza.

The mobile monitoring campaign was confined to an area of approximately 2 km² bounded by the Niagara River to the west, spanning the Peace Bridge plaza, and extending about eight city blocks into the residential west side neighborhood of Buffalo to the east. The residential streets within the study area run in a grid pattern from the Peace Bridge plaza, starting with Busti Avenue and extending 900 m east to Normal Avenue, and extending from Hampshire Street to the north, down to Connecticut Street to the south. The western boundary of the study area was Bird Island Pier, which at its nearest point is 350 m west of the Peace Bridge plaza with a north-south orientation. Bird Island Pier is within 50 m to 100 m of the U.S. side of the Niagara River where it passes underneath the Peace Bridge, and it extends to a point southwest of the GLC site on the shore.

The fixed sampling sites were selected for their locations relative to the Peace Bridge plaza with respect to the predominant wind vectors coming out of the southwest, the availability of electricity, and physical security for the instruments. The GLC Aquatic Field Station, operated by Buffalo State College, is 560 m southwest of the plaza center. The Chapel site is 80 m directly east of the plaza center, 40 m east of the plaza boundary, and 640 m from the GLC site. Measurements made at the Chapel site reflect traffic emissions emanating from plaza activities and from roadways farther west when the winds blow from the lake. The Chapel and GLC sites were established to identify MSATs and other compounds associated with plaza activities.

The School site is approximately 600 m east of the Peace Bridge plaza. It is an infrequently used paved parking lot near the corner of Fargo Avenue and Vermont Street. The site is four blocks northeast of the plaza and two blocks northwest of Porter Avenue, a commercial route leading from Buffalo to the plaza entrance and interstate highway access. The School site was chosen to represent residential exposures in the community of west Buffalo. It is central to the study neighborhood and downwind of the plaza for the prevailing southwest winds off Lake Erie. We learned after the site was established that community volunteers were distributing meals from the community center to people in the neighborhood. A van or panel truck delivered prepackaged meals to the school once a day, and about five volunteers arrived in the morning in their own cars to pick up the meals for distribution in the community.

Sampling Frequency

At each fixed sampling site 12-hour integrated samples of ambient air were taken daily from 7:00 AM to 7:00 PM for 1 week in January 2005, 2 weeks in July 2005, and 2 weeks in January 2006, to assess the suite of compounds listed in Table 6. The daytime sampling interval included hours of high traffic volume on the bridge. On average, 640 cars and 150 trucks crossed the bridge each hour. One duplicate sample and one blank sample were collected daily for each group of compounds. Weekend sampling lasted 48 hours,

PM Components and Elements	VOCs	NPAHs	PAHs
PM ₁₀	1,3-Butadiene	1-Nitronaphthalene	Naphthalene
PM _{2.5}	MTBE	2-Nitronaphthalene	2-Methylnaphthalene
EC (reflectance)	Benzene	2-Nitrobiphenyl	Azulene
Aluminum (Al)	Toluene	3-Nitrobiphenyl	1-Methylnaphthalene
Antimony (Sb)	Ethylbenzene	4-Nitrobiphenyl	Biphenyl
Arsenic (As)	<i>m&p-</i> Xylene	1,3-Dinitronaphthalene	2,7-Dimethylnaphthalene
Beryllium (Be)	Styrene	1,5-Dinitronaphthalene	1,3-Dimethylnaphthalene
Cadmium (Cd)	<i>o</i> -Xylene	5-Nitroacenaphthalene	1,6-Dimethylnaphthalene
Calcium (Ca)	Chloroform	2-Nitrofluorene	1,4-Dimethylnaphthalene
Cesium (Cs)	1,1,1-Trichloroethane	2,2'-Dinitrobiphenyl	1,5-Dimethylnaphthalene
Chromium (Cr)	Carbon tetrachloride	9-Nitroanthracene	Acenaphthylene
Cobalt (Co)	2-Methylhexane	2-Nitroanthracene	1,2-Dimethylnaphthalene
Copper (Cu)	2,3-Dimethylpentane	9-Nitrophenanthrene	1,8-Dimethylnaphthalene
Iron (Fe)	3-Methylhexane	3-Nitrophenanthrene	Acenaphthene
Lanthanum (La)	Trichloroethene	4-Nitrophenanthrene	2,3,5-Trimethylnaphthalene
Lead (Pb)	2,2,4-Trimethylpentane	2-Nitrofluoranthene	Fluorene
Magnesium (Mg)	Methylcyclohexane	3-Nitrofluoranthene	1-Methylfluorene
Manganese (Mn)	Tetrachloroethene	1-Nitropyrene	Dibenzothiophene
Nickel (Ni)	1,4-Dichlorobenzene	2-Nitropyrene	Phenanthrene
Potassium (K)	Methylene chloride ^a	2,7-Dinitrofluorene	Anthracene
Scandium (Sc)	<i>N</i> -hexane ^a	7-Nitrobenz[<i>a</i>]anthracene	2-Methyldibenzothiophene
Selenium (Se)	Formaldehyde	6-Nitrochrysene	4-Methyldibenzothiophene
Silver (Ag)	Acetaldehyde	1,3-Dinitropyrene	2-Methylphenanthrene
Sodium (Na) Strontium (Sr) Sulfur (S) Thallium (Tl)	Acetone Acrolein ^b	1,6-Dinitropyrene 9,10+1,8-Dinitroanthracene 6-Nitrobenzo[<i>a</i>]pyrene 1-Nitrobenzo[<i>e</i>]pyrene	2-Methylanthracene 4,5-Methylenephenanthrene 1-Methylanthracene 1-Methylphenanthrene
Tin (Sn) Titanium (Ti) Vanadium (V) Zinc (Zn)		3-Nitrobenzo[<i>e</i>]pyrene 1+3-Nitrobenzo[<i>a</i>]pyrene	9-Methylanthracene 9,10-Dimethylanthracene Fluoranthene Pyrene 3,6-Dimethylphenanthrene
			Benzo[<i>a</i>]fluorene Retene Benzo[<i>b</i>]fluorene Cyclopenta[<i>c,d</i>]pyrene
			Benz[<i>a</i>]anthracene Chrysene+Triphenylene Naphthacene 4-Methylchrysene
			Benzo[<i>b</i>]fluoranthene Benzo[<i>k</i>]fluoranthene Dimethylbenz[<i>a</i>]anthracene

Benzo[*e*]pyrene Benzo[*a*]pyrene Perylene 3-Methylchloanthrene Indeno[1,2,3-*c*,*d*]pyrene Dibenz[*a*,*h*+*a*,*c*]anthracene Benzo[*g*,*h*,*i*]perylene Anthranthrene Coronene

 Table 6. Air Pollutants Measured over Integrated Time Periods

^a Samples may have been contaminated by solvents used in PAH samples and were voided.

^b Levels measured were below method detection limits.

instead of 12 hours, to reduce the potential of nondetection. To capture nighttime pollutant levels, 60-hour composite samples were collected at each site during each of the 4 weeks of the summer 2005 and winter 2006 field campaigns from 7:00 PM to 7:00 AM. Between sampling periods, 60-hour samples were stored at the GLC under refrigeration to reduce evaporative loss. Daytime 60-hour composite samples were also collected. For stable analytes like PM_{2.5}, EC reflectance (EC-r), and metals, we expected correspondence between the 60-hour composites and the sum of the matching 12-hour samples.

Across the 2-week campaign periods, 10 daytime, one weekend, and four 60-hour samples were collected at each site. In addition, blanks and duplicate samples were collected. Table 7 is a summary of the fixed-site sampling details for each integrated sampling period.

Meteorologic Data

Meteorologic data for the sampling sites were obtained for our study by the GLC Davis Weather Station, operated by Buffalo State College. The weather station is located at the GLC near the riverbank and is 6 m above ground level. It is mounted on top of a shortwave radio antenna tower and, except for the Peace Bridge, is the tallest structure within a mile in all directions. The Davis Weather Station reports data for each minute, in contrast to the Buffalo Airport weather station, which reports data hourly. We obtained 1-minute values of wind direction, wind speed, temperature, humidity, rainfall, and pressure.

The Davis Weather Station has a wind threshold of 1 mph. During the summer 2005 campaign, for the 12-hour daytime sampling interval the wind was greater than 1 mph (0.44 m/sec) 91.8% of the time and greater than 2 mph (0.9 m/sec) 86.8% of the time. Because of the wind speeds measured and the use of 10-minute averages, we do not think this wind threshold is a significant limitation in our analysis. During the summer 2005 campaign, we compared the values for wind speed and wind direction obtained from the Davis Weather Station with the values reported at the Buffalo Airport. The difference in wind speed between the GLC Davis instrument value and the value reported at the Buffalo Airport for 300 hourly averages was -0.88 mph, with a standard error of 0.10 mph (t = -8.48; P < 0.001). The difference in wind direction values obtained from the GLC Davis Weather Station and at the Buffalo Airport for 293 hourly measurements was -10.6° with a standard error of 1.21° (t = -8.74; P < 0.001). Although the differences in wind speed and wind direction were significant, they were small in magnitude and most likely represent actual meteorologic differences between locations. The values at the GLC Davis Weather Station were considered

comparable to the values reported at the Buffalo Airport for wind speed and wind direction. More information on this analysis can be found in Appendix A: Data Quality.

Continuous Sampling

Real-time continuous monitors were collocated with the integrated samplers at the three fixed sites depending on the availability of equipment. Data were collected every minute for ozone (O_3) , NO_x , $PM_{2.5}$, carbon dioxide (CO_2) , UFPs, and PAHs. All continuous monitors were collocated upwind and downwind of the Peace Bridge plaza to ensure reliability under similar sampling ranges. These data can be compared directly with the 1-minute weather measurements from the GLC and aggregated to 1-hour periods for analyses using traffic counts.

Mobile Monitoring Scheme

To understand spatial patterns of air pollution, we deployed staff carrying monitors in backpacks to traverse established routes across the entire study area. Each backpack contained a continuous particle counter (P-Trak, TSI Inc., Shoreview, MN), a continuous PAH monitor (PAS 2000CE, EcoChem, League City, TX), and a handheld GPS (eTrex Vista, Garmin, Olathe, KS), as well as a Harvard integrated personal exposure monitor (PEM), to capture average $PM_{2.5}$ mass, reflectance, and element concentrations across the study area.

Four principal routes for mobile monitoring were established within the study area by grouping sequential streets. A discussion on instrumentation, sampling frequency, duration, and specific details about sampling patterns follows in the Mobile Monitoring section.

Traffic Data

We obtained hourly car and truck counts from the Peace Bridge Authority (2004–2006), which reports counts for buses, trucks, and passenger cars in each direction of travel. As buses were a very small fraction of the total traffic, we included them in the truck category. Figure 3 shows an example of the cyclic nature of truck traffic and total traffic for the period of our first pilot study during summer 2004. Truck counts were low late at night and throughout the weekend, a pattern that holds true throughout the year. Total traffic tended to fall below 200 counts per hour from 1:00 AM to 5:00 AM. In contrast, during peak traffic times, from 10:00 AM to 7:00 PM, counts exceeded 1000 vehicles per hour. Also, three times the number of diesel trucks traveled on weekdays during peak hours as on weekends. Although truck counts remained fairly constant across all seasons, car counts in the winter were less than half those in the summer. Perhaps most

	Flow	Sampla	Number of Samples					
Sample ^a	Rate	Volume	Chapel	GLC	School	Duplicates	Blanks	Total
12-Hour Sampling	g Summary, Winter	2005						
PAH–C	16.7 L/min	12 m ³	10	9	9	5	5	38
Metals	16.7 L/min	12 m ³	10	9	9	6	5	39
EC/OC ^b	10 L/min	7.2 m^3	10	9	9	6	8	42
PM ₁₀	4 L/min	$2.9 { m m}^3$	10	9	9	5	5	38
CARB	100 cm ³ /min	72 L	8	7	8	5	6	34
ACR	100 cm ³ /min	72 L	8	7	8	5	5	33
12-Hour Sampling	g Summary, Summe	er 2005 and Wi	nter 2006					
PAH–C	16.7 L/min	12 m ³	10	10	10	10	10	50
Metals	16.7 L/min	12 m ³	10	10	10	10	10	50
PM_{10}	10 L/min	7.2 m^3	10	10	10	10	10	50
CARB	100 cm ³ /min	72 L	10	10	10	10	10	50
VOC _t , summer	30 cm³/min	22 L	10	10	10	10	10	50
VOC _t , winter	50 cm³/min	36 L						
ACR, summer	100 cm ³ /min	72 L	10	10	10	10	10	50
ACR, winter	450 cm ³ /min	324 L						
48-Hour Weekend Sampling Summary, Summer 2005 and Winter 2006								
PAH–C	16.7 L/min	48 m ³	1	1	1	1	1	5
Metals	16.7 L/min	48 m ³	1	1	1	1	1	5
PM_{10}	10 L/min	28.8 m^3	1	1	1	1	1	5
CARB	100 cm ³ /min	288 L	1	1	1	1	1	5
VOC _t , summer	30 cm ³ /min	86 L	1	1	1	1	1	5
VOC _t , winter	50 cm³/min	144 L						
ACR, summer	100 cm ³ /min	288 L	1	1	1	1	1	5
ACR, winter	450 cm ³ /min	1296 L						
60-Hour (Ам/Рм) I	ntegrated Samplin	g Summary, Su	mmer 2005 a	nd Winte	r 2006 ^c			
PAH–C	16.7 L/min	60 m ³	4	4	4	4	4	20
Metals	5 L/min	18 m ³	4	4	4	4	4	20
PM ₁₀	10 L/min	36 m ³	4	4	4	4	4	20
CARB	100 cm ³ /min	360 L	4	4	4	4	4	20
CARB, backup			4	4	4	4	4	20
ACR, summer	100 cm ³ /min	360 L	4	4	4	4	4	20
ACR, winter	450 cm ³ /min	1620 L						
ACR, backup			4	4	4	4	4	20
VOC _t , summer	30 cm ³ /min	108 L	4	4	4	4	4	20
VOC _t , winter	50 cm³/min	180 L						
VOC _t , backup			4	4	4	4	4	20

Table 7. Fixed-Site Sampling Summary for 12-Hour Weekday, 48-Hour Weekend, and 60-Hour Weekday and WeeknightSamples by Sampling Campaign

^a Abbreviations: PAH–C indicates ChemComb PAH samples analyzed at the University of Maryland; Metals indicates PM_{2.5}, EC reflectance, and elements analyzed at LDEO; CARB indicates carbonyl samples (Sep-Pak cartridges) for analysis of formaldehyde, acetone, acetaldehyde, and propionaldehyde by HPLC at HSPH; ACR indicates acrolein samples (XAD-2-[hydroxymethyl]piperidine tubes); VOC_t indicates VOC samples in triple-sorbent tubes, analyzed by HSPH. Sampling rates for acrolein and VOCs were higher in winter to capture lower levels. EC/OC indicates ratio of elemental to organic carbon, used to calibrate the regression equation for the calculation of EC-r.

^b EC/OC analysis was only performed during the winter 2005 sampling session.

^c Samples were collected on weekdays from 7:00 AM to 7:00 PM, or on weeknights from 7:00 PM to 7:00 AM, for 60 hours (5 days).



Figure 3. Hourly counts of total traffic and truck traffic on the Peace Bridge (June 20–26, 2004), showing a cyclic pattern with lows late at night and peaks during the day. Note different scales for *y* axes.

central to our specific aims is the fact that diesel trucks made up between 20% and 50% of the total vehicles crossing the bridge during peak traffic times.

Fixed-Site Sampling

Integrated samples for $PM_{2.5}$, PM_{10} , VOCs, aldehydes, and PAHs were taken at the three fixed sites. Integrated acrolein samples and continuous NO_x samples were also obtained; data quality issues are discussed further in Appendix A: Data Quality. The methods used to analyze these samples are described below.

Analytic Methods for Integrated Samples

PM2.5, EC-r, and Multielement Analysis Samples for analyses of PM_{2.5}, EC-r, and multiple elements were collected on Teflon filters with rings (37 mm, 2-µm pore; Gelman Sciences). The sampling system consisted of modified Harvard impactors. Traditional Harvard impactors use impactor oil to lubricate the impaction surface (Marple et al. 1987). However, for the multielement analysis this oil presented the potential for unacceptable contamination. We replaced the inertial impaction heads of the Harvard impactors with two-stage polyurethane foam (PUF) impaction heads, which require no lubrication. Each impaction head had a 2.5-µm cutoff at 16.7 L/min ± 10% for the 12-hour samples and 5 L/min ± 10% for the 60-hour (5 day) samples. A 2.5-µm cut was selected so that a single sample could be analyzed for PM_{2.5}, EC-r, and multielement analysis. As the purpose of the study was to assess exposure to air toxics emanating from the Peace Bridge plaza, a PM_{2.5} cutoff was selected to focus on elements of combustion origin. The Teflon filters were assembled in the laboratory on acid-washed filter-holder cassettes, supported by acid-washed drain disks. The assembled filterholder cassette was placed inside an acid-washed Petri dish. Samples were collected for 12 hours, 48 hours, or 60 hours. Flows were adjusted to 16.7 L/min before sampling for the 12-hour and 48-hour samples, and to 5 L/min before sampling, with readjustment daily as needed, for the 60-hour samples. Final flows were checked at the end of the sampling period. Sampled filters were stored chilled when not being analyzed.

 $PM_{2.5}$ filters were weighed before and after sampling on a Mettler microbalance at the HSPH laboratory after being conditioned in an environment controlled for temperature and humidity for at least 24 hours (by cracking the Petrislide cover) and statically discharged via a polonium source. Both before and after sampling, filters were weighed twice; if these two masses were not within 5 µg of each other, then the sample was weighed a third time. After the third weighing, the mean of the two masses that were within 5 µg of each other was used for calculating concentrations. In every batch of 10 samples, the zero, span, and linearity of the balance were checked using a standardized set of calibration weights (class "S" weights).

Before PM_{2.5} gravimetric analyses, the Teflon filters were analyzed for reflectance, a measure of filter blackness. Reflectance measurements were made inside a class 100 flow bench using a smoke stain reflectometer (EEL Model 43D, Diffusion Systems Ltd). The measurements were made following the standard operating procedures of the European study ULTRA: Exposure and Risk Assessment for Fine and Ultrafine Particles in Ambient Air, whereby measurements of five separate locations are made on each filter (Pekkanen et al. 2000). Because this conventional method has the potential for the reflectometer head to touch the active filter area, we designed a new filter holder that prevents any contact of the measurement device with the active area of the filter. The filter holder only touches the outer plastic ring, holding the filter in a fixed flat geometry. These modifications enabled us to make reflectance measurements without a significant risk of contaminating the filter for later multielement analysis. The reflectance measurement is sensitive to the distance between the reflectometer head and the filter (which is 2.5 mm longer with our filter holder).

EC-r measurements were calculated using concurrent measurements from quartz filters (x) according to Method 5040, Elemental Carbon (National Institute for Occupational Safety and Health 2003) and reflectance measurements from the Teflon filters (y) collected during the summer 2004 and winter 2005 pilot studies. The regression equation calculated from an independent set of paired samples collected elsewhere in Buffalo shows a similar relationship (y = 34.5x + 0.023). We used the regression equation generated with data from both the summer and winter pilot studies to estimate EC-r values, where EC (µg/filter) is 3.45 times ln(reflectance blank/reflectance sample) plus 0.023.

After reflectance and $PM_{2.5}$ gravimetric measurements, the filters were returned to the Petri dish until sample digestion took place in preparation for multielement analysis by magnetic sector high-resolution inductively-coupledplasma mass spectrometry (HR-ICP-MS) at the Lamont-Doherty Earth Observatory (LDEO), Columbia University, Palisades, New York. All sample handling was done in a class 100 laminar flow bench. We used 18-Mohm water and Optima or trace-metal-grade acids. All plasticware was acid-leached and triply rinsed with 18-Mohm water.

The procedures for sample digestion and analysis have been standardized for several years (Kinney et al. 2002) and are summarized below. Of the digests in each batch, 20% were procedural blanks (acids only). Field blanks were treated as samples. Samples and procedural blanks from digestion batches were analyzed on the same day. The supporting ring was cut from filters. The filter was transferred to a 7-mL perfluoroalkoxy (PFA) vial. We added 20 µL of ethanol to wet the filter, then 60 µL of water and 225 μ L of concentrated Optima nitric acid (HNO₃). After the ethanol and HNO3 reacted, the vial was sealed and placed in a microwave vessel with 10 mL of 65% HNO₃ (outside the vial). The microwave program was run for 52 minutes (with the samples being held near 200°C for the last 20 minutes). Then the vials were taken out and 10 µL ethanol, 100 µL HNO₃, and 40 µL hydrogen fluoride were added. The vials were returned to the microwave vessels with a second 10-mL aliquot of 65% HNO₃, and the program was run again.

After the digestion, the mass of remaining digest was calculated gravimetrically. Based on the amount remaining, the digest was diluted with 5 mL of water, or 1% HNO₃, or 2% HNO₃, to make the acid strength of the resulting solution as close to 3% as possible.

Aliquots of standard reference material (SRM) 1648, urban particulate matter, were weighed on a microbalance and digested several times during the course of the analyses. The mass of SRM 1648 digested was similar to the total mass of $PM_{2.5}$ collected on the sample filters. The SRM aliquots were then digested using the same quantities of acids and the same microwave program.

Diluted digests were analyzed using an Axiom (VG-Elemental) HR-ICP-MS at LDEO, Columbia University. Data were collected for all isotopes of interest at the appropriate resolving power (RP) to avoid isobaric interferences. Beryllium, silver, cadmium, tin, antimony, cesium, lanthanum, platinum, thallium, and lead, for which interferences are not a problem, were run at RP 400; sodium, magnesium, aluminum, sulfur, calcium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, and zinc were run at RP 3000 to 4300; and potassium, arsenic, and selenium were run at RP > 9300. Indium was added to all samples, blanks, and standards as an internal drift corrector and run in all RPs. External and internal standards were used to quantify the elements. On each analysis date, several sets of multielement standards were analyzed in both clean acid-washed blanks and sample matrices.

Three multielement standards were used for the external calibration. All were prepared at LDEO from primary, single-element standards acquired from SPEX CertiPrep (Metuchen, NJ) or High-Purity Standards (Charleston, SC). HR-ICP-MS data were reduced in an Excel spreadsheet. Data were drift-corrected using indium, quantified, converted to a mass, and corrected for blanks. Samples below the limit of quantitation according to daily procedural blanks were flagged.

 PM_{10} PM₁₀ was collected using 10-L/min Harvard impactors and measured using gravimetric analysis similar to that for PM_{2.5}. Blanks for PM₁₀ and PM_{2.5} were combined to increase the number of blanks for determinations of blank correction and limit of detection (LOD).

Volatile Organic Compounds VOC samples were collected on stainless steel, multibed thermal desorption tubes (TDTs) from Supelco, with the three following adsorbents: 200 mg of Carbopack B, 230 mg of Carbopack X, and 170 mg of Carboxen 1001 (Supelco/Perkin-Elmer), according to EPA Compendium Method TO-17 (U.S. EPA 1999). The triple-sorbent tubes were conditioned before use, as described in Method TO-17, by heating them at 350°C for 2 hours and passing pure helium gas (50 mL/min) through them. In addition, used tubes were reconditioned for 15 minutes after analysis before being returned to the field.

Samples were analyzed on a Perkin-Elmer Automatic Thermal Desorber interfaced to a Hewlett Packard gas chromatograph with mass selective detector using EPA Method TO-17. The thermal desorber's transfer line connects directly to the DB-1 column (J&W Scientific, Folsom, CA) inside the gas chromatography oven. Dry purge and addition of internal standard were accomplished in one step. Sample tubes were placed on a spiking device (tubing connected to an ultra-high-purity nitrogen tank with fitting for the tube) with carrier flow of 75 mL/min. A vaporphase internal standard was injected into the device, and the tube was kept in place for 5 to 30 minutes. The vaporphase internal standard was made from liquid standards in solution (usually methanol) of a known concentration that are injected as a known volume into a 2-L static dilution bottle. A volume of vapor was drawn up with a gas-tight syringe and injected into the injector-port/spiking device with flow onto the sample tube. Initial calibration standards were prepared the same way. Drawing different volumes yields different masses and thus the different levels of calibration.

Results for hexane and methylene chloride samples are not reported due to contamination from the PAH sampling system, which contained both of these solvents. The surrogate spiking solution for the PAH samples was prepared in hexane, and all components including PUF and XAD-2 resin were cleaned in methylene chloride before sampling. High levels of these two compounds were occasionally detected in blanks and samples.

Carbonyls Formaldehyde, acetaldehyde, and acetone were sampled actively using a commercially available sampler with silica cartridges coated with 2,4-dinitrophenylhydrazine (DNPH) (Waters Associates, Milford, MA). Samples were collected at 100 cm³/min and stored at -4° C. The samples were prepared by desorbing the DNPH derivative from the substrate with 5 mL of acetonitrile. This was done in a vacuum chamber with 12 sample positions, each fitted with a valve to control the extractant flow rate to approximately 1 mL/min. The extracts were collected directly into 5-mL volumetric flasks or graduated test tubes. After removing the vacuum we diluted the samples to 5 mL with acetonitrile. Aliquots were pipetted into special 1-mL amber vials (Whatman mini-prep vials with a 0.45-µm filter) for chemical analysis.

Samples were analyzed by high-performance liquid chromatography (HPLC) with ultraviolet detection using Agilent 1100 series HPLC equipped with a quaternary pumping system, a degassing unit, a 100-position autosampler, a column compartment with thermostat, and an ultraviolet-visible variable wavelength detector set at 360 nm. The mobile phase was a mixture of water, acetonitrile, and tetrahydrofuran at a flow rate of 1.5 mL/min. A 20- μ L sample was injected, and the compounds including the DNPH derivatives were separated in less than 30 minutes with a gradient on a Waters reverse-phase Nova-Pak C₁₀ column (150 mm \times 3.9-mm internal diameter). The data were processed automatically with Agilent ChemStation software.

Acrolein Acrolein samples were analyzed by Assay Technology Laboratory, Pleasanton, California, using Occupational Safety and Health Administration (OSHA) Method 52, which is specific for acrolein. Additional acrolein samples were collected at the Chapel and GLC sites by our collaborators at the University of California–Davis using the mist chamber method (Seaman et al. 2006). The sample collection period was 10 minutes per sample. The method uses a mist chamber to collect carbonyls by forming water-soluble carbonyl-bisulfite adducts. The carbonyls are then liberated from the bisulfite, derivatized, and quantified by gas chromatography with electron-capture negative ionization mass spectrometry.

Acrolein samples were also collected by a passive method based on the use of dansylhydrazine (DNSH) (Zhang et al. 2000). The Personal Aldehydes and Ketones Sampler employs DNSH-coated solid sorbent to collect aldehydes and ketones (carbonyls). The DNSH-carbonyl derivatives are analyzed using a sensitive HPLC-fluorescence technique.

PAHs and NPAHs PAHs and NPAHs were sampled using two ChemComb organic samplers (Thermo Fisher Scientific, Milford, MA) operating at 16.7 L/min. The Chem-Comb organic sampler consists of a 2.5-µm size-selective inlet, a prefired quartz filter, and a glass sleeve containing purified XAD-2 (Supelpak-2B) sandwiched between two PUF pads. A third PUF pad was added to 60-hour samples to evaluate sample breakthrough. The quartz filters were removed from the sampler and placed in precleaned glass jars. The glass sleeve containing the PUF pads and XAD-2 were capped and wrapped in foil. All samples were stored at 4°C and shipped cold. Filter and PUF/XAD-2 components were transferred to a Soxhlet apparatus, and the jars for filter samples and PUF/XAD-2 sleeves were rinsed with dichloromethane into the extraction apparatus. The filter/PUF/XAD-2/PUF plugs were placed on top of precleaned sodium sulfate and glass wool to prevent XAD-2 from cycling into the reflux flask.

Before extraction, the following recovery standards were added to each filter/PUF/XAD-2/PUF Soxhlet: a mixture of acenaphthylene- d_8 , fluorene- d_8 , and pyrene- d_{10} and a mixture of 1-nitronaphthalene- d_7 , 9-nitroanthracene- d_9 , and 1-nitropyrene- d_9 . The samples were concentrated using a gentle stream of nitrogen and exchanged to hexane to a final volume of approximately 1 mL. Each concentrate was transferred to 2-mL vials with Teflonlined lids. Each analyte was quantified by comparing the response of the molecular ion signal with that of the corresponding internal standard in the respective selected ion monitoring window. The mass spectrometer was calibrated by analyzing mixed standards containing known masses of the analytes and internal standards. Analyte identities were often confirmed by analysis of a secondary ion. Instrumental detection limits are defined as three times the signal-to-noise ratio of each monitored ion in the region of each analyte. Method detection limits are defined as three times the average field matrix blank.

After quantification of the PAHs, the remainder of each sample was fractionated for NPAH analysis using the method developed by Bamford and Baker (2003). Briefly, each extract was eluted through an aminopropyl solid-phase extraction cartridge (Sep-Pak, Waters, Milford, MA) using 40 mL of a 1:4 dichloromethane-to-hexane solution, concentrated under nitrogen gas, and exchanged to hexane. Normal phase liquid chromatography was then employed for the final cleanup procedure using a 5-µm Chromegabond amino/cyano column (30 cm \times 9.6-mm internal diameter, ES Industries, West Berlin, NJ) with 1:5 dichloromethane-tohexane solution as the mobile phase. The fractions containing NPAHs were retained and concentrated under a gentle stream of nitrogen to 1 mL. An NPAH internal standard containing 5-nitroacenaphthene- d_9 , 2-nitrofluorene- d_9 , 3-nitrofluoranthene- d_9 , and 6-nitrochrysene- d_{11} was then added to all of the vials before NPAH analysis.

Sample quantification was performed using a gas chromatograph and mass spectrometer (Models 6890 and 5973, Agilent, Palo Alto, CA) in electron ionization mode and negative chemical ionization (methane gas) mode for PAHs and NPAHs, respectively (Crimmins and Baker 2006). This instrument was equipped with a programmable temperature vaporizer (PTV, Gerstel, Germany) for injection. The PAH method employed hot splitless injection (250°C) coupled to a DB-5MS gas chromatograph column (30 m imes 0.25mm internal diameter \times 0.25-µm film thickness, J&W Scientific). The oven was held at 40°C during the injection. ramped to 280°C at 10°C/min, and then ramped to 310°C at 5°C/min. NPAH analysis was performed using a DB-17MS capillary column (30 mimes 0.25-mm internal diameter imes0.25-µm film thickness). The oven temperature program was 40°C (held for 1.7 minutes during injection), ramped to 150°C at 20°C/min, held for 10 minutes, ramped to 220°C at

10°C/min, held for 10 minutes, and finally ramped to 310°C and held for 15 minutes. The PTV injector (in solvent vent mode) was configured to perform ten 5-µL injections venting at 100 mL/min at 2 psi for 1.10 minutes. At 1.2 minutes the PTV was ramped at 600°C/min to 280°C.

Cubic regressions of the molecular weight of the target analyte against the percentage of each laboratory and field surrogate recovered (eight data points) were calculated for each PAH sample. Each of the samples, including each blank, was corrected for recovery using the regression equation calculated from that sample's surrogates. NPAH samples were corrected by molecular weight group of the laboratory surrogates. All NPAH samples, including blanks, were corrected for recovery based on the percentage recovery of the surrogate representing each molecular weight group.

Analytic Methods for Continuous Measurements Continuous sampling was done both at the fixed sites (Chapel, GLC, and School) and in the mobile monitoring campaign, with the sampling record shown in Table 8. We measured PM_{2.5}, UFPs, pPAHs, O₃, CO₂, and nitric oxide (NO).

Particle-Bound PAHs Continuous measurements of pPAHs were taken using the EcoChem PAS 2000CE, a photoelectric aerosol sensor (PAS) that measures the excitation of surface-bound PAHs. It uses a krypton-bromide lamp (excimer laser) that emits radiation at 207 nm, a wavelength specific to the photoelectric threshold of surfacebound PAH. The PAS is limited in that it cannot measure vapor-phase PAHs, cannot provide values for speciated PAH, and can only detect 4- and 5-ring PAHs adsorbed on particles with diameters generally less than 2 µm, because larger particles are more likely to recapture the ionized photons before they reach the electrometer (Wilson et al. 1994). The advantages of using the PAS, however, are that it is battery operated, does not require a warm-up period, and can be operated continuously for 4 to 6 hours. The output of

Table o. Continu	ous sampning summary for white	r 2005, Suin	mer 2005, and	t winter 200	o Campaigns	
		Valio	d 10-Minute A	werage Meas	surements	Mobile
Analyte	Instrument	GLC	Chapel	School	Total	(minutes)
PM _{2.5}	DustTrak	4104	3662	3892	11,658	0
UFPs	P-Trak 8525	3799	3719	3709	11,227	15,861
pPAHs	PAS 2000CE	4448	4294	3120	11,862	17,073
O ₃	2B Technologies 202	4049	1023	0	5,072	0
\tilde{CO}_2	Telaire 7001	1999	2294	1469	5,762	0
NO	2B Technologies 400	0	0	0	0	0

Table 8. Continuous Sampling Summary for Winter 2005, Summer 2005, and Winter 2006 Cam	paigns
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this monitor is a direct reading of the total concentration of pPAHs (ng/m³) and is calibrated by the manufacturer. As an additional check, we collocated all instruments to ensure high correlation among instruments.

Ultrafine Particles The P-Trak (Model 8525, TSI Inc.) was used to measure ambient UFP number concentrations (particles/cm³) within the size range of 0.02 to 1 μ m in median aerodynamic diameter. The P-Trak uses an internal pump that draws the air through the instrument. As particles enter the P-Trak they pass through a saturator tube, where isopropyl alcohol evaporates into the sample stream, saturating the sample with alcohol vapor. The sample then goes to the cooled condenser tube, where the alcohol vapor supersaturates and condenses onto the particles, increasing their diameters to more than 10 nm. These particles then pass through a small laser beam. The particles scatter this light, and an optical system collects and focuses the light onto a photometer. The instrument then converts the light signal into a particle count. The high sensitivity and portable nature of the P-Trak 8525 made it ideal for this study. However, a limitation for this instrument is that alcohol is typically consumed within 3 hours, and thus long-term sampling requires that the alcohol wick be recharged frequently. P-Traks were zeroed daily with an external high-efficiency particulate air (HEPA) filter. All instruments were factory calibrated within the past year, as recommended by the manufacturer. As an additional check, all instruments were collocated before we began sampling. Comparisons of the P-Trak with a general-purpose condensation particle counter (CPC) suggest that the P-Trak underreports particle counts when it is close to combustion sources such as traffic (Zhu et al. 2006b). Correlations between the P-Trak and CPC values improve with increasing particle size and distance from the road. Studies in Los Angeles by Zhu and colleagues (Zhu et al. 2002a, 2002b, 2004) showed that UFP values tended to drop off exponentially with distance from major sources such as roadways.

Particle Mass We measured continuous $PM_{2.5}$ particle counts using the DustTrak Aerosol Monitor (TSI Inc.), a portable, battery-operated laser-photometer. The DustTrak measures particles within the range of 0.001 to 100 mg/m³ and is equipped with a size-selective inlet for $PM_{2.5}$. Output from this optical light-scattering device was adjusted by applying a correction factor based on daily ratios from measurements of gravimetric mass concentrations.

Ozone For O_3 , we used a monitor (Model 202 Ozone Monitor, 2B Technologies, Boulder, CO) designed to obtain accurate measurement in the mixing ratio range of 0 to 1000 ppbv. The instrument works on the principle of absorption of ultraviolet light, and has long been used for measurements of O_3 with high precision and accuracy. The O_3 molecule has an absorption maximum at 254 nm, coincident with the principal emission wavelength of a low-pressure mercury lamp.

Nitric Oxide For NO, we used a monitor (Model 400 Nitric Oxide Monitor, 2B Technologies) designed to obtain measurements in the range of 2 to 2000 ppbv. The technology employed by the monitor is based on the quantitative reaction of NO with O_3 : NO + $O_3 \rightarrow NO_2 + O_2 + h\nu$, where h is Planck's constant and ν is the frequency of light.

This reaction has long been used as a gas-phase titration for the measurement of either NO or O_3 in laboratory kinetics experiments. The reaction is stoichiometric; that is, one O_3 molecule is consumed for every NO molecule oxidized to nitrogen dioxide (NO₂) in the reaction. In the monitor, a small concentration of O_3 (approximately 3 to 5 ppm) is added to the gas sample stream, and the resulting decrease in concentration of O_3 is measured by the absolute method of absorption of ultraviolet light. Providing adequate time for the reaction to go to completion allows the O_3 concentration to decrease to a level that is equal to the original concentration of NO in the gas stream.

Carbon Dioxide We measured CO_2 with a CO_2 monitor (Model 7001, Telaire, Goleta, CA), which uses a dual-beam infrared absorption sensor to detect CO_2 . It has a range of 1 to 10,000 ppm and an accuracy of $\pm 5\%$.

MOBILE MONITORING

To define spatial patterns of UFPs and pPAHs in the neighborhood, monitors in backpacks were carried by staff walking along predetermined paths across the entire study area. Each backpack contained a P-Trak, a PAS 2000CE, and a handheld GPS (eTrex Vista, Garmin), as well as a Harvard PEM to capture average $PM_{2.5}$ mass, EC-r, and element concentrations across the study area. The measurements were recorded every minute. Location information was matched to concentration data through their time stamps.

One staff member with a backpack was assigned to each mobile monitoring route (Figure 4). The first route covers a walking path on Bird Island Pier, which extends into the Niagara River to create a slow-moving channel for small watercraft. The river walkway lies roughly 50 to 100 m west of the western edge of Interstate 190 and is representative of air pollution in the air masses passing over Buffalo from the west. The other three routes are east of the Peace Bridge plaza, and each comprises a set of three streets parallel to the plaza. Over the course of a 3-hour sampling session, a staff member assigned to each route walked those streets in



Figure 4. Mobile monitoring routes. Data points represent GPS points recorded by devices that field staff carried in their backpacks as they walked the routes.

a figure-8 pattern. Four zones were created by grouping data by routes: (1) the Bird Island Pier, about 300 m west of the center of the Peace Bridge plaza, which represented upwind background conditions; (2) the near zone, 90 m to 300 m east of the center of the plaza, comprised Busti Avenue and Columbus Parkway/7th Street, as well as the west side of Niagara Street; (3) the mid zone, 300 m to 550 m east of the center of the plaza, consisted of the east side of Niagara Street, as well as Prospect and Fargo Avenues; and (4) the far zone, 650 m to 900 m east of the plaza, consisted of West, Plymouth, and Normal Avenues.

Study staff members wearing backpacks were deployed during the same time periods on all four routes whenever feasible. Sampling duration lasted between 2 and 3 hours per session. Sampling sessions were consistently held each morning and early evening, or from roughly 8:30 AM to 11:30 AM and again from 4:30 PM to 7:30 PM. Occasionally sessions would occur midday and on weekends. More than 40 hours of data were collected by this method during the summer 2005 campaign, while the winter 2006 campaign resulted in a total of 42 hours of data. Sampling did not occur during inclement conditions, such as periods of heavy rain. During cold weather, backpacks were insulated to keep instruments at temperatures within recommended operating ranges. Each staff member kept a field log on instrument checks, location, time, and pertinent observations such as when a school bus or a person smoking passed by.

The Garmin eTrex Vista GPS is a small cell-phone-sized unit that provides location accuracy from 3 to 22 m, depending on satellite coverage and reception. It is capable of recording location, direction, and pace of travel. Locations were recorded every minute and were linked to measured concentrations through the time stamp. Therefore, synchronizing instrument times and ensuring that clock drift was minimal were critical quality control functions that occurred daily.

Each backpack contained a PEM (SKC Personal Environmental Monitor) with a $PM_{2.5}$ cutpoint at 10 L/min. A Teflo 37-mm filter identical to those used at each fixed sampling site was the sampling medium. A portable 10-L/min pump (BGI Inc., Waltham, MA) with a lithium battery generated the required flow rate to each PEM. For every batch of samples, one field blank was handled and processed identically to the actual sample and was attached to a backpack.

Temperature and relative humidity were measured and stored on HOBO data loggers (Onset Computer Corp., Pocasset, MA). A HOBO device was placed in every backpack during each use to identify any periods when the manufacturer's suggested operating temperature range for the instruments recording continuous measurements were violated during sampling.

QUALITY ASSURANCE AND QUALITY CONTROL

Strict quality assurance and quality control procedures were implemented during each sampling period, including the collection of blanks, duplicates, and collocated samples in the field. Before any statistical analysis, all data collected were checked against performance criteria outlined for this study in our Quality Assurance Project Plan. These criteria included measures of data capture, accuracy, comparability, and precision.

Devices to measure instrument flow rates in the field were calibrated to a reference standard, and flow tolerance limits were established and followed. Chain-of-custody forms were generated for all samples. Duplicates and field blanks were tracked with the rest of the samples. The data quality of each integrated sample type has been summarized in data quality report tables that list the LOD, percentage of samples above the LOD, and the relative precision of the duplicate pairs. Additional tables with recoveries of field spikes for the VOC analyses and surrogates for the PAH and NPAH analyses are presented in Appendix A: Data Quality.

Integrated Samples

In Appendix A data quality reports for each analytic sample are presented in tabular form. For each sampling session the following data quality indicators are presented for each target analyte: mean blank value, the LOD calculated from the standard deviation of the field blanks (three times standard deviation), the percentage of samples above the LOD, and the relative precision (100 \times root mean square error [RMSE]/ $\sqrt{2}$) calculated from the duplicate pairs. Data quality reports assessing analytic recoveries for VOC, PAH, and NPAH analyses are also presented in Appendix A, and the 60-hour daytime samples are compared with the average of the five corresponding 12-hour samples for VOC, elemental, and PAH analyses.

Treatment of Samples Below the LOD

For all sample types actual values below the LOD were used in all calculations of summary statistics and statistical tests. This is known as the instrument-generated data method (Antweiler and Taylor 2008). In summary tables in Appendix B (available on the HEI Web site), negative and zero sample values are represented with a dashed line (---). For log transformations, zero values and negative values were replaced with a value at half the instrument detection limit.

Continuous Samples

Appendix A presents the results of the collocation of the PAS 2000CE instruments used in this study. Also in Appendix A is an analysis comparing the PAS 2000CE continuous values of pPAHs with the sum of 15 PAHs derived from the 12-hour PUF sampling.

The storage system for O₃ data had a software flaw that would reset the data logger time stamp to the previous date when the instrument was turned off for routine zero, parameter checks, and downloads. The date on the display read correctly, while the date on the data logger returned to the date it had been set to initially. This resulted in multiple readings for the same date and time, which made the data unreliable. The source of the error was not discovered until the end of the summer 2005 campaign, when we realized that to correct the data logger time stamp, we needed to run the instrument for 10 minutes and shut it off again. After the restart, the instrument would log the correct date. We have since learned from other users of the instrument that this software flaw is common to this model. We discovered that the manufacturer was aware of the problem yet made no effort to notify its customers of the software flaw. The O₃ data from the winter 2006 campaign are not presented because the levels are at or near the LOD of the instruments. The CO₂ instruments had a drift of over 100 ppm, which made detection of any differences between sites questionable. The NO_x monitors did not provide reliable data; these were the first two models produced, and there were issues with zero drift and data logging.

Data Management

Integrated samples were sent to laboratories for analysis. Data were returned to the manager of quality assurance and quality control, who performed blank corrections, calculated relative standard deviations for precision, inspected laboratory-reported recovery rates, and validated samples against control standards in the quality assurance plan. A data set for each sampling period containing all integrated measures was created using Microsoft Access software.

Continuous measurements were downloaded at the end of each day or as often as possible to ensure data capture. Files were descriptively named to include the instrument serial number and type and a location identifier. Then these files were read into SAS to remove duplicates, clean extraneous fields, add site and location information, and merge the data on the date and time of the sample. P-Trak (UFP) data with values below 500 particles/cm³ and Dust-Trak (PM_{2.5}) data with negative values were deleted from the cleaned data set. Data from the fixed-site sampling and from mobile monitoring were placed in separate data sets. Ten-minute averages of fixed-site continuous data were calculated. Only complete 10-minute periods were used in data analyses.

DustTrak continuous data were adjusted using correction factors derived from integrated samples collected at the fixed sites. For daytime samples the ratio of the Dust-Trak 12-hour mean to the corresponding $PM_{2.5}$ concentration from the 12-hour integrated sample was used as the correction factor. For nighttime samples the average of these ratios for the previous-day and the next-day integrated samples was used.

GPS coordinates were converted to spatial data sets compatible with GIS software. The GPS devices would occasionally lose contact with one or more satellites, resulting in deterioration of their accuracy. Inaccurate locations were identified by flagging points that deviated from what would be expected from a typical walking pace, for example, more than 100 m from the location recorded for the previous minute. Flagged points that veered away from the expected sampling routes were deleted. If fewer than four points in a row were deleted during a period when the instruments were traveling in a straight line at a steady pace, then they were replaced by points interpolated from the previous and next accurate points. After the GPS location data were cleaned, they were linked to the corresponding continuous monitoring data by route, date, and time to the nearest minute.

Accurate spatial data sets for streets were obtained from "NYS Streets for Erie County" (New York State GIS Clearinghouse 2006). The study streets parallel to the Peace Bridge plaza were manually selected and merged by street name. In order to calculate summary statistics by street, GIS software was used to assign mobile locations within 30 m of study area streets, to the nearest street.

All measurements were identified by fixed sampling site or mobile monitoring route, type of measurement, latitude, and longitude, as well as being time-stamped using official government time.

Hourly traffic counts for cars and trucks by direction of travel were obtained from the Peace Bridge Authority. Meteorologic data recorded every minute were obtained from the GLC Davis Weather Station. These data were averaged for 10-minute and 1-hour intervals. Vector addition was used to average the wind directions.

The Internet-based Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Version 4.8 was used to calculate 24-hour trajectories of air parcels every 6 hours for the study sampling periods (National Oceanic and Atmospheric Administration [NOAA] 2006). The model output contained hourly latitudes and longitudes for each air parcel trajectory. These were converted into arcs in a GIScompatible format (shapefiles), which could be displayed in relation to potential pollution sources such as major cities and to geographic features such as the Great Lakes.

Traffic counts and meteorologic variables were matched to all ambient measurements by time of day and were averaged when necessary. Units for concentrations are reported as follows: $PM_{2.5}$, PM_{10} , VOCs, carbonyls, and EC-r in μ g/m³; pPAHs, PAHs, and elements in ng/m³; NPAHs in pg/m³; UFPs in particles/cm³; and O₃ and NO in ppbv.

STATISTICAL METHODS AND DATA ANALYSIS

The Peace Bridge Plaza Study was designed to identify MSATs emanating from an area of concentrated traffic. Taking advantage of the geographic location on the east shore of Lake Erie and the prevalent winds from the west and southwest direction, we structured the analysis around sets of cases. Analysis focused on contrasting air pollutant concentrations measured at the site that was upwind during lake-wind conditions (GLC site) with concentrations measured at the downwind site immediately adjacent to the plaza (Chapel site). When the winds blew from an easterly direction, the upwind and downwind designations for these two sites reversed. Consistent with the meteorologic records for this area, lake winds were most prevalent, particularly in the warm season. Thus, there were twice as many "lake-wind" cases as "city-wind" cases. Furthermore, the imbalance in the percentages of lake-wind and city-wind cases between summer and winter campaigns prevented analysis by season.

Groupings of analytes possibly associated with traffic at the bridge were established to explore differences between sites. Pearson product-moment correlations helped to identify relations among analytes both within and between sites. A simple *t* test on log-transformed data established significant differences among analytes. The correlation structure for VOCs was obvious for BTEX compounds, so additional analysis was not done.

Principal component analysis was applied to the elemental data to derive linear combinations of the original variables with orthogonal eigenvectors. Exploratory analyses included 3, 4, 5, and 10 vector spaces, but given the limited number of cases available for this analysis, the PRINCOMP procedure for principal component analysis in SAS (Version 9.0) provided useful interpretation.

PAH and NPAH data were analyzed by positive matrix factorization using an EPA model. Windows-based PMF software developed by the EPA (EPA PMF 1.1) is used as a receptor model to solve a least squares problem using the measured concentration and concentration uncertainties. PMF solves the following equation:

$$x_{ij} = \Sigma(g_{ik} f_{kj}) + e_{ij} \tag{1}$$

where x_{ij} is the concentration of species j in sample i, f_{kj} is the chemical profile of j species in kth factor, g_{ik} is the source contribution of kth factor in sample i, and e_{ij} is the model-generated error of species j in sample i. This equation is solved to minimize the sum of squares described as:

$$Q = \Sigma \Sigma (e_{\rm ij}/s_{\rm ij})^2 \tag{2}$$

where s_{ij} is the input error estimate of species j in sample i (concentration). EPA PMF 1.1 is set in robust mode to prevent the outliers from influencing the fitting of the contribution and profiles (Eberly 2005). Species not detected in each sample are replaced by one half of the method detection limit (MDL), which is three times the average mass of analyte in the field blanks divided by sample volume. Error estimates are determined based on the following equation:

$$s_{ij} = [(\alpha_i x_{ij})^2 + (\beta_i DL_i)^2]^{1/2}$$
(3)

where α_i is the measurement uncertainty for species j (fraction), β_i is the MDL uncertainty for species j (fraction), and DL_i is the MDL for species j (concentration) (Brinkman et al. 2006). The standard deviations of blank and sample

surrogate recovery values are used for α and β . In this study, equation 3 was modified to incorporate the error associated with the quartz filter (QF) and PUF/XAD-2 sampling component, in addition to the error associated with volume measurement in each sample i. The propagation of error was used to modify the equation to:

$$s_{ij} = x_{ij} \{ \{ \{s'_{ij} / (QF_{ij} + PUF / XAD - 2_{ij}) \} \}^2 + (\gamma_i / v_{ij})^2 \}^{1/2}$$
(4)

where s'_{ij} is the error estimate of mass (QF + PUF/XAD-2) for species j in sample i, QF_{ij} is the mass measured on the filter for species j in sample i, PUF/XAD-2_{ij} is the mass measured in the PUF/XAD-2 for species j in sample i, γ_i is the volume measurement uncertainty for species j, and v_{ij} is the volume of species j in sample i. The error estimate for values below the MDL was multiplied by a factor of 10 to down-weight their influence.

The theoretical optimal Q value equals the number of data points in the concentration data set. The Q value is used as a guide to determine whether the model is appropriate for the data and the uncertainties specified truly reflect the data (Eberly 2005). The optimal number of sources is a balance between the Q value and the explainable source profile. As the number of sources increases, the calculated Q value decreases (i.e., is closer to the theoretical Q value). However, this also increases the number of unexplainable sources. Each PMF factor is identified by its profile and temporal pattern.

PMF was also applied to the elemental data sets but did not provide additional information beyond principal component analysis.

Continuous measurements of pollution variables were analyzed as 1-minute, 10-minute, or 1-hour averages depending on the circumstance. Because the UFP and pPAH data, both from fixed-site sampling and from mobile monitoring, were not normally distributed, we examined differences with nonparametric methods, using both the Wilcoxon rank sum test and the Kruskal-Wallis test for one-way analysis of variance. These tests were used to examine differences between fixed sampling sites, between streets, and between zones for periods of time categorized by wind direction.

Wind speed, traffic counts for cars and trucks, and site differences in pollutant concentrations were compiled as hourly averages. Univariate and multivariate analyses were applied to untransformed and transformed predictor variables in an attempt to explain variations in differences of UFPs and pPAHs between the measurements made at the Chapel site and the GLC site.

GIS software was used for exploratory analysis of the continuous data collected during the summer 2005 and winter 2006 campaigns according to the mobile monitoring routes. ArcGIS 9.2 Geostatistical Analyst Extension was used to create surfaces representing UFP concentrations measured using P-Traks and pPAH concentrations measured using PASs. Ordinary kriging using K-Bessel functions, assuming anisotropy, and typically using 50 neighbors (and at least 2 neighbors), was used to estimate surfaces from the data points. The results were converted to raster files with 10-m cell size masked to display only the study area. A series of figures was created for different conditions using the same cutpoints.

RESULTS

OVERVIEW AND SUMMARY OBSERVATIONS

Brief descriptions of concentrations measured at each of the fixed sampling sites and the relative differences among sampling locations and campaigns, and between weekend and weekday values and day and night values, are provided here to orient the reader for the following analyses. Full details of the data are found in Appendix B (available on the HEI Web site).

PM and Carbon

Across the two winter sampling sessions (N = 14 days) and one summer session (N = 10 days), the 12-hour daily PM_{10} mean concentration at the Chapel site (23.8 µg/m³) was only slightly higher than that at the School site $(22.6 \ \mu g/m^3)$ but almost $4 \ \mu g/m^3$ higher than that at the GLC site (19.1 μ g/m³). The PM_{2.5} means at the three sites reflected similar proportional differences (15.7 µg/m³, 14.6 μ g/m³, and 13.4 μ g/m³ for the Chapel, School, and GLC sites, respectively). The impact of proximity to Peace Bridge traffic is revealed in comparisons of the median fraction of EC in PM_{2.5}. EC was 17% of PM_{2.5} at the Chapel site, 7.6% at the School site, but only 5.4% at the GLC site. The proportion of coarse fraction particles (PM_{2.5-10}) was apparently higher at the Chapel site as well: 45% of the median PM₁₀ concentration was coarse fraction at the Chapel site versus 35% at the GLC site.

Integrated 48-hour samples were collected over weekends and compared with the 12-hour daytime samples described above. Overall, when the number of trucks crossing the Peace Bridge dropped on weekends, levels of PM_{10} , $PM_{2.5}$, and EC were lower. The Chapel and School sites had identical PM_{10} levels (12 µg/m³), while the GLC level was lower (9 µg/m³). All three sites had similar $PM_{2.5}$ levels (approximately 7 µg/m³), and only the Chapel site showed a higher EC level (0.6 µg/m³ versus 0.4 µg/m³ at the School and GLC sites). During the summer and winter campaigns, we ran integrated daytime samplers (7:00 AM to 7:00 PM) for 5 days and integrated nighttime samplers (7:00 PM to 7:00 AM) for 5 nights over each of the 2 weeks. As expected, nighttime PM_{10} and $PM_{2.5}$ levels were lower, with the difference primarily in the changes in $PM_{2.5}$. The nighttime EC levels were only slightly lower.

VOCs and Carbonyls

Details for VOCs and carbonyls are provided in Appendix B (available on the HEI Web site). We created a composite variable to represent BTEX compounds, BTEX plus (BTEX plus 1,3-butadiene, MTBE, and styrene), as well as a variable to represent the sum of six chlorinated compounds. The median values for BTEX and BTEX plus were higher at the School site than at the Chapel site, and the values at the GLC site were less than half of those at the Chapel site. The benzene median concentration was 1.1 µg/m³ at the Chapel and School sites and 0.6 µg/m³ at the GLC site. Concentrations of chlorinated compounds were similar across all three sites, indicating an association with the regional air mass rather than local sources. The ratio of four of the BTEX plus compounds consistent with fuel is 3:2:1:0.1 for toluene, *m&p*-xylene, benzene, and 1,3-butadiene. The overall median values of the 67 12-hour samples collected were as follows: toluene, 2.5 µg/m³; *m&p*-xylene, 1.2 µg/m³; benzene, 1.0 μ g/m³; and 1,3-butadiene, 0.1 μ g/m³.

For the three reported carbonyls, acetone was more abundant at the GLC site, with median values higher than those at either of the other two sites. Acetaldehyde values were similar at the GLC and School sites, but these were higher than the value at the Chapel site. Formaldehyde showed a different pattern, with the highest median value at the School site. Overall, the mean 12-hour concentrations were formaldehyde, 1.2 µg/m³; acetaldehyde, 4.3 µg/m³; and acetone, 5.9 µg/m³ (Table B.4 in Appendix B). Formaldehyde showed an interesting seasonal pattern: high summertime levels, particularly at the School site where summer levels were five times the winter levels. Conversely, at the GLC site winter levels were twice the summer level, which most likely reflects the influence of urban air at the GLC site in the winter, but not during the summer sampling period.

Elements

Overall, we analyzed samples for 28 elements using HR-ICP-MS. Of the 20 elements listed in IRIS as compounds emitted by mobile sources (see Table 3), 13 were detected. The analysis of elements can provide insight into the sources influencing west Buffalo. The most abundant element was sulfur, about 1.5 μ g/m³, followed by several earth-crustal

elements (sodium, magnesium, aluminum, potassium, calcium, titanium, iron, and zinc), which were two to three orders of magnitude lower in abundance than sulfur.

The elements could be broadly grouped into two categories. One category comprised those that had similar median concentrations across the three sites, which were the coal and oil-derived elements (sulfur, arsenic, selenium, vanadium, and nickel) and another group of elements (beryllium, sodium, potassium, zinc, silver, cadmium, tin, cesium, and thallium). The other category comprised elements that displayed substantial enrichment at the Chapel site (calcium, chromium, manganese, iron, copper, and antimony); the concentrations of these elements at the School site were intermediate between the concentrations at the Chapel and GLC sites, which reinforces the suggestion that they are related to sources at the plaza. It should be noted that the winter 2006 samples from the School site were not analyzed for elements for financial reasons.

Concentrations of most elements in this study were similar to or lower than concentrations reported for a New York City study using the same analytic method of HR-ICP-MS (Kinney et al. 2002). As expected, nickel, cobalt, and vanadium concentrations were one or more orders of magnitude higher in New York City because of residual oil combustion. Five elements measured during the summer 2005 campaign had concentrations consistently higher across the three sites than median summer values reported for 36 sites in New York City; they are cesium, thallium, selenium, scandium, and arsenic. Because of similar values at all three sites, we suspect regional coal or industrial sources for these elements in the current study. The close proximity to traffic at the Chapel site resulted in concentrations of magnesium, calcium, and chromium that were higher (at that site only) than the median concentrations in New York City.

There were no clear trends in daytime-to-nighttime comparisons. Only the combustion elements vanadium, arsenic, potassium, and selenium showed distinctly elevated concentrations during the winter (approximately 40%), when the west Buffalo sites experienced more citywind conditions.

PAHs and NPAHs

Of the PAHs lighter than 2,3,5-trimethylnaphthalene, naphthalene is the most abundant. Levels of naphthalene and many of the methylated naphthalene compounds were consistently higher at the Chapel site, followed by the School site, and then the GLC site. This pattern was more striking during the summer when car traffic was heavier and temperatures were substantially warmer. Of 14 lower-molecularweight compounds (naphthalene through acenaphthene in

Table B.11 in Appendix B), 8 of the compounds' median values were substantially higher at the Chapel site than at the GLC site. These include naphthalene, 2-methylnaphthalene, and biphenyl. The median naphthalene value at the GLC site was less than 50% of that at the Chapel site, whereas the median naphthalene value at the School site was 62% of that at the Chapel site. The median values at the School site were about 10% and 25% less than the values at the Chapel site for 2-methylnaphthalene and biphenyl, respectively. For the two main sampling campaigns, the median naphthalene level at the Chapel site was twice as high in the summer (100 ng/m³), when winds from the lake sector were most prevalent, as in the winter. Seasonal differences in naphthalene concentrations were not apparent at the GLC and School sites. (Summary statistics for all of the PAH and NPAH samples appear in Tables B.11 through B.14 in Appendix B.)

Three general groupings were identified for the 38 PAH compounds included in the PMF analysis in the main report. These are lightweight compounds characterized by fluorene and phenanthrene, middle-molecular-weight compounds like the methylated PAH compounds, and heavier-molecular-weight compounds including pyrene, chrysene+triphenylene, and benzo[g,h,i]perylene, among others. Concentrations were always lower at the GLC site than at the Chapel or School sites; however, they were not higher at the Chapel site than at the School site. During the summer 2005 campaign, most of the lightweight and methylated compounds were actually higher at the School site, while compounds heavier than benzo[k]fluoranthene were routinely higher at the Chapel site. The pattern was different during the winter 2006 campaign. Fluorene and phenanthrene were still higher at the School site, but most of the methylated PAHs were higher at the Chapel site.

Tunnel and truck-stop studies and emissions tests have characterized PAH and NPAH emitted from diesel engines. The profiles vary for many reasons including fuel, engine design, emission controls, engine load, and atmospheric conditions. Complicating interpretation of atmospheric samples are PAHs from other sources, including coal and other biomass combustion, and evaporation from asphalt, tars, and lubricants. Among PAH compounds with molecular weights greater than 188, several have been identified as probable indicators of diesel emissions: among them are fluorene, phenanthrene, fluoranthene, pyrene, methylated compounds, anthracene, and the sum of PAHs with molecular weights greater than 202 (chrysene+triphenylene, benzo[b]fluoranthene, indeno[1,2,3-c,d]pyrene, and benzo[g,h,i]perylene).

When the overall means and medians for these compounds across the three fixed sites were examined, the School site concentrations were slightly higher and the GLC site concentrations were slightly lower than the Chapel site concentrations (Table B.11 in Appendix B). Summing the mean values for the methylated compounds along with the mean for anthracene shows that the School site level (20 ng/m³) was actually twice the level of the GLC site (9.4 ng/m³) and 60% higher than the sum of the means at the Chapel site (12 ng/m³). Comparing coronene, which has been associated with gasoline emissions, across our sites, revealed that the median concentration for the Chapel site was six times the GLC site median and twice the School site median. The median values for retene, a reported marker for wood (Ramdahl 1983), were similar at the Chapel and School sites and slightly lower at the GLC site.

Diesel truck traffic decreased substantially over the weekends, while car traffic over the bridge did not. The weekend car traffic was substantially higher during the summer sampling session. When all 72 of the 12-hour daytime samples were compared with the 9 weekend samples for dieselrelated compounds (naphthalene, 2-methylnaphthalene, biphenyl, fluorene, phenanthrene, benzo[b]-flouranthene, chrysene+triphenylene, benzo[g,h,i]perylene, and indeno[1,2,3-c,d]pyrene), most had weekday values approximately twice the weekend median values (Table B.12 in Appendix B). The median value of coronene was nearly three times the weekday median. The higher weekend median for coronene suggests a higher contribution from gasoline-related PAHs to overall PAH levels during the weekend.

The 12-hour integrated samples collected on weekdays and on weeknights during the summer 2005 campaign contrast daytime and nighttime conditions. For diesel markers (methylated phenanthrene/anthracene, chrysene+ triphenylene, and benzo[g,h,i]perylene), the levels measured at the Chapel site were somewhat higher at night (Table B.13 in Appendix B). The number of truck crossings at night was around 20% of the daytime number, but wind speeds and the height at which pollutants mix in the air drop off at night, which may have increased their concentrations near the plaza. In general, the School site showed higher concentrations for these marker compounds during the day. This pattern is consistent with more transport away from the plaza and more local PAH sources or evaporative emissions during the day.

According to a truck-stop sampling study (Minegishi 2007) and other studies (Schuetzle et al. 1982; Paputa-Peck et al. 1983; Zielinska et al. 2004; Havey et al. 2006), the following NPAHs are possible indicators of diesel emissions: 1- and 2-nitronaphthalene, 1- and 2-nitropyrene, 9-nitroanthracene, and nitrophenanthrene. Detailed analysis in the current study was restricted to 19 NPAHs that were

Table 9. Peace Bridge Authority Hourly Traf.	fic Coun	ts: Annual, Sea	sonal, and	During Sampl	ing Campai	gns
	Total		Cars		Trucks	
Time Period of Traffic Data	Mean	90th Percentile	Mean	90th Percentile	Mean	90th Percentile
Annual and seasonal						
Annual (1/1/2004–12/31/2004)	789	1381	640	1217	149	258
Winter (12/1/2004–2/28/2005)	630	1074	490	914	140	253
Summer (6/1/2004–8/31/2004)	982	1633	829	1444	153	256
During sampling campaigns						
Winter 2005 (1/9 6:00 PM-1/18 5:59 PM)	601	1003	448	816	153	257
Summer 2005 (7/18 8:00 AM-7/30 5:59 PM)	966	1608	887	1522	161	253
Winter 2006 (1/6 6:00 PM-1/20 5:59 PM)	593	995	445	802	148	256

more reliably and frequently detected. During the summer 2005 campaign when the predominant wind direction was from the GLC site across the Peace Bridge plaza to the Chapel site (lake winds), NPAHs were about 100 to 1000 times less abundant than PAHs overall. Among the NPAHs, four compounds had median concentrations greater than 10 pg/m³ at the Chapel and School sites: 1- and 2-nitronaphthalene, 2- and 3-nitrobiphenyl, 5-nitroacenaphthalene, and 9-nitroanthracene (Tables B.14 and B.22 in Appendix B). In addition, at the School site the 2-nitrofluoranthene median concentration was greater than 10 pg/m³ and the 2-nitrobiphenyl concentration was greater than 200 pg/m³. The median values for NPAHs measured at the GLC site were all less than those at the other two sites. (Winter results are not discussed because winter 2006 samples at the School site were not analyzed for NPAHs.)

The differences in the summer 2005 median concentrations of NPAHs across the sites are better indicators of diesel emissions near the Chapel site than the differences in median PAH concentrations (Table B.14 in Appendix B). Compared with the median values at the GLC site, the Chapel site median concentrations were 8 or more times higher for both 9-nitrophenanthrene and 1-nitropyrene; approximately 1.9 to 4.9 times higher for 1- and 2-nitronaphthalene and 2-nitroanthracene; and 1.5 to 2.5 times higher for 2-nitrofluorene and 9-nitroanthracene. For 9-nitroanthracene, the School site's median value was slightly higher than the Chapel site's value. The School site had higher median values for 2-nitrobiphenyl, 5-nitroacenaphthalene, 3-nitrophenanthrene, 2-nitrofluoranthene, and 2-nitropyrene.

Five of the six NPAH diesel markers had substantially higher values at the Chapel site. The one exception was 2-nitropyrene, for which the median value at the School site exceeded the value at the Chapel site by more than a factor of two. The median value of 2-nitrofluorene at the Chapel site was twice the median values at the GLC and School sites, suggesting that 2-nitrofluorene might be another marker for diesel emissions.

CONTRIBUTIONS OF PEACE BRIDGE PLAZA ACTIVITIES TO LOCAL AIR CONTAMINANTS

An objective of the Buffalo Peace Bridge Study was to identify air contaminants possibly associated with localized congestion of traffic, with specific attention to those contaminants labeled as MSATs. Our first analyses were undertaken to broadly identify contaminants found in higher concentration at the Chapel site next to the Peace Bridge plaza. To help clarify local source impacts, we classified all our 12-hour sampling periods based on persistence of wind direction as lake wind, city wind, or other wind. Summary statistics of all samples collected in the winter 2005 pilot study and summer 2005 and winter 2006 campaigns can be found in Appendix B.

Traffic Data

As expected, hourly traffic data from the Peace Bridge Authority showed temporal variability, with consistent patterns for diurnal, weekday, weekend, holiday, and seasonal traffic. We first compared the hourly traffic counts during the specific periods we selected for our field campaigns with annual and seasonal counts (Table 9). Figure 5 displays the cumulative distributions of vehicle counts (total traffic, trucks, and cars) for the three sampling sessions compared with seasonal averages for summer 2004 and winter 2004-2005, and annual averages for 2004. The hourly truck and car counts for the winter 2005 campaign are displayed in Figure 6, summer 2005 in Figure 7, and winter 2006 in Figure 8. As shown in Table 9 and displayed in Figure 5, the car and total traffic counts during the sampling sessions are representative of the respective seasonal counts. Wilcoxon rank sum tests showed that total traffic during sampling



Figure 5. Cumulative distributions of hourly counts of total traffic, trucks, and cars on the Peace Bridge during sampling sessions, compared with seasonal and annual data.



Figure 6. Peace Bridge vehicle counts per hour, winter 2005 sampling session.



Figure 7. Peace Bridge vehicle counts per hour, summer 2005 sampling session.



Figure 8. Peace Bridge vehicle counts per hour, winter 2006 sampling session.

campaigns did not differ from seasonal counts; however, truck counts during the winter 2005 and 2006 sampling campaigns were slightly, but not significantly, higher than the comparison seasonal (winter) truck count.

Meteorologic Conditions

The general air mass transport across the Buffalo region was determined by trajectory analysis. HYSPLIT backward trajectories showing the paths of air arriving in Buffalo at midnight, 6:00 AM, noon, and 6:00 PM are displayed in Figures 9 through 14. Also shown are the 10-minute wind vectors across the sampling periods as recorded at the GLC meteorologic tower. The trajectories and wind vectors are presented corresponding to each week in the sampling campaigns: winter 2005 (Figures 9 and 10), summer 2005 (Figures 11 and 12), and winter 2006 (Figures 13 and 14).

The following criteria were used to classify the 12-hour daytime monitoring period as being representative of lake winds, city winds, or other winds. A sampling day was classified as a lake-wind day when for 75% of the time the wind vector was between 180° and 280°. Because winds were more variable when blowing from an easterly direction, a city-wind day was defined less rigidly as a day that had a wind vector between 1° and 179° for at least 25% of the time, but did not have wind blowing from the lake for more than 5% of the time. Other-wind days either had a strong northerly component, a vector between 281° and 360°, or were quite variable and failed to meet the definition of the other two cases. We note that downtown Buffalo at the U.S. shoreline of Lake Erie is actually to the south-southeast of the Peace Bridge plaza. Further, the southern area of Ontario, Canada, is actually west of the plaza. So we defined "lake winds" to represent conditions when plaza emissions were likely to affect the adjacent neighborhood defined as our study area. Our classification scheme is generally supported by radial plots that show the 10-minute differences in pollutant concentrations between the GLC site and the Chapel site, by wind vectors (see Figures 34 and 40).



Figure 9. Backward air mass trajectories and wind directions for the first week of the winter 2005 sampling session.



Figure 10. Backward air mass trajectories and wind directions for the second week of the winter 2005 sampling session.



Figure 11. Backward air mass trajectories and wind directions for the first week of the summer 2005 sampling session.



Figure 12. Backward air mass trajectories and wind directions for the second week of the summer 2005 sampling session.



Figure 13. Backward air mass trajectories and wind directions for the first week of the winter 2006 sampling session.



Figure 14. Backward air mass trajectories and wind directions for the second week of the winter 2006 sampling session.

Table 10.	Summary o	f Local Wind	All 12-Hour Weekda	y Sampling Pe	eriods ^a		
		Local Winds	8		Air Mass Origir	1	
Season	Lake Winds	City Winds	Other Winds	Hamilton, ON / Toronto, ON (NW, N)	Detroit, MI / London, ON (W)	Ohio (SW)	Other
Summer Winter	9 6	1 6	2	5 1	3 3	2 8	2

^a Values are number of sampling periods. Total = 24.

Table 11. Wind Direction on Days That 12-Hour Weekday Integrated Samples Were Obtained

Winter 2005	2005 St		r 2005	Winte	er 2006
Date	Winds	Date	Winds	Date	Winds
January 11	City / other	July 18	Lake	January 9	Lake
January 12	City / other	July 19	Lake	January 10	Lake
January 13	City / other	July 20	Lake	January 11	Lake
January 14	City / other	July 21	Lake	January 12	Lake
	U U	July 22	Lake	January 13	City / other
		July 25	Lake	January 16	City / other
		July 26	Lake	January 17	City / other
		July 27	City / other	January 18	Lake
		July 28	Lake	January 19	City / other
		July 29	Lake	January 20	Lake

The backward trajectories of the air mass for midnight, 6:00 AM, noon, and 6:00 PM were used to characterize the recent history of the air being sampled and to confirm the classification described above. In addition, days were classified by recent air mass origin in an effort to understand better the background concentrations of the constituents of the regional background air. Table 10 summarizes the wind classifications and air mass origins for 12-hour weekday sampling periods during the different campaigns. Out of a possible 24 weekdays during our sampling campaigns, 15 had lake-wind conditions, which is consistent with historic wind rose data for the Buffalo area.

Considering all the sampling periods for the winter 2005, summer 2005, and winter 2006 field campaigns, we had 24 possible 12-hour weekday sampling periods. Table 11, derived from data on air mass trajectories (Figures 9 through 14), lists the local wind classification during each 12-hour weekday sampling period. In the summer, the winds were more frequently from the southwest and west; hence, only one summer sampling period was classified as having city/other winds.

Overall, we had 15 lake-wind samples and 9 city-wind or other-wind samples. These last two categories were combined for the subsequent analysis and termed as "city/other winds." We examined analytes by site as well as between sites, testing for differences and exploring correlations. First, all sampling days were combined, and then they were examined by the classifications discussed above. Composite variables were created by grouping some of the analytes.

PM_{2.5} Mass, EC-r, and Sum of All PAHs

At the highest level of aggregation, we examined upwind-downwind relationships for PM_{2.5}, EC-r, and the sum of PAHs at the GLC and Chapel sites. Table 12 contrasts the median, minimum, and maximum concentrations and the between-site (Chapel-to-GLC) ratios for these three composite variables. Concentrations at the Chapel site were slightly higher than those at the GLC site for city/other-wind sampling days. The between-site ratios for PM_{2.5} were higher for lake-wind days than for city/otherwind days. The ratio of the Chapel site median EC-r value to

Amalanta /	City	y / Other Winds (N	er Winds ($N = 9$)		Lake Winds ($N = 13$)		
Site ^a	Median	Minimum	Maximum	Median	Minimum	Maximum	
PM _{2.5} (µg/m ³)							
Chapel	11	4.4	16	16	7.8	55	
GLC	10	4.3	15	14	6.6	44	
Ratio	1.06	0.66	1.37	1.24	1.03	1.41	
EC-r (µg/m³)							
Chapel	1.7	0.74	3.1	2.40	0.79	2.90	
GLC	1.0	0.41	1.6	0.53	0.11	0.75	
Ratio	1.57	0.95	3.86	4.92	3.42	7.42	
PAHs (ng/m³)							
Chapel	430	220	1500	380	140	550	
GLC	280	260	1200	120	83	480	
Ratio	1.37	0.82	1.90	2.67	0.83	4.51	

^a "Ratio" is the median Chapel-to-GLC ratio.



Figure 15. Chapel-to-GLC ratios for the sum of PAH measurements and EC-r measurements: 12-hour weekday integrated samples (N = 22).

the GLC site median shows levels were 3.42 to 7.42 times higher over the 13 lake-wind sampling events (2 lake-wind days had incomplete or missing values for one of the three measurements and are not included in Table 12). The Chapel-to-GLC ratio range for EC-r on city/other-wind days was 0.95 to 3.86. The between-site ratio for the sum of all PAHs for lake-wind days ranged from 0.83 to 4.51, with a median value of 2.67. EC-r was 10% of the PM_{2.5} at the Chapel site under lake-wind conditions. Under city/otherwind conditions, EC-r was 10% of PM_{2.5} at the GLC site, as compared with only 2% under lake-wind conditions. Traffic activities between the shoreline and the Peace Bridge plaza increased the PM_{2.5} in the air by about 2 μg/m³, which is almost entirely accounted for by the increase in EC.

Figure 15 rank orders all 22 sampling days with valid measurements according to the ratio between EC-r concentrations at the Chapel and GLC sites, and also shows the Chapel-to-GLC ratios for the sum of PAHs. Note that city/other-wind days predominate across the lower ratios and lake-wind days across the higher ratios. In general, for the sum of PAHs, the lower ratios are to the left while higher ratios are to the right. Closer scrutiny of the PAH and NPAH compounds will help clarify which compounds behaved more like EC.

VOCs and Aldehvdes

Log-transformed values for each of the 19 VOCs and three carbonyls were tested for significance of differences between the Chapel and GLC sites (Table 13). In addition, three composite variables were created: the sum of the BTEX compounds; the sum of BTEX and 1,3-butadiene, MTBE, and styrene (BTEX plus); and the sum of all six chlorinated compounds. BTEX, BTEX plus, and all the individual compounds except MTBE differed significantly between sites

	L	og-Trans	formed Data		Nontransformed Data					
	(Ln) <i>P</i> (<i>t</i> Test)		Pearso	n <i>r</i>	City / Other Winds			Lake Winds		
Analyte	City / Other Winds	Lake Winds	City / Other Winds	Lake Winds	Mean Ratio	n SD o Ratio	Median Ratio	Mean Ratio	SD Ratio	Median Ratio
BTEX	0.00	0.00	0.95	0.15	1.35	0.23	1.37	2.78	1.36	2.35
Benzene	0.01	0.00	0.96	0.10	1.24	0.19	1.18	2.47	1.83	1.95
Toluene	0.01	0.00	0.92	-0.29	1.39	0.31	1.32	2.61	1.23	2.28
Ethylbenzene	0.01	0.00	0.95	-0.03	1.32	0.26	1.29	3.18	1.81	2.76
m&p-Xylene	0.01	0.00	0.93	0.37	1.40	0.34	1.30	3.69	1.99	3.17
o-Xylene	0.01	0.00	0.91	0.49	1.38	0.30	1.33	3.67	1.93	3.19
BTEX plus	0.01	0.00	0.92	0.49	1.37	0.28	1.37	2.78	1.34	2.45
1,3-Butadiene	0.10	0.00	0.95	0.08	1.28	0.35	1.29	2.52	1.74	2.10
MTBE	0.24	0.41	0.20	0.30	0.95	0.54	0.89	1.17	0.77	1.11
Styrene	0.04	0.00	0.80	0.50	1.55	0.63	1.45	2.70	1.50	2.45
Formaldehyde	0.14	0.23	0.86	0.38	1.57	0.96	1.42	0.93	0.35	0.82
Acetaldehyde	0.39	0.11	0.60	0.97	1.58	1.57	1.09	1.07	0.53	0.73
Acetone	0.26	0.13	0.46	0.71	1.08	0.67	1.32	0.57	0.54	0.48
Methylcyclohexane	0.10	0.00	-0.45	0.94	1.70	1.52	1.22	2.91	2.17	2.53
3-Methylhexane	0.23	0.00	0.77	0.27	2.67	4.41	1.10	2.33	0.94	2.20
2-Methylhexane	0.14	0.00	0.50	0.50	2.55	3.84	1.20	2.38	0.84	2.36
2, 3-Dimethylpentane	0.19	0.00	0.64	0.52	2.57	3.87	1.20	2.50	1.18	2.13
2,2,4-Trimethylpentane	e 0.41	0.00	0.55	0.42	1.11	0.59	1.14	2.21	1.20	1.86
Chlorinated compounds	0.05	0.26	0.36	0.12	1.32	0.49	1.19	1.03	0.15	1.03
Chloroform	0.05	0.20	0.42	0.82	0.79	0.18	0.79	1.30	0.47	1.36
1,1,1-Trichloroethane	0.11	0.24	0.74	0.63	1.16	0.32	1.05	1.06	0.22	1.03
Carbon tetrachloride	0.14	0.45	-0.84	0.39	1.29	0.65	1.05	1.02	0.11	1.01
Trichlorethene	0.24	0.20	-0.66	0.73	2.50	3.50	1.02	1.05	0.11	1.04
Tetrachloroethene	0.01	0.49	0.60	0.98	1.46	0.40	1.39	1.14	0.63	0.99
1,4-Dichlorobenzene	0.39	0.29	0.87	-0.22	1.02	0.39	1.13	0.96	0.26	0.97

Table 13. Statistical Values for Chapel-to-GLC Ratios of VOCs by Wind Directiona

^a Values in **bold**: P < 0.05; Pearson r value > 0.8; city/other winds, mean or median ratio less than 1; and lake winds, mean or median ratio greater than 1. City/other winds, N = 7; lake winds, N = 14.

under lake-wind conditions. In addition, the methylated hexane and pentane compounds were also significantly higher at the Chapel site for the analysis of log-transformed data. These compounds and the BTEX compounds were not correlated between sites under lake-wind conditions. However, all the BTEX compounds were correlated (Pearson product-moment correlation coefficient r > 0.8) when there were city/other winds. Mobile sources appeared to affect both the Chapel and GLC sites under city/other-wind conditions; however, there must be some dilution of city and plaza mobile-source pollution by the time the air reaches the GLC site. This is inferred because the Chapel-to-GLC mixing ratio for BTEX compounds was still greater than one, even for non-lake-wind conditions. Under lake-wind conditions there was no evidence that the mobile sources from the Peace Bridge added to the chlorinated compounds or the carbonyls. Concentrations at the Chapel and GLC sites were highly correlated for lake-wind conditions but not at all for city-wind conditions. One can see in Table 13 that the median ratios for 1,1,1-trichloroethane, carbon tetrachloride, and trichlorethene were close to unity for both city/other-wind and lake-wind days. From the Chapel-to-GLC site ratio for chloroform, it appears that chloroform increased between the GLC and Chapel sites on lake-wind days. Buffalo's intake station for drinking water is just south of the GLC site. With southwest (lake) winds, emissions from the plant would miss the GLC site but affect the Chapel site. There were three days in 2005 (January 12, July 20, and July 28) when chloroform was substantially higher at the Chapel site than at the GLC site. On each of these days there were several hours during the sampling period when the winds were from 210°, which would favor transport from the water intake station. Table 14 presents the median, minimum, and maximum concentrations of carbonyls and chlorinated compounds and Chapel-to-GLC ratios for lake-wind and city/other-wind days. Figure 16 shows the distribution of Chapel-to-GLC ratios for concentrations of the VOCs, three carbonyls, $PM_{2.5}$, and EC-r for city/other-wind and lake-wind days. Many of the nonchlorinated compounds were higher at the Chapel site than at the GLC site for city/other-wind days. For the lake-wind days, BTEX and the methylated hexanes and pentanes were clearly elevated at the Chapel site, but chlorinated and carbonyl compounds were not.

Table 14. Chapel and GLC Site Concentrations (μg/m³) of BTEX, BTEX Plus, Formaldehyde, Acetaldehyde, and Chlorinated Compounds by Wind Direction, with Between-Site Ratios

Angleta /	(City / Other Win	ds	Lake Winds			
Site ^a	Site ^a Median Minimum Maximu		Maximum	Median	Minimum	Maximum	
BTEX							
Chapel	7.8	2.8	13.2	6.1	2.0	11.0	
GLC	5.8	2.8	8.4	2.2	1.4	4.6	
Ratio	1.37	0.99	1.67	2.35	1.49	5.85	
BTEX plus							
Chapel	8.15	2.83	13.89	6.36	2.11	11.39	
GLC	6.06	3.01	8.73	2.34	1.45	4.82	
Ratio	1.37	0.94	1.71	2.45	1.43	5.76	
Formaldehyde ^b							
Chapel	0.83	0.27	2.12	0.90	0.06	4.54	
GLC	0.71	0.41	4.16	0.89	0.19	1.16	
Ratio	1.42	0.66	3.22	0.78	0.00	1.55	
Acetaldehyde							
Chapel	1.10	0.12	6.12	1.29	0.24	51.32	
GLC	1.24	0.20	51.32	1.64	0.06	59.05	
Ratio	1.09	0.18	4.30	0.73	0.06	4.52	
Chlorinated compounds ^c							
Chapel	1.21	0.80	2.00	0.83	0.69	1.15	
GLC	0.94	0.81	1.31	0.82	0.57	1.17	
Ratio	1.19	0.90	2.33	1.03	0.78	1.35	

^a "Ratio" is the median Chapel-to-GLC ratio.

^b Formaldehyde values in the summer had only one ratio in which both pairs were above the LOD.

^c Values are for the sum of chlorinated compounds: chloroform, 1,1,1-trichloroethane, carbon tetrachloride, trichloroethane, tetrachloroethane, and 1,4-dichlorobenzene.



Figure 16. Box and whisker plots of Chapel-to-GLC ratios for VOC, $PM_{2.5}$, and EC-r values on city-wind days (N = 7 pairs) and lake-wind days (N = 14 pairs). Minimum, bottom whisker; 25th percentile, bottom of the box; median, center line in the box; mean, "x"; 75th percentile, top of the box; and maximum, top whisker. For city/other-wind days all compounds, except chloroform, had at least 5 pairs of samples above LOD (chloroform is not shown). For lake-wind days formaldehyde, 1,4-dichlorobenzene, acetone, and trichloroethene had 5 of 14 sample pairs above LOD. Compounds are ranked by the median ratio.

Table 15. University	ersity of California–Davis Acro	olein Sample Summ	ary (10-Minute San	nples), Summer 2005	
Site / Date ^a	Average (μg/m ³)	Range (µg/m³)	Average (ppb)	Range (ppb)	Ν
Chapel					
July 25	0.30	0.17 - 0.46	0.13	0.07-0.20	26
July 26	0.27	0.17-0.37	0.12	0.07-0.16	7
July 27	0.21	0.09 - 0.42	0.09	0.04 - 0.18	6
GLC					
July 26	0.04	0-0.10	0.016	0-0.044	7
July 27	0.01	0-0.024	0.004	0-0.011	7
MDL	0.037		0.016		

Table 15.	University	y of California–Dav	is Acrolein Sam	ple Summary	(10-Minute Sam	ples), Summer 200
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^a Sampling occurred from 7 AM to 7 PM.



Figure 17. University of California–Davis average acrolein levels obtained at the Chapel site on July 25, 2004.

Acrolein

At the Chapel site the highest acrolein level measured by the University of California–Davis method (Seaman et al. 2006) was 0.46 μ g/m³ (Table 15). In the University of California-Davis samples, acrolein levels were higher at the Chapel site than at the GLC site, with the highest levels being found during times of heavy traffic (Figure 17). Concurrently with the University of California-Davis effort, we sampled for acrolein using the Environmental and Occupational Health Sciences Institute (EOSHI) DNSH passive method (Zhang et al. 2000) on consecutive weekdays. We employed a nested sampling strategy in which a pair of samples was exposed for 4 days, a second pair was exposed for 3 days, a third pair was exposed for 2 days, and a final pair was exposed for 1 day. The acrolein levels in the samples, though higher than the field blanks, were around the filter detection limit of 0.01 µg/m³ reported by EOSHI. Table 16 presents the results of the DNSH analysis. The levels measured in the current study were comparable to those that Weisel and colleagues (2005) obtained in the Relationships of Indoor, Outdoor, and Personal Air (RIOPA) study using a DNSH-based sampler. They reported median concentrations outdoors in Los Angeles,

Table 16. Acrolein Sample Results by EOSHI DNSH Method During Summer 2005^a

Paired Samples / Date of Exposure	Acrolein (ng)	Acrolein (µg/m³)
First pair, 96 hours		
June 25–29	19	0.51
June 25–29	8	0.19
Second pair, 72 hours		
June 25–28	12	0.43
June 25–28	25	0.96
Third pair, 48 hours		
June 25–27	11	0.55
June 25–27	9	0.41
Fourth pair, 24 hours		
June 25–26	6	0.46
June 25–26	7	0.57
Blank 1	1	
Blank 2	3	

^a We employed a nested sampling strategy: a pair of samples was exposed for 4 days, Monday to Friday; a second pair was exposed for 3 days, Monday to Thursday; a third pair was exposed for 2 days, Monday to Wednesday; and a final pair was exposed for 1 day, Monday to Tuesday.

California; Elizabeth, New Jersey; and Houston, Texas, of 0.4, 0.39, and 0.95 μ g/m³, respectively. In the current study the range of values obtained using the University of California–Davis method was 0.01 to 0.46 µg/m³ and the range obtained using the EOSHI DNSH method was 0.19 to 0.96 µg/m³. After assessing the acrolein levels measured by the University of California-Davis method, we chose not to analyze any of the acrolein samples collected for analysis by OSHA Method 52 because the detection limit of the OSHA method, based on the sample volumes collected, was 1 µg/m³, which is substantially higher than the

highest reported value obtained using the University of California–Davis method.

Elements

Elements analyzed in the 12-hour integrated PM_{2.5} samples were resolved by HR-ICP-MS. Mean and median ratios of values at the Chapel site to those at the GLC site were examined for city/other-wind and lake-wind days. We calculated Pearson correlations for pairs of measurements, as well as testing for significant difference in the log-transformed and nontransformed data (Table 17). Nine elements had median ratios greater than 1.75 for lake-wind days (aluminum, calcium, titanium, chromium, iron, cobalt, copper, strontium, and antimony). Of these, only titanium and cobalt had a significant correlation (Pearson r > 0.80 for logtransformed values) between sites on lake-wind days. On city/other-wind days, the median ratio was 1.0 ± 0.24 for all elements except chromium (4.26), iron (1.32), and copper (2.23). The values for copper at the two sites were uncorrelated (Pearson r < 0.80 for log-transformed values) and significantly different only for lake-wind conditions.

A second set of elements (sodium, magnesium, potassium, manganese, nickel, tin, and lanthanum) had significantly different Chapel-to-GLC ratios on lake-wind days, between 1.25 and 1.75, and on city/other-wind days they had ratios near one (1.0 ± 0.16), except nickel had a median ratio of 0.78. Similar to the first set, these elements were significantly different between sites for the lake-wind days but not for the city/other-wind days. Neither zinc nor silver differed significantly between sites for either of the classified wind conditions.

Elements measured at the two sites that were highly correlated (Pearson r > 0.80 for log-transformed values) on lake-wind days and did not show enrichment downwind of traffic are most likely associated with the regional air mass as opposed to local sources. Sulfur and arsenic meet these criteria; their Chapel-to-GLC ratios for city/otherwind days were also near unity, and their correlation coefficients were also high (> 0.80). These elements have been identified as tracers for fossil fuel.

Figure 18 plots the distributions of Chapel-to-GLC ratios for 28 elements, $PM_{2.5}$, PM_{10} , and EC-r for samples collected on days with lake-wind and city/other-wind conditions. On city/other-wind days, only for EC-r, chromium, and copper were 75% of the between-site ratios greater than unity. EC has many urban sources, and the lower concentration at the GLC site reflects dilution as air flows from the city and plaza toward Lake Erie. The reason for high copper and chromium ratios for days when winds were not from the lake is unknown. On lake-wind days, the distributions suggest that the Peace Bridge plaza traffic resulted in an increase of calcium, iron, zinc, chromium, copper, aluminum, antimony, strontium, cobalt, titanium, manganese, magnesium, EC-r, and PM_{10} . Other elements, although to a lesser extent, also had 75% or more of the paired ratios greater than unity on lake-wind days.

Principal component analysis was applied to the elemental data in an attempt to confirm element groupings observed from correlations and ratios of differences between sites. Analysis of 25 elements was carried out using the PRINCOMP procedure in SAS (Version 9.0). Chromium and thallium were excluded because of the low number of samples in which they were detected on lakewind days. We used this analysis to explore whether the number of variables could be logically reduced by clustering elements as linear combinations. The first principal component is the best fit to the data as measured by the sum of squared perpendicular distances from each data point to the vector.

In our application the next vector is orthogonal to the first, and so forth. Principal component analysis was performed multiple times on the entire data set (52 observations) for subsets classified by sampling site and wind direction. When five factors or components were allowed, a total of 72% of the variance was explained. One component contained elements indicative of both coal combustion and traffic-related emissions (beryllium, sulfur, potassium, titanium, manganese, iron, cobalt, arsenic, selenium, antimony, and lead). A second component comprised silver, vanadium, nickel, and to some extent sodium and lead, suggesting residual fuel oil. A third component had magnesium, aluminum, and calcium, which is indicative of crustal material, but the fourth component (sodium and strontium) and the fifth component (tin and cadmium) were not clearly interpretable. Owing to financial constraints, the combined data set was missing the winter 2006 elemental analysis from the School site, leading to an imbalance in the days and locations represented. For this reason, and because of the limited number of sample days, the analysis was restricted to three factors when examining samples classified by wind sector. For lake-winds days the three factors explained 65% of the variance at the GLC site and 69% of the variance at the Chapel site.

Table 18 presents the factor loadings of the principal component analysis for elements measured at the Chapel site under lake-wind conditions. Factor 1 had moderate loadings of sulfur, arsenic, selenium, cadmium, and tin, which were all negatively associated with the other factors. This factor had the marker elements for coal combustion and regional transport. A similar first factor was found for the GLC data under lake-wind conditions (not shown).

Log-Transformed Data Notice Transformed Data Log-Transformed Data Notice Transformed Data Analyse Transformed Data Notice Transformed Data Analyse Try/Other Take Transformed Data Notice Transformed Data Analyse Try/Other Take Transformed Data Notice Transformed Data Analyse Other Take Try/Other Take Transformed Data Notice Transformed Data Analyse Other Data Take Try/Other Take Transformed Data Notice Transformed Data Analyse Other Data Other Take Try/Other Take Transformed Data Notice Transformed Data Analyse Other Data Other Data Take Try/Other Take Transformed Data Notice Transformed Data Analyse Other Data Data Other Data Data Data Data Data Data Data Note Other Data Data Other Data Data Data Data Data Data Data Note Other Data Data Data Data Data <thd< th=""><th>-</th><th></th><th></th><th></th><th></th><th>\$</th><th></th><th></th><th></th><th></th><th></th><th></th><th></th></thd<>	-					\$							
$ \begin{array}{ $			Log-Trar	ısformed Data				ľ	Vontransfor	med Data			
		(Ln) <i>P</i> (<i>t</i>	Test)	Pears	on <i>r</i>	Pearso	n r	City	/ Other Wi	nds		Lake Winds	
	Analyte	City / Other Winds	Lake Winds	City / Other Winds	Lake Winds	City / Other Winds	Lake Winds	Mean Ratio	SD Ratio	Median Ratio	Mean Ratio	SD Ratio	Median Ratio
	Be	0.30	0.01	0.23	0.89	0 40	0.80	4 25	8 40	1 08	1.38	0.54	1.24
	Na	0.16	0.01	0.35	0.80	0.17	0.76	0.90	0.46	0.94	1.64	1.05	1.36
	Mg	0.13	0.00	0.56	0.26	0.86	0.40	0.81	0.40	0.88	1.97	1.22	1.72
S0.160.110.850.930.960.970.860.970.980.320.941.100.221.13K0.130.050.740.730.160.330.931.110.261.130.231.26K0.130.050.430.740.730.160.730.160.231.160.231.16K0.110.050.040.930.740.740.731.160.261.771.691.76T0.300.010.070.010.070.060.740.840.731.160.731.161.271.69T0.300.010.070.010.070.740.840.731.160.731.170.661.77V0.010.070.040.030.060.740.940.731.161.790.661.77V0.010.070.040.030.040.731.161.232.341.16V0.010.020.040.030.040.731.161.232.341.16V0.010.020.030.040.030.040.231.161.24V0.030.120.130.140.130.140.130.141.24V0.130.140.130.140.130.140.130.141.24V0.130.14<	Ă	0.46	0.01	0.73	0.55	0.76	0.52	1.30	1.08	0.91	2.24	1.39	2.17
	s	0.16	0.11	0.85	0.93	0.98	0.97	0.88	0.32	0.94	1.10	0.22	1.12
Ca0.230.000.49-0.080.440.351.211.260.323.812.94T0.310.500.930.450.450.731.160.401.271.681.07T0.300.070.410.930.740.731.160.951.170.691.77V0.190.070.410.960.660.686.551.190.951.170.321.17V0.010.070.910.070.940.930.711.190.531.170.321.17V0.100.090.970.440.930.160.150.190.171.130.170.321.17V0.100.090.940.930.711.190.301.130.311.161.130.321.17V0.110.000.930.740.170.171.130.311.141.26V0.120.000.940.930.711.161.130.311.14V0.120.010.140.170.171.161.161.16V0.110.100.550.940.930.741.161.161.16V0.120.100.120.140.170.131.161.161.16V0.110.110.110.120.140.190.141.161.16 <td< td=""><td>Х</td><td>0.13</td><td>0.05</td><td>0.74</td><td>0.77</td><td>0.93</td><td>0.83</td><td>0.80</td><td>0.33</td><td>0.93</td><td>1.18</td><td>0.28</td><td>1.26</td></td<>	Х	0.13	0.05	0.74	0.77	0.93	0.83	0.80	0.33	0.93	1.18	0.28	1.26
X_c 0.310.500.930.450.740.731.160.401.271.681.00T10.300.000.740.410.990.741.190.961.171.681.01C0.070.010.070.010.070.090.060.051.190.061.771.681.01C0.070.010.970.090.060.060.060.060.171.160.331.57C0.070.010.970.070.090.060.060.161.390.711.322.561.092.54Ci0.370.120.000.970.440.930.161.190.331.241.722.661.01Ci0.370.120.000.970.470.090.870.471.092.542.45Ci0.450.100.550.330.530.540.090.561.091.232.561.092.54Ci0.170.120.100.550.330.570.440.572.350.452.452.45Ci0.170.100.550.380.560.161.771.092.761.16Ci0.170.100.550.390.561.190.771.261.452.45Ci0.170.100.550.940.960.761.611.771.66	Ca	0.23	0.00	0.49	-0.08	0.48	0.35	1.21	1.26	0.92	3.82	3.81	2.94
	\mathbf{Sc}	0.31	0.50	0.93	0.45	0.74	0.73	1.16	0.40	1.20	1.77	1.68	1.00
$ \begin{array}{rcccccccccccccccccccccccccccccccccccc$	ïT	0.30	0.00	0.74	0.84	0.89	0.74	1.19	0.96	1.01	1.78	0.66	1.76
	Λ	0.19	0.07	0.41	0.96	0.67	0.91	0.93	0.48	0.95	1.17	0.32	1.17
	C	0.07	0.01	0.03	0.69	0.06	0.88	6.45	6.61	4.26	2.39	1.53	2.18
	Mn	0.23	0.00	0.97	0.72	0.96	0.55	1.09	0.23	1.16	1.50	0.33	1.57
	Fe	0.12	0.00	0.87	0.44	0.95	0.16	1.39	0.71	1.32	2.56	1.04	2.54
Ni 0.37 0.12 0.43 0.71 0.17 0.71 1.60 1.35 0.78 1.69 1.94 1.24 Cu 0.43 0.00 0.24 0.03 0.47 -0.09 3.87 3.97 2.23 4.53 6.43 2.45 Zn 0.10 0.55 0.33 0.53 0.04 2.53 3.50 1.02 1.64 1.10 1.44 Zr 0.09 0.99 0.92 0.94 0.94 0.79 0.36 0.84 1.10 0.17 1.06 Zr 0.01 0.05 0.92 0.94 0.94 0.79 0.79 0.84 1.10 1.10 Zr 0.01 0.05 0.92 0.94 0.94 0.79 0.78 0.77 0.77 Zr 0.00 0.77 0.78 0.94 0.10 0.78 0.97 0.77 0.79 0.77 Zr 0.01 0.00 0.77 0.92 0.96 0.78 0.97 0.77 0.79 0.79 Zr 0.01 0.00 0.77 0.92 0.96 0.74 0.10 0.79 0.79 0.79 Zr 0.17 0.00 0.77 0.28 0.96 0.87 0.76 0.79 0.79 0.79 Zr 0.17 0.00 0.78 0.96 0.98 0.96 0.87 1.76 1.76 1.76 Zr 0.01 0.00 0.98 0.96	Co	0.10	0.00	0.93	0.84	0.93	0.69	1.19	0.30	1.24	1.72	0.58	1.85
	Ż	0.37	0.12	0.43	0.71	0.17	0.71	1.60	1.35	0.78	1.69	1.94	1.28
	Cu	0.43	0.00	0.24	0.03	0.47	-0.09	3.87	3.97	2.23	4.53	6.43	2.45
As 0.12 0.09 0.89 0.92 0.84 0.94 0.79 0.36 0.84 1.09 0.21 1.06 Sr 0.17 0.05 0.98 0.98 0.96 0.96 0.17 1.06 0.17 1.07 Sr 0.46 0.00 0.85 0.54 0.96 0.96 0.96 1.00 2.35 2.09 1.16 Ag 0.11 0.05 0.57 -0.14 0.19 0.89 0.62 0.87 1.76 1.70 1.25 Ag 0.12 0.91 0.53 0.96 0.68 0.87 1.69 0.79 1.28 Ag 0.12 0.00 0.77 0.90 0.57 0.97 0.87 0.77 1.76 1.70 Sh 0.27 0.90 0.91 0.69 0.87 0.87 0.87 1.26 1.26 Sh 0.21 0.00 0.77 0.82 0.97 0.87 1.26 1.26 Sh 0.27 0.90 0.82 0.97 0.87 0.99 1.36 Sh 0.77 0.90 0.92 0.97 0.97 0.97 0.99 1.26 Sh 0.21 0.01 0.92 0.92 0.92 0.97 0.99 1.26 Sh 0.21 0.01 0.90 0.92 0.97 0.99 1.26 0.79 La 0.21 0.01 0.90 0.92 0.92 0.92 0.92 0.72 <	Zn	0.19	0.10	0.55	0.33	0.53	0.04	2.53	3.50	1.02	1.64	1.10	1.44
Se 0.17 0.05 0.98 0.98 0.96 0.96 0.95 0.18 0.90 1.08 0.17 1.07 Sr 0.46 0.00 0.85 0.54 0.80 0.64 1.51 1.60 1.00 2.35 2.09 1.86 Ag 0.14 0.11 0.05 0.57 -0.14 0.19 0.89 0.65 0.87 1.76 1.70 1.28 Cd 0.12 0.00 0.77 0.87 0.97 0.87 0.87 1.05 0.33 1.17 Sh 0.27 0.00 0.77 0.87 0.97 0.87 0.87 1.76 1.70 1.28 Sh 0.27 0.00 0.77 0.87 0.97 0.87 0.87 0.77 0.33 1.17 Sh 0.27 0.00 0.77 0.87 0.97 0.87 0.97 0.77 0.39 1.36 Sh 0.21 0.01 0.99 0.96 0.97 0.87 0.97 0.77 0.99 1.36 Sh 0.27 0.01 0.99 0.96 0.97 0.97 0.17 0.99 1.26 0.33 1.27 La 0.21 0.01 0.99 0.96 0.99 0.99 0.99 1.26 0.99 1.26 La 0.21 0.01 0.99 0.99 0.99 0.99 0.72 0.99 1.112 1.01 1.22 La 0.21 0.09	\mathbf{As}	0.12	0.09	0.89	0.92	0.84	0.94	0.79	0.36	0.84	1.09	0.21	1.08
Sr 0.46 0.00 0.85 0.54 0.80 0.64 1.51 1.60 1.00 2.35 2.09 1.86 Ag 0.14 0.11 0.05 0.57 -0.14 0.19 0.89 0.62 0.87 1.76 1.70 1.28 Cd 0.12 0.36 0.91 0.57 0.97 0.96 0.82 0.87 1.66 1.76 1.70 1.28 Sh 0.21 0.00 0.77 0.82 0.97 0.87 0.87 0.87 1.36 1.17 Sh 0.27 0.00 0.77 0.80 0.69 1.11 0.69 1.26 0.39 1.36 Sh 0.27 0.01 0.90 0.92 0.90 0.98 0.88 0.47 0.99 1.06 1.06 La 0.27 0.01 0.90 0.90 0.90 0.91 0.91 0.72 0.99 1.12 La 0.27 0.01 0.90 0.90 0.90 0.90 0.72 0.99 1.12 0.79 1.01 La 0.21 0.01 0.90 0.90 0.90 0.99 0.72 0.99 1.12 0.30 1.24 La 0.21 0.07 0.90 0.90 0.99 0.72 0.99 1.12 0.30 1.24 T 0.21 0.07 0.91 0.92 0.99 0.72 0.92 0.91 1.12 0.37 1.14 Ph_{2.5 </td <td>Se</td> <td>0.17</td> <td>0.05</td> <td>0.98</td> <td>0.98</td> <td>0.98</td> <td>0.95</td> <td>0.95</td> <td>0.18</td> <td>06.0</td> <td>1.08</td> <td>0.17</td> <td>1.07</td>	Se	0.17	0.05	0.98	0.98	0.98	0.95	0.95	0.18	06.0	1.08	0.17	1.07
	Sr	0.46	0.00	0.85	0.54	0.80	0.64	1.51	1.60	1.00	2.35	2.09	1.86
$ \begin{array}{ ccccccccccccccccccccccccccccccccccc$	Ag	0.14	0.11	0.05	0.57	-0.14	0.19	0.89	0.62	0.87	1.76	1.70	1.28
Sn 0.21 0.00 0.77 0.82 0.97 0.87 0.97 0.47 0.99 1.39 0.39 1.31 Sb 0.27 0.00 0.38 0.90 0.92 0.69 1.11 0.69 1.36 0.39 1.35 Cs 0.17 0.01 0.98 0.90 0.98 0.94 0.17 0.99 1.23 0.30 1.22 La 0.50 0.03 0.78 0.90 0.96 0.73 1.12 0.42 1.15 1.86 2.03 1.31 T1 0.21 0.06 1.00 0.93 0.96 0.96 0.17 0.99 1.23 0.30 1.24 T1 0.21 0.06 1.00 0.98 0.96 0.72 0.96 0.10 1.16 1.23 1.14 Pb 0.21 0.07 0.90 0.93 0.96 0.10 0.37 1.15 1.24 1.14 Pb 0.21 0.07 0.98 0.96 0.07 0.93 0.26 0.14 1.16 1.22 0.37 1.14 PM $_{25}$ 0.43 0.01 0.97 0.98 0.96 0.99 0.10 0.37 1.14 PM $_{25}$ 0.43 0.01 0.97 0.99 0.12 1.01 1.22 0.37 1.14 PM $_{25}$ 0.91 0.09 0.02 0.91 0.12 1.01 1.24 0.13 1.14 PM $_{25}$ 0.99	Cd	0.12	0.36	0.91	0.53	0.96	0.68	0.82	0.35	0.87	1.05	0.38	1.17
Sb 0.27 0.00 0.38 0.800.920.69 1.11 0.69 1.06 2.30 0.79 2.03 Cs 0.17 0.010.980.900.980.94 0.17 0.99 1.23 0.30 1.22 La 0.50 0.03 0.78 0.69 0.96 0.73 1.12 0.42 1.15 1.86 2.03 1.31 T1 0.21 0.06 1.00 0.930.96 0.93 0.96 0.10 1.36 1.31 Pb 0.21 0.07 0.80 0.93 0.96 0.10 0.99 1.15 0.28 1.14 Pb 0.21 0.07 0.98 0.96 0.72 0.93 0.97 1.12 1.22 0.37 1.14 Pb 0.21 0.07 0.90 0.97 0.93 0.91 0.17 1.01 1.22 0.38 1.14 Pb 0.21 0.07 0.90 0.96 0.10 0.37 1.14 1.14 PM ₂₅ 0.43 0.01 0.97 0.98 0.04 0.07 0.37 1.12 1.24 0.13 1.14 PM ₂₅ 0.43 0.01 0.97 0.98 0.04 0.07 1.13 0.12 1.14 1.14 PM ₂₅ 0.99 0.00 0.53 0.98 0.04 0.07 1.13 1.01 1.24 0.13 1.24 PM ₂₅ 0.99 0.00 <	Sn	0.21	0.00	0.77	0.82	0.97	0.87	0.97	0.47	0.99	1.39	0.39	1.35
$ \begin{array}{r[rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	Sb	0.27	0.00	0.38	0.80	0.92	0.69	1.11	0.69	1.06	2.30	0.79	2.03
$ \begin{array}{r[r]rcccccccccccccccccccccccccccccccccc$	$\mathbf{C}_{\mathbf{S}}$	0.17	0.01	0.98	06.0	0.98	0.88	0.94	0.17	0.99	1.23	0.30	1.22
$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	La	0.50	0.03	0.78	0.69	0.96	0.73	1.12	0.42	1.15	1.86	2.03	1.31
$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	ΓΙ	0.21	0.06	1.00	0.93	0.98	0.93	0.96	0.10	0.99	1.15	0.28	1.14
$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	Pb	0.21	0.07	0.80	0.72	0.96	0.72	0.93	0.37	1.01	1.22	0.37	1.14
EC-r 0.09 0.00 0.53 0.84 0.04 -0.37 1.98 1.01 1.79 4.95 1.31 4.83	$PM_{2.5}$	0.43	0.01	0.97	0.98	-0.26	0.97	1.13	0.12	1.12	1.24	0.13	1.24
	EC-r	0.09	0.00	0.53	0.84	0.04	-0.37	1.98	1.01	1.79	4.95	1.31	4.83



Figure 18. Box and whisker plots of Chapel-to-GLC ratios for 28 elements, PM₁₀, PM_{2.5}, and EC-r on city/other-wind days (*N* = 8 pairs) and lake-wind days (*N* = 15 pairs). Minimum, bottom whisker; 25th percentile, bottom of the box; median, center line in the box; mean, "x"; 75th percentile, top of the box; and maximum, top whisker. Compounds are rank ordered by median ratio.

Element	Factor 1 Regional	Factor 2 Plaza	Factor 3 Oil
Be	0.26	-0.16	-0.17
Na	0.10	-0.21	0.30
Mg	0.21	0.22	-0.02
Al	0.26	0.17	0.02
S	0.23	-0.23	-0.01
К	0.25	-0.14	0.08
Ca	0.16	0.34	-0.03
Ti	0.19	0.11	0.01
V	0.06	-0.04	0.62
Mn	0.15	0.13	-0.31
Fe	0.14	0.24	-0.16
Со	0.20	0.15	-0.06
Ni	0.14	0.14	0.26
Cu	0.08	0.39	0.18
Zn	0.18	0.14	0.03
As	0.23	-0.26	-0.12
Se	0.25	-0.24	-0.06
Sr	0.21	0.18	0.26
Ag	0.16	0.04	-0.36
Cd	0.23	-0.28	-0.01
Sn	0.27	-0.19	-0.07
Sb	0.27	-0.01	0.02
Cs	0.14	-0.12	0.11
La	0.21	-0.09	0.18
Pb	0.20	0.26	-0.03
% of Variance ^b	0.43	0.17	0.08

Table 18. Principal Component Factor Loadings forElements Measured at Chapel Site Under Lake-WindConditions^a

^a Values in **bold**: P < 0.05.

^b Percentage of the variance explained by the factor.

Factor 2 at the Chapel site had many of the elements that appeared to be enriched relative to the GLC site (Figure 18), namely, magnesium, calcium, iron, copper, and lead. This factor might be considered to be related to the Peace Bridge plaza traffic. The second factor at the GLC site under lake-wind conditions included aluminum, manganese, and strontium, elements that might be interpreted as reflecting a transported crustal component. Factor 3 at the Chapel site had vanadium, nickel, and sodium loadings, which could be indicators of residual oil combustion. A similar factor was not apparent in principal component analysis for the GLC site.

Principal component analysis has limited application in this study, but it does help to confirm the grouped patterns of elements suggested by pairwise correlation and by the values for the downwind Chapel site in Table 17. We previously reported that the concentrations of several elements were highly correlated at all three sites. This was interpreted as indicative of contaminants more uniformly distributed in an air mass. Arsenic and sulfur were examples of such transported elements. Edge plots are simple scatter plots of ambient concentrations used to visualize data for source apportionment (Henry 2003). Plotting sulfur as sulfate against arsenic in an edge plot has proved quite interesting (Figure 19).

We used the wind trajectory analysis shown in Figures 9 through 14 to classify the general direction for each 12-hour daytime sampling period. As shown in Figure 19, when the air mass came from the southwest, the ratios of arsenic to sulfate were similar at all three sites. With air masses from the northwest and east, values also tended to plot along this summertime southwest trend. In contrast, when the wind came from the north, the ratio was very different, showing much more enrichment in arsenic with respect to the relatively low sulfate levels. This suggests that



Figure 19. Edge plot of ratios of arsenic to sulfate concentrations with air mass trajectories from different directions. Data for the north, east, and northwest trajectories are for all sites and seasons; data for the southwest trajectory are presented by site and season.

the northerly air masses have a much more distant and distinct source for arsenic and sulfate. When the wind came from the southwest in wintertime, there was little evidence for an association between arsenic and sulfate at either of the two sites monitored, consistent with power plant coal combustion being much less prevalent in winter.

PAHs and NPAHs

Analyses of PAHs and NPAHs are particularly challenging. These compounds are emitted from a variety of sources, including vehicles and construction equipment, combustion of fossil and biomass fuels from stationary sources, and evaporation from surface materials. Many of them undergo chemical transformations, some of which are dependent on other constituents in the atmosphere such as hydroxyl radicals or nitrogen compounds, or on the presence or absence of sunlight. Parsing our Buffalo Peace Bridge data by site, season, and wind direction provides some insight into the behavior of PAH and NPAH compounds, but the analysis is limited in statistical power. We first examined the relationship between PAH and NPAH values at the Chapel site and at the GLC site, then applied PMF to a subset of the PAH and NPAH data from all three sites. In support of our study, the Chesapeake Biological Laboratory (CBL) collected 12-hour high-volume daytime and nighttime PAH samples (obtained using Graseby Andersen high-volume samplers) at the Chapel, GLC, and School sites for 1 week during the summer 2005 campaign. The samples were added to the Harvard data sets to enhance the interpretation of PMF output and explore diurnal differences. The primary differences between our data sets and those of CBL were that CBL's analysis excluded PAHs with molecular weight below 188 and had greater sensitivity and temporal resolution due to larger sampling volumes. The source-related PAH profiles derived for PMF analysis had been collected earlier and were restricted to compounds with molecular weight above 188 because the high-volume samplers CBL used to collect supplemental samples for specific sources and at the study site did not contain XAD-2 resin or deuterated surrogates, which are necessary for collecting the lightermolecular-weight compounds. The CBL Peace Bridge samples were compared with samples that CBL collected from other locations using the same method and analyte list. The CBL samples were higher-volume samples that provided higher resolution for diurnal analysis at all sites.

Between-Site Comparison of PAHs by Wind Direction

Figure 20 presents the distributions of Chapel-to-GLC ratios for the PAH compounds with at least five pairs of observations for city/other-wind conditions, and Figure 21

presents results for lake-wind conditions. The compounds are rank ordered by the median ratios. Note that for all but a few compounds PAH concentrations were higher at the Chapel site when winds were classified as city/other. Only azulene, 2,2,5-trimethylnaphthalene, and 1-methylnaphthalene had ratios close to or less than one. This finding suggests that many PAHs are added to air masses as they pass over an urbanized area. Median ratios for compounds that are likely from diesel emissions ranged from 1.1 to 1.4, with naphthalene and benzo[*a*]pyrene in the middle at 1.25, for city/other-wind conditions. Plaza and highway traffic activity added to urban background levels of many PAHs, but when the wind flow was from the urban area across the plaza to the GLC site, the between-site ratios were lower, suggesting possible dilution. In general, the ratios were larger for lake-wind conditions. All of the methylated compounds (lower molecular weights) were substantially higher at the Chapel site for lake winds. Because of the previously noted limitation of the highvolume samplers, data for these lighter-weight compounds are not often reported. Naphthalene, an MSAT compound associated with diesel emissions, was up to 10 times higher at the Chapel site than at the GLC site during lakewind events. The concentrations at the two sites were correlated (at 0.95) for city/other winds and uncorrelated (at 0.01) for lake winds. Another PAH associated with diesel emissions, benzo[*a*]pyrene, showed a similar pattern.

Table 19 shows the correlations and median ratios for select PAHs. Several PAHs related to diesel combustion show a pattern of nonsignificant correlations between sites and higher between-site median ratios with lake winds (benzo[a]anthracene, chrysene+triphenylene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, dibenz[a,h+a,c]anthracene, and benzo[g,h,i]perylene), while winds classified as city/other carried these compounds over both sites, and thus the between-site correlation values were 0.80 or higher. Among the few exceptions were 1,3-dimethylnaphthalene and 1,4-dimethylnaphthalene, which had higher betweensite correlations for lake winds than for city/other winds. These compounds had substantially higher median ratios for lake winds. These observations suggest that these PAH compounds are present in the background air but have strong local sources at the plaza. Minegishi (2007) also identified benz[a]anthracene, chrysene+triphenylene, benzo[*a*]pyrene, benzo[*g*,*h*,*i*]perylene, and to a lesser extent dibenz[a,h+a,c,]anthracene as mobile-source pollutants. Other studies of diesel emissions in which direct exhaust measurements were made also have shown the presence of these compounds to varying degrees (Zielinska et al. 2004; Shah et al. 2005). Retene has been associated with biomass combustion, but concentrations do not



Figure 20. Box and whisker plots of Chapel-to-GLC ratios for PAHs and sum of PAHs (N = 8 pairs) with city/other winds. Minimum, bottom whisker; 25th percentile, bottom of the box; median, center line in the box; mean, "x"; 75th percentile, top of the box; and maximum, top whisker. All compounds have at least five pairs of samples above the LOD. 3-Methylchloanthrene, 9-methylanthracene, 3,6-dimethylphenanthrene, benzo[b]fluorene, naphthacene, 4-methylchrysene, dimethylbenz[a]anthracene, perylene, dibenz[a,h+a,c]anthracene, anthranthrene, and coronene are not shown. Compounds are ordered by the median ratio.



Figure 21. Box and whisker plots of Chapel-to-GLC ratios for PAHs and sum of PAHs (*N* = 14 pairs) with lake winds. Minimum, bottom whisker; 25th percentile, bottom of the box; median, center line in the box; mean, "x"; 75th percentile, top of the box; and maximum, top whisker. All compounds have at least five pairs of samples above the LOD. 3-Methylchloanthrene, 9-methylanthracene, 3,6-dimethylphenanthrene, benzo[*b*]fluorene, naphthacene, 4-methylchrysene, dimethylbenz[*a*]anthracene, and anthranthrene are not shown. Compounds are ordered by the median ratios.

Table 19. Statistical values	for Chapel-to	-GLU Kal	105 OI PAHS DY	wind Dire	CUON ^a				
		Log-Trans	sformed Data		Nontransformed Data				
	(Ln) <i>P</i> Value (<i>t</i> Test)		Pearson <i>r</i>		City / Ot	City / Other Winds		Winds	
РАН	City / Other Winds	Lake Winds	City / Other Winds	Lake Winds	Pairs Above LOD	Median Ratio	Pairs Above LOD	Median Ratio	
Naphthalene	0.04	0.00	0.95	0.01	8	1.25	13	2.32	
1,3-Dimethylnaphthalene	0.20	0.00	0.55	0.82	8	1.20	14	3.10	
1,4-Dimethylnaphthalene	0.20	0.00	0.58	0.80	8	1.16	14	2.70	
Acenaphthylene	0.00	0.00	0.87	0.14	8	1.95	14	3.70	
1-Methylfluorene	0.37	0.00	0.98	0.52	8	1.02	14	3.85	
Phenanthrene	0.02	0.10	0.97	0.40	8	1.27	14	1.49	
Pyrene	0.02	0.23	0.92	0.67	8	1.29	14	1.40	
Retene	0.21	0.36	0.13	0.54	7	1.25	14	1.15	
Benz[<i>a</i>]anthracene	0.16	0.00	0.83	0.45	8	1.10	13	2.34	
Chrysene+Triphenylene	0.07	0.00	0.85	0.49	8	1.26	14	1.50	
Benzo[<i>a</i>]pyrene	0.03	0.06	0.98	0.08	8	1.23	7	1.72	
Dibenz[a,h+a,c]anthracene	0.22	0.00	0.93	-0.21	4	1.31	5	1.48	
Indeno[1,2,3- <i>c,d</i>]pyrene	0.05	0.16	0.79	0.48	8	1.40	10	1.44	
Benzo[g,h,i]perylene	0.00	0.00	0.84	0.63	8	1.43	12	2.26	
Anthranthrene	0.06	0.06	0.46	0.29	4	1.56	5	1.25	
Coronene	0.02	0.00	0.84	0.80	5	1.46	6	2.04	

Table 19. Statistical Values for Chapel-to-GLC Ratios of PAHs by Wind Direction

^a Values in **bold**: *P* < 0.05; Pearson *r* > 0.8; city/other winds, mean or median ratio less than 1; and lake winds, mean or median ratio greater than 1.

appear correlated between sites for either wind condition. Coronene, a reported marker for gasoline combustion, showed high correlation between sites for both wind conditions. Although only five pairs of samples obtained under city/other-wind conditions were available, the Chapel-to-GLC ratio of 1.46 indicates that concentrations were higher at the Chapel site because gasoline in the urban air was diluted somewhat as the air mass moved away from the city. The median ratio of 2.04 for lake-wind conditions, with between-site correlations of 0.8, suggests that the level of coronene, which is in the background air, is also enriched by local plaza traffic.

Concentrations of PAHs in city air that are not related to vehicles, as well as MSATs arising from activities at the plaza, were diluted up to a factor of four between the Chapel and GLC sites. For example, overall the concentration of 1-methylfluorene was twice as high at the Chapel site as at either the School or GLC site under lake-wind conditions. Yet when the wind came from the plaza to the lake (city/other-wind conditions), the values at the Chapel and GLC sites were similar and highly correlated.

The ratios of median PAH values on lake-wind days to those on city/other-wind days are displayed for the Chapel

and GLC sites in Figure 22; the Chapel site ratios for the two wind conditions are rank ordered, with the GLC site ratios superimposed. The heavier-molecular-weight compounds identified with diesel emissions were equally or more abundant in air from an urban direction (Table B.20 in Appendix B). Ratios of median city/other-wind concentrations to median lake-wind concentrations reported at the Chapel site were: chrysene+triphenylene 2.5; benzo[b]fluoranthene 4.8; benzo[k]fluoranthene 5.0; benzo[e]pyrene 5.0; benzo[*a*]pyrene 5.0; perylene 2.0; indeno[1,2,3-*c*,*d*]pyrene 4.8; benzo[g,h,i]perylene 3.5; and coronene 3.3. However, over a third of the compounds had higher concentrations (ratios < 1) in the air coming from the lake and passing over the Peace Bridge plaza: acenaphthene 0.95; 2,3,5-trimethylnaphthalene 0.86; fluorene 0.62; 1-methylfluorene 0.64; dibenzothiophene 0.34; phenanthrene 0.48; anthracene 0.61; 2-methyldibenzothiophene 0.67; 4-methyldibenzothiophene 0.66; 2-methylphenanthrene 0.69; 2-methylanthracene 0.51; 4,5-methylenephenanthrene 0.54; 1-methylanthracene 0.43; 1-methylphenanthrene 0.49; 9,10-dimethylanthracene 0.45; fluoranthene 0.38; and pyrene 0.58.

At the GLC site, unlike the Chapel site, more of the compounds had higher median concentrations with city/other winds. However, there were some exceptions, including



Figure 22. Ratios of median lake-wind PAH concentrations to median city/other-wind PAH concentrations measured at the Chapel and GLC sites. Compounds are rank ordered by Chapel site values.

2,3,5-trimethylnaphthalene, retene, benzo[b]fluorene, and a few others. All the compounds with ratios of median lake-wind concentrations to city/other-wind concentrations greater than 1 at the GLC site also had ratios greater than 1 at the Chapel site, suggesting that although plaza emissions might have added to the concentrations at the Chapel site, the compounds were already in the air mass.

Analysis by Edge Plots and Ratio-to-Ratio Plots Certain ratios between the compounds in emissions are characteristic of specific sources. In an edge plot a straight line representing the ratio between two emitted compounds at different concentrations is plotted for each source. When a single source is contributing to ambient concentrations, data will fall along the source line. When two sources are contributing, the ambient data will fall between the two source lines. Data falling outside the source lines indicate a source is present that is not accounted for. The closer the ambient data fall to the line representing the emission rate for a specific source, the stronger the contribution from that source. Diesel, coke, and gasoline emissions have specific ratios of benzo[*e*]pyrene and indeno[1,2,3-*c*,*d*]pyrene. Figure 23 shows edge plots of benzo[e]pyrene and

indeno[1,2,3-c,d]pyrene concentrations by season (summer and winter) and by sampling site paired with wind direction. The signal from coke emissions was stronger in the winter, when there were more city-wind conditions than in the summer. A strong diesel signal was present at the Chapel site on lake-wind days compared with city-wind days. The same signal was not apparent at the GLC or School sites. Concentrations of benzo[e]pyrene and indeno[1,2,3-c,d]pyrene were higher on city-wind days than they were on lake-wind days. Edge plots are more difficult to interpret when a mixture of multiple sources is present.

Ratio-to-ratio plots include a third dimension of information that produces more easily interpretable data (Robinson et al. 2008). In Figure 24 a ratio-to-ratio comparison of (benzo[g,h,i]perylene \times 1000)/EC and (indeno[1,2,3c,d]pyrene \times 1000)/EC shows the strong diesel signal at the Chapel site during lake-wind days. At the other two sites, the effect of wind direction was not as distinct, and the data for the GLC and School sites for both wind directions were similar to those for the Chapel site during citywind days, suggesting that the dilution of the diesel signal was the dominant process occurring with distance from the plaza.



Indeno[1,2,3-c,d] pyrene (ng/m³)

Figure 23. Edge plots of benzo[e]pyrene and indeno[1,2,3-*c*,*d*]pyrene by season (summer and winter), and by sampling site paired with wind direction. The plots at the bottom are magnifications of the low values in the top plots.



Figure 24. Ratio-to-ratio plots of (benzo[*g,h,i*]perylene × 1000)/EC and (indeno[1,2,3-*c,d*]pyrene × 1000)/EC. The plot on the right is a magnification of the low values in the plot on the left.

NPAH Analyses by Wind Direction NPAHs in ambient air have been associated with adverse health effects (Arey et al. 1988; IARC 1989; Gupta et al. 1996). NPAHs are byproducts of combustion (Arey et al. 1987) or are formed through the oxidation of PAHs in the atmosphere (Arey 1998). Individual NPAHs are specific in origin to either combustion or oxidation and thus may help identify primary and secondary aerosol sources (Cecinato et al. 1996; Crimmins and Baker 2006). The truck-stop study by Minegishi (2007) identified 9-nitroanthracene and 1-nitropyrene as emissions from diesel engines. Figure 25 shows the distributions of Chapel-to-GLC ratios of NPAH concentrations for lake-wind days. The data confirm the presence of these two compounds at the Chapel site. The median ratios suggest nearly a 10-fold increase for 1-nitropyrene and 9-nitrophenanthrene at the Chapel site. Most of the NPAHs for which there were sufficient paired measurements had 75% of the Chapel-to-GLC ratios above unity. A few compounds, 2-nitropyrene and 9-nitroanthracene among them, had little differences in their concentrations between the Chapel and GLC sites for lake-wind conditions, implying that these were not related to mobile sources.

Table 20 lists the NPAH samples above the LOD for both lake-wind and city/other-wind conditions. For 5-nitroacenaphthalene, 9-nitroanthracene, 3-nitrophenanthrene, and 2-nitrofluoranthene, all 20 samples (10 at each site) taken with a lake wind blowing had levels above the LOD, but none of the 8 samples taken under city/other-wind conditions had detectable levels. Compounds detected predominantly in air from the lake and not in air from the city or other directions are noted in Table 20. Other compounds that were detected primarily in lake-wind directions were 1,3-dinitronaphthalene (18 of 20 samples were detected with lake winds and 0 of 8 with city/other winds), 2-nitrofluorene (17 of 20 samples with lake winds and 0 of 8 with city/other winds), 3-nitrophenanthrene (20 of 20 samples with lake winds and 1 of 8 with city/other winds), and 1nitropyrene (18 of 20 samples with lake winds and 1 of 8 with city/other winds). The only NPAH compound behaving contrary to the others was 3-nitrofluoranthene: it was detected at both sites only when the wind came from the city/other direction and was not detected at either site when the wind came from the lake.

Diurnal PAH and NPAH Concentrations The diurnal variations in PAH and NPAH concentrations in Buffalo during summer 2005 (July 20–26) are summarized in Table 21, which shows daytime and nighttime 12-hour geometric mean concentrations in samples collected by CBL using high-volume Graseby Andersen samplers. Generally, the total PAH concentration measured was higher during the day and the total NPAH concentration was elevated at



Figure 25. Box and whisker plots of Chapel-to-GLC ratios for NPAHs (*N* = **10 pairs**) with lake winds. Minimum, bottom whisker; 25th percentile, bottom of the box; median, center line in the box; mean, "x"; 75th percentile, top of the box; and maximum, top whisker.

night at all three fixed sampling sites. The total PAH geometric mean daytime concentration varied between sampling sites, with the School site having the highest concentration (84 ng/m³), then the Chapel site (34 ng/m³), and then the GLC site (11 ng/m³). Figure 26 shows a unique diurnal pattern of PAHs at the School site, where the total concentration was higher during the day. No similar consistent trend was observed at the GLC or Chapel site. Similarly, the highest NPAH geometric mean nighttime concentration was at the School site (317 pg/m³), and the Chapel site mean (233 pg/m³) was higher than the GLC site mean (117 pg/m³). NPAH showed a strong diurnal pattern, with the nighttime concentration twice as high as that in the daytime. This pattern was relatively consistent among sampling sites.

Positive Matrix Factorization Analysis PMF was performed on the seasonal PAH data collected in the winter 2005, summer 2005, and winter 2006 sampling sessions. The analysis was applied separately among the sampling sites to characterize the different sources at each site. Species that were not detected in at least 80% of the samples were removed from the analysis. Seventeen PAHs were used in an analysis with an additional 2% uncertainty error to achieve a realistic Q value. The minimal value for the additional uncertainty error that resulted in the calculated Q value closest to the theoretical optimal Q value was 2%. The optimal number of sources for the winter 2005, summer 2005, and winter 2006 data for each site appeared to be two or three. The GLC site was characterized by two factors, but three factors were necessary to sufficiently characterize the sources at the Chapel and School sites.

NPAH	City / Other Winds			Lake Winds		
	Chapel	GLC	Overall	Chapel	GLC	Overall
1-Nitronaphthalene	4	4	8	10	10	20
2-Nitronaphthalene	4	4	8	10	10	20
2-Nitrobiphenyl	4	4	8	10	10	20
3-Nitrobiphenyl	4	4	8	10	10	20
4-Nitrobiphenyl	0	0	0	3	1	4
1,3-Dinitronaphthalene ^a	0	0	0	9	9	18
1,5-Dinitronaphthalene ^a	0	0	0	1	2	3
5-Nitroacenaphthalene ^a	0	0	0	10	10	20
2-Nitrofluorene ^a	0	0	0	10	7	17
9-Nitroanthracene ^a	0	0	0	10	10	20
2-Nitroanthracene	3	4	7	7	5	12
9-Nitrophenanthrene	2	2	4	10	6	16
3-Nitrophenanthrene ^a	0	1	1	10	10	20
4-Nitrophenanthrene	2	2	4	2	1	3
2-Nitrofluoranthene ^a	0	0	0	10	10	20
3-Nitrofluoranthene ^b	4	4	8	0	0	0
1-Nitropyrene ^a	1	0	1	10	8	18
2-Nitropyrene ^a	4	2	6	8	10	18
7-Nitrobenz[<i>a</i>]anthracene ^a	2	1	3	10	10	20
6-Nitrochrysene	2	2	4	1	0	1
1,3-Dinitropyrene	0	0	0	0	0	0
1,6-Dinitropyrene	0	0	0	0	0	0
6-Nitrobenzo[a]pyrene	0	1	1	3	4	7
1-Nitrobenzo[<i>e</i>]pyrene	1	0	1	4	6	10
3-Nitrobenzo[<i>e</i>]pyrene	0	0	0	1	2	3

Table 20 NDAH S th 1 d CI C Sito by Wind Dir 1. . L I OD at th CL -+;

^a NPAHs primarily detected on lake-wind days at both sites.

^b NPAH primarily detected on city/other-wind days at both sites.

Table 21. Total PAH and NPAH Concentrations Measured at the Three Sampling Sites, Using Graseby Andersen High-Volume Samplers, During July 20-26, 2005^a

	Day Samples		Night Samples		
Site	Mean	Range	Mean	Range	
PAHs (ng/m ³)					
GLC	11	3–40	20	8-37	
School	84	54-107	58	50-65	
Chapel	34	19–55	29	18–40	
NPAHs (pg/m ³)					
GLC	47	19–89	117	45-299	
School	192	169-226	417	145-833	
Chapel	134	77–200	233	81–577	

^a Values are the geometric means of 6 samples (except the value for the GLC night samples is the geometric mean of 5 samples).



Figure 26. Diurnal pattern of total PAH and NPAH concentrations at the GLC, School, and Chapel sites during July 2005, from data obtained using Graseby Andersen high-volume samplers.



Figure 27. Light PAH profile and heavy PAH profile based on lighter-molecular-weight and heavier-molecular-weight PAHs, resolved by two-source PMF analysis of seasonal data (winter 2005, summer 2005, and winter 2006 samples). (*Figure continues next page*)

The two PAH profiles resolved by PMF were similar for the GLC, School, and Chapel sites. One of the sources is predominantly loaded with lighter-molecular-weight PAHs (light PAH profile), and the other source is enriched with heavier-molecular-weight PAHs (heavy PAH profile) (Figure 27). The temporal patterns of the light and heavy PAH profiles were consistent among the sampling sites (Figure 28). The light PAH profile was dominant in the summer (July), and the heavy PAH profile in the winter (January). The two sources resolved by PMF characterize the summer and winter profiles common among the sampling sites.



Figure 27 (Continued).



Figure 28. Temporal patterns of light PAH profile and heavy PAH profile concentrations resolved by two-source PMF analysis. (Figure continues next page)


Figure 28 (Continued).

In the three-source PMF analysis, a medium PAH profile was resolved in addition to the light and heavy profiles (Figure 29). The light PAH profile is dominated by fluorene and phenanthrene, which have molecular weights of 166 and 178, respectively. The medium profile is dominated by the methylated compounds, with molecular weights ranging from 190 to 198. In the heavy profile, molecular weights are 216 or greater. The light and heavy PAH profiles resolved from the GLC, School, and Chapel sites were relatively similar, but the medium profile varied among the sampling sites. As in the two-source PMF analysis, the light PAH profile was dominated by lighter-molecularweight PAHs, especially phenanthrene and fluorene, which suggests volatilization (from ground surfaces).



Figure 29. Light, medium, and heavy PAH profiles resolved by three-source PMF analysis of PAH data. (Figure continues on next two pages)

Phenanthrene, fluoranthene, and pyrene were included in the heavy PAH profile to determine their associations to the heavier PAHs, such as chrysene+triphenylene, benzo[b]fluoranthene, and benzo[g,h,i]perylene, which represent combustion sources. Though the medium profiles differed among the sampling sites, all were enriched with methylated PAHs. The profile patterns from the School and Chapel sites were similar, but there were approximately four times the number of individual species at the School site. The medium PAH profile represents volatilization from surface materials nearby (asphalt paving and roofing).



Figure 29 (Continued).

The temporal pattern showed that the light PAH profile was more abundant at the GLC site compared with the School and Chapel sites (Figure 30). At all of the sampling sites, the light profile had higher concentrations in the summer than in the winter. The correlation between ambient temperature and the PAH concentration indicated that the lighter-molecular-weight PAHs were positively correlated with warmer temperature (P < 0.01). This suggests that the higher concentration of lighter-molecularweight PAHs in the summer sampling session was due to volatilization.

The medium PAH profile was not prevalent at the GLC site, but was a dominant source at the School and Chapel sites during the summer sampling session (Figure 30). The



Figure 29 (Continued).



Figure 30. Temporal pattern of the light, medium, and heavy PAH profiles in winter 2005, summer 2005, and winter 2006, resolved by three-source PMF analysis. (*Figure continues on next two pages*)

concentration of the medium profile at the School site was approximately five times greater than that at the Chapel site. The medium profile, like the light profile, was characterized by lighter-molecular-weight PAHs. The medium PAH profile is enriched with methylated PAHs, and its abundance at the School site indicates that volatilization from surface material near the School site is a possible PAH source. The heavy PAH profile was relatively abundant in the winter sampling sessions at all three sites (Figure 30). The ambient temperature was negatively correlated with the concentration of heavier-molecular-weight PAHs (P < 0.05). The heavier-molecular-weight PAHs are common tracers of combustion sources (Greenberg et al. 1981; Rogge et al. 1993a, Miguel et al. 1998; Kado et al. 2000; Kavouras et al.



Figure 30 (Continued).

2001). As seen in Figures 5 through 8, the number of vehicles on the Peace Bridge in the winter was half of that in the summer. However, with a lower atmospheric boundary layer and less mixing of compounds in the air, vehicle emissions could contribute to the heavier-molecularweight PAHs in the winter. Also, increased use of heating appliances during colder temperatures could be a source of oil, wood, and coal combustion (Freeman and Cattel 1990; Rogge et al. 1997; Simcik et al. 1999; Kavouras et al. 2001). With the limited number of PAH species in this analysis, the winter source could not be specified.



Figure 30 (Continued).

Comparisons with PAH and NPAH Levels in Other

Cities The PAH and NPAH concentrations measured in Buffalo were compared with those collected in other cities during summer and winter sampling sessions (Figure 31). Fluoranthene had the lowest molecular weight of the PAHs available in the comparison database. It was selected to represent PAHs found primarily in the gas phase (light profile). Chrysene+triphenylene were selected to represent PAHs that occur in both the gas and particle-bound phases (medium profile), and benzo[g,h,i] perylene was selected to represent PAHs found in the particle phase (heavy profile). The three compounds selected for NPAH analysis were those that occurred in all of the data sets.



Figure 31. Comparison of selected PAHs and NPAHs measured at the three sampling sites in Buffalo (GLC, School, Chapel) during the summer and winter with those reported in other locations: Buffalo, means of 15 samples measured in January 2005 and 2006 and 10 samples (9 for School site) in July 2005 (this study); Baltimore, geometric means of 69 samples measured in summer 2002 and winter 2003 (Crimmins 2006); Birmingham, means of 55 samples collected in February and August 1992 (Harrison et al. 1996); Los Angeles and Riverside, means of four 5-day samples collected at different time intervals in August 2002 and four collected in January 2003 (Reisen and Arey 2005).

The mean of PAH concentrations measured in the winter at Buffalo was an order of magnitude less than means of concentrations measured in Birmingham, United Kingdom (Harrison et al. 1996) and in Baltimore, Maryland (Crimmins 2006). In the summer, PAH concentrations measured in Buffalo were similar to those reported in Baltimore. The concentration of fluoranthene during the summer was approximately 3-fold higher at the School site than in either Baltimore or Birmingham. Seasonal patterns varied among locations, possibly due to meteorologic differences. The PAH concentrations were higher during the winter than in the summer in Birmingham. In Baltimore, the volatile PAHs (e.g., fluoranthene) had a higher concentration during the summer, and the semivolatile PAHs (e.g., benzo[a]pyrene and benzo[g,h,i]perylene) were more abundant in the winter, which was a similar trend to that in Buffalo. The mean PAH concentration in Buffalo was within the range of concentrations in other urban areas.

For NPAHs, the mean concentration of 9-nitroanthracene in Buffalo was comparable to the concentrations in Los Angeles and Riverside, California (Reisen and Arey 2005), but the mean concentrations of 2-nitrofluoranthene and 1-nitropyrene were 10 to 100 times less during both summer and winter (Figure 31). The seasonal patterns of NPAHs were different among locations. The concentration of 2-nitrofluoranthene in Riverside was twice as high in the summer as in the winter. In Baltimore (Crimmins 2006) the 9-nitroanthracene concentration was three times greater in the summer, and the 1-nitropyrene concentration in the winter was 7-fold above the concentration measured in the summer. In Buffalo the concentrations of all of the NPAHs were higher during the summer. The NPAH concentrations in Buffalo were relatively lower than those in the other urban areas, which could be because there is less production of secondary NPAHs (e.g., 2-nitrofluoranthene) in the atmosphere and there are fewer combustion sources that emit primary NPAHs (e.g., 1-nitropyrene).

The PAH and NPAH concentrations measured in Buffalo were compared with concentrations in other studies that characterized diurnal differences. In general, the individual PAH concentration did not change dramatically between day and night at any of the locations (Figure 32). The day and night PAH concentrations measured at the Chapel and GLC sites were comparable to those measured in Los Angeles and Riverside, California (Reisen and Arey 2005). The concentrations of benzo[a] pyrene and benzo[g,h,i]pervlene at the School site were most similar to those that were measured in samples collected during a photochemical smog episode in Torrance, California, which is 20 km south of central Los Angeles (Arey et al. 1987). The concentration of NPAHs was typically higher at night, but there were differences in individual species concentrations at different locations (Figure 32). In Buffalo the concentration of 9-nitroanthracene increased three to seven times at night, and in Riverside, California, the concentration of 2-nitrofluoranthene was twice as high at night (Reisen and Arev 2005). The concentration of 1-nitropyrene did not differ significantly between day and night at any of the locations. The higher NPAH concentration during the night could be due to NPAH production via gas-phase reaction with NO₃ radicals, to a lower atmospheric boundary layer, or to less photodegradation.

CONTINUOUS MEASUREMENTS AT FIXED SAMPLING SITES AND RELATIONSHIPS TO WIND DIRECTION AND TRAFFIC

This section focuses on the continuous measurements of PM_{2.5}, UFPs, and pPAHs collected at the fixed sampling sites. Attempts to obtain continuous measurements of O_3 , NO, and CO_2 were less successful. The NO device was the first edition from 2B Technologies and had problems with data storage. The O₃ device, also from 2B Technologies, developed problems that required factory repairs, so simultaneous measurements upwind and downwind of the Peace Bridge plaza were limited. Although the CO₂ instruments worked reasonably well, simultaneous measurements recorded at the GLC and Chapel sites also were limited; therefore, in this report we chose to focus on the particle measurements. In the integrated sample analysis, the "other-wind" cases were combined with "city-wind" cases because of the limited number of 12-hour city-wind cases. It was not necessary to include the other-wind cases for the continuous samples because the data set was reduced to 10-minute sampling periods and the number of city-wind cases was sufficient to conduct the analysis.

The P-Trak was used for UFP measurements. Even though the manufacturer claims that the P-Trak responds to particles as small as 20 nm, comparisons of particle counts made at the Peace Bridge plaza by Clarkson University during the summer 2004 pilot study showed strong correlations between counts by a CPC (Model 2007, TSI Inc.) and by the engine exhaust particle spectrometer (EEPS, Model 39090, TSI Inc.). The EEPS continuously measures number concentration in the particle size range of 6 to 500 nm (Ogulei et al. 2007). From one of the Clarkson researchers, Tim McAuley (personal communication, March 2007), we learned that the CPC was responsive to particles as small as 15 nm, but the EEPS showed that at locations very close to combustion sources a majority of the particles counted will be smaller than this. At a location near our Chapel site with a truck idling, the CPC number counts tracked with the EEPS number counts but were always lower by 10% to 50% (data not shown). In the absence of local mobile sources, the CPC counts were lower than the EEPS number counts, even for regional air masses. Zhu and coworkers (2006b) reported on comparisons between the P-Trak and CPCs for their Los Angeles freeway studies. Consistent with McAuley's point, the Los Angeles group claimed that the P-Trak underreported particle number counts (25% of CPC with $r^2 = 0.68$ when within 30 m of a freeway). Upwind of the freeway and farther downwind of the freeway there was less undercounting by the P-Trak and correlations increased (Zhu et al. 2006b). Zhu and colleagues were able to demonstrate



Figure 32. Comparison of selected PAHs and NPAHs measured at the three sampling sites in Buffalo (GLC, School, Chapel) during the daytime and nighttime with those reported in three California locations: Buffalo, means of 4 samples measured during the daytime (7:00 AM to 7:00 PM) in July 2004 and during the nighttime (7:00 PM to 7:00 AM) in July 2005 (this study); Torrance, means of 6 filter samples measured during the daytime (6:00 AM) in February 1986 (Arey et al. 1987); Los Angeles and Riverside, means of 5-day sampling at 4 time intervals during the daytime (7:00 AM to 6:30 PM) and nighttime (7:00 PM to 6:30 AM) in August 2002 (Reisen and Arey 2005).

Table 22.	Ten-Minu	te Average	e UFP Cour	its at Fixe	d Samplin	g Sites fo	r Winter 2	005, Sum	mer 2005,	and Wint	er 2006 ^a
							Percentil	9			
Site	N	Mean	SD	5th	10th	25th	50th	75th	90th	95th	Maximum
GLC	3799	10,842	12,620	1792	2401	3794	6,411	11,431	26,273	37,341	139,156
Chapel	3719	17,974	14,412	3836	6005	9591	14,153	21,736	32,820	45,426	158,555
School	3709	10,785	7,604	2514	3670	5690	8,463	14,084	21,578	25,931	101,420

^a Values are particles/cm³.

Table 23. Ten-Minute Average UFP Counts at Fixed Sampling Sites by Season^a

	Sui	nmer 20	05	W	inter 200	06
Site	Ν	Mean	SD	N	Mean	SD
GLC Chapel School	1067 1067 1203	6,232 14,528 6.512	4060 8222 3705	1682 1618 1673	12,033 20,922 13,031	13,241 18,195 7,585

^a Values are particles/cm³.

that for particles between 20 nm and 50 nm, the ratio of P-Trak counts to CPC counts ranged from 20% to 50% (Zhu et al. 2006b). For particles larger than 60 nm, the ratio approached unity. Thus, although the P-Trak instruments when operated side-by-side are within 1000 particles/cm³ of each other, comparative interpretation of particle number counts among locations will depend on the particle size distributions of fresh and aging aerosols. Only during the final preparation of this report did the number counts by particle size made by Clarkson researchers become available. These detailed data from EEPS measurements upwind and downwind of the Peace Bridge plaza are relevant to the interpretation of our UFP measurements.

First, we explored the between-site differences in UFPs, pPAHs, and PM_{2.5} by wind direction and wind speed. Then, for a select portion of the data, we looked at the influence of traffic on the differences in the UFPs and pPAHs between the Chapel site measurements and the GLC site measurements.

Ultrafine Particle Counts

More than 600 hours of UFP measurements were made at each of the three sites. Table 22 provides the statistical distribution of the 10-minute UFP counts for each site. We decided to use 10-minute averages for the fixed-site continuous measurements, rather than complicate the analvsis with lags adjusted for wind speed. With a wind speed of 5 m/sec, which is typical for the study area, the time for wind to travel between sites is less than 2 minutes. UFP counts at the Chapel site were two to three times those at the GLC site over the lower half of the distribution, but the difference diminished above the 75th percentile. UFP counts at the GLC site were less than those at the School site for all of the distribution except the higher percentiles.

The UFP counts were substantially higher during the wintertime than the summertime (Table 23) (P < .001 for each site). The wintertime means for both the GLC and the School sites were twice the summer means. For the Chapel site, the summer mean was approximately 70% of the winter mean.

The paired differences in UFP counts were calculated for combinations of the fixed sampling sites and displayed as cumulative frequency distributions (Figure 33). UFP counts at the GLC site exceeded counts at the Chapel site only 20% of the time, and rarely were the differences greater than 10,000 particles/cm³. In contrast, UFP counts at the Chapel site exceeded counts at the GLC site by 10,000 particles/cm³ or more about 25% of the time, and by 20,000 particles/cm³ or more 10% of the time. UFP counts at the Chapel site were greater than counts at the School site more than 80% of the time. The shape of the cumulative frequency distribution of the differences between the Chapel and School sites was similar to that between the Chapel and GLC sites for the portion where the Chapel site had higher concentrations. The Chapel site experienced substantially higher UFP counts than either the GLC or School sites. Across the lower end of the distribution, a different pattern was observed. The School site rarely exceeded the Chapel site by more than 5000 particles/cm³, suggesting fewer local UFP sources. The two sites are in west Buffalo and experience similar wellmixed particle pollution with winds from the city. With winds from the lake, each site experiences the regional background air as well as pollution from sources between the shoreline and the site; under lake-wind conditions, UFP counts would be reduced from the levels observed at the plaza through dilution and coagulation of the particles as they are transported to the School site.



Figure 33. Cumulative frequency distributions of the differences in 10-minute average UFP counts between fixed sampling sites.



Figure 34. Radial plots of differences in UFP concentrations (particles/cm³) between the Chapel and School, School and GLC, and Chapel and GLC sites, by wind direction. From a data set of average wind direction and concentration data for 10-minute periods during winter 2005, summer 2005, and winter 2006 sampling sessions, the average of the 10-minute average differences in concentration was calculated for each wind direction degree.

The long tail of negative readings in the cumulative frequency distribution of differences between the Chapel and GLC site UFP counts indicates that, on occasion, the GLC site experienced local emissions. To examine the difference in more detail, we created a radial plot. Figure 34 shows the difference in 10-minute average UFP counts between the Chapel and GLC sites plotted by the wind vector over the entire sampling period. Between approximately 145° and 315° the count was always higher at the Chapel site than at the GLC site. For winds from about 5° to 135° (city-wind conditions) the count was typically higher at the GLC site than at the Chapel site. If there were no UFP sources between the Chapel site and the shore of Lake Erie, one would expect that with winds from the city, the GLC site would have lower UFP counts due to dilution and coagulation of particles.

With city winds between 100° and 135° the UFP counts at the GLC site were pronouncedly higher than those at the

бам брм бам

Jan 20 Jan 21

Jan 19



Figure 35. UFP counts (hourly moving average) at the three sampling sites during the summer 2005 sampling session.



Figure 36. UFP counts (hourly moving average) at the three sampling sites during the winter 2006 sampling session.

Chapel site. When examining the temporal record, we noted a period between midday on January 15 through late morning on January 17, 2006, when UFPs at the GLC site often exceeded those at the other two sites. The air mass trajectory and wind data for this period show that on January 15 local surface winds and air mass movement were from the north. By late morning on January 15, winds had shifted to north-northeast, and they had moved easterly by that evening. With easterly winds, UFP counts increased at all sites, with substantial increases recorded at the GLC site. We speculate that the GLC was downwind of the Interstate 190 highway and the Peace Bridge plaza during times when winds were from the northeast quadrant and was possibly downwind of some local source when winds were from the 90° to 110° direction. As winds shifted further, first to 150° and then from the southwest quadrant, UFPs decreased at all three sites.

Moving hourly averages were created for each fixed sampling site from the 10-minute average UFP counts. Figure 35 shows a plot of the 1-hour averages for the summer 2005 campaign, and Figure 36 shows the same for the winter 2006 campaign. Wintertime particle counts, as noted, were typically higher than summertime counts. A diurnal pattern was apparent for periods of time, particularly during the summer. The overnight decrease in UFP counts was more distinct nearer the bridge. There were a few times in the summer (on July 23 and 27, 2005) and a longer period in the winter (January 15-17, 2006) when UFP counts at the three sites appeared more correlated. It was during this winter period that the GLC site had higher UFP counts than the School and Chapel sites, which had similar UFP counts. The air mass arriving over Buffalo during these summer periods was from Ontario to the north, with surface winds from the north-northeast and northeast. The air mass trajectories for January 15 and 16 were very similar. In contrast, from early morning on January 9 through January 10, winds were consistently from the west or west-southwest for about 36 hours, with the air mass arriving in Buffalo after crossing southern Ontario and Lake Erie. UFP counts were low at the GLC site, reached 20,000 to 30,000 particles/cm³ at the School site, and were 40,000 to more than 80,000 particles/cm³ at the Chapel site. These observations suggest that in typical urban air UFP values might be 15,000 to 20,000 particles/cm³, but local sources of traffic (cars and trucks) might double those levels as measured by the P-Trak. If the P-Trak values were adjusted to CPC values as described by Zhu and colleagues (2006b), the local number counts for particles of 10 nm and smaller might be three to four times higher.

To explore further the relationship of UFP counts to the Peace Bridge plaza traffic, we created scatter plots comparing 10-minute average values at the Chapel site versus the GLC site. Figure 37 displays a plot of data from all paired readings and a plot of data restricted to readings obtained under lake-wind conditions. The two plots clearly show that restricting the data to those obtained when the winds were from the southwest sector greatly reduced the number of times when UFP counts at the GLC site exceeded those at the Chapel site. In Figure 38, the lake-wind cases were divided among wind speeds greater than and equal to or less than 3.1 m/sec. With the higher wind speeds, only a few 10-minute UFP counts at the GLC site exceeded those at the Chapel site.

Particle-Bound PAHs

Mean pPAH concentrations were highest at the Chapel site. The ratio of the pPAH concentrations (medians and means) among the GLC, School, and Chapel sites was approximately 1:2:4. Table 24 provides summary statistics on pPAHs at the three sampling sites. Like UFP counts, pPAH



Figure 37. UFP counts at the Chapel site versus those at the GLC site: all data and data obtained under lake-wind conditions (wind direction, 180° -280°).



Figure 38. UFP counts at the Chapel site versus those at the GLC site obtained during lake winds of low speed (\leq 3.1 m/sec) and higher speed (> 3.1 m/sec).

Table 24.	Ten-Mini	ite Average	рган Со	Jucentrati	ons (ng/m	°) at Fixed	i Samping	g Sites				
				Percentile								
Site	Ν	Mean	SD	5th	10th	25th	50th	75th	90th	95th	Maximum	
GLC	4448	3	8	1	1	1	2	3	5	9	308	
Chapel	4294	13	13	2	3	4	8	17	30	38	130	
School	3120	5	5	2	2	3	4	6	9	13	76	

Table 24. Ten-Minute Average pPAH Concentrations (ng/m³) at Fixed Sampling Sites

concentrations were higher in the winter than in the summer. Further, the daytime values at the Chapel and School sites were higher than the nighttime values (Table 25).

Figure 39 is the cumulative frequency distribution of the between-site differences in pPAH concentrations. The 95th percentile for the difference between the School site and the GLC site was about 9 ng/m^3 , and the difference between the Chapel and GLC sites exceeded this value about 30% of the time. The pPAH values were higher at the Chapel site than at the other two sites more than 70% of the time. To complete this analysis, we prepared radial plots of the differences in pPAH concentrations between the individual sites (Figure 40). The pPAHs were slightly elevated at the School site in comparison with the GLC site for wind directions from about 135° through 215°. Although the difference was not as pronounced as the differences between the Chapel and GLC sites, the patterns were similar. The small increase in pPAH concentration from the GLC site to the School site may or may not be due to the traffic at the Peace Bridge plaza; other sources between these two sites may contribute to the difference. For city-wind directions, the School and GLC sites had equivalent levels of pPAHs. As shown in Figure 40, for the north-to-east wind sector, the Chapel and School sites were equivalent in pPAH concentrations. For the east-tosoutheast wind sector, pPAHs were slightly higher at the School site than at the Chapel site. However, for wind directions from about 160° to 340°, the PAHs were higher at

	Sum	mer 2005		Wir	ter 2006	
Site / Time	N (10-min Averages)	Mean of 12-hr Averages	SD	N (10-min Averages)	Mean of 12-hr Averages	SD
GLC						
Day	851	2	19	982	4	5
Night	817	2	24	997	3	15
Chapel						
Day	855	22	22	954	13	8
Night	775	16	28	931	8	18
School						
Day	623	6	28	986	7	5
Night	564	3	32	947	5	22

Table 25. Twelve-Hour Average pPAH Concentrations (ng/m^3) for Day versus Night, by Season

the Chapel site. The southwest sector shows the same consistent pattern as seen on the previous radial plots for UFPs (see Figure 34).

Next, differences between the Chapel and GLC sites were explored by wind sector and two categories of wind speed. Figure 41 shows the scatter plot of simultaneous pPAH measurements made at the Chapel and GLC sites under lake-wind conditions. There was a substantial



Figure 39. Cumulative frequency distributions of the differences in pPAH 10-minute average concentrations between sampling sites.



Figure 40. Radial plots of differences between pPAH concentrations (ng/m³) at the Chapel and School, School and GLC, and Chapel and GLC sites, by wind direction. From a data set of 10-minute average wind directions and pPAH concentrations for winter 2005, summer 2005, and winter 2006 sampling sessions, the average difference of the 10-minute average concentrations was calculated for each wind direction degree.





Figure 41. Scatter plot of all pPAH concentrations from the summer 2005 and winter 2006 sampling sessions for the Chapel site versus the GLC site; and scatter plot of concentrations measured under lake-wind conditions (wind direction, 180°–280°).

reduction in the number of 10-minute values at the GLC site that were greater than those at the Chapel site. As with UFPs, the number of 10-minute pPAH values at the GLC site that exceeded those at the Chapel site was reduced with higher wind speeds, as indicated in Figure 42, which classifies the lake-wind conditions into two categories of wind speeds.

Figure 42. Scatter plot of pPAH concentrations from the summer 2005 and winter 2006 sampling sessions for the Chapel site versus the GLC site measured during lake winds of low speed (≤ 3.1 m/sec); and scatter plot of concentrations measured under lake winds of higher speed (> 3.1 m/sec).

Figure 43 shows the temporal variations in pPAHs for the summer 2005 campaign, and Figure 44 for the winter 2006 campaign. Some diurnal and weekend-versus-weekday patterns were apparent. We would have expected to see higher pPAH concentrations at the Chapel site starting on Monday, January 16, except it was a national holiday (birthday of Martin Luther King, Jr.). For most of the previous 2 days, the



Figure 43. One-hour moving average pPAH concentrations during the summer 2005 sampling session for the three sampling sites.



Figure 44. One-hour moving average pPAH concentrations during the winter 2006 sampling session for the three sampling sites.

wind flow had been from Canada to the north. By Monday, winds had shifted and were blowing from the northeast quadrant. The Chapel site was not affected by air that came across the Peace Bridge plaza until Wednesday, January 18. On Tuesday, January 17, one can observe elevated pPAH levels at all three sites (Figure 45).

Continuous PM_{2.5} Measurements

The laser-based nephelometer used to collect $PM_{2.5}$ measurements operated continuously at each fixed sampling site for more than 600 hours. The instrument is subject to interference from humidity, which causes small particles to agglomerate. To correct for this interference, each 12-hour daytime integrated $PM_{2.5}$ measurement was used to adjust the instrument's electronic output for that period. The mean of the values obtained for mass gravimetric measurements during the previous and following sampling periods was used to adjust the values for periods when we were not making these measurements.

Table 26 provides the statistical summary for the 10minute average PM_{2.5} (µg/m³) concentrations, while Figure 46 shows the cumulative frequency distribution of the differences in DustTrak PM_{2.5} measurements between sites for summer and winter periods. During the summer, the differences between the Chapel and GLC sites were within $\pm 5 \,\mu\text{g/m}^3$ about 80% of the time; however, a small fraction of the Chapel site PM_{2.5} concentrations did exceed the corresponding GLC values by more than 10 μ g/m³. Although the GLC and the School sites had similar mean values, the tails of the distribution for the differences in the summer suggest the influence of local sources at both sites, leading to more extreme differences. During the winter, PM_{2.5} values at both the Chapel and School sites were more likely to exceed the GLC values than during the summer. The Chapel site exceeded the simultaneously recorded GLC site PM_{2.5} levels by more than 5 µg/m³ 25% of the time versus 20% of the time in the summer. The School site PM_{2.5} levels in the winter were greater than the



Figure 45. Ten-minute average pPAH concentrations and wind directions for selected days in winter 2006.

1able 26.	able 20. Statistical Summary of 10-Winute Average $FM_{2.5}$ (µg/m ²) Measurements from Dust mak											
	Percentile											
Site	N	Mean	SD	5th	10th	25th	50th	75th	90th	95th	Maximum	
GLC	4104	10.1	5.7	2.0	3.3	6.1	9.6	13.3	17.0	19.5	47.9	
Chapel	3662	11.7	6.9	3.8	4.4	5.9	10.6	15.4	21.4	25.2	39.8	
School	3892	10.6	6.7	2.7	3.6	5.8	9.2	14.0	18.8	24.2	46.3	

Table 26 Statistical Summary of 10 Minute Average PM (ug/m3) Measurements from DustTral

GLC site levels 80% of the time versus only 45% of the time during the summer (Figure 46).

UFP and pPAH Data Analysis by Wind Factors and Traffic Counts

To understand the mechanism by which traffic-related UFPs and pPAHs were transported, we stratified 1-hour average wind directions by wind-angle increments of 10 degrees. For robustness in data analysis, we included the data for wind directions between -30° and $+30^{\circ}$ of every wind-angle increment of 10 degrees. The coefficient of determination (R^2) was computed between the UFP concentrations measured from each of the three fixed sampling sites and the hourly traffic counts categorized by vehicle types reported by the Peace Bridge Authority. We were not able to find a clear relationship between Peace

Bridge traffic counts and UFP concentrations at the Chapel site when the wind direction was from the southwest to west (Figure 47). The same procedure was applied to pPAH analysis. We found that the Chapel site had the highest variability when the wind was blowing from the west. Figure 47 demonstrates the highest variability between pPAH concentration and total truck counts at the Chapel site when the wind was blowing from averaged vector directions of 190° to 230°, and we attributed this to emissions from diesel trucks southwest of the Chapel site.

Analysis by Wind Speed and Direction Ogulei and colleagues (2007), in another study of this location, found that the highest average UFP concentrations were recorded at the Chapel site and the lowest at the GLC site. A number of physical and chemical factors affect the dispersion and



Figure 46. Cumulative frequency distributions of the differences in 10-minute average $PM_{2.5}$ concentrations between sampling sites, for the summer 2005 and winter 2006 sampling sessions.

dilution of UFPs as the air mass moves away from the Peace Bridge. Seasonal changes and meteorologic conditions play an important part in particle emissions. As shown by Hussein and colleagues (2004), UFP concentrations vary seasonally. Hussein and colleagues (2006) observed that UFP concentrations in Helsinki, Finland, were higher during winter than summer. Among the meteorologic factors influencing UFP concentrations, low wind speed has been found to be important (Hussein et al. 2006; Kerminen et al. 2007). Hence, we stratified the continuous data in our study by wind speeds equal to or less than 1.8 m/sec and greater than 1.8 m/sec and divided the data into three different wind sectors of city winds (1° through 179°), lake winds (180° through 280°), and other winds (281° through 359°) based on the 1-hour vector average wind directions. The data were then separated by sampling session. Note that the 12-hour integrated data were assigned to wind sectors using 10-minute vector average wind directions and considering



Figure 47. Coefficient of determination (R^2) for the Chapel site UFP concentrations and pPAH concentrations versus car, truck, and total traffic counts reported by the Peace Bridge Authority. R^2 was computed between the pollutant concentrations for each average wind direction stratified by wind-angle increment of $10^{\circ} \pm 30^{\circ}$ and the hourly traffic counts categorized by vehicle types.

not only the direction, but also the length of time that the wind came from that direction. The mean, standard deviation, and median were computed for hourly average UFP concentrations at each sampling site (GLC, Chapel, and School sites), and the variance in concentrations explained by traffic counts was compared for all vehicles, cars, and trucks.

We observed a systematic pattern during both summer and winter: when the wind was blowing from southwest to west (lake winds), the UFP concentrations at the Chapel site were the highest and background concentrations at the upwind GLC site were lowest. The traffic-related particles moved from the major roads (Niagara Thruway) and the Peace Bridge toward the downwind location at the Chapel site, and the average concentrations measured at the School site, located 520 m away from the Chapel site, were lower than the values at the Chapel site but higher than those at the GLC site. Total pollutant concentrations have been found to gradually decrease with distance from the Peace Bridge (Ogulei et al. 2007), and this may be because the particles are diluted by mixing before they reach the School site. Analyses by Hussein and colleagues (2006) have shown that low wind speed and stable atmospheric stratification can reduce the transport of local pollution.

The total UFP concentrations at the Chapel site were slightly higher when the wind speed was equal to or less than 1.8 m/sec, and the average winter UFP concentration was greater than the average summer concentration by a factor of 1.5 (Table 27). We observed a similar pattern for pPAH concentrations at the Chapel site when the wind was blowing from the lake. The 1-hour average pPAH concentration was greater by a factor of 1.3 when the wind speed was equal to or less than 1.8 m/sec, and the average pPAH concentration was higher during winter than summer by a factor of 1.3. Studies carried out in Finland found that aerosol particle concentrations were elevated with low wind speed and low ambient temperatures (Hussein et al. 2006).

Analysis by Traffic Counts After stratifying the 1-hour average counts of all vehicles, cars, and trucks on the Peace Bridge by wind speed (1.8 m/sec) and season, we examined the relationship between traffic counts and the total UFP concentration and pPAH concentration when the prevailing wind direction was from the southwest to west (lake winds). In Table 28, R_1^2 is the coefficient of determination between the total traffic counts and UFP concentration. R_2^2 represents the variability in the UFP concentration explained by the total number of trucks, and R_3^2 is a linear regression between the total number of cars and the UFP concentration. The same procedure was applied to pPAH analysis. According to Table 28 the highest variability was explained by the relationship between truck counts and UFP concentration at the Chapel site during the summer with a low wind speed ($R_2^2 = 0.96$). At the School site, the UFP concentration showed a strong relationship to the total traffic count $(R_1^2 = 0.63)$ and the total number of cars $(R_3^2 = 0.66)$ during summer with a low wind speed. For the pPAH analysis, we found a strong relationship between the total number of trucks and the pPAH concentration at the Chapel site during summer with a low wind speed $(R_2^2 = 0.61)$.

MOBILE MONITORING TO CHARACTERIZE NEIGHBORHOOD POLLUTANT CONCENTRATIONS

Mobile monitoring was used to characterize pollutant concentrations across the 10-block residential neighborhood adjacent to the Peace Bridge plaza. Previous studies have explored the use of portable equipment to record real-time particle concentrations with GPS tracking of the locations. A study in the Dudley Square neighborhood of Boston established the feasibility of profiling pollutant concentrations over a complex network of urban streets (Levy et al. 2003).

		-	UFPs (Part	ticles/cm ³	3)	1 0			pPAHs (ng/m ³)		
Sito /	Wind S	Speed ≤ 1	.8 m/sec	Wind S	Speed > 1	.8 m/sec	Wind Sp	peed ≤ 1	1.8 m/sec	Wind Sp	beed > 1	.8 m/sec
Winds	Mean	SD	Median	Mean	SD	Median	Mean	SD	Median	Mean	SD	Median
2005 Sur	nmer											
GLC												
City	7,908	2,892	8,273	7,978	3,166	8,026	1.4	0.7	1.3	1.7	0.7	2.0
Lake	5,034	2,877	5,358	5,180	3,052	4,928	2.0	1.8	1.5	2.3	3.2	1.7
Other	7,944	4,743	6,345	8,154	4,070	7,158	1.8	0.7	1.7	1.8	0.6	1.8
Chapel												
City	12,455	3,574	11,597	14,773	4,182	15,343	6.4	5.4	4.5	16.4	10.8	14.5
Lake	19,277	14,316	19,277	13,648	6,053	13,077	22.5	11.2	20.4	24.2	11.0	24.3
Other	19,608	10,258	15,100	16,195	8,461	12,780	12.1	11.8	5.4	13.7	8.5	10.8
School												
City	5,993	2,469	5,440	6,587	1,356	6,006	4.2	2.2	3.8	3.3	0.9	3.4
Lake	6,566	1,053	6,868	5,726	3,400	5,412	12.7	23.5	3.5	4.1	3.3	3.0
Other	9,085	3,782	8,171	8,849	3,227	7,905	4.4	1.8	3.9	4.4	3.9	3.1
2005 Wir	aton											
2003 WI	itei											
City	44 140	22 017	20.960	10 202	16 000	17 400	10/	11.0	105	51	25	4.2
Lako	44,140 N 4	23,017 NA	39,000 NA	19,202	10,200	17,403	10.4	11.5	10.0	0.1 2.6	2.0	4.3
Other	14 097	16 864	7 017	8 716	9.687	6 103	25	0.5	25	27	0.7	2.5
	14,057	10,004	7,017	0,710	5,007	0,100	2.0	0.5	2.0	2.7	0.7	2.0
Chapel	.		0= 400						- -	- 0		
City	24,591	1,129	25,190	14,846	6,923	13,295	6.2	5.4	3.7	5.9	3.4	5.0
Lake	NA 10 794	NA 10.046	NA 16 EG4	9,063	5,219	7,296	0 E	1 5	• •	4.5	3.1	2.8
Other	19,704	10,040	10,304	22,150	14,300	21,020	3.0	1.5	3.3	3.7	0.9	3.0
School												
City	21,244	11,396	25,886	13,565	8,082	11,387						
Lake	NA	NA	NA	9,149	6,472	7,411						
Other	11,691	6,635	10,104	15,696	7,778	13,158						
2006 Wir	nter											
GLC												
City	23,230	13,357	19,703	17,519	13,156	12,011	6.8	5.7	5.0	4.3	3.4	3.0
Lake	9,616	8,981	8,074	4,269	2,542	3,349	2.9	3.2	2.1	1.8	0.6	1.8
Other	45,443	8,953	45,443	5,205	3,179	3,973	25.9	4.3	25.9	4.1	7.9	2.1
Chapel												
Citv	21.642	10.447	19.059	14.821	6.057	13.445	11.4	11.5	6.7	9.3	6.5	6.6
Lake	30,571	14,190	28,517	24,926	21,859	17,172	19.7	12.0	18.1	10.2	5.6	8.9
Other	36,633	7,342	36,633	9,901	6,064	9,332	54.1	27.0	54.1	4.5	2.3	3.9
School												
Citv	NA	NA	NA	12,646	6.497	10.376	8.6	6.5	7.1	5.3	2.4	5.2
Lake	NA	NA	NA	10,991	6.663	9,560	6.4	4.4	4.9	4.7	1.9	4.3
Other	NA	NA	NA	10,105	4,813	9,339	32.2	7.0	32.2	4.4	2.2	3.7
				,	, -	,						

 Table 27. UFP and pPAH Concentrations Stratified by Sampling Session, Wind Direction, and Wind Speed (1.8 m/sec)

C'1. /		UF	P Concentrat	ion	pPA	AH Concentra	tion
Site / Wind Speed (m/sec)	Season	R_{1}^{2}	R_{2}^{2}	R_{3}^{2}	R_{1}^{2}	R_{2}^{2}	R_3^2
GLC							
≤ 1.8	Winter	0.09	0.07	0.08	0.10	0.06	0.09
	Summer	0.01	0.02	0.00	0.00	0.10	0.01
> 1.8	Winter	0.05	0.03	0.10	0.05	0.00	0.05
	Summer	0.00	0.00	0.00	0.01	0.01	0.01
Chapel							
≤ 1.8	Winter	0.19	0.33	0.11	0.18	0.39	0.11
	Summer	0.46	0.96	0.35	0.10	0.61	0.07
> 1.8	Winter	0.10	0.00	0.09	0.12	0.23	0.06
	Summer	0.05	0.02	0.02	0.05	0.48	0.03
School							
≤ 1.8	Winter	0.26	0.43	0.18	0.19	0.25	0.14
	Summer	0.63	0.29	0.66	0.18	0.16	0.16
> 1.8	Winter	0.16	0.06	0.15	0.23	0.28	0.14
	Summer	0.00	0.00	0.00	0.03	0.05	0.02

Table 28. Multiple Linear Regression of Traffic Counts by Vehicle Type and Lake-Wind UFP and pPAH ConcentrationsStratified by Wind Speed and by Season

^a R_1^2 is the coefficient of determination between the UFP or pPAH concentrations and all vehicles; R_2^2 , all trucks; R_3^2 , all cars.

The summer 2004 pilot study convinced us that a moveable platform containing many instruments and a meteorologic station was not feasible for the Peace Bridge plaza area, even in warm weather. Moving the platform proved to be awkward on uneven sidewalks, and we could obtain air pollution data for only a limited number of locations with this system. After comparing the advantages of data collection by staff members using handheld UFP counters, instruments to measure $PM_{2.5}$ and pPAHs, and a GPS, we abandoned the moveable platform concept in the winter 2005 pilot study. In the first pilot study we had been contrasting air pollution profiles of different streets and intersections in west Buffalo. By the second pilot study, we were convinced that a survey of the neighborhood was feasible.

A schedule was established to deploy three staff members, equipped as described above, across the network of streets parallel to the Peace Bridge plaza and extending in a grid to the east-northeast, and a fourth staff member to the Bird Island Pier, approximately 50 m to 100 m off the eastern bank of the Niagara River. The Bird Island Pier monitoring route started in a public park northeast of the Peace Bridge and extended under the bridge to a point west of the GLC fixed sampling site. With lake winds or Canadian winds from the southwest or northwest sectors, measurements along Bird Island Pier reflected upwind conditions.

The staff members collected UFP and pPAH data across the network of streets (see Figure 4). In our analysis we pooled all data first by street and then by neighborhood zone (Bird Island Pier, near zone, mid zone, and far zone) to determine whether there were significant spatial differences in UFP and pPAH concentrations.

Mobile monitoring was conducted during the summer 2005 and winter 2006 field campaigns. We first explored the data to determine if there might be overall differences between the morning and afternoon mobile monitoring sessions or between seasons. Table 29 provides a summary of the morning and afternoon mobile monitoring sessions for UFPs and pPAHs, by season; the data were split to examine Bird Island Pier monitoring separate from monitoring on the neighborhood streets east of the Peace Bridge plaza. Table 30 shows results for the individual streets. The Wilcoxon rank sum test (two sided) for differences in the mean ranked score does not require assumptions about the form of the distribution. The Kruskal-Wallis test examines the equality of the medians but does not assume a normal distribution. The mean of UFP concentrations at Bird Island Pier was significantly lower (P < 0.01) than the mean UFP concentrations measured on any of the eight streets to the east of the plaza.

We made between-street comparisons for the pPAH data as well (Table 30). Again, as expected, the mean of pPAH concentrations on Busti Avenue was significantly higher than that on Bird Island Pier. Proceeding east, the next four streets (Columbus Parkway/7th Street, Niagara Street,

Table 29. Mobile Monitoring Summary

			Summer			Winter	
Measurements Time of Day	/ Pollutant	Hours	Mean Value	SD	Hours	Mean Value	SD
All Measureme	ents						
Morning	UFPs (particles/cm ³)	53	12,007	8,055	80	22,792	21,434
0	pPAHs (ng/m ³)	56	16	36	92	9	27
Afternoon	UFPs (particles/cm ³)	48	12,113	9,710	63	30,441	21,471
	pPAHs (ng/m ³)	46	11	25	76	15	37
Bird Island Pie	r						
Morning	UFPs (particles/cm ³)	12	7,665	6,102	19	8,487	9,039
0	pPAHs (ng/m ³)	16	3	3	24	4	5
Afternoon	UFPs (particles/cm ³)	14	12,396	12,233	17	14,643	14,375
	pPAHs (ng/m ³)	15	3	2	20	13	56
All Study Stree	ets						
Morning	UFPs (particles/cm ³)	41	13,276	8,115	61	27,294	22,218
0	pPAHs (ng/m ³)	40	21	41	68	11	31
Afternoon	UFPs (particles/cm ³)	34	12,002	8,519	46	36,238	20,717
	pPAHs (ng/m ³)	31	15	30	56	16	28

Table 30. Overall Summary of UFP and pPAH Data by Street

Charact		UFPs (Particl	.es/cm ³)			pPAHs (ng/	m ³)	
(West to East)	Minutes	Mean Value	SD		Minutes	Mean Value	SD	
Bird Island Pier	3684	10,863	11,403		4413	6	29	
Busti	756	28,939	24,656	<u>a</u>	877	24	45	<u>a</u>
Columbus	1638	23,793	19,924	a,b	1869	21	32	<u>a</u>
Niagara	1851	25,263	20,206	<u> a,b</u>	2202	18	33	a,b
Prospect	1524	24,030	19,980	a,b	1885	12	20	a,b
Fargo	809	22,065	19,654	a,b	1046	11	23	a,b
Westc	935	20,081	16,063	<u> a,b</u>	731	9	57	<u>b</u>
Plymouth	1602	20,109	16,755	<u> a,b</u>	1336	8	26	<u>b</u>
Normal	804	20,677	16,599	a,b	633	8	30	b

^a Significantly different from Bird Island Pier value at P < 0.01 (Wilcoxon rank sum test, two sided).

^b Significantly different from Busti Avenue value at P < 0.01 (Wilcoxon rank sum test, two sided).

^c The difference between median pPAH concentrations at West Avenue and Bird Island Pier was significant at P < 0.01.

Prospect Avenue, and Fargo Avenue) all had significantly higher mean pPAH concentrations than Bird Island Pier. For the next street, West Avenue, the difference in mean pPAH concentrations was barely significant at P = 0.04 (though the difference in median values remained significant at P < 0.01). For the next two streets (Plymouth Avenue and Normal Avenue), the differences in pPAH means compared with Bird Island Pier mean were not significant. These findings might indicate that the effects of activities related to the Peace Bridge plaza and highway emissions are discernible about 500 m to 700 m into the neighborhood.

We also compared UFP counts on Busti Avenue, the road next to the Peace Bridge plaza, with counts collected while traversing the streets to the east of it. For this comparison, the results obtained with the Wilcoxon and Kruskal-Wallis tests of significance were similar, so only

		UFI	Ps (Particles	s/cm³)			pPAHs (ng/m ³)						
				Differen	t from	Busti ^a				Differer	nt from	Busti ^a	
		Moon			Perce	entile		Moon			Perce	entile	
Street	Minutes	Value	SD	Median	75th	90th	Minutes	Value	SD	Median	75th	90th	
Busti	756	28,939	24,656				877	24	45				
Columbus	1638	23,793	19,924	~			1869	21	32				
Niagara	1851	25,263	20,206	~	~		2202	18	33	✓			
Prospect	1524	24,030	19,980	~			1885	12	20	~		~	
Fargo	809	22,065	19,654	~	~		1046	11	23	~			
West	935	20,081	16,063	~	~	~	731	9	57	~			
Plymouth	1602	20,109	16,755	~			1336	8	26	~			
Normal	804	20,677	16,599	~	~	~	633	8	30	~			

Table 31. Test of Differences in Upper Tail of UFP and pPAH Distributions by Street

^a Check mark indicates significant difference from Busti Avenue value at P < 0.01 (Kruskal-Wallis test).

the Kruskal-Wallis test results are reported. We also examined the upper tail of the distribution using Q-Reg STATA to test differences at the 90th percentile (Table 31). Median UFP counts on Busti Avenue were significantly greater than UFP counts on all other streets.

The median pPAH concentrations were significantly different between Busti Avenue and all of the other streets (P < 0.01) except for Columbus Parkway/7th Street, the first street east of Busti Avenue. Like the UFP values, the streetaveraged pPAH values generally decreased with distance from the Peace Bridge plaza.

Correlation Between UFP and pPAH Measurements

We examined the relationship between the continuous UFP and pPAH measurements, believing that both might serve as proxies for the spatial and temporal impact of diesel emissions. In Table 32, Pearson correlation coefficients were derived for all paired UFP and pPAH data collected on Bird Island Pier, on each of the eight neighborhood streets, and by zone (near, mid, and far). Overall, the correlations were low, but some were statistically significant. A subset of the data was defined for measurements made under lake-wind conditions to see if correlations strengthened, but these correlations were not substantially higher.

For Bird Island Pier, the UFP and pPAH values were significantly correlated (P < 0.01), and the correlation coefficient increased from 0.11 to 0.27 when the data were restricted to those obtained under lake-wind conditions (Table 32). During mobile monitoring, staff had noted occasional increases in UFP counts and pPAH values when vessels would pass by on the Niagara River. No correlations between UFP and pPAH values were observed for Busti Avenue, Columbus Parkway/7th Street, and Niagara Street,

Table 32. Correlations between pPAH and UF	Ρ
Measurements by Street and by Zone ^{a,b}	

Location	Overall	Lake Winds
Bird Is. Pier	0.11	0.27
Busti	0.015	-0.012
Columbus	0.035	0.030
Niagara	0.042	0.055
Near Zone	0.027	0.026
Prospect	0.26	0.17
Fargo	0.058	0.025
Mid Zone	0.17	0.11
West	0.21	0.24
Plymouth	0.30	0.13
Normal	0.085	0.050
Far Zone	0.17	0.16

^a Values are Pearson correlation coefficients.

^b **Bold** indicates P < 0.01.

or for the combined data in the near zone. Prospect Avenue (mid zone) is a low-traffic residential street, east of Niagara Street, which is a commercial route with mixed zoning. Prospect Avenue's UFP and pPAH measurements were strongly correlated (P < 0.01). However, the correlation coefficient was lower in the lake-wind data. Measurements were uncorrelated for Fargo Street, the next street east of Prospect. However, for the combined data collected on these two midzone streets, there was a modest correlation between the UFP and pPAH measurements. Of the three streets in the far zone of the neighborhood, two (West Avenue and Plymouth Avenue) had a significant correlation (P < 0.01) between



Figure 48. Cumulative frequency distribution of 1-minute UFP data collected during summer 2005 and winter 2006 mobile monitoring campaigns, classified by street.



Figure 49. Cumulative frequency distribution of 1-minute UFP data collected during summer 2005 and winter 2006 mobile monitoring campaigns, classified by neighborhood zone.

these two measures. In the combined data for these three farzone streets, the correlation was significant, albeit modest.

The continuous PAH monitor (PAS 2000CE) has considerable signal noise, particularly at the lower concentrations. Therefore, we examined the data that were above the median pPAH measurements from the neighborhood streets in the near zone, and found that the correlation was significant at P < 0.0001.

Examination of UFP and pPAH Data by Neighborhood Zones

Figure 48 shows the cumulative distribution of the 1-minute UFP measurements (particles/cm³) collected during the summer 2005 and winter 2006 mobile monitoring campaigns by street. Figure 49 presents the distributions classified by neighborhood zone and, along with Table 33 (a statistical summary), shows that the streets closest to the plaza (the near zone) had UFP counts consistently higher across the entire distribution. The distinction was not as great between the near and mid zones as it was for the other pairings. The median value for Bird Island Pier (background) was about 6000 particles/cm³, which is half of the median value for the far zone but a third of the median value for the near zone.

The pPAH data, displayed as cumulative distributions classified by street (Figure 50), by neighborhood zone (Figure 51), and by percentile values (Table 34), show a

Table 33. One-Minute UFP Measurements (Particles/cm³) Collected on Weekdays During Summer 2005 and Winter 2006Mobile Monitoring Campaigns^a

				Percentile							
Zone	N	Mean	SD	5th	10th	25th	50th	75th	90th	95th	Maximum
Overall											
Near	3866	26,062	22,169	6,017	7,546	11,107	19,906	33,210	51,550	68,480	214,616
Mid	3427	23,970	20,032	5,516	6,737	10,026	17,201	32,573	48,696	62,885	264,295
Far	3628	20,174	16,341	5,732	6,925	9,295	13,542	26,711	42,060	52,415	186,050
Birds Is. Pier	3684	10,863	11,403	1,248	2,461	3,842	5,984	15,023	25,276	34,106	80,383
Lake Winds											
Near	2853	22,134	20,373	5,533	6,767	9,625	15,285	27,148	45,785	63,068	186,668
Mid	2555	19,325	17,051	5,083	6,059	8,862	13,178	24,168	40,665	52,843	264,295
Far	2733	16,436	13,630	5,398	6,405	8,480	11,611	18,773	35,108	42,666	186,050
Birds Is. Pier	2499	7,468	9,143	1,021	1,680	3,653	5,174	7,052	13,618	24,523	80,383
City Winds											
Near	1013	37,126	23,267	13,925	17,490	24,280	31,401	41,796	62,511	81,948	214,616
Mid	872	37,579	21,847	11,978	15,568	24,617	32,149	44,574	66,635	82,920	156,205
Far	895	31,589	18,507	9,113	10,468	18,650	28,075	41,940	56,905	66,828	116,191
Birds Is. Pier	1185	18,024	12,348	2,799	3,195	7,997	16,972	23,815	32,263	43,580	74,155

^a Sampling periods included rush hours and did not include weekends.



Figure 50. Cumulative frequency distribution of 1-minute pPAH data collected during summer 2005 and winter 2006 mobile monitoring campaigns, classified by street.

somewhat different picture than the UFP data. For pPAHs, the data collected on streets in the near zone, close to the Peace Bridge plaza, were distinct from those collected in the mid zone across the entire distribution. For example, the relative difference in measurements was greater at the 90th percentile than at the 50th percentile. The distribution for the neighborhood streets in the far zone resembled the Bird Island Pier distribution for much of the data up to the

Table 34. One-Minute pPAH Measurements (ng/m³) Collected on Weekdays During Summer 2005 and Winter2006 Mobile Monitoring Campaigns^a

				Percentile							
Zone	Ν	Mean	SD	5th	10th	25th	50th	75th	90th	95th	Maximum
Overall											
Near	4710	22	37	1	2	5	10	22	50	78	833
Mid	4689	12	19	0	0	2	7	15	26	36	505
Far	3029	8	36	0	0	1	3	7	18	30	1374
Birds Is. Pier	4645	6	28	0	0	1	3	5	9	13	1120
Lake Winds											
Near	3277	24	41	1	2	5	10	25	58	94	480
Mid	3206	11	16	0	0	2	7	14	25	34	505
Far	1865	8	43	0	0	1	3	6	13	20	1374
Birds Is. Pier	3093	3	4	0	0	1	3	4	7	9	121
City Winds											
Near	1113	17	30	1	3	6	11	21	38	50	833
Mid	1133	15	26	1	2	4	9	18	30	41	469
Far	1071	9	22	0	0	1	3	10	28	40	545
Birds Is. Pier	1320	12	52	0	1	2	5	8	15	22	1120

^a Sampling periods included rush hours and did not include weekends.



Figure 51. Cumulative frequency distribution of 1-minute pPAH data collected during summer 2005 and winter 2006 mobile monitoring campaigns, classified by neighborhood zone.

70th percentile; the distribution for higher concentrations did not follow this pattern. Plymouth Avenue and Normal Avenue have public bus routes, with an extra route on school days. Other public buses transit the study area on Niagara Street.

In addition to carrying the continuous monitoring equipment, each staff member wore a PEM to collect an integrated $PM_{2.5}$ sample. The ratio between exposures to elements on backpack routes in the near, mid, and far zones and values on the Bird Island Pier (background) route are shown in Figure 52 for the summer 2005 mobile



monitoring campaign. Values are the arithmetic mean of four samples obtained by staff while walking the routes, and each sample was a composite of several route-days. Typically, the exposures measured on the mid-zone route were less than those on the near-zone or far-zone routes. For some elements related to mobile sources, the exposures were higher on the near-zone route (nickel, chromium, strontium, and antimony), but for others the exposures were higher on the far-zone route (calcium, titanium, iron, copper, and lead).

Spatial Patterns of UFPs and pPAHs in West Buffalo

To generate patterns of neighborhood levels of UFPs and pPAHs, we combined all the data from both the summer 2005 and winter 2006 mobile monitoring campaigns in the west Buffalo neighborhood, and then separated them according to whether they were obtained under lake-wind or city/other wind conditions (see Table 33 for UFP particle counts and Table 34 for pPAH concentrations).

Figure 53 displays the summer and winter UFP counts (particles/cm³) under lake-wind conditions. Counts were



Figure 52. Ratio of exposures to elements on the mobile monitoring routes in the near, mid, and far zones to values on the Bird Island Pier route (background). Values are the means of data from 4 samplers worn by staff in summer 2005 while walking the routes. Each sample is a composite of several route-days.

Figure 53. Spatial pattern of combined summer and winter UFP measurements (N = 10,808) made under lake-wind conditions in west Buffalo using P-Trak.

elevated along Busti Avenue adjacent to the Peace Bridge plaza. Higher readings occurred at a busy intersection at the northwest end of Niagara Street. Figure 54 represents seasonally pooled UFP data under city-wind conditions. In general, the particle counts were elevated across the study region with city winds. Traffic along Busti Avenue and Niagara Street and around the plaza appeared to contribute to the UFP levels. An area of elevated particle counts on the southeast side of Niagara Street, between Connecticut Street and Porter Avenue, is near D'Youville College, where a dormitory was under construction during the summer 2005 campaign.

The wintertime UFP data obtained under lake-wind conditions show a decreasing gradient with distance into the neighborhood (away from the Peace Bridge plaza), with higher counts more narrowly confined near Busti Avenue for the morning sampling sessions (Figure 55). The spatial profile of afternoon UFP data (Figure 56)





Figure 54. Spatial pattern of combined summer and winter UFP measurements (N = 3980) made under city-wind conditions in west Buffalo using P-Trak.

Figure 55. Spatial pattern of UFP measurements (N = 2478) made on winter mornings under lake-wind conditions in west Buffalo using P-Trak.



Figure 56. Spatial pattern of UFP measurements (N = 2373) made on winter afternoons under lake-wind conditions in west Buffalo using P-Trak.



Figure 57. Spatial pattern of UFP measurements (N = 2331) made on winter mornings under city-wind conditions in west Buffalo using P-Trak.

shows higher concentrations extending over much of the neighborhood.

Figure 57 displays the wintertime morning UFP values under city-wind conditions. The spatial pattern is similar to that for combined UFP data shown in Figure 54, with the most elevated UFP counts north of the Peace Bridge plaza.

The pPAH concentrations (ng/m^3) are displayed spatially in the next series of figures. The seasonally aggregated data

plotted by wind sector ArcGIS are shown in Figure 58 (lake winds) and Figure 59 (city winds). Although the noisy lower-end signal from the PAS 2000CE instrument used to collect PAH data resulted in contour lines that are not as smooth as they were for the UFPs, these figures do illustrate the probable transport of diesel-derived PAHs into the neighborhood. Under city-wind conditions, there were areas of elevated pPAHs from other sources. At the southeast end of



Figure 58. Spatial pattern of combined summer and winter pPAH measurements (N = 12,821) made under lake-wind conditions in west Buffalo using a PAS.



Figure 59. Spatial pattern of combined summer and winter pPAH measurements (N = 4637) made under city-wind conditions in west Buffalo using a PAS.

Busti Avenue, where it intersects with Porter Street, there is a fast-food restaurant that may have contributed to the increased level of pPAHs in the air.

The final two figures in this series show the patterns of pPAH concentrations measured on winter mornings under lake-wind and city-wind conditions in west Buffalo. Focusing on one season and time of day reduces the noise in the data. The contour lines are somewhat smoother for these two cases, as the lake-wind condition was defined to

include a rather large set of wind vectors. Figure 60 shows that under lake-wind conditions, pPAH concentrations were higher due east of the Peace Bridge plaza. A persistent west wind could fetch along the bridge and across the plaza to yield this pattern of pPAHs. Figure 61 shows that under city-wind conditions, pPAH concentrations were slightly higher in the vicinity of Niagara Street, and the highest pPAH concentrations were in patches in the south corner and along the northeast side of the neighborhood grid.



Figure 60. Spatial pattern of pPAH measurements (N = 2978) made on winter mornings under lake-wind conditions in west Buffalo using a PAS.

DISCUSSION AND CONCLUSIONS

Each year tens of thousands of cars, trucks, and buses use the Peace Bridge at one of the busiest international border crossings in the United States. Idling vehicles, stopand-go traffic for passport control, customs inspections, and use of duty-free shops are responsible for motor vehicle emissions near the plaza on the New York side of the bridge. The type of vehicular activity at the Peace Bridge results in emissions that are unlike emissions measured by dynamometer tests, along roadways or in tunnels. Vehicles transit the Peace Bridge plaza slowly, with frequent stops and starts. In addition, vehicles are usually in low gear, particularly heavy-duty vehicles, as they slow down while descending from the bridge, stopping for passport control and inspection, or are accelerating up the incline to the bridge as they leave the United States.

The Peace Bridge plaza is considered a hot spot for mobile-source emissions. Measurements at the Chapel site



Figure 61. Spatial pattern of pPAH measurements (N = 2522) made on winter mornings under city-wind conditions in west Buffalo using a PAS.

on Busti Avenue, adjacent to the plaza on the northeast side, clearly indicated elevated concentrations of PM_{2.5}, EC-r, and vehicle-related VOCs, metals, PAHs, NPAHs, UFPs, and pPAHs when meteorologic conditions were such that the air flowed from Lake Erie.

More than 62% of the total daily heavy-duty truck traffic crossed the bridge during the daytime 12-hour weekday sampling periods. The Chapel site concentrations ranged from 1.5 to 10 times the concentrations at the upwind GLC site, located 560 m to the southwest of the Peace Bridge plaza at the shore of Lake Erie and the start of the Niagara River. Under lake-wind conditions concentrations measured at the GLC site reflected the regional air mass, while the Chapel site concentrations reflected regional air with the addition of emissions from the Peace Bridge plaza and surrounding roadways.

Table 35 groups the different types of analytes by the ratio of Chapel median concentrations to GLC median concentrations under lake-wind conditions. The ratios are grouped into four categories to indicate a gradient in the strength of the Peace Bridge plaza as a source of enrichment: \geq 1.5 but < 2.0 enriched; \geq 2.0 but < 2.5 strongly enriched; \geq 2.5 but < 3.0 substantially enriched; \geq 3.0 very enriched.

Other analytes appeared to be enriched even though their ratios of median concentrations for the Chapel and GLC sites were less than 1.5. For example, PM_{2.5} was, on average, 30% higher at the Chapel site under lake-wind conditions.

Higher levels of fine PM and EC have been associated with diesel exhaust in several studies. Schauer and coworkers (1996) applied source apportionment techniques to PM samples collected in Los Angeles. Although they reported multiple sources of organic aerosol, diesel exhaust was a major contributor to PM_{2.5} in downtown Los Angeles. Miguel and colleagues (1998) compared PAHs with particle and black carbon concentrations collected in the Caldecott Tunnels near Berkeley, California. Trucks were restricted to two bores, while a third bore permitted only cars. Black carbon levels in the truck-influenced samples were five times the levels in the car-only samples, with chemical mass balance analysis associating 93% of the black carbon with heavyduty diesel trucks. In a multicity study in Europe, where diesel-fueled personal vehicles are a more substantial fraction of the fleet than in the U.S., Brauer and colleagues (2003) examined the variation in air pollutant measures,

including an indicator for EC, and found reasonable prediction of measurements by geographic variations in traffic density and distance from high-volume roadways.

Many studies have consistently associated benzene, toluene, ethylbenzene, m&p-xylene, and o-xylene with emissions from gasoline-fueled vehicles; so universal are these reports that verifying references are not needed. This study showed that in addition to the compounds methylated hexane and pentane, which are consistently associated with vehicle emissions, 1,3-butadiene and styrene were also enriched downwind of the plaza.

Analysis of PM by HR-IPC-MS identified 11 elements (including 8 metals) that were clearly enriched in downwind samples. These elements were not necessarily from vehicle tailpipe emissions. Air passing over the plaza also might have carried a resuspended complex mixture of road dust, which could contain abraded asphalt, oil-coated particles, latex tire fragments, pollens, sand, salt, soil, and engine-wear and brake-wear debris. Vehicles in tunnel and roadway traffic can disperse road dust by the friction of their tires on the road surface and the microturbulence of displaced air; however, with the slower-moving traffic at the plaza, these factors would be less effective in resuspending settled debris.

Table 33. Analytes Enriched at the Downwind Chaper Site Relative to the Opwind GLC Site, with Lake winds										
	Chapel-to-GLC Ratio of Median Concentrations									
Analytes	Very Enriched (≥ 3)	Substantially Enriched (≥ 2.5 but < 3)	Strongly Enriched (≥ 2.0 but < 2.5)	Enriched $(\geq 1.5 \text{ but} < 2.0)$						
VOCs	m&p-Xylene o-Xylene	Benzene Ethylbenzene Styrene	Toluene 1,3-Butadiene 3-Methylhexane 2-Methylhexane 2,3-Dimethylpentane	2,2,4-Trimethylpentane						
Elements		Ca Fe Cu	Al Cr Sb	Mg Ti Mn Co Sr						
PAHs	1,3-Dimethylnaphthalene Acenaphthalene 1-Methylfluorene	1,4-Dimethylnaphthalene	Naphthalene Benz[<i>a</i>]anthracene Benzo[<i>g,h,i</i>]perylene Coronene	Phenathrene Chrysene+Triphenylene Benzo[<i>a</i>]pyrene						
NPAHs	9-Nitrophenathrene 1-Nitropyrene	1,3-Dinitronaphthalene 2-Nitronaphthalene	7-Nitrobenz[<i>a</i>]anthracene 2-Nitronaphthalene	1-Nitronaphthalene 3-Nitrophenathrene 2-Nitroflouranthene						

Analytes Enriched at the Downwind Chanel Site Relative to the Unwind CLC Site, with Lake Winds Table 25

Dynamometers have been used to identify metals originating from brake, tire, and engine wear that are not related to tailpipe emissions. Schauer and colleagues (2006) found that iron and barium were an order of magnitude higher than other elements. The next most abundant elements were zinc, manganese, and copper. Interestingly, in the test cycles featuring the most extreme vehicle acceleration and deceleration, most elements had higher emission rates than during the more standard federal driving test cycles. During the test with aggressive braking and acceleration, emission rates of chromium and strontium were equivalent to those of zinc and copper. Other elements reported as being emitted during the wear test were vanadium, molybdenum, and to a lesser extent antimony. They noted that this type of driving probably volatilized material from the hot surfaces of brakes and tires, which then condensed to smaller-size particles.

Schauer and colleagues (2006) also reported on sampling conducted in the Howell Tunnel (Seattle, WA) on weekdays and weekends to contrast traffic with higher and lower proportions of heavy-duty trucks (approximately 7% on weekdays and 2% on weekends). They noted that in the weekday PM_{10} emissions the ratio of EC to total metals was about three times that in weekend emissions. Emissions of many crustal elements were higher on weekends (sodium, magnesium, aluminum, silicon, calcium, and iron), most likely from resuspension. Emissions of some "wear" elements (copper, zinc, antimony, and barium) were also higher.

Schauer and colleagues (2006) pointed out that dust from brake housing comprises debris from pad and rotor wear. The composition of brake pads varies considerably, coming in two basic types: semimetallic and low-metallic versions. The wear of rotors contributes iron and copper, whereas the pads mostly contain barium as barium sulfate. In roadway situations the distinction is less important; tunnel studies indicated that brake dust is a substantial component of the resuspended road dust. Schauer and colleagues (2006) suggested that tire wear is a negligible contributor of trace metals compared with other sources. This may be the case in general, but the correlation between traffic activities and zinc concentrations in airborne PM, as well as roadside soil samples, suggests otherwise. Pierson and Brachaczek (1974) first reported the association between traffic activities and zinc. Twenty years later Ahlbom and Duus (1994) estimated that about 10% of the particulate zinc in Swedish cities came from tire wear. Fauser (1999) showed that organic zinc might be a marker for tire-generated PM, and Fauser and colleagues (2002) reported that 20% of the total zinc in samples of airborne particles collected in Copenhagen was from tire wear.

Organic zinc may be a marker for tire wear, but elemental zinc comes from other vehicle sources as well. Metals in tailpipe emissions are primarily from lubricating oils that contain antiwear agents and surfactants, along with engine-wear debris. Okada and colleagues (2003) demonstrated that the metals in diesel PM emissions came from lubricating oils. Zinc was a measurable component in both gasoline and diesel tailpipe emissions, as reported by Schauer and colleagues (2006). Schauer and coworkers (2006) showed that the EC fraction of $PM_{2.5}$ from diesel emissions ranged from 70% to 84%, whereas it was only 17% to 28% of the $PM_{2.5}$ mass from gasoline emissions. Zinc, calcium, and iron were significant components of the $PM_{2.5}$ mass, along with lesser amounts of copper, molybdenum, and lead.

In its Commentary on the report by Schauer and colleagues (Schauer et al. 2006, p. 84), HEI's Health Review Committee states: "They [Schauer and colleagues] conclude that much of the lighter crustal elements (sulfur, magnesium, aluminum, potassium, calcium, iron, and titanium), as well as the trace elements strontium, cadmium, and lead, were attributable to road dust. They also concluded that brake dust contributed to a larger portion of the roadway emissions of iron, chromium, manganese, copper, zinc, strontium, antimony, and barium. The investigators report that diesel-vehicle tailpipe emissions contributed to a large percentage of PM₁₀, vanadium, and cadmium and a smaller amount of calcium, chromium, zinc, strontium, and lead. The combination of gasolinevehicle tailpipe emissions and tire dust were shown to account for a large percentage of the roadway emission of vanadium, chromium, zinc, strontium, lead, molybdenum, and silver."

Measurements made at the Chapel site on lake-wind days showed that the PM_{2.5} mass had substantially elevated concentrations of many metals and elements associated with vehicle-related emissions, such as iron, copper, and chromium, and with brake dust, such as manganese, copper, zinc, strontium, and antimony (barium was not measured). Elevated levels of EC, along with calcium and other trace elements (strontium, chromium, and zinc), suggest the contribution of diesel-vehicle tailpipe emissions. Calcium, magnesium, aluminum, and iron are also markers for road dust. It was difficult to attribute vanadium, silver, and lead concentrations to plaza emissions, although on lake-wind days both silver and lead were higher in the Chapel $PM_{2.5}$ (> 75% of cases) than in the GLC PM_{2.5}. Exploratory principal component analysis for the Chapel site revealed five components, including a dominant first component (factor 1 in Table 18) that contained clear markers for regional transport (sulfur, selenium, and arsenic) and some trace metals associated with vehicle emissions (tin and antimony). The analysis reasonably separated a component associated with iron, copper, magnesium, calcium, and lead (factor 2) from two other components. A third component (factor 3) also distinguished vanadium, nickel, and sodium from the other two components. More sampling events would strengthen these observations.

Several PAHs and NPAHs were elevated in the air downwind of the plaza. Although these and other compounds were also present in the urban air of Buffalo, the Chapel-to-GLC ratios for lake-wind days indicate local sources. Truckstop, tunnel, and emissions tests, as reported by Minegishi (2007), have confirmed the association of some of these compounds with heavy-duty diesel emissions. Analysis profiles were dominated by benzo[*b*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*c*,*d*]pyrene, chrysene+triphenylene, as well as many methylated PAH compounds that



Figure 62. Box and whisker plots of concentrations of MSAT elements at the Chapel (C), GLC (G), and School (S) sites for all data (N = 24) and for data obtained on lake-wind days (N = 15). Minimum, bottom whisker; 25th percentile, bottom of the box; median, center line in the box; mean, "x"; 75th percentile, top of the box; and maximum, top whisker.

are characteristic of diesel exhaust. Naphthalene, a lightermolecular-weight PAH also associated with diesel emissions, was elevated downwind of the plaza, as was coronene, a PAH associated with gasoline emissions.

1-Nitropyrene was substantially elevated at the downwind Chapel site and highly correlated with truck counts. It appears that several other locally generated PAHs reacted quickly with hydroxyl and NO_3 radicals to form NPAH compounds. Several nitrogenated derivatives of naphthalene, phenanthrene, and benz[*a*]anthracene were elevated as well. These parent compounds, along with 9-nitrophenanthrene and 3-nitrophenathrene, 1-nitronaphthalene, 2-nitronaphthalene, and 1,3-dinitronaphthalene, appear to be good markers for diesel exhaust, along with 1-nitropyrene (Collier et al. 1995; Nasrin et al. 1995; Rhead and Pemberton 1996).

COMPARISON OF MSATS AT THE PEACE BRIDGE PLAZA AND OTHER SITES

We sampled 43 of the 93 compounds identified in the IRIS list of MSATs (Table 3). Hexane could not be measured reliably because of field contamination. Acrolein was not present above the limits of detection. Chromium III and chromium VI were not differentiated from elemental chromium. Figures 62, 63, and 64 provide an overall summary for MSAT elements, PAHs, and VOCs, respectively, as measured at the GLC, Chapel, and School sites under lake-wind conditions. In addition to the VOC MSATs, Figure 64 includes the sum of BTEX compounds, the sum of BTEX plus compounds, and the chlorinated compounds.

Of the MSAT elements, manganese, zinc, strontium, antimony, and lead were elevated at the Chapel site, as discussed previously. All the vehicle-related VOC compounds, with the possible exception of MTBE, showed consistently higher concentrations at the site downwind of the Peace Bridge plaza, while none of the chlorinated MSAT VOCs did. Formaldehyde tended to be higher at the Chapel site with lake-wind conditions.

Most of the concentration distributions for the MSAT PAHs were higher at the Chapel site. This was not the case for some compounds identified as diesel-related, notably pyrene and fluoranthene. Yet 1-nitropyrene and 2-nitrofluoranthene were substantially higher at the Chapel site than at the GLC site.

Very few studies of traffic hot spots were as comprehensive as the Peace Bridge Study in terms of the number of target analytes. Furthermore, in this study with the location of the Peace Bridge at the eastern edge of Lake Erie and the prevailing wind flow, the upwind site (GLC) was not influenced by local sources. We compared 12-hour daytime integrated measurements collected during



Figure 63. Box and whisker plots of concentrations of MSAT PAHs at the Chapel (C), GLC (G), and School (S) sites for all data (N = 24) and for data obtained on lake-wind days (N = 14). Minimum, bottom whisker; 25th percentile, bottom of the box; median, center line in the box; mean, "x"; 75th percentile, top of the box; and maximum, top whisker.


Figure 64. Box and whisker plots of concentrations of MSAT VOCs, BTEX, and BTEX plus compounds, chlorinated compounds, and carbonyls at the Chapel (C), GLC (G), and School (S) sites for all data (N = 24) and for data obtained on lake-wind days (N = 14). Minimum, bottom whisker; 25th percentile, bottom of the box; median, center line in the box; mean, "x"; 75th percentile, top of the box; and maximum, top whisker.

summer and winter with measurements from a variety of studies conducted in different settings, for different purposes, and using different protocols. Nevertheless, it is important to place the Peace Bridge measurements in context. For $PM_{2.5}$, we compared our values with values that the EPA reported for selected cities in 2005 (U.S. EPA 2005). The metropolitan areas used as references were those reported in the 2007 article linking cardiovascular mortality and morbidity in postmenopausal women to particulate air pollution (Miller et al. 2007). Annual average PM_{2.5} concentrations ranged from 5 μ g/m³ in Honolulu, Hawaii, to 21.4 μ g/m³ in Pittsburgh, Pennsylvania; in the Buffalo-Niagara Falls area, the annual average was 14.7 μ g/m³. The mean PM_{2.5} concentrations across each of our sites ranged from 13.4 μ g/m³ at the GLC site to a high of 15.7 μ g/m³ at the Chapel site. The mean at the School site $(14.6 \,\mu\text{g/m}^3)$, in a residential neighborhood of west Buffalo, was consistent with the overall metropolitan average.

As shown in Figure 65, we compared the Buffalo Peace Bridge VOC and carbonyl data with data collected and analyzed by similar methods in the Toxics Exposure Assessment Columbia and Harvard (TEACH) study in Los Angeles (Sax et al. 2006), as well as the Boston Exposure Assessment in Microenvironments (BEAM) study (Dodson 2007). Levels measured in the Buffalo Peace Bridge Study were generally comparable to levels measured in the BEAM study in metropolitan Boston and lower than levels measured in the TEACH study in Los Angeles.

Elements measured in the Buffalo Peace Bridge Study were compared with ambient 48-hour concentrations sampled in the TEACH study in New York City (Sax et al. 2006). Collaborator Dr. Steve Chillrud, of LDEO at Columbia University, was responsible for the analysis by HR-ICP-MS in both studies. Figure 66 compares the Peace Bridge summer 2005 and winter 2006 data with the TEACH New York City summer and winter data. Elements



Figure 65. Box and whisker plots of VOC concentrations at the Chapel, GLC, and School sites in this study and outdoor concentrations from the TEACH study in Los Angeles and the BEAM study in Boston. Minimum, bottom whisker; 25th percentile, bottom of the box; median, center line in the box; mean, "x"; 75th percentile, top of the box; and maximum, top whisker.



Figure 66. Seasonal comparison of median element concentrations in Buffalo (this study) and in New York City (TEACH study, in which N = 36 for both winter and summer).

are rank ordered by mean ratios based on the Chapel site. Comparison of the data from the two studies shows that more sulfur and thallium were found in Buffalo than in New York City. These elements were correlated to each other in mass concentrations, suggesting a similar source. Potential sources of thallium have been reported to include coal combustion, cement factories or resuspension of cement dust, and electronics industries.

The Peace Bridge PAH data were compared with PAH measurements taken by the Integrated Atmospheric Deposition Network on the shores of the Great Lakes from two monitoring stations: Eagle Harbor, Michigan (on Lake Superior), which represents regional background levels, and Sturgeon Point, New York (on Lake Erie), which is relatively near Buffalo and is affected by PAHs from the metropolitan Buffalo area (Cortes et al. 2000). Sturgeon Point data were compared with the overall means of the Peace Bridge data set, while the Eagle Harbor regional background data were compared with the GLC (upwind) data on lake-wind days. There was good agreement between the data for the primarily particle-bound PAHs, those PAHs starting at benz[a]anthracene and including heavier compounds, at the Peace Bridge and the other two sites (Figure 67). For the three other PAHs to the left of benz[*a*]anthracene (pyrene, fluoranthene, and phenanthrene) in Figure 67, which are primarily gas-phase PAHs with some particle-bound component, levels were higher in the Peace Bridge samples.

It is clear that many MSATs were added to the air as it passed over the plaza from the west, as evidenced by contrasting MSAT levels at the downwind site. When winds blow from the lakefront across the plaza, as they do 60% of the time, they are unimpeded for the most part. Wind velocities are higher during the day, when truck traffic is the highest, than at night. The mean wind speed for lakewind conditions during our campaigns was 4.83 m/sec, in contrast to 2.64 m/sec for city/other-wind conditions. Even though vehicle traffic through the Peace Bridge plaza is substantial, benzene concentrations - a good marker for gasoline emissions in outdoor settings — were less than half the concentrations reported in Los Angeles and Houston for the RIOPA study (Weisel et al. 2005), but slightly higher than outdoor levels measured across metropolitan Boston in the BEAM study (Dodson 2007). Several chlorinated compounds, such as trichloroethene, chloroform, and tetrachloroethene, were higher in the TEACH Los Angeles urban samples than in samples obtained near the Peace Bridge plaza. In contrast, as an informal check on analytic methods, we measured carbon tetrachloride, a ubiquitous compound in the atmosphere with regional rather than local sources, and found similar concentrations at all three study sites (Chapel, GLC, and School).

The situation was quite different for elements. Levels of several elements were actually higher in Buffalo than in New York City. Some of the MSAT metals (chromium, arsenic, manganese, and scandium) were higher in the Buffalo samples during the summer than they were in New York City ambient samples in the summer, but not during the winter. Concentrations of many of the metals in this study, particularly those identified with vehicles (iron, zinc, vanadium, tin, copper, and calcium), were lower than concentrations found in New York City during the TEACH study (Sax et al. 2006).

Differences in the sampling and analytic methods used make it problematic to compare PAH measurements in the Peace Bridge Study with values obtained elsewhere. However, the study by Choi (2006) of eight heavier-molecularweight PAHs and pyrene in Krakow, Poland, offers an opportunity for comparison because similar methods were used to capture PAHs in both particle and gaseous phases. Table 36 presents the mean values for the nine PAHs available from the Krakow study and mean data for the Peace Bridge Study. The Krakow measurements were from 48-hour integrated samples taken outside homes or apartments of participants living in the metropolitan area, whereas the Peace Bridge samples were 12-hour integrated samples obtained during weekdays. Nevertheless, except



Figure 67. Left: Mean PAH concentrations at the GLC site under lake-wind conditions (N = 14), in the Peace Bridge Study samples overall (N = 67), and in samples taken by the Integrated Atmospheric Deposition Network at Eagle Harbor and Sturgeon Point (N = 100; analyte detection, 42%–100%). Right: Reported relative standard deviations of measurements (SD/mean) in these sample sets. Eagle Harbor is on the shore of Lake Superior and represents regional background levels; data were from November 1990 through December 1997. Sturgeon Point is on the shore of Lake Erie, in the Buffalo area; data were from December 1991 through December 1997. (Data are from Cortes et al. 2000.)

Table 36.	Ambient Concentrations	(ng/m ³) of Eight H	łeavy-Molecular-V	Veight PAHs an	d Pyrene at the Pe	eace Bridge and in
Krakow, P	'oland					

		Peace Bridge ^a			Krakow, Poland ⁱ	b
РАН	Ν	Mean	SD	N	Mean	SD
Benz[a]anthracene	72	0.11	0.09	70	7.50	1.39
Benzo[b]fluorene	72	0.07	0.05	70	9.28	1.43
Benzo[k]fluoranthene	72	0.05	0.08	70	2.75	0.42
Benzo[g,h,i]perylene	72	0.15	0.13	70	4.50	0.72
Benzo[a]pyrene	72	0.06	0.10	70	5.46	0.96
Chrysene+Triphenylene	72	0.19	0.16	70	6.82	1.12
Dibenz $[a,h+a,c]$ anthracene	72	0.01	0.01	70	1.11	0.19
Indeno[1,2,3-c,d]pyrene	72	0.14	0.12	70	5.64	0.88
Sum of eight PAHs (above)	72	0.78	0.58	70	43.06	7.02
Pyrene	72	4.67	7.84	70	12.45	2.10

^a Peace Bridge data are for the three fixed sampling sites combined.

^b Krakow data are from Choi (2006).

for pyrene, the Peace Bridge levels are only 3% or less of the Krakow levels. For pyrene, the median value is 1.6 ng/m³; the School site experienced one measurement of pyrene four times the next-highest measurement. For some PAHs from diesel emissions, such as indeno[1,2,3-*c*,*d*]pyrene, chrysene+triphenylene, and benzo[g,h,i]perylene, the Peace Bridge levels range from 2% to 3% of the Krakow values. These compounds showed spatial differences within the Peace Bridge Study consistent with local sources. For the PAHs that are primarily coal-derived, there were no spatial differences across the Buffalo sites, and the levels are less than 2% of those in Krakow. Pyrene, for which diesel emissions are a substantial contribution in the Peace Bridge Study, has a mean value at the Chapel site of 2.82 ng/m³, which is 23% of the Krakow mean. The primary source of these PAHs in Krakow was coal combustion, with outdoor levels showing distinct seasonal and spatial patterns (Choi et al. 2008a).

Schauer and colleagues (2003) reported on historic and more recent PAH levels in Munich, Germany. The pyrene levels from year-round sampling at a traffic-oriented site in 2001–2002 were about 25% less than the Peace Bridge plaza levels, but other compounds, such as benzo[*g*,*h*,*i*]perylene, indeno[1,2,3-*c*,*d*]pyrene, and benz[*a*]anthracene, were comparable. Schauer and colleagues (2003) also reported that PAH concentrations observed in Munich were similar to levels reported in metropolitan areas in the U.S. (Baltimore), Australia (Melbourne), Finland (Helsinki), and Hong Kong. Similar to the Buffalo–Krakow comparison, contemporary PAH levels in Munich were lower than values in Seoul, Naples, London, and Manchester by factors of 6 to 20 (Schauer et al. 2003).

The Peace Bridge Study utilized a novel approach for acquiring temporally and spatially resolved air pollution profiles in the community. Staff equipped with continuously recording monitors and GPS instruments walked the neighborhood near the Peace Bridge plaza. During periods when the winds were from the west (lake winds), residential streets experienced pPAH concentrations and UFP counts two to five times the upwind levels measured along Bird Island Pier, a jetty in the Niagara River that passes under the Peace Bridge. The distributions of concentrations show a clear gradient by distance from the plaza.

The association of elevated UFP counts and higher concentrations of pPAHs with heavy-duty vehicles passing through the plaza was previously reported by Clarkson University researchers (Ogulei et al. 2007), who creatively used size-resolved particle counts to identify seven independent source profiles: fresh tailpipe diesel exhaust, local street diesel traffic, aged or evolved diesel particles, spark-ignition gasoline emissions, background urban emissions, heavy-duty diesel agglomerates, and secondary or transported material. Whereas our P-Trak instruments only provided total UFP counts per cubic centimeter, the Clarkson mobile van had an EEPS to measure concentrations of submicron-size particles (5.6 to 560 nm) at a time resolution of seconds.

Figure 68 is a map showing locations where the Clarkson mobile van parked to record concentrations of submicron-size particles. The reported distances are measured to an arbitrary center point of the Peace Bridge. The wind direction was generally southwesterly over the sampling period. The Clarkson study upwind (GLC) and R1 sites are collocated with the GLC and Chapel sites of the Peace Bridge Study. In addition, Clarkson sites R2, R3, and R4 are within the neighborhood of our Peace Bridge Study. Ogulei and colleagues (2007) operated the mobile van during the period of our summer 2004 pilot study. Figure 69 shows the size profiles of particles that the Clarkson researchers measured during this time period, when the winds were consistently from the southwest and west. The elevated number of small particles at the R1 site indicates the presence of fresh diesel emissions. Zhu and his colleagues (Zhu et al. 2002a, 2002b) showed that particle counts shift to larger sizes as the distance from roadways with heavy traffic increases. Consistent with this finding the Clarkson data for R2 and R3 sites showed an elevation in counts of particles in the very small size ranges (< 20 nm) and higher number counts than the R1 site in the larger particle size range of 50 to 60 nm. Statistical analysis by Ogulei and colleagues (2007) found that the site-specific size-resolved particle counts could be attributed to the seven factors reflecting source profiles.

Table 37 indicates that in the Clarkson analysis (Ogulei et al. 2007), fresh diesel particles (factor 1) and aged/processed diesel particles (factor 3) accounted for 54% of the particle counts at the Chapel (R1) site and 30% at the R2 and R3 sites. By the time the air traveled to the R4 site, some 800 m downwind of the Peace Bridge plaza, the fresh diesel contribution had dropped to less than half of what it was at the closer sites, but the aged/processed diesel particle contribution had increased from what it was at the R2 and R3 sites by nearly as much.

From the results of our mobile monitoring campaigns, we could infer an influence of plaza-related diesel emissions a few hundred meters downwind into the neighborhood. The neighborhood has residential streets and some commercial streets, and additional emissions from mobile and stationary sources make it difficult to discern an influence of bridge-related congestion. The case study presented by Ogulei and colleagues (2007) shows promising results to support the possibility of attributing particle



Figure 68. Map showing the location and sampling sites used in the Clarkson University study. The reported distances are measured to an arbitrary center point of the Peace Bridge, marked with a star on the map. The wind direction was generally southwesterly over the sampling period. Adapted with permission from Ogulei et al. 2007, and from the Air and Waste Management Association.



Figure 69. Average number concentrations (particles/cm³) measured at the six Clarkson University sampling sites on June 24, 2004, when winds consistently blew from the southwest. Main Street measurements were made on June 23, 2004. For completeness the entire particle size range measured is shown (6–500 nm). Adapted with permission from Ogulei et al. 2007, and from the Air and Waste Management Association.

Table 37. Average Source Contributions	from All of the R	Particles/cm	³ (% of Total) at	Sampling Site	
Resolved Factor	R1	R2	R3	R4	Main Street
 Fresh tailpipe diesel exhaust Local/street diesel traffic Aged/processed diesel particles 	21,450 (25.5) 16,195 (19.3) 24,287 (28.9)	8,910 (19.6) 12,094 (26.6) 4,718 (10.4)	8,084 (21.2) 5,789 (15.2) 3,549 (9.3)	1887 (9.8) 5227 (27.1) 3526 (18.3)	3812 (15.4) 5250 (21.2) 3844 (15.5)
 Spark-ignition gasoline emissions Urban background emissions Heavy-duty diesel agglomerates Secondary/transported material 	12,053 (14.3) 9,173 (10.9) 845 (1.0)	6,475 (14.2) 13,097 (28.8) 159 (0.3)	10,207 (26.7) 10,583 (27.7)	2106 (10.9) 6530 (33.9)	1075 (4.3) 9760 (39.5) 995 (4.0)

Source: Adapted with permission from Ogulei et al. 2007, and from the Air and Waste Management Association.

contributions to specific or generic sources. In the traffic and weather conditions prevailing during their discrete sampling times, they found submicron-size particles influenced strongly by diesel emissions that reflect the agglomerate size range of 50 to 70 nm from more aged (not fresh) sources at distances of 800 m (R4 site) into the neighborhood.

In a meta-analysis by Zhou and Levy (2007), our HSPH colleagues reviewed published reports and government documents that presented spatial measurements of air pollution near roadways or mobile-source hot spots. From these studies they concluded that the effects could be discerned at distances on the order of 100 to 400 m for EC or PM mass concentration, and 100 to 300 m for UFP counts. For studies reporting on NO₂, spatial effects were seen to a distance of 500 m. The street-by-street comparisons of UFPs and pPAHs in the Peace Bridge Study, together with the GIS analysis of the data collected for both summer and winter days with lake winds, suggest that plaza-associated traffic emissions were still discernible 400 m to 500 m into the community. Our findings are consistent with the findings of the meta-analysis (Zhou and Levy 2007). However, the spatial measurements and GIS analysis of pPAH concentrations in our Peace Bridge Study indicate that mobile-source pollutants perhaps extended farther into the west Buffalo neighborhood than 500 m.

IMPLICATIONS OF FINDINGS

Air pollution clearly has distinct spatial and temporal variability. The 2003 RFA issued by HEI called for an examination of hot spots where traffic congestion might elevate exposures. There are many examples of permanent, transitory, or episodic hot spots, including ports, truck stops, construction sites, airports, shopping and sports centers, and a variety of roadway configurations. The distinguishing condition is the concentration of mobile sources (construction equipment, ships, aircraft, etc.) that leads to spatially distinct patterns of pollution concentrations.

California's MATES-II study (SCAQMD 2000) demonstrated the spatial heterogenicity of mobile-source air pollution and the importance of diesel sources as contributors to the risks associated with air toxics. The Los Angeles freeway studies of Zhang, Zhu, and their colleagues (Zhang et al. 2004, 2005; Zhu et al. 2004, 2006a) have demonstrated that particle dynamics and concentration gradients change as air flows across and downwind of congested freeways. A multicity study in Europe found that traffic indicators and distance measures were strongly predictive of NO₂ and carbon measurements (Brauer et al. 2003). Using a sophisticated time- and size-resolved particle counter, Ogulei and colleagues (2007) were able to distinguish "fresh" diesel emissions in proximity to the Peace Bridge plaza in west Buffalo.

In their meta-analysis, Zhou and Levy (2007) reviewed many studies of mobile-source air pollution to determine the spatial extent of pollution impacts. Of course, the extent to which concentrations of mobile sources can be distinguished downwind would vary depending on source configuration, meteorology, and analytic factors associated with equipment, study design, and laboratory methods. Zhou and Levy (2007) concluded that the spatial extent over which distinct mobile sources might be discerned ranged from 100 m to 500 m downwind. Dilution, coagulation, transformation, and the addition of other sources eventually make it difficult in an urban setting to establish with certainty that a mobile-source hot spot has great spatial influence.

In 2004 we responded to the HEI RFA on hot spots with a proposal to study air pollution in a neighborhood of west Buffalo, adjacent to the Peace Bridge plaza. Thousands of cars and trucks cross over the Niagara River at the eastern edge of Lake Erie each day. Vehicles stop for tolls, customs inspection, and duty-free shopping at this busy international border crossing between the U.S. and its northern neighbor. NAFTA has increased the volume of traffic, and since September 11, 2001, security concerns have extended wait times for vehicles at the bridge. During our study period, 2005–2006, tollbooths were moved to the Canadian side (where there is more room) to alleviate congestion on the U.S. side.

The Peace Bridge plaza was an almost ideal location for a hot spot study, as the bridge authority counted and classified all vehicles every hour. Winds prevailed from the southwest quadrant 45% of the time (more in summer), which provided a long fetch across Lake Erie to the west of the plaza. The plaza was approximately 500 m from the lakeshore, where a site was established at the Great Lakes Center to monitor background pollutant levels. Dr. Jamson Lewbuga-Mukasa had excellent relationships within the community because of his long-term asthma studies. We arranged for secure monitoring sites directly across the street from the plaza at an Episcopal church (Chapel site) and at a community center school (School site) that is central to the neighboring community and 520 m from the Chapel site. In addition, the streets of west Buffalo formed a convenient parallel and perpendicular grid for mobile monitoring along the downwind axis of a southwest wind flow.

Through two pilot studies we established a comprehensive study design. All three sites had instruments to obtain integrated samples capturing 12-hour daytime concentrations of 10 targeted VOCs, 4 carbonyls, 28 elements, 30 PAHs, and 13 NPAHs, along with PM_{10} , $PM_{2.5}$, and EC. Though the daytime weekday periods accounted for more than 80% of the overall truck traffic, we also obtained integrated weekend and nighttime samples. Continuous monitoring instruments recorded values of $PM_{2.5}$, pPAHs, UFPs, and several gases (O₃, NO_x, and CO₂) every minute.

Our staff were equipped with portable instruments and a GPS to examine spatial patterns of UFPs and pPAHs upwind and across the grid of streets downwind (usually) of the Peace Bridge plaza. Two-week mobile monitoring campaigns were conducted in summer 2005 and winter 2006.

Air mass trajectories and local wind measurements were useful in characterizing the meteorologic conditions influencing local transport conditions. For sampling periods characterized as having lake-wind conditions (the majority), contaminants associated with mobile sources were identified by comparison between sites, particularly contrasting the Chapel site to the GLC site on the lakeshore, where the meteorologic tower is located.

The Chapel site, as expected, had substantially higher concentrations of MSATs (as well as other mobile-source contaminants) than the GLC site with southwest winds. Chapel-to-GLC ratios of 2 to 10 were found for EC, BTEX VOCs, acrolein, several metals, PAHs, and NPAHs. Although the levels of many MSATs increased in the air passing over the plaza, their absolute concentrations were less than or comparable to pollution in other urban locations. Formaldehyde levels, for example, were comparable to levels reported in Boston but one fourth of levels reported in Los Angeles. Benzene levels were half the Los Angeles levels, with 1,3-butadiene levels equal to those in Boston. Acrolein levels measured during summer days and immediately downwind of the plaza were comparable to other urban measurements in the U.S. Only a few elements were present at levels higher than the average levels reported for New York City or elsewhere, and these were not MSATs.

Several PAHs and NPAHs substantially increased in the air measured adjacent to the plaza. Benzo[a]pyrene concentrations, which had a Chapel-to-GLC ratio of 5, were higher across all three fixed sampling sites with city winds. Overall values were about one half of the benzo[a]pyrene levels reported for Elizabeth, New Jersey (Naumova et al. 2002), and for Quebec (Sanderson and Farant 2004), and one seventh of the New York City levels (Choi et al. 2008b). Although residents near the plaza clearly experience higher vehicle-related pollution than they would without the Peace Bridge, the concentrations we measured are comparable to or less than those found in many urban settings. The good ventilation (higher wind speeds and lack of upwind sources) with airflow off Lake Erie provides some benefit in diluting MSATs emitted from bridge traffic.

The Peace Bridge plaza and the adjacent neighborhood represent a classic mobile-source hot spot. Congestion of car, bus, and truck traffic results in a persistent source of emissions. Persistent southwest to northwest winds increase PM and EC. We have presented evidence that many compounds emitted directly from cars and heavy-duty vehicles were substantially elevated immediately downwind of the plaza. For example, at the Chapel site the mean benzene concentration was only 1.1 μ g/m³ overall, but on days when the winds were from Lake Erie, it was twice as high as the background level recorded at the (upwind) GLC site. Similar associations were observed for all BTEX compounds, as well as styrene and 1,3-butadiene.

The impact of the Peace Bridge traffic on BTEX compounds at the School site, only 600 m west of the plaza center but surrounded by a network of residential and commercial streets, was difficult to distinguish. Results for other indicators of gasoline emissions, such as coronene, azulene, and 1-methylfluorene, indicate a greater impact of mobile sources at the Chapel site. The two NPAHs showing the most enrichment at the Chapel site (with reference to the GLC site) under lake-wind conditions were 1-nitropyrene and 9-nitrophenanthrene; however, their concentrations at the School site were less than half the mean concentrations over the summer campaign.

A different pattern was seen for secondary pollutants, such as formaldehyde, which had higher concentrations at the School site than at either the GLC site or Chapel site. Furthermore, we inferred the influence of PAH sources on the School site that were not prominent at the Chapel site or GLC site.

The mobile UFP and pPAH monitoring with GPS was an innovation of our project. It demonstrated how concentration contours can be mapped in urban areas to show subblock spatial patterns of pollution. We contrasted the UFP and pPAH levels across the west Buffalo streets to those at Bird Island Pier in the Niagara River, which is upwind from the plaza under lake-wind conditions. Across all spatial case studies based on the mobile monitoring results, the median difference between UFP counts for Busti Avenue (the street adjacent to the plaza) and Bird Island Pier (upwind from the plaza) was 15,000 particles/cm³. The difference at the 90th percentile was 25,000 particles/cm³. The 50th and 90th percentile spread between these two locations was even more distinct for pPAHs. The ratio between the differences at the 90th percentile and the 50th percentile was 5 (8 ng/m³ for the 50th percentile difference and 42 ng/m³ for the 90th percentile). Spatial plots showed that the UFP concentration dropped by half across a distance of about eight city blocks from the plaza, while the pPAH concentration decreased by two thirds across the same distance. Statistical analysis showed that at least to a distance of six blocks (600–700 m) from the plaza, UFP and pPAH levels were different from levels monitored along Bird Island Pier.

Radial plots of differences in 10-minute average UFP and pPAH values between pairs of sites support the contention that mobile sources at the plaza influenced pollution levels at least 600 m downwind. For all wind directions from about 60° to 340°, both UFP and pPAH levels were consistently higher at the Chapel site than at either the GLC site (as expected) or the School site. The differences between the values at the Chapel and School sites are not as great as those between either of these sites paired with the GLC site, but they are discernible (particularly for UFPs).

The results of our mobile monitoring and geographic analysis appear consistent with the size-resolved particle counts obtained using an EEPS in the Clarkson mobile van (Ogulei et al. 2007). The EEPS measurements by Ogulei and colleagues (2007) demonstrated that the P-Trak device was not responding to particles in the size range below 20 nm, where fresh tailpipe diesel exhaust dominates. A similar point was made by Zhu and colleagues (2006b). Perhaps the undercounting of very small UFPs by the P-Trak, which is more problematic near the Peace Bridge plaza, is an explanation why, at least qualitatively, the geographic analysis provides more resolution of the pPAH data than the UFP data. The issues about the particle-size response ranges of different types of equipment used in field studies need further attention. There are obvious trade-offs among practical considerations of probability, cost, and data analysis. While the study by Ogulei and coworkers (2007) provides valuable insight with 15 hours of data, our Peace Bridge Plaza Study provides spatially and temporally resolved information on the distribution of pPAHs.

Birmili and colleagues (2008) have reported the results of detailed time- and size-resolved particle measurements in Berlin, Germany. They used two sites characterized as near and distant background urban sites to compare roadside monitoring and plotted the concentration of particles by size relative to the average background concentration. Several interesting features of that study are pertinent to our study. The three size classes of particles (11 nm, 17 nm, and 26 nm) were clearly enriched by 8- to 10-fold in the morning (6:00 AM) and by 5- to 7-fold in the evening (7:00 PM). The P-Traks used for UFP measurements in our study most likely were not responding to these freshly produced vehicle-exhaust particles and would have underestimated the true particle counts near the source, leading to an underestimate of the spatial gradients.

Birmili and colleagues (2008) did show that for particles between 41 nm and 96 nm the roadside values were 4 to 6 times the background counts and displayed a temporal pattern similar to that for the smaller particles. Concentrations of larger particles (229–352 nm), while twice as high near the motorway during high-traffic times of the day, did not display the same temporal pattern as concentrations of smaller particles.

Observations and methodologies developed from these Buffalo studies need to be considered in the context of exposure and health risk. Observed associations between asthma and proximity to the Peace Bridge plaza by Lwebuga-Mukasa and colleagues (2002) and Oyana and colleagues (2004) were based on geographic correlations, as were other studies reporting associations between health effects and proximity to roadway traffic (White et al. 2005; HEI Air Toxics Review Panel 2007). However, the extent to which differential exposures to size- and compositionresolved particle pollution would alter the reported associations with traffic remains uncertain.

Several studies support the observations of increased incidence of asthma and asthma symptoms near mobilesource hot spots, typically defined geographically or by NO_2 concentrations. The Southern California Children's Health Study is now a 12-year follow-up of 5500 children with chronic exposure to air pollution (McConnell et al. 2006). Adverse effects were reported for those whose residences were closer to major roadways. Asthma prevalence and school absences decreased with the distance of the child's residence from a major roadway. An increase in the probability of asthma was most distinct for the first 100 m away from the road but still significant to nearly 200 m.

From this same southern California study, Gauderman and colleagues (2005) showed that childhood asthma increased by 89% with closer residential proximity to freeways. McConnell and colleagues (2006) showed that treatment for current asthma was 2.5 times higher and wheezing was 2.7 times higher in the group at high risk of traffic exposure.

In an asthma study of children living in Oakland, California, Kim and colleagues (2004) reported a 5% to 8% increase in risk of acute respiratory symptoms when the child's school was close to traffic. More recently Kim and colleagues (2008) reported on an expanded study in the San Francisco Bay area. This cross-sectional study of 1080 children was designed to examine the possible association of current asthma and other respiratory symptoms with the distance of their residences from high-traffic roadways. Relevant to the west Buffalo situation, this San Francisco Bay area study included urbanized areas with coastal locations characterized by good regional air quality. Children whose residences were in the highest quintile of exposure had approximately twice the adjusted odds for current asthma compared with children whose residences were in the lowest quintile. Children living within 75 m of a heavily trafficked roadway had the highest risk.

Gauderman and colleagues (2007) examined lung growth for a subset of 1500 children over an 8-year period. At 18 years of age, the forced expiratory volume in 1 second (FEV₁) of children who lived within 500 m of a freeway was 5.5% less over 8 years than the FEV₁ for children living more than 1500 m from a freeway. At age 18, by this measure of lung performance, these children were 7.5% behind "non-freeway exposed children." Effects of intermediate distances (500–1000 m and 1000–1500 m) were consistent with an exposure-response function. It is noteworthy that even children living 500 m to 1000 m from a freeway had 5.5% lower FEV₁, a difference that was statistically significant (P < 0.05) by age 18.

In our study, the UFP and pPAH concentration profiles near the Peace Bridge plaza and the difference in concentrations of MSATs, PM, and EC between the GLC and Chapel sites are consistent with effects of mobile sources on the west Buffalo neighborhood. The literature on traffic-related health effects includes associations with increased cardiovascular, developmental, and cancer risks. Mills and colleagues (2007) demonstrated ST-segment depression and

ischemic burden in 20 subjects when they were exposed to dilute diesel exhaust during 15-minute intervals of exercise-induced stress as compared with breathing clean filtered air. In a European study, Peters and colleagues (2004) showed a consistent association between time spent in cars, on public transport, or on motorcycles and an increased risk of myocardial infarction. This case-crossover study examined activities before onset of myocardial infarction in 691 subjects who survived for at least 24 hours. Exposure to traffic within 1 hour of the event had an odds ratio of 2.92 (confidence interval, 2.22–3.83). Exposure to vehicle exhaust was associated with a 36% increase in low birthweights and a 27% increase in premature births in a Los Angeles County study by Wilhelm and Ritz (2005). Earlier, Ritz and colleagues (2002) had associated a 3-fold increase in cardiac birth defects with trafficrelated pollutants in a southern California study. PAHs are mutagens as well as carcinogens in humans and may play a role in both prenatal and postnatal reproductive and developmental outcomes (Perera et al. 1998; Dejmek et al. 2000; Perera et al. 2003). Choi and colleagues (2008b) associated prenatal exposures to PAHs with a risk of intrauterine growth restriction, including small size for gestational age and preterm delivery, among African Americans (but not Dominicans) in New York City. Adverse birth outcomes were also reported by Choi and colleagues (2006) in a study conducted in Krakow, Poland. We compared the concentrations of eight heavy-molecular-weight PAHs measured at the Chapel site with concentrations reported for New York City and Krakow (Choi 2006; Choi et al. 2008b). As expected, wintertime coal combustion was the dominant source of PAHs in Krakow. For the sum of the eight heavy-molecular-weight PAHs, the Krakow concentration (43.06 ng/m³) was more than 50 times the mean Chapel concentration (0.78 ng/m³) and more than 10 times the New York City concentration (3.2 ng/m^3) . The individual PAH concentrations at the Chapel site averaged between one fifth and one half of the New York City levels.

We conducted intensive field campaigns to provide a comprehensive assessment of many MSATs. The purpose was to characterize the influence of a permanent mobilesource hot spot on neighborhood air pollution. To our knowledge this study is among only a few comprehensive examinations of VOCs, carbonyls, PAHs, and NPAHs, along with particle mass and EC, conducted at mobile-source hot spots. The study also demonstrated the use of portable air monitors and GIS analysis to assess spatial and temporal variability in air pollution across a community. Although it is reasonable to infer from published reports a health risk to a community chronically and differentially exposed to mobile-source air pollutants, this study provides only a partial examination of long-term exposures. Since the study period, changes have occurred in the configuration of the plaza, the neighborhood, fuel composition, vehicle controls, and fleet composition that could moderate the influence of the Peace Bridge plaza on the community. With these qualifications in mind, we nevertheless recommend that ambient air monitoring, as well as respiratory and cardiovascular health studies, be conducted in west Buffalo.

LIMITATIONS

The UFP counts and pPAH levels were elevated and more uniformly spatially distributed when the wind came from the east of our study neighborhood (city-wind conditions). There are many urban sources for pPAHs and UFPs, which complicates any analysis of traffic-related hot spots or plumes in this area.

The risk associated with traffic congestion at the Peace Bridge crossing for this community cannot be adequately assessed with the results of our field campaigns. Ambient concentrations for these MSATs would be substantially lower in the absence of the plaza. Actual exposures and the corresponding risks will depend on meteorologic conditions, the penetration of pollutants into dwellings, and a complex set of demographic factors.

Although the two pilot studies and two field campaigns captured the predominant wind and traffic profiles for the study area, our sampling sessions only covered a few weeks in summer and winter. Combining the data for three of the sampling sessions only gave us 24 weekdays, with 9 classified as city/other-wind days and 15 classified as lake-wind days. This number of cases allowed for only limited statistical analysis, even though inferences could be made because of the distinction between results at the upwind and downwind sites. In addition, the nighttime data are limited. To maximize resources we focused on 12-hour daytime samples. Although the measured concentrations were much lower at night than during the day for all pollutants, lower nighttime wind speeds may have revealed nightto-night variations for those pollutants, as well as different spatial patterns. In our limited nighttime data, NPAHs were much more prevalent than they were in the daytime.

Acrolein levels in the vicinity of the Peace Bridge were lower than expected. In the first (summer 2004) pilot study, we sampled for acrolein passively using the EOSHI DNSHbased method. None of our acrolein samples were significantly different from the field blanks. We switched to an active system, OSHA Method 52 for acrolein, for the second (winter 2005) pilot study and two subsequent field campaigns. The detection limits for this method were 2.8 μ g/m³ for a 12-hour sample and 0.5 μ g/m³ for a 60-hour sample. During the summer 2005 sampling session, University of California–Davis colleagues working on a sensitive acrolein sampling method offered to collect samples alongside our samples at the Chapel and GLC sites using their mist chamber method (Seaman et al. 2006), which has an analytic acrolein detection limit of 0.04 μ g/m³. For these 10-minute samples, the highest value at the Chapel site was 0.46 μ g/m³ and the average value measured at the Chapel site was 0.28 μ g/m³ (10 times lower than the detection limit for the 12-hour OSHA Method 52 samples). The average concentration measured by the University of California–Davis method at the GLC site was < 0.04 μ g/m³.

This study focused on measurements of toxic pollutants without linking them to health effects. It identified many traffic-related toxic pollutants that penetrated deep into the nearby community. Except for UFP counts, most other measurements were integrated over time and may not reveal short-term spikes that might be of clinical or health consequence, because a short-term exposure may trigger a prolonged adverse response that lasts for hours or days in a susceptible individual. Furthermore, sensitized individuals may respond to very low levels of pollutants that would normally not bother nonsensitized persons. It is also apparent that numerous pollutants are involved; the combined health effects of chronic exposure to such mixtures, especially during periods of lung development and growth (up to 20 years of age), are unknown. When comparing pollutant levels and implying health effects, it is important to take into account the individual susceptibility factors: for example, in Los Angeles, the predominant Latino population is of Mexican descent, a group in which asthma prevalence is low. On Buffalo's west side, the Latino population is predominantly of Puerto Rican descent, a group that, for unknown reasons, has high asthma rates that are well documented. We do not yet have any information on how traffic-related pollutants interact with or affect other environmental exposures that also impact the respiratory or cardiovascular health of nearby residents. We recommend mechanistic studies of the factors and pathways that contribute to inception of asthma and maintenance of high asthma morbidity in Buffalo's west-side community.

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Major Scott Newberg (U.S. Army), while on assignment at HSPH, made significant contributions to our study. He assembled equipment and built the sampling platform; he designed and managed the mobile monitoring component of the study; and he supervised the team of field staff throughout the three campaigns, including cold winters and hot summers. Scott was always on duty, and we are very grateful for his invaluable participation.

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APPENDIX A. Data Quality

INTEGRATED SAMPLES

For each analytic sample, data quality reports are presented in tabular form. The reports present the following indicators of data quality for each target analyte in each sampling session: mean blank value, the LOD calculated from the standard deviation of the field blanks ($3 \times SD$), of the total samples the percentage that were above the LOD, and the relative precision ($100 \times RMSE/\sqrt{2}$) calculated from the duplicate pairs. The data quality reports are presented in Table A.1 for PM_{2.5}, PM₁₀, and reflectance analysis; Table A.2 for carbonyls; and Table A.3 for VOCs. An additional data quality indicator is presented in Table A.4

		PM _{2.5}			PM_{10}	
Indicator ^a	Winter 2005	Summer 2005	Winter 2006	Winter 2005	Summer 2005	Winter 2006
Mean blank value (µg)	-2.65	4.33	14.83	4.52	4.33	0.74
LOD (µg)	13.5	21.4	16.8	14.95	21.4	16.2
Samples above LOD (%)	100	100	100	100	100	100
Precision (%)	5.4	6.1	6.3	9.3	11	4
Reflectance precision (%)	25.2	20.5	29.4			

 a LOD is 3 times SD of blanks; relative precision is 100 \times RMSE/V2.

Table A.2. Carbonyl Data	Quality Stat	tistics ^a											
		Winter	2005				Summe	r 2005			Winter	r 2006	
Carbonyl	Mean Bla Value (_I	ank I 1g) (, (gu)	Sample > LOD (se (%	Mean Bl Value (ank I µg) (,0D (µg) >	Samples LOD (%)	Mean I Value	3lank (µg)	LOD >	Samples LOD (%)
Formaldehyde Acetaldehyde Acetone	0 0.03 0.02		0 0.08 0.06	$\begin{array}{c} 100\\ 100\\ 100 \end{array}$		0.1 0.16 0.82		0.08 0.11 2.83	85 95 14	0.00 0.00 0.02		0.03 0.01 0.11	88 88 75
^a LOD is 3 times SD of blanks.													
Table A.3. VOC Data Qual	ity Statistic	S ^a											
		Winte	er 2005				Summe	er 2005			Winter	2006	
VOC	(ng)	Samples > LOD (%)	Dup Paire > LO	s Rel D (9	Pre %)	LOD (ng)	Samples > LOD (%)	Dup Pairs > LOD	Rel Pre (%)	(ng)	Samples > LOD (%)	Dup Pairs > LOD	Rel Pre (%)
1,3-Butadiene	1.02	27.6	0			0.00	100	6	33	2.09	98	11	34
MTBE	0.00	86.2	с о	4,	01 0	0.00	57	6	89	1.21	35	11	32
benzene Toluene	0.10	96.6 100.0	ກຕ	7 1	0 4	3.U8 2.25	100	იი	37	2.00 1.52	98 98	11	18 17
Ethylbenzene	0.94	96.6	3	1	2	0.00	100	6	24	0.10	98	11	18
$m\mathcal{E}p$ -Xylene	0.48	82.8	3	1	9	0.86	100	6	24	0.43	98	11	17
Styrene o-Xylene	0.07 0.00	79.3 89.7	n n	1 2	4	0.00	$90 \\ 100$	66	48 24	0.80 0.11	98 98	11 11	34 17
Chloroform	0.00	24.1	1			0.00	55	3	62	0.17	98	11	46
1,1,1-Trichloroethane	0.00	82.8 07.0	നറ		L 1	0.00	100	6	32	0.21	98 00	11	23 7E
2-Methylhexane	0.00	96.6	ເພ		r 6	0.00	100	6	25 25	0.17	98 86	11	34
2,3-Dimethylpentane	0.00	93.1	3	1	2	0.00	100	6	27	0.17	98	11	42
3-Methylhexane	0.00	96.6	3	1	2	0.00	100	6	28	0.25	98	11	45
Trichloroethene 2.2.4-Trimethvlnentane	0.12	62.1 96.6	(-) cr	LC.	0	2.26 23.4	100 23	ο 12	79 74	0.15	98 80	11	19
				, () ,							4 .	
Methylcyclonexane	0.00	90.0 70.2	ກເ		- 1	0.00	98	י ת	17	0.13	90	1;	17
teuracintoroleurene 1.4-Dichlorobenzene	0.36 0.36	72.4	ກຕ	N 67.		0.00	00 38	ο –	3U 62	0.07 0.38	06 86	11	12
ן-תווז- עסיי ס -י עס ז					1		1					1	
^a LOD is 3 times SD of blanks. Kel	Pre is relative	precision: 10	$00 \times \text{KMS}$	E/V2.									

114

		Mean Percentage Recovery	
VOC	Winter 2005	Summer 2005	Winter 2006
1,3-Butadiene	114	116	115
Methylene chloride	57	103	90
MTBE	49	97	74
2-Methylpentane	90	106	94
Chloroform	35	122	103
1,1,1-Trichloroethane	70	117	103
Benzene	81	103	103
Carbon tetrachloride	82	115	103
2-Methylhexane	91	104	93
2,3-Dimethylpentane	89	105	95
3-Methylhexane	87	102	88
Trichloroethene	86	108	104
2,2,4-Trimethylpentane	89	104	95
1,3-Dichloropropene (<i>cis+trans</i>)	52	105	95
Methylcyclohexane	85	103	96
Toluene	87	106	99
Tetrachloroethene	94	113	111
Ethylbenzene	83	112	92
m&p-Xylene	82	111	96
Styrene	78	116	105
o-Xylene	84	115	100
1,4-Dichlorobenzene	74	128	123

Table A.4. Mean Percentage Recovery of VOC Field Spikes^a

^a Tubes were spiked before departure on the field trip, taken to the field, stored with the samples, and returned to the lab and analyzed with the samples. These quality control samples were collected to document that there was no 1,3-butadiene loss in the actual VOC samples. All compounds were recovered within the range of \pm 30% to 100%. Recoveries between 70% and 130% are considered acceptable. a-Pinene and d-limonene were not included in the spike mixture. All compounds were spiked with 49.75 ng except for dichloropropene, which was spiked with 199.00 ng.

for the VOC analysis containing the percentage recoveries of the VOC field spikes for each sampling session. In Table A.5, VOC data for the 60-hour daytime samples are compared with the average of the five corresponding 12-hour daily samples per week by site.

Table A.6 presents the data quality statistics for the winter 2005, summer 2005, and winter 2006 elemental analysis. In Table A.7, the elemental data for the 60-hour daytime samples are compared with the average of the five corresponding 12-hour daily samples per week and site. Table A.8 presents the data quality report for the winter 2005, summer 2005, and winter 2006 PAH analyses, and Table A.9 presents the data quality report for the NPAH analyses. NPAH analysis was not performed on the winter 2006 samples. Table A.10 contains descriptive statistics of

the laboratory and field surrogates of the PAHs and NPAHs for the winter 2005, summer 2005, and winter 2006 campaigns. Cubic regressions of molecular weight of the target analyte against percentage recoveries of each laboratory and field surrogate (eight data points) were calculated for each PAH sample. The PAH samples, including blanks, were each corrected for recovery from the regression equation calculated from that sample's surrogates. NPAH samples were corrected by molecular weight group of the laboratory surrogates. All NPAH samples, including blanks, were corrected for recovery based on the percentage recovery of the surrogate representing each molecular weight group. In Table A.11, the PAH data for the 60-hour daytime samples are compared with the average of the five corresponding 12-hour daily samples per week and site.

Table A.5. VOC ConcSamples for the Week	entration (r by Field S	ıg/m ³) in 60 ampling Site	-Hour Dayti e in Summer	me (5-Day) ' 2005	Weekday Saı	mples Com	oared with A	verage Conc	centration of	the Five 12	-Hour
	Cha (July 18	pel , 2005)	Cha (July 25	pel , 2005)	GL (July 18	رC , 2005)	Sch (July 18	ool , 2005)	Sch (July 25	.ool 1, 2005)	Dolotico
NOC	12-Hour	5-Day	12-Hour	5-Day	12-Hour	5-Day	12-Hour	5-Day	12-Hour	5-Day	Precision ^a
1,3-Butadiene	144.05	61.32	138.05	89.77	43.95	18.60	98.98	77.87	93.88	100.32	16.6
MTBE	15.88	0.00	14.63	11.48	5.44	3.28	23.18	10.04	15.97	9.17	28.6
Benzene	1,286.01	1416.49	1383.48	1749.56	448.43	623.40	1,128.43	1043.01	1070.70	1467.40	7.2
Toluene	2,826.05	3541.44	3009.49	2967.31	894.39	1311.35	3,142.57	4464.38	4344.92	5556.55	8.7
Ethylbenzene	559.39	474.92	578.23	535.34	164.71	154.69	443.55	379.89	493.26	571.99	4.5
$m\mathcal{E}p$ -Xylene	1,875.97	1518.47	1926.76	1791.92	460.27	468.82	1,467.71	1278.95	1650.80	2024.69	5.5
o-Xylene	716.56	608.22	741.38	686.87	185.85	201.07	598.14	498.86	649.09	780.08	5.1
Styrene	136.45	80.68	114.14	90.70	27.18	33.60	96.81	89.78	130.27	146.65	9.5
Chloroform	15.75	35.77	27.22	17.07	7.47	22.51	62.47	49.50	58.43	17.73	22.8
Trichloroethane	101.47	93.40	91.35	97.88	87.21	65.51	98.10	89.19	98.06	107.47	4.2
Carbon tetrachloride	600.28	509.06	600.78	488.82	537.63	387.14	494.06	489.40	614.32	552.75	5.8
2-Methvlhexane	476.40	370.54	431.29	449.47	191.34	82.63	356.32	421.34	495.42	454.45	6.5

^a Relative precision is 100 \times RMSE/V2.

7.0 24.0

 $169.81 \\ 986.26$

149.66 592.44

 $198.70 \\ 296.65$

137.54275.19

68.68 67.62

 $\begin{array}{c} 60.13\\ 12.08 \end{array}$

 $172.98 \\ 98.92$

 $147.76 \\ 23.75$

155.15

153.033.60

49.14

19 $1520 \\ 562$

856 12,34117,411

1,4-Dichlorobenzene Methylcyclohexane

Formaldehyde

Acetaldehyde

Acetone

39 18,52522,726

18.1

211.41

225.03

454.45

495.42

421.34406.86

356.32 153.61

82.6364.03

191.3489.48

449.47

431.29208.84

370.54 202.01

476.40

2-Methylhexane

213.51

2,3-Dimethyl-

pentane

227.47

11.522.8 12.3

521.6350.86

609.80 109.95 726.68

 $721.61 \\ 96.78$

389.84 50.55 279.71

 $\begin{array}{c} 120.88 \\ 49.77 \\ 241.01 \end{array}$

524.48 30.57 670.39

 $\begin{array}{c} 477.18\\ 10.83\\ 1045.27\end{array}$

425.8877.41648.23

487.3131.78434.00

3-Methylhexane

2,2,4-Trimethyl-Trichlorethene

pentane

218.3949.13199.56

454.26

698.80

65.5 67.8 70.0

 $328 \\ 1215 \\ 36$

3651 3448 3979

443 259 1889

3,8462,76619,185

 $\begin{array}{c} 11\\ 655\\ 0\end{array}$

97 73 241

 $\begin{array}{c} 1674\\ 4106\\ 1505 \end{array}$

		Μ	inter 200	10			Sun	nmer 2005			Win	ter 2006	
I	M		OD			Maan	< I	[OD			Moon		CO.
Element	Mean Blank Value (ng)	Ν	%	– Pairs > LOD	Rel Pre (%)	Blank Value (ng)	Ν	%	- Dup Pairs > LOD	Rel Pre (%)	Blank Value (ng)	Ν	%
Be	0.5	23	66	3	36.7	0.02	12	28	9	7	0.01	1	ŋ
Na	110	1	3	9	11.6	140	7	16	8	5.3	68	0	0
Mg	29	0	0	9	21.4	21	0	0	10	4	11	1	2
Al	720	33	94	0		360	24	56	4	29.6	21	1	ŋ
S	230	0	0	9	5.8	140	0	0	10	1.9	60	0	0
К	360	0	0	9	18.1	110	1	2	10	3.5	38	1	2
Ca	140	7	20	9	30	790	1	2	10	13	110	0	0
\mathbf{Sc}	0.02	5	14	9	43.6	0.32	42	98	0		0.06	15	75
Ï	42	0	0	9	30.9	120	0	0	10	3.8	7.7	4	20
Λ	8.1	5	14	9	8.5	2.9	4	6	6	3.4	0.50	0	0
C	22	27	77	0		7.1	31	72	33	9.5	20	19	95
Mn	4.0	1	3	9	13.7	4.0	0	0	10	3.3	0.82	1	5
Fe	240	0	0	9	22.9	420	6	21	8	5.9	66	1	2
Co	0.06	2	9	9	21.4	0.07	0	0	10	5.2	0.05	1	2
Ni	21	6	26	9	72.3	6.7	31	72	3	21	9.9	16	80
Cu	23	20	57	2	115.5	20	17	40	ß	74.9	3.4	1	2
Zn	450	24	67	3	103.2	170	28	65	1	16.2	69	2	10
As	16	10	27	9	74.9	1.6	0	0	10	6.3	0.91	1	IJ
Se	1.8	9	17	9	14.4	2.8	7	16	7	3.8	0.75	0	0
Sr	0.53	0	0	9	18.7	5.8	30	70	2	15.7	0.39	0	0
Ag	0.31	0	0	9	12.1	0.25	35	81	2	16.3	0.07	2	25
Cd	0.63	2	9	9	20.8	0.80	13	30	4	9.1	0.06	1	ŋ
Sn	0.54	0	0	9	18.1	1.9	0	0	10	4.6	0.33	1	ŋ
Sb	0.20	0	0	9	6.9	0.41	0	0	10	2	0.30	1	5
Cs	0.00	0	0	9	6.7	0.08	15	35	2	5.4	0.01	1	2
La	0.21	0	0	9	15.8	0.48	10	23	8	7.1	0.09	0	0
T				0		0.02	0	0	10	4.8	0.02	2	10
Pb	6.1	1	с,	9	8.2	7.1	0	0	10	14.2	1.9	1	2

1	1	8

	Sch (July 25	ool , 2005)	Sch (July 18	ool , 2005)	GL (July 25	, 2005)	GL (July 18	C 2005)	Cha (July 25	tpel (, 2005)	Cha (July 18	pel , 2005)	- - -
Element	12-Hour	5-Day	12-Hour	5-Day	12-Hour	5-Day	12-Hour	5-Day	12-Hour	5-Day	12-Hour	5-Day	Relative Precision
Вe	000	00.0	0.00	0.01	0.00	00.0	000	00.0	00.0	0.00	000	000	16.5
Na	28	34	22	34	27	24	19	23	24	27	24	32	7.5
Mg	11	30	13	44	13	15	11	23	17	29	18	40	24.4
Al	30	71	23	83	32	46	22	50	36	60	44	67	21.3
S	1400	1500	2500	2500	1800	1200	2200	2100	1300	1100	2500	2200	4.4
K	36	55	51	68	34	39	33	42	31	37	39	54	8.8
Ca	49	150	36	160	53	59	37	71	92	160	68	160	25.6
Sc	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	28.8
Ti	39	81	29	95	31	49	20	39	43	63	31	99	22.1
Λ	1.1	1.2	0.90	1.2	1.2	0.77	0.74	0.87	0.84	0.82	0.88	1.1	6.9
Ū.	0.49	1.0	1.6	0.60	0.49	0.32	0.24	0.52	1.0	0.78	0.45	1.1	22.4
Mn	1.8	2.8	2.3	3.9	1.5	1.8	1.9	2.6	2.1	2.5	2.9	4.4	11.7
Fe	63	120	61	140	44	64	41	65	89	120	94	190	18.3
Co	0.03	0.05	0.03	0.07	0.03	0.03	0.02	0.04	0.04	0.06	0.04	0.07	16.1
Ni	0.58	0.83	0.31	0.60	0.55	0.52	0.27	67	0.70	0.69	0.36	0.90	128.7
Cu	2.5	4.1	4.1	5.7	1.4	1.8	1.5	3.1	5.1	4.2	8.7	5.5	12.9
Zn	22	13	21	22	7.5	32	26	12	13	11	18	18	19.9
\mathbf{As}	0.59	0.72	0.55	0.51	0.58	0.42	0.47	0.53	0.55	0.49	0.57	0.48	5.4
Se	1.2	1.4	1.8	1.3	1.6	0.76	1.3	1.7	1.1	1.0	1.6	1.6	8.9
Sr	0.30	0.62	0.32	0.80	0.46	0.50	0.30	0.47	0.66	0.75	0.49	0.89	15.6
Ag	0.01	0.02	0.01	0.08	0.01	0.02	0.02	0.01	0.02	0.02	0.01	0.01	43.5
Cd	0.10	0.10	0.35	0.19	0.13	0.11	0.11	0.07	0.22	0.13	0.10	0.35	23.0
Sn	1.0	1.4	0.90	1.1	1.1	1.1	0.88	0.77	1.9	1.3	1.0	1.1	8.4
Sb	0.42	0.56	0.46	0.74	0.35	0.31	0.40	0.47	0.65	0.75	0.86	1.1	8.1
Cs	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02	8.3
La	0.09	0.13	0.09	0.20	0.07	0.09	0.07	0.11	0.07	0.11	0.09	0.16	16.7
Pb	3.3	4.7	29	23	2.9	2.5	3.3	3.4	3.8	2.8	4.9	3.9	9.3

			Samples	s > LOD	Dup	
РАН	Mean Blank Value (ng)	LOD (ng)	N > LOD	%	- Pairs > LOD	Rel Pre (%)
Winter 2005			-			-
Naphthalene	12.70	38.09	32	91.4	6	6.2
2-Methylnaphthalene	4.45	13.36	33	94.3	6	5.6
Azulene	0.01	0.04	12	34.3	1	73.1
1-Methylnaphthalene	1.92	5.76	32	91.4	6	5.6
Biphenyl	0.67	2.01	33	94.3	6	7.0
2 7-Dimethylnaphthalene	0.89	2.68	34	97 1	6	6.1
1 3-Dimethylnaphthalene	0.88	2.65	34	97.1	6	5.4
1.6-Dimethylnaphthalene	0.00	1 46	34	97.1	6	5.4
1 4-Dimethylnaphthalene	0.15	0.84	33	94.3	6	7.0
1 5-Dimethylnaphthalene	0.20	0.61	33	94.3	6	6.9
	0.10	0.10	0.4	07.4	0	11.0
Acenaphthylene	0.07	0.22	34	97.1	6	11.6
1,2-Dimethylnaphthalene	0.18	0.54	33	94.3	6	7.5
1,8-Dimethylnaphthalene	0.02	0.05	17	48.6	2	57.7
	0.62	1.86	34	97.1	6	10.3
2,3,5-Irimethyinaphthalene	0.26	0.79	33	94.3	6	10.1
Fluorene	0.70	2.10	33	94.3	6	16.8
1-Methylfluorene	0.30	0.90	34	97.1	6	13.1
Dibenzothiophene	0.16	0.47	34	97.1	6	12.4
Phenanthrene	1.82	5.47	34	97.1	6	6.3
Anthracene	0.05	0.15	35	100.0	6	10.2
2-Methyldibenzothiophene	0.09	0.27	34	97.1	6	17.3
4-Methyldibenzothiophene	0.09	0.28	32	91.4	5	21.2
2-Methylphenanthrene	0.27	0.82	35	100.0	6	31.5
2-Methylanthracene	0.38	1.14	34	97.1	6	12.9
4,5-Methylenephenanthrene	0.11	0.33	34	97.1	6	16.1
1-Methylanthracene	0.23	0.70	31	88.6	4	14.6
1-Methylphenanthrene	0.25	0.70	32	00.0 91 4	4	16.0
9-Methylanthracene	0.10	0.10	3	86	0	10.5
9 10-Dimethylanthracene	0.04	0.11	30	85.7	4	28.6
Fluoranthene	0.10	1 99	34	97.1	6	10.5
Deserves	0.00	1.00	0.4	07.1	0	10.0
Pyrene	0.46	1.39	34	97.1	6	10.9
3,6-Dimetnyipnenantnrene	0.01	0.04	2	5.7	0	40 5
Benzolajiiuorine	0.03	0.08	34	97.1	6	40.5
Retene	0.19	0.57	28	80.0	3	63.1 - 0.0
Benzolojiluorine	0.02	0.05	34	97.1	6	58.3
Cyclopenta[<i>c</i> , <i>d</i>]pyrene	0.07	0.20	33	94.3	5	32.0
Benz[a]anthracene	0.02	0.06	35	100.0	6	12.8
Chrysene+Triphenylene	0.07	0.20	34	97.1	6	10.5
Naphthacene	0.04	0.11	20	57.1	2	12.7
4-Methylchrysene	0.05	0.15	20	57.1	2	7.5
Benzo[b]fluoranthene	0.09	0.26	34	97.1	6	11.1
Benzo[<i>k</i>]fluoranthene	0.06	0.19	34	97.1	6	5.6

Table A.8. PAH Data Quality Statistics^a

^a LOD is 3 times SD of blanks. Rel Pre is relative precision: $100 \times RMSE/\sqrt{2}$. Only analytes with both samples in the duplicate pair above the LOD were included in the relative precision calculation.

	Maar Dlaad		Samples	s > LOD	Dup	
РАН	Value (ng)	LOD (ng)	N > LOD	%	- Pairs > LOD	Rel Pre (%)
Winter 2005 (Continued)						
Benzo[<i>e</i>]pvrene	0.07	0.22	35	100.0	6	11.7
Benzo[<i>a</i>]pyrene	0.12	0.37	34	97.1	6	9.4
Pervlene	0.03	0.09	26	74.3	4	67.9
3-Methylchloanthrene	0.15	0.45	0	0.0	0	
Indeno[1,2,3- <i>c,d</i>]pyrene	0.09	0.28	34	97.1	6	21.0
Dibenz[<i>a</i> . <i>h</i> + <i>a</i> . <i>c</i>]anthracene	0.15	0.45	0	0.0	0	
Benzo[<i>g</i> . <i>h</i> . <i>i</i>]pervlene	0.11	0.34	34	97.1	6	19.6
Anthranthrene	0.25	0.76	3	8.6	0	
Coronene	0.17	0.50	10	28.6	0	
Summer 2005						
Nanhthalene	74 48	138 90	40	89	7	23
2-Methylnanhthalene	7 1 .40 50 70	105 14	40	05	2 8	23
Azulene	0.52	2 09	-1-5 	30 47	6	79
1-Methylnanhthalene	25.18	43.76	43	96	8	24
Binhenvl	8 96	14 45	40	89	8	22
2.7. Dimentional and the large	0.50	45.45	10	55	0	22
2,7-Dimetnyinaphthalene	28.10	45.47	32	71	8	30
1,3-Dimetryinaphthalene	21.37	31.35	30	/8	ð	27
1,6-Dimetryinaphthalene	19.03	37.62	28	62	ð	43
1,4-Dimethylnaphthalene	5.80	8.09	40	89 E1	ð	29
1,5-Dimetryinaphthalene	3.88	9.26	23	51	ð	50
Acenaphthylene	1.00	2.12	44	98	8	58
1,2-Dimethylnaphthalene	2.40	7.39	24	53	8	42
1,8-Dimethylnaphthalene	0.80	2.05	11	24	1	22
Acenapthene	8.48	17.60	42	93	8	19
2,3,5-Trimethylnaphthalene	6.43	11.08	36	80	8	27
Fluorene	12.51	22.49	44	98	8	29
1-Methylfluorene	2.75	11.31	29	64	8	34
Dibenzothiophene	1.38	2.26	45	100	8	32
Phenanthrene	17.16	31.84	45	100	8	33
Anthracene	2.87	21.12	31	69	8	37
2-Methyldibenzothiophene	0.40	1.04	45	100	8	32
4-Methyldibenzothiophene	0.46	0.47	45	100	8	39
2-Methylphenanthrene	1.27	1.69	45	100	8	25
2-Methylanthracene	2.16	1.95	45	100	8	31
4,5-Methylenephenanthrene	0.12	0.54	45	100	8	50
1-Methvlanthracene	0.69	1.48	45	100	8	28
1-Methylphenanthrene	0.55	1.16	45	100	8	30
9-Methylanthracene	0.09	0.27	15	33	1	40
9,10-Dimethylanthracene	0.10	0.31	45	100	8	39
Fluoranthene	2.70	4.27	45	100	8	114
Pyrene	0.61	1 74	45	100	8	04
3 6-Dimethylphenanthrene	0.01	1.7 1 0 2 9		24	1	73
Benzo[a]fluorine	0.10	0.23	45	100	8	80
o [a]aoo	0.00	5.61	10	100		30

Table A.8 (Continued). PAH Data Quality Statistics^a

Table continues next page

^a LOD is 3 times SD of blanks. Rel Pre is relative precision: $100 \times \text{RMSE}/\sqrt{2}$. Only analytes with both samples in the duplicate pair above the LOD were included in the relative precision calculation.

	Moon Plank		Samples	s > LOD	Dup	
РАН	Value (ng)	LOD (ng)	N > LOD	%	> LOD	Rel Pre (%)
Summer 2005 (Continued)						
Retene	0.30	0.80	28	62	8	121
Benzo[<i>b</i>]fluorine	0.06	0.22	45	100	8	98
Cyclopenta[<i>c,d</i>]pyrene	0.11	0.64	7	16	4	104
Benz[a]anthracene	0.13	0.57	22	49	8	93
Chrysene+Triphenylene	0.13	0.58	41	91	8	70
Naphthacene	0.08	0.30	4	9	2	88
4-Methylchrysene	0.08	0.34	1	2	1	98
Benzo[<i>b</i>]fluoranthene	0.12	0.26	35	78	4	65
Benzo[k]fluoranthene	0.20	0.71	7	16	1	10
Dimethylbenz[<i>a</i>]anthracene	0.16	0.68	2	4	1	61
Benzo[e]pyrene	0.21	0.71	12	27	8	128
Benzo[a]pyrene	0.31	0.59	12	27	2	31
Pervlene	0.10	0.24	1	2	1	60
3-Methylchloanthrene	0.35	0.67	4	9	2	57
Indeno[1,2,3- <i>c</i> , <i>d</i>]pyrene	0.20	0.82	11	24	5	87
Dibenz[<i>a</i> . <i>h</i> + <i>a</i> . <i>c</i>]anthracene	0.14	0.63	1	2	1	99
Benzo[g.h.i]pervlene	0.11	0.44	25	56	6	63
Anthranthrene	0.16	0.67	0	0	1	65
Coronene	0.07	0.00	8	18	1	21
Winter 2006						
Naphthalene	19.12	15.90	46	92	12	15
2-Methylnaphthalene	32.07	35.99	45	90	10	28
Azulene	0.35	0.64	42	84	11	18
1-Methylnaphthalene	12.57	11.88	45	90	10	27
Biphenyl	5.31	14.63	45	90	12	31
2.7-Dimethylnaphthalene	10.15	21.55	45	90	12	23
1.3-Dimethylnaphthalene	21.64	44.47	45	90	12	23
1,6-Dimethylnaphthalene	12.12	25.35	45	90	12	23
1,4-Dimethylnaphthalene	5.86	11.53	45	90	12	23
1,5-Dimethylnaphthalene	2.82	7.25	43	86	12	26
Acenanhthylene	1 4 3	2 34	45	90	12	43
1 2-Dimethylnanhthalene	3 59	6 74	45	90	12	23
1.8-Dimethylnaphthalene	1 31	5 35	3	6	0	20
Acenaphthene	4 90	10.60	44	88	12	35
2 3 5-Trimethylnaphthalene	2.64	2.49	46	92	12	5
	4.00	4.50	16	02	10	F
r 10010110 1 Methylfluorona	4.Uð 2.26	4.09	40	94	12	Э
Dibonzothionhone	0.00 5.04	44.37 17 00	1	4	0	
Phonanthrono	0.04 7 5 Q	47.00 10.02	46	0 02	U 1 2	Ω
Anthracana	0 3 3 7 . 7 0	0.47	40	94 Q4	12	Ο Ω
	0.00	0.47	=/	34	14	U
2-Methyldibenzothiophene	0.49	0.60	47	94	12	6
4-Methylaibenzothiophene	0.38	0.48	47	94	12	7

^a LOD is 3 times SD of blanks. Rel Pre is relative precision: $100 \times RMSE/\sqrt{2}$. Only analytes with both samples in the duplicate pair above the LOD were included in the relative precision calculation.

	Moon Dlank		Samples	> LOD	Dup	
РАН	Value (ng)	LOD (ng)	N > LOD	%	> LOD	Rel Pre (%)
Winter 2006 (Continued)			-			
2-Methylphenanthrene	0.93	1.31	47	94	12	6
2-Methylanthracene	1.66	2.32	47	94	12	6
4,5-Methylenephenanthrene	0.11	0.14	31	62	7	18
1-Methylanthracene	0.75	1.09	47	94	12	7
1-Methylphenanthrene	0.67	0.87	47	94	12	6
9-Methylanthracene	0.09	0.23	4	8	0	
9,10-Dimethylanthracene	0.17	0.24	47	94	12	6
Fluoranthene	1.15	1.44	47	94	12	7
Pyrene	1.08	1.35	47	94	12	5
3,6-Dimethylphenanthrene	1.96	7.20	0	0	0	
Benzo[<i>a</i>]fluorine	0.10	0.15	45	90	12	4
Retene	0.38	0.71	14	28	3	16
Benzo[b]fluorine	0.05	0.13	46	92	12	3
Cyclopenta[<i>c,d</i>]pyrene	0.08	0.13	46	92	12	7
Benz[a]anthracene	0.04	0.19	45	90	12	2
Chrysene+Triphenylene	0.09	0.17	47	94	12	3
Naphthacene	0.01	0.02	25	50	4	16
4-Methylchrysene	0.01	0.01	43	86	12	5
Benzo[b]fluoranthene	0.01	0.06	47	94	12	2
Benzo[k]fluoranthene	0.01	0.02	47	94	12	3
Dimethylbenz[a]anthracene	0.00	0.00	37	74	8	18
Benzo[e]pyrene	0.19	0.71	9	18	2	15
Benzo[a]pyrene	0.03	0.17	40	80	11	3
Perylene	0.00	0.00	47	94	12	3
3-Methylchloanthrene	0.00	0.00	4	8	0	
Indeno[1,2,3- <i>c,d</i>]pyrene	0.06	0.22	48	96	12	2
Dibenz[a,h+a,c]anthracene	0.00	0.01	48	96	12	3
Benzo[g,h,i]perylene	0.11	0.28	48	96	12	2
Anthranthrene	0.02	0.04	44	88	11	5

Table A.8 (Continued). PAH Data Quality Statistics^a

^a LOD is 3 times SD of blanks. Rel Pre is relative precision: $100 \times \text{RMSE}/\sqrt{2}$. Only analytes with both samples in the duplicate pair above the LOD were included in the relative precision calculation.

		V	Vinter	2005				Su	nmei	r 2005		
	Mean	LOD	>	LOD	Dup	n l	Mean	LOD	>	LOD	Dup	D 1
NPAH	Value (pg)	(pg)	Ν	%	PairsLOD	Rei Pre	Blank Value (pg)	(pg)	Ν	%	PairsLOD	Rel Pre
1-Nitronaphthalene	5.1	15.24	30	85.7	5	11.1	25.19	118.98	45	100	8	20
2-Nitronaphthalene	2.6	7.85	23	65.7	4	25.6	28.70	116.22	45	100	8	28
2-Nitrobiphenyl	2.5	7.37	31	88.6	4	23.0	36.48	88.33	45	100	8	41
3-Nitrobiphenyl	2.0	5.97	26	74.3	3	53.0	0.00	0.00	45	100	8	27
4-Nitrobiphenyl	11.6	34.68	0	0.0	0		0.00	0.00	14	31	1	40
1,3-Dinitronaphthalene	1.2	3.47	0	0.0	0		2.62	8.98	15	33	6	71
1,5-Dinitronaphthalene	0.5	1.60	0	0.0	0		0.71	7.02	1	2	0	
5-Nitroacenaphthalene	5.0	14.89	0	0.0	0		11.32	76.13	44	98	8	45
2-Nitrofluorene	0.8	2.28	4	11.4	0		0.79	4.79	5	11	4	20
2,2'-Dinitrobiphenyl	73.0	218.86	3	8.6	5	55.9						
9-Nitroanthracene	14.5	43.55	29	82.9	0		41.09	52.30	45	100	8	33
2-Nitroanthracene	1.5	4.62	11	31.4	0		0.00	0.00	27	60	1	74
9-Nitrophenanthrene	2.2	6.56	7	20.0	0		0.52	3.54	26	58	4	37
3-Nitrophenanthrene	1.4	4.27	8	22.9	0		1.50	8.19	44	98	8	26
4-Nitrophenanthrene	191.8	575.35	0	0.0	0		0.97	10.08	10	22	0	
2-Nitrofluoranthene	0.9	2.65	32	91.4	0		1.57	4.31	45	100	8	8
3-Nitrofluoranthene	0.7	1.96	9	25.7	0		0.14	1.39	0	0	0	
1-Nitropyrene	5.4	16.32	9	25.7	0		2.90	6.29	39	87	8	15
2-Nitropyrene	5.6	16.66	0	0.0	0		1.24	4.10	9	20	2	86
2,7-Dinitrofluorene	1.3	3.95	6	17.1	2	48.2						
7-Nitrobenz[<i>a</i>]anthracene	4.6	13.72	17	48.6	0		1.15	3.18	9	20	4	124
6-Nitrochrysene	3.1	9.27	1	2.9	0		4.66	23.34	0	0	0	
1,3-Dinitropyrene	2.8	8.51	0	0.0	0		0.00	0.00	0	0	0	
1,6-Dinitropyrene	6.8	20.37	0	0.0	0		0.00	0.00	0	0	0	
9,10+1,8- Dinitroanthracene	102.8	308.53	1	2.9	0							
6-Nitrobenzo[<i>a</i>]pyrene	2.8	8.26	2	5.7	0		1.18	11.75	8	18	0	
1-Nitrobenzo[<i>e</i>]pyrene	2.5	7.62	1	2.9	0		1.40	13.94	0	0	1	81
3-Nitrobenzo[<i>e</i>]pyrene	2.4	7.20	3	8.6	0		0.00	0.00	3	7	0	
1+3-Nitrobenzo[a]pyrene	8.4	25.28	3	8.6	0							

Table A.9. NPAH Data Quality Statistics5^a

^a LOD is 3 times SD of blanks. Rel Pre is relative precision: $100 \times \text{RMSE}/\sqrt{2}$. Only analytes with both samples in the duplicate pair above the LOD were included in the relative precision calculation.

			Reco	very (%)	
Surrogate	Mol. Wt.	Mean	RSD	Maximum	Minium
Winter 2005					
Lab Surrogates					
Acenaphthylene-d ₈	160	44.3	0.4	74.1	1.4
Fluorene- d_{10}	176	43.0	0.3	75.2	7.4
Pyrene- d_{10}	212	61.3	0.2	72.8	0.9
Field Surrogates					
Naphthalene- d_8	136	25.7	0.4	51.2	0.0
Fluoranthene- d_{10}	212	56.6	0.2	91.4	48.2
Benz[a]pyrene-d ₁₂	264	106.0	0.1	151.5	98.6
NPAH Lab Surrogates					
1-Nitronaphthalene- <i>d</i> ₇	180	19.7	0.4	53.1	8.6
9-Nitroanthracene- d_9	232	48.4	0.2	66.1	30.4
1-Nitropyrene-d ₉	256	53.2	0.2	69.0	36.1
Summer 2005					
Lab Surrogates					
Acenaphthylene- d_8	160	27.0	0.4	74.8	2.5
Fluorene-d ₁₀	176	26.2	0.4	61.6	4.9
Pyrene- d_{10}	212	70.0	0.2	108.7	50.4
Field Surrogates					
Naphthalene-d ₈	136	15.7	0.7	61.9	0.9
Anthracene- d_{10}	188	52.6	0.3	123.8	1.9
Fluoranthene- d_{10}	212	73.4	0.3	155.7	10.4
Benz[a]pyrene- d_{12}	264	100.2	0.3	214.9	21.4
Indeno[1,2,3- c,d]pyrene- d_{12}	288	98.0	0.3	232.4	18.7
NPAH Lab Surrogates	100	7.0	0.4	1 17 1	1 5
1-Nitronaphtnaiene- a_7	180	7.8	0.4	17.1	1.5
9-Nitroanthracene- a_9	232	39.5	0.1	48.9	20.4
1-intropyrene- a_9	250	59.1	0.1	/3.9	28.8
Winter 2006					
Lab Surrogates					
Acenaphthylene-d ₈	160	27.0	0.4	74.8	2.5
Fluorene- d_{10}	176	26.2	0.4	61.6	4.9
Pyrene- d_{10}	212	70.0	0.2	108.7	50.4
Field Surrogates	100		0.7	61.0	0.0
Naphthalene- <i>a</i> ₈	136	15.7	0.7	61.9	0.9
Anufracene- a_{10}	100	0∠.0 72.4	U.3	123.8 155 7	1.9
Find an anti-array d	212	/ J.4	0.3	100.7	10.4
Indono[1,2,3,c,d]pyrono_d	20 4 288	08.0	0.3	414.9 222 4	41.4 19.7
NPAH Lab Surrogates	200	90.0	0.5	232.4	10./
1-Nitronaphthalene- <i>d</i> _π	180	7.8	0.4	17.1	1.5
9-Nitroanthracene- d_{2}	232	39.5	0.1	48.9	20.4
1-Nitronvrene-do	256	59.0	0.1	73.9	28.8

Table A.10. Surrogate Recovery Statistics for PAH and NPAH Samples

	Cha (July 18	pel , 2005)	Cha (July 25	ipel (, 2005)	GI (July 18	رC (, 2005)	GI (July 25	,C , 2005)	Sch (July 18	ool , 2005)	
PAH	12-Hour	5-Day	12-Hour	5-Day	12-Hour	5-Day	12-Hour	5-Day	12-Hour	5-Day	Precision
Naphthalene 2-Methylnaphthalene Azulene	94 51 0.65	0.0 79 0.0	130 58 0.97	39 60 0.60	44 24 0.06	7.7 6.4 0.02	39 23 0.14	$64 \\ 14 \\ 0.40$	74 52 0.28	47 32 0.22	36.4 14.0 33.6
1-Methylnaphthalene Biphenyl 2,7-Dimethylnaphthalene	21 5.5 12	34 3.8 9.3	24 4.8 14	23 3.4 8.8	9.0 2.9 3.6	2.5 1.4 1.9	$\begin{array}{c} 9.1 \\ 2.0 \\ 5.6 \end{array}$	5.4 1.2 2.9	20 5.8 10	13 4.0 7.0	14.7 13.6 13.7
1,3-Dimethylnaphthalene 1,6-Dimethylnaphthalene 1,4-Dimethylnaphthalene	9.4 10 2.8	8.1 5.4 2.5	11 8.1 3.2	8.5 3.3 2.6	2.6 2.5 1.0	$1.6 \\ 0.85 \\ 0.58$	4.8 3.0 1.5	2.6 1.0 0.78	8.3 6.5 2.5	5.7 3.7 1.9	10.4 24.2 8.7
1,5-Dimethylnaphthalene Acenaphthylene 1,2-Dimethylnaphthalene	2.1 2.3 1.5	$1.0 \\ 0.71 \\ 1.1$	$\begin{array}{c} 1.4\\ 2.5\\ 1.4\end{array}$	$0.71 \\ 0.92 \\ 0.73$	0.48 1.0 0.44	$0.20 \\ 0.11 \\ 0.16$	$\begin{array}{c} 0.35 \\ 1.1 \\ 0.54 \end{array}$	$0.20 \\ 0.15 \\ 0.17$	$1.2 \\ 2.5 \\ 1.1$	0.66 0.78 0.81	24.3 36.7 17.2
1,8-Dimethylnaphthalene Acenaphthene 2,3,5-Trimethylnaphthalene	0.0 8.4 4.1	$0.31 \\ 6.5 \\ 3.1$	0.23 4.5 4.5	0.47 3.4 2.6	$\begin{array}{c} 0.0\\ 14\\ 1.2 \end{array}$	$\begin{array}{c} 0.19 \\ 6.5 \\ 0.91 \end{array}$	$\begin{array}{c} 0.40\\ 4.9\\ 1.7\end{array}$	0.42 4.0 0.86	$\begin{array}{c} 0.40\\ 17\\ 2.9\end{array}$	$\begin{array}{c} 0.34\\ 12\\ 2.6\end{array}$	22.8 17.0 13.3
Fluorene 1-Methylfuorene Dibenzothiophene	20 2.1 2.7	$\begin{array}{c} 12\\ 1.6\\ 2.1\end{array}$	14 2.0 2.2	7.8 1.7 2.2	24 0.92 3.4	$\begin{array}{c} 14\\ 0.66\\ 2.8\end{array}$	$\begin{array}{c} 13\\ 0.61\\ 1.8\end{array}$	$8.1 \\ 0.61 \\ 2.3$	39 2.0 12	$\begin{array}{c} 37\\2.3\\15\end{array}$	11.6 6.4 8.5
Phenanthrene Anthracene 2-Methyldibenzothiophene	49 3.9 0.92	$39 \\ 3.2 \\ 0.72$	38 2.4 0.87	47 2.9 0.77	59 3.4 0.74	55 2.3 0.46	$\begin{array}{c} 31\\1.7\\0.39\end{array}$	38 2.0 0.47	$\begin{array}{c} 260\\ 20\\ 1.8\end{array}$	370 27 2.0	16.4 15.2 6.3
4-Methyldibenzothiophene 2-Methylphenanthrene 2-Methylanthracene	0.55 3.4 5.1	0.36 2.9 3.8	0.49 3.1 4.1	$\begin{array}{c} 0.41\\ 3.4\\ 4.0 \end{array}$	0.53 2.5 3.6	0.30 2.0 2.6	$\begin{array}{c} 0.24 \\ 1.4 \\ 1.9 \end{array}$	0.28 1.5 1.8	1.4 10 14	$\begin{array}{c} 1.7\\ 14\\ 20\end{array}$	9.8 12.6 14.4
									Table	e continue	s next page

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<i>Continued</i> r Samples
Fable A.11 (Five 12-Hou

	Cha (July 18	pel , 2005)	Cha (July 25	pel , 2005)	GI (July 18	LC (, 2005)	GI (July 25	LC (, 2005)	Sch (July 18	100l 3, 2005)	ייייה ויי די
PAH	12-Hour	5-Day	12-Hour	5-Day	12-Hour	5-Day	12-Hour	5-Day	12-Hour	5-Day	Precision
4.5-Methvlenephenanthrene	0.38	0.07	0.39	60.0	0.38	0.06	0.32	0.14	0.69	0.43	29.6
1-Methylanthracene	2.0	1.7	1.8	1.8	1.4	1.0	0.74	0.75	4.3	5.9	10.8
1-Methylphenanthrene	1.6	1.3	1.3	1.4	1.2	0.75	0.69	0.58	4.5	6.2	12.9
9-Methylanthracene	0.02	0.03	0.02	0.03	0.02	0.02	0.02	0.02	0.01	0.03	16.0
9,10-Dimethylanthracene Fluoranthene	0.38 17	0.28 3.7	0.32 5.3	$0.19 \\ 4.6$	0.23 13	$\begin{array}{c} 0.16 \\ 7.4 \end{array}$	0.13 12	$0.12 \\ 3.8$	0.50 79	$\begin{array}{c} 0.74 \\ 130 \end{array}$	13.7 25.8
Pvrene	7.3	2.4	3.1	2.6	6.1	с. С	5.2	2.0	31	52	26.6
3,6-Dimethylphenanthrene	0.02	0.05	0.02	0.03	0.01	0.01	0.01	0.01	0.02	0.09	37.1
Benzo[a]fluorene	0.10	0.05	0.08	0.05	0.11	0.06	0.08	0.06	0.32	0.57	25.6
Retene	0.09	0.06	0.07	0.05	0.15	0.07	0.05	0.06	0.15	0.20	15.0
Benzo[b]fluorene	0.08	0.04	0.07	0.05	0.08	0.04	0.06	0.04	0.19	0.38	27.4
Cyclopenta[<i>c</i> , <i>d</i>]pyrene	0.02	0.01	0.04	0.01	0.02	0.01	0.01	0.01	0.17	0.06	46.6
Benz[<i>a</i> }anthracene	0.06	0.02	0.06	0.03	0.03	0.01	0.02	0.02	0.11	0.16	21.0
Chrysene+Triphenylene	0.11	0.03	0.12	0.08	0.09	0.04	0.09	0.04	0.66	0.84	14.0
Naphthacene	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.0	0.01	0.00	47.7
4-Methylchrysene	0.0	0.0	0.01	0.0	0.00	0.0	0.00	0.0	0.0	0.00	87.7
Benzo[b]fluoranthene	0.05	0.01	0.06	0.02	0.04	0.02	0.03	0.02	0.13	0.07	25.6
$\operatorname{Benzo}[k]$ fluoranthene	0.02	0.00	0.04	0.00	0.01	0.00	0.01	0.00	0.04	0.03	36.9
Dimethylbenz[a]anthracene	0.00	0.0	0.03	0.0	0.01	0.0	0.00	0.0	0.0	0.0	105.9
Benzo[<i>e</i>]pyrene	0.03	0.01	0.06	0.02	0.03	0.01	0.03	0.01	0.06	0.04	27.7
Benzo[a]pyrene	0.03	0.01	0.04	0.02	0.02	0.01	0.02	0.01	0.0	0.02	33.7
Perylene	0.00	0.0	0.01	0.0	0.01	0.0	0.0	0.0	0.0	0.0	84.1
3-Methyl-chloanthrene	0.04	0.0	0.05	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.9
Indeno[1,2,3-c,d]pyrene	0.04	0.02	0.04	0.02	0.05	0.01	0.04	0.02	0.08	0.04	25.4
Dibenz[<i>a</i> , <i>h</i> + <i>a</i> , <i>c</i>]anthracene	0.00	0.0	0.02	0.0	0.01	0.00	0.0	0.0	0.0	0.0	90.4
$\operatorname{Benzo}[g,h,i]\operatorname{perylene}$	0.07	0.02	0.09	0.06	0.03	0.02	0.04	0.02	0.08	0.04	23.4
Anthranthrene	0.0	0.0	0.01	0.0	0.00	0.0	0.0	0.0	0.0	0.0	111.8
Coronene	0.02	0.00	0.02	0.01	0.01	0.01	0.0	0.00	0.0	0.01	42.7

TREATMENT OF SAMPLES BELOW THE LOD

For all sample types actual values of samples below the LOD were used in all calculations of summary statistics and statistical tests. This is known as the instrument-generated data method (Antweiler and Taylor 2008). In summary tables of Appendix B, negative and zero values were replaced with a dashed line (---). For log transformations, zero values and negative values were replaced with a value at half of the instrument detection limit.

ACROLEIN SAMPLES

Based upon an assessment of the acrolein levels measured by the University of California–Davis method, we chose not to analyze any of the acrolein samples collected by OSHA Method 52. The detection limit of OSHA Method 52, based on the sample volumes collected, was $1 \mu g/m^3$, which is substantially higher than the highest value reported by the University of California–Davis of 0.46 $\mu g/m^3$.

CONTINUOUS SAMPLES

The results of the collocation of the PAS 2000CE instruments used in our study are presented in Table A.12. The results from multiple instruments were compared. In two sessions we collected a total of 374 minutes of data from collocated instruments. Levels measured during this exercise were below the reported analytic sensitivity; the instruments were responding to PAH concentrations in the range of 1 to 10 ng/m³, with a coefficient of variation of approximately 35%. Most values obtained during the collocation exercises were at or below the analytic sensitivity of the instrument of 10 ng/m³; however, the mean ranges were 2.4 ng/m³ for summer 2005 and 3 ng/m³ for winter 2006 on an instrument with a sensitivity of 1 ng/m³. Two instruments borrowed from other researchers for the summer 2005 campaign had not arrived on site at the time the collocation exercise was performed. The summer 2005 collocation was conducted at the GLC site, and the winter 2006 collocation was conducted at the Chapel site.

We also compared the PAS 2000CE continuous values of pPAHs and the sum of 15 PAHs derived from the 12-hour PUF sampling. These 15 PAHs were a subset of all of the PAHs measured and represent heavier-molecular-weight compounds more likely to be in the particle-bound phase versus the gas phase. Analysis was restricted to data collected at the GLC and School sites to avoid ambiguities of "fresh" PAHs generated by mobile sources near the Chapel site. The correlation coefficient between PAS 2000CE and the sum of 15 PAHs was 0.64. The ratio of PAS to PUF (15 PAHs) was approximately 8.

The PAS 2000CE only samples pPAHs, while both the particle-bound phase and the gas phase are captured in the integrated samples. Separate analyses can be performed on the integrated sample filter and PUF to separate these fractions, but this would double the sampling cost. To address the correspondence between the integrated and continuous PAH methods, we compared the average PAS 2000CE values at the School and GLC sites with the sum of values for compounds primarily found in the particle phase (high-molecular-weight PAHs) with the integrated Chem-Comb samples: chrysene+triphenylene, naphthacene, 4-methylchrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, dimethylbenz[a]anthracene, benzo[e]pyrene, benzo[a]pyrene, perylene, 3-methylchloanthrene, indeno[1,2,3-c,d]pyrene, dibenz-[a,h+a,c]anthracene, benzo[g,h,i]perylene, anthranthrene, and coronene. Some

Table A.12. PAH	H Results (ng/m³) f	rom Collocated	PAH Instruments			
DAS	Sum (T	ımer 2005, GLC otal, 113 Minut	C Site res)	Wint (T	ter 2006, Chape otal, 261 Minut	l Site es)
ID Number	Mean	SD	Median	Mean	SD	Median
20	3.0	2.3	3	6.6	4.7	5
63	0.6	1.1	0	4.8	7.5	3
111				5.6	7.5	4
121	3.0	2.3	3	4.0	2.8	4
168	2.6	1.9	2	7.0	6.0	6
173	3.0	2.4	3	4.0	2.3	4
180				5.9	7.7	4
Total	2.6	0.9		5.4	1.2	
Range	1.4			3		

of the high-molecular-weight PAHs listed above occur in the gas phase as well as the particle-bound phase; in addition, some lower-molecular-weight PAHs that are prevalent in higher concentrations than the high-molecularweight PAHs may have a small fraction in the particlebound phase. The closer (fresher) the aerosol is to its source, the higher its gas-phase portion. For this reason, the Chapel site values were left out of this exercise. The Chapel site is closer to local traffic sources than the other two sites, and this means there was a much greater impact on the portion of PAHs in the semivolatile fraction of the gas phase that is not detected by the PAS than at the other two sites. By averaging over the entire sampling session, the day-to-day variation in the ratio of compounds in the gas phase to compounds in the particle phase can be smoothed out. Figure A.1 displays the average high-molecular-weight



Figure A.1. Comparison of the mean concentration of high-molecularweight PAHs (ng/m³) for the GLC and School sites overall against the corresponding mean PAS PAH reading. By averaging over all of the sampling sessions, the day-to-day variation in the ratio between compounds in the gas phase and compounds in the particle can be smoothed out.



Figure A.2. Comparison of high-molecular-weight PAH concentrations (ng/m³) in the integrated 12-hour samples and the mean PAS samples for the corresponding time periods (winter and summer sampling sessions) for all samples where air mass trajectories were primarily over water.

PAH concentration (in ng/m³) at the GLC and School sites combined, for the three sampling sessions (winter 2005, summer 2005, and winter 2006), against the corresponding average PAS PAH reading.

Figure A.2 presents a comparison of high-molecularweight PAHs in the integrated samples to the mean PAS reading for the corresponding time periods for all samples whose trajectories were primarily over water for the winter and summer periods. This included most lake-wind days and some days when the air mass trajectories were over Lake Huron to the northwest. Our intention was to focus on conditions where most of the high-molecular-weight PAHs would be found in the particle-bound phase, which is detected by the PAS 2000CE, rather than in the gas phase, which the instrument does not detect. Both plots show a distinct relationship between the PAS 2000CE and the integrated PAH samples.

EVALUATION OF DAVIS WEATHER STATION AT THE GLC

During the summer 2005 campaign, we compared data on wind speed and direction obtained from the Davis Weather Station at the GLC with values reported at the Buffalo Airport. Figure A.3 plots the wind speed (mph) reported at the Buffalo Airport against the wind speed reported by the GLC Davis Weather Station. Table A.13 shows the regression output from the data plotted in Figure A.3. Figure A.4 is a histogram showing the distribution of differences in wind speed between the values reported at the GLC and the Buffalo Airport. For 300 hourly averages, the difference in wind speed values between the GLC Davis Weather Station and the Buffalo Airport was -0.88 mph, with a standard error of 0.10 mph, and the *t* value was -8.48, which had a *P* value < 0.001.



Figure A.3. Comparison of wind speeds (mph) between the Buffalo Airport and the GLC Davis Weather Station for summer 2005 sampling session.

Table A.13. Summary Regression Output for the Comparison of Wind Speeds (mph) between the Buffalo Airport and theGLC Davis Weather Station for the Summer 2005 Sampling Session

Regression Statistics

Multiple <i>R</i>	0.94
R ²	0.89
Adjusted R ²	0.89
Standard error	1.80
Observations	300

Analysis of Variance

	Degrees of Freedom	Sum of Squares	Mean Square	F	Significance F			
Regression Residual Total	1 298 299	7491 963 8454	7491 3.23	2317	$1.37 imes 10^{-142}$			
	Coefficients	Standard Error	t	Р	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept × Variable 1	$\begin{array}{c} -0.54 \\ 0.96 \end{array}$	0.21 0.02	$\begin{array}{c} -2.63\\ 48.14\end{array}$	$\begin{array}{c} 0.0089 \\ 1.37 \times 10^{-142} \end{array}$	$\begin{array}{c} -0.95\\ 0.92 \end{array}$	-0.14 1.00	$\begin{array}{c} -0.95\\ 0.92\end{array}$	$\begin{array}{c} -0.14 \\ 1.00 \end{array}$



Figure A.4. Histogram of wind speed differences (mph) between the Buffalo Airport and the GLC site for summer 2005 sampling session.

Figure A.5 plots the wind direction (degrees) reported at the Buffalo Airport against the wind direction reported by the GLC Davis Weather Station. Table A.14 shows the regression output from the data plotted in Figure A.5. Figure A.6 is a histogram showing the distribution of differences in wind direction between the values reported at the GLC Davis Weather Station and the Buffalo Airport. The difference in wind direction obtained from the GLC



Figure A.5. Comparison of wind direction (degrees) between the Buffalo Airport and the GLC Davis Weather Station for summer 2005 sampling session (seven pairs of measurements with one value greater than 0 and the other less than 360 have been removed).

Davis Weather Station and the values reported at the Buffalo Airport for 293 hourly measurements was -10.6° with a standard error of 1.21°, and the *t* value was -8.74 with a *P* value < 0.001. Although the differences in wind speed and wind direction were significant, they were small in magnitude. The GLC Davis Weather Station values were considered comparable to the values reported at the Buffalo Airport for wind speed and wind direction.

 Table A.14.
 Summary Regression Output for the Comparison of Wind Direction (Degrees) between the Buffalo Airport and the GLC Davis Weather Station for the Summer 2005 Sampling Session

Regression Statistics

Multiple R	0.97
R ²	0.93
Adjusted R ²	0.93
Standard error	20.64
Observations	293

Analysis of Variance

	Degrees of Freedom	Sum of Squares	Mean Square	F	Significance F			
Regression Residual	1 291	1,781,167 123,976	17,811,678 426.03	4180	$1.08 imes 10^{-174}$			
Total	292	1,905,143						
	Coefficients	Standard Error	t	Р	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept × Variable 1	-17.54 1.03	3.58 0.016	$\begin{array}{c}-4.90\\64.66\end{array}$	$1.57 imes 10^{-6} \ 1.08 imes 10^{-174}$	$\begin{array}{c}-24.57\\1.00\end{array}$	-10.50 1.06	$\begin{array}{r}-24.58\\1.00\end{array}$	-10.50 1.066



Figure A.6. Histogram of differences in wind speed directions (degrees) between the Buffalo Airport and the GLC Davis Weather Station for summer 2005 sampling session.

APPENDIX AVAILABLE ON THE WEB

Appendix B contains supplemental material not included in the printed report. It is available on the HEI Web site *http://pubs.healtheffects.org*.

Appendix B. Overview, Summary, and Comparison of Integrated Data

ABOUT THE AUTHORS

John D. Spengler, Ph.D., is Akira Yamaguchi Professor of Environmental Health and Human Habitation at the Harvard University School of Public Health. Over the past 30 years, he has conducted research in the areas of personal monitoring, air pollution health effects, aerosol characterization, indoor air pollution, and air pollution meteorology.

Jamson Lwebuga-Mukasa, M.D., Ph.D., is founder, president, and CEO of the Respiratory and Environmental Exposure Consultants LLC, Getzville, New York. At the time of the HEI study, Dr. Lwebuga-Mukasa was associate professor of medicine at the School of Medicine and Biomedical Sciences, University at Buffalo, State University of New York, and director of the Pulmonary and Critical Care Division at Buffalo General Hospital; he also founded and served as director of the Center for Asthma and Environmental Exposure at Buffalo General Hospital. Dr. Lwebuga-Mukasa has
published work on the high prevalence of and morbidity due to asthma and other chronic respiratory illnesses among residents of communities close to Buffalo, New York, and Fort Erie, Ontario, a NAFTA corridor. His current research focuses on the role of combustion-generated particles in human diseases.

Jose Vallarino, M.S., is a project manager working with Dr. Spengler at the Harvard School of Public Health.

Steve Melly, M.A., M.S., is a data analyst/data manager and GIS specialist working with Dr. Spengler at the Harvard School of Public Health.

Steve Chillrud, Ph.D., is Lamont Research Professor at Lamont-Doherty Earth Observatory of Columbia University and codirector of Columbia's Exposure Assessment Core Facility, which supports Columbia's National Institute for Environmental Health Sciences Center for Environmental Health in Northern Manhattan. Dr. Chillrud is known for his work on the analysis and geochemistry of pollutants in air and water and has collaborated with public health investigators on a variety of exposure assessment projects.

Joel Baker, Ph.D., is Port of Tacoma Chair in Environmental Science, science director of the Center for Urban Waters, and professor at the University of Washington–Tacoma. His research team studies the environmental behaviors of anthropogenic organic chemicals in surface waters and the atmosphere, including air-sea exchange, bioaccumulation, and organic aerosol source characterization.

Taeko Minegishi, M.S., is currently a staff scientist at Environmental Health and Engineering, Inc., in Newton, Massachusetts. In 2007, she completed her master's degree research, under the supervision of Dr. Joel Baker, at the University of Maryland.

ABBREVIATIONS AND OTHER TERMS

BEAM	Boston Exposure Assessment in Microenvironments study
BTEX	benzene, toluene, ethylbenzene, and xylenes
BTEX plus	BTEX plus 1,3-butadiene, MTBE, and styrene
CBL	Chesapeake Biological Laboratory
CO	carbon monoxide
CO_2	carbon dioxide

CPC condensation particle counter

DNPH	2,4-dinitrophenylhydrazine
DNSH	dansylhydrazine
EC	elemental carbon
EC-r	elemental carbon estimated by reflectance analysis
EEPS	engine-exhaust-particle spectrometer
EOSHI	Environmental and Occupational Health Sciences Institute
EPA	Environmental Protection Agency (U.S.)
FEV_1	forced expiratory volume in 1 sec
GIS	geographic information system
GLC	Great Lakes Center
GPS	Global Positioning System
HAP	hazardous air pollutant
HEPA	high-efficiency particulate air
HNO_3	nitric acid
HPLC	high-performance liquid chromatography
HR-ICP-MS	high-resolution inductively-coupled- plasma mass spectrometry
HSPH	Harvard School of Public Health
HYSPLIT	Hybrid Single-Particle Lagrangian Integrated Trajectory
IRIS	Integrated Risk Information System
LDEO	Lamont-Doherty Earth Observatory
LOD	limit of detection
MATES-II	California Multiple Air Toxics Exposure Study II
MDL	method detection limit
MSAT	mobile-source air toxic
MTBE	methyl <i>tert</i> -butyl ether
NAFTA	North American Free Trade Agreement
NATA	National-Scale Air Toxics Risk Assessment
NO	nitric oxide
NO_2	nitrogen dioxide
NO_3	nitrate
NO_x	nitrogen oxides
NPAH	nitrogenated polycyclic aromatic hydrocarbon
O_3	ozone
OC	organic carbon
PAH	polycyclic aromatic hydrocarbon
PAS	photoelectric aerosol sensor
PEM	personal exposure monitor

PFA	perfluoroalkoxy	Be	beryllium
PM	particulate matter	Ca	calcium
$PM_{2.5}$	$PM \leq 2.5~\mu m$ in aerodynamic diameter	Cd	cadmium
PM ₁₀	$\text{PM} \leq 10~\mu\text{m}$ in aerodynamic diameter	Co	cobalt
PMF	positive matrix factorization	Cr	chromium
pPAH	particle-bound polycyclic aromatic	Cs	cesium
	hydrocarbon	Cu	copper
PTV	programmable temperature vaporizer	Fe	iron
PUF	polyurethane foam	K	potassium
QF	quartz filter	La	lanthanun
RFA	Request for Applications	Mg	magnesiu
RIOPA	Relationships of Indoor, Outdoor, and	Mn	manganes
	Personal Air study	Mo	molybden
RMSE	root mean square error	Na	sodium
RP	resolving power	Ni	nickel
SCAQMD	South Coast Air Quality Management	Pb	lead
	District	Pt	platinum
SRM	standard reference material	S	sulfur
TEACH	Toxics Exposure Assessment Columbia	Sb	antimony
	and Harvard study	Sc	scandium
UFP	ultrafine particle	Se	selenium
VOC	volatile organic compound	Sn	tin
		Sr	strontium
ELEMENTS		Th	thorium
Ag	silver	Ti	titanium
Al	aluminum	Tl	thallium
As	arsenic	V	vanadium

Ba barium

- m
- m
- ım
- um
- ese
- enum

- y
- m
- m
- vanadium v
- Zn zinc

COMMENTARY Health Review Committee

ΗE

Research Report 158, Air Toxics Exposure from Vehicle Emissions at a U.S. Border Crossing: Buffalo Peace Bridge Study, J. Spengler et al.

INTRODUCTION

Motor vehicles and other combustion sources emit many air toxics that are either known or suspected, with sufficient exposure, to cause adverse health effects. Characterization of exposure to air toxics has been challenging, in part, because of the low ambient levels of individual compounds.

HEI has had a long-standing commitment to improving methods for measuring selected air toxics and increasing our understanding of exposure and health effects. The accompanying Preface to Research Report 158 describes the actions that the U.S. Environmental Protection Agency (EPA*) has taken to regulate emissions of air toxics in general and of mobile-source air toxics (MSATs) specifically. It also describes HEI's rationale for issuing Request for Applications (RFA) 03-1, "Assessing Exposure to Air Toxics," which was to support research to identify and characterize exposure to air toxics at so-called hot spots, areas where concentrations of one or more air toxics are expected to be elevated. HEI's objective through this RFA was to identify hot-spot areas (and populations that live in such areas) that may be appropriate for health effects studies.

In response to RFA 03-1, Dr. John Spengler, of the Harvard School of Public Health in Boston, Massachusetts, submitted an application entitled "Air Toxics Exposure from Vehicular Emissions at a U.S. Border Crossing." Spengler, along with colleagues from other institutions, proposed measuring levels of air toxics and EPA criteria air pollutants in the area surrounding the Peace Bridge in Buffalo, New York, as a potential hot spot for mobile-source emissions.

During the study period, approximately 5000 trucks crossed the border between the United States and Canada daily at this location, each requiring customs and passport inspection. Increased security after the terrorist attacks of September 11, 2001, lengthened the waiting time for vehicles at the border, especially for trucks, which often idled while in traffic or during layovers near the bridge. The investigators proposed measuring ambient levels of air toxics, including those of polycyclic aromatic hydrocarbons (PAHs), a variety of metals, aldehydes, benzene, butadiene, methyl tert-butyl ether (MTBE), and styrene, as well as particulate matter with aerodynamic diameter $\leq 2.5 \ \mu m$ (PM_{2.5}), black carbon, carbon monoxide, nitric oxide, and ozone. Spengler and colleagues hypothesized that the vehicle-related emissions from traffic backed up around the plaza adjacent to the bridge on the U.S. side of the border would result in higher exposures in the community directly downwind of the plaza than in upwind areas, constituting an air toxics hot spot.

On the strength of the location proposed for study as a potential hot spot and Spengler's extensive experience with air toxics measurement, the RFA 03-1 Review Panel ranked the application second among the 17 that HEI received. The Research Committee requested some modifications to this initial proposal, and they agreed to approve the study for funding after review of the revised proposal, with the stipulation that a site visit by Research Committee members take place in conjunction with the pilot phase of the project.

During the summer pilot study in July 2004 and the winter pilot study in January 2005, the investigators sampled air at sites upwind and downwind of the plaza adjacent to the Peace Bridge and tested routes for mobile monitoring. The Research Committee visited the site in August 2004 to audit the first pilot sampling campaign for the feasibility of the investigators' methods and the quality of results and approved funding for the main phase of sampling. Using their experience and data from the two pilot studies, Spengler's team planned and conducted campaigns in summer 2005 and winter 2006 with fixed-site sampling, and they collected information on meteorologic conditions and bridge traffic counts for all sampling days.

This Commentary is intended to aid HEI sponsors and the public by highlighting the strengths and limitations of the study and discussing the HEI Health Review Committee's interpretation of the results.

Dr. John Spengler's 2-year study, "Air Toxics Exposure from Vehicular Emissions at a U.S. Border Crossing," began in April 2004. Total expenditures were \$861,426. The draft Investigators' Report from Spengler and colleagues was received for review in June 2007. A revised report, received in April 2009, was accepted for publication in June 2009. During the review process, the HEI Health Review Committee and the investigators had the opportunity to exchange comments and to clarify issues in both the Investigators' Report and the Review Committee's Commentary.

This document has not been reviewed by public or private party institutions, including those that support the Health Effects Institute; therefore, it may not reflect the views of these parties, and no endorsements by them should be inferred.

^{*} A list of abbreviations and other terms appears at the end of the Investigators' Report.

STUDY AIMS

Spengler and his research team hypothesized that the traffic backed up on the U.S. side of the Peace Bridge results in high levels of motor vehicle emissions, which then blow with prevailing winds into the nearby residential areas. They argued that these emissions, particularly emissions from diesel-powered trucks waiting for customs inspection, may locally elevate levels of MSATs, creating a hot spot of emissions and exposure. To explore this hypothesis, the authors pursued three specific aims:

- 1. Characterize the ambient levels of air contaminants including MSATs across a series of days to obtain upwind and downwind concentrations in the vicinity of the Peace Bridge plaza.
- 2. Examine the relation between traffic at the Peace Bridge and pollutant concentrations in ambient air.
- 3. Explore geographic patterns of ambient air pollutants.

STUDY DESIGN AND METHODS

The study area is centered on the Peace Bridge plaza in Buffalo, on the U.S. side of one of the nation's busiest border crossings. At the beginning of the study, the 17-acre plaza comprised the U.S. Customs Building, a customs inspection and holding area, tollbooths, a duty-free store, the Peace Bridge Authority Administration Building, and parking space. Residential and commercial areas abut the plaza to the east, north, and south, with Lake Erie and the Niagara River to the west. The Commentary Figure shows the study area. Typical weekly traffic counts on the Peace Bridge are shown in Figure 3 of the Investigators' Report.

PILOT STUDIES

To establish fixed sampling sites representative of downwind and upwind conditions, assess wind and weather patterns relevant to the transport of pollutants and MSATs, and investigate routes for mobile monitoring, Spengler's team conducted pilot studies in summer 2004 and winter 2005.

Prevailing wind directions were determined from 10 years of weather records obtained from the Buffalo Niagara International Airport, northeast of the plaza. The authors' analysis of these data demonstrated that the wind blows from the west side of the plaza, off Lake Erie and the Niagara River, about 45% of the time (lake winds) and from the east on the Buffalo side of the plaza (city winds) about 31% of the time. A representative wind rose for this area may be seen in Figure 2 of the Investigators' Report.

Based on the wind analysis, the investigators established two fixed sampling sites, with integrated sampling equipment and real-time continuous monitoring equipment (taking readings every minute), during the summer 2004 pilot study: one to the southwest of the plaza at the Great Lakes Center (GLC site), which they describe as an upwind site, and the other in front of the Episcopal Church Home (Chapel site), adjacent to the east side of the plaza, which they describe as a downwind site. They also tested routes, equipment, and protocols for mobile monitoring intended to determine the spatial variability of pollutant levels around the Peace Bridge plaza area, including the Buffalo neighborhood to the east and downwind of the plaza.

During the winter 2005 pilot study, the researchers added a third fixed sampling site in the neighborhood to the east of the plaza (School site), to reflect potential pollutant exposure of the residents. They also established the integrated sampling schedule of 12 hours per weekday and weeknight, with 48-hour weekend samples, which was used in subsequent campaigns, and they continued to experiment to determine the best routes, schedules, and equipment for their mobile monitoring program to characterize the spatial variation of MSAT levels near the plaza.

MAIN SAMPLING CAMPAIGNS

After the two pilot studies, Spengler's team conducted two larger-scale sampling campaigns featuring both fixedsite and mobile monitoring components. The team simultaneously collected samples at all three fixed sampling sites for two weeks in July 2005 and two weeks in January 2006. Before their summer 2005 campaign, the tollbooths in the Peace Bridge plaza were relocated to the Canadian side of the bridge, which changed the location and number of idling vehicles, and this should be considered when comparing data from the pilot studies with those from the main sampling campaigns.

The three locations used for fixed-site sampling in the winter 2005 pilot study, the GLC site, the Chapel site, and the School site (shown on the map in the Commentary Figure), were retained for the main sampling campaigns in summer 2005 and winter 2006. Weather information for the fixed sampling locations was collected at the GLC site using a Davis Weather Station, and the prevailing wind direction at the GLC site was assumed to be representative of conditions in the entire Peace Bridge plaza area during the sampling campaigns. The research team obtained



Commentary Figure. The study area comprised the Peace Bridge plaza and the three fixed sampling sites (GLC, Chapel, and School), as well as Bird Island Pier and the neighborhood of west Buffalo (boxed), where routes for mobile monitoring were located. (This map appears as Figure 1 in the Investigators' Report.)

hourly counts of passenger vehicles, buses, and trucks crossing the bridge in each direction from the Peace Bridge Authority. An overview of the sampling dates and locations and the elements and compounds sampled is presented in Commentary Table 1.

A summary of the sampling instruments and equipment and analytical methods for each type of sample collected during the study is presented in Commentary Table 2; they are described in more detail in the Investigators' Report. The research team collected 12-hour integrated samples on weekdays (7:00 AM to 7:00 PM) and weeknights (7:00 PM to 7:00 AM) and 48-hour integrated samples over each weekend during the campaigns. In addition, two 60-hour composite samples were collected over five 12-hour weekdays and five 12-hour weekday nights for each week of each sampling campaign. When available, real-time continuous monitors collecting data every minute were also placed at the three fixed sampling sites. These instruments measured ozone (O_3) , nitrogen oxides (NO_x) , $PM_{2.5}$, carbon dioxide (CO₂), ultrafine particles (UFPs, particles $< 0.1 \,\mu m$ in aerodynamic diameter), and particle-bound PAHs (pPAHs). Problems with the equipment and data storage limited the available sampling data for O_3 and NO_x , in particular, and instrument downtime limited the amount of directly comparable data for upwind and downwind measurements for all measured species.

Each of the main two-week sampling campaigns included a mobile monitoring component. Dr. Spengler designed the mobile monitoring campaign to assess the spatial variability of levels of selected pollutants in the neighborhood adjacent to the Peace Bridge plaza. Researchers from Harvard School of Public Health and the University at Buffalo, State University of New York, recruited staff to wear backpacks containing air monitoring equipment while walking along designated routes near the plaza. The staff also carried GPS (Global Positioning System) units that logged their progress along the routes during sampling. The four designated mobile monitoring routes are displayed in Investigators' Report Figure 4, and a summary of the mobile sampling equipment and the sampled species is presented in Commentary Table 2.

STATISTICAL METHODS AND DATA ANALYSIS

Primary analysis of the sampling data focused on comparing and contrasting pollutant levels measured at the GLC and Chapel sites, on opposite sides of the Peace Bridge plaza. According to the prevailing winds in the area, the GLC site was typically upwind of the plaza and the Chapel site was typically downwind, as determined from weather data before the study and verified during the sampling campaigns. Sampling data from these two sites were further compared with data from the School site representing pollutant levels in the residential area farther downwind of the Peace Bridge plaza, and results for all three sites were also stratified by season (summer and winter).

The investigators note that they selected statistical methods for summarizing data according to the forms of the data distributions. Thus they report measures of central tendency and data variability according to whether the distributions of measured values for a given pollutant were normally or lognormally distributed, log-transformed, nonparametric, and so forth. This accounts for the variety of different statistics for different measured species of pollutants reported. Detailed information on how data from integrated sampling were handled is presented in Appendix A of the Investigators' Report, along with data quality statistics.

The investigators were most interested in the levels of MSATs, which they expected to be elevated as a result of the traffic congestion in the Peace Bridge plaza area. They measured levels of a large number of compounds that



Commentary Table 1. Overview of Sampling Campaigns			
Monitoring Type / Pollutants Measured ^a	Campaign (Sampling Dates)	Locations	
Fixed-Site, Integrated			
PM ₁₀ , PM _{2.5} , EC-r, elements, VOCs, PAHs, NPAHs	Summer 2004 (June 20–26) Winter 2005 (January 9–18) Summer 2005 (July 18–30) Winter 2006 (January 6–20)	Chapel, GLC Chapel, GLC, School Chapel, GLC, School Chapel, GLC, School	
Fixed-Site, Continuous			
PM _{2.5} , UFPs, pPAHs, O ₃ , CO ₂ , NO _x	Summer 2004 (June 20–26) Winter 2005 (January 9–18) Summer 2005 (July 18–30) Winter 2006 (January 6–20)	Chapel, GLC Chapel, GLC, School Chapel, GLC, School Chapel, GLC, School	
Mobile			
UFPs, pPAHs	Summer 2004 (June 20–26) Winter 2005 (January 9–18) Summer 2005 (July 18–30) Winter 2006 (January 6–20)	Routes under development Routes 1, 2, 3, 4 ^b Routes 1, 2, 3, 4 ^b Routes 1, 2, 3, 4 ^b	

^a See Table 6 of the Investigators' Report for a complete list of elements, VOCs, PAHs, and NPAHs measured.

^b See Figure 4 of the Investigators' Report for a map of the mobile monitoring routes.

might be expected to be in exhaust from diesel and gasoline vehicles, including volatile organic compounds (VOCs), PAHs, and nitrogenated PAHs (NPAHs). The Investigators' Report presents extensive comparisons of data from samples designated as upwind or downwind of the plaza at the time of measurement. Traffic counts from the Peace Bridge were matched to all ambient air measurements. Where appropriate, traffic counts were averaged to match the interval of the integrated pollutant samples. Further comparisons were made to assess the degree of correlation among measurements of selected elements and compounds (and summed values for specific groupings of compounds), typically using Pearson correlations or *t*-test statistics on log-transformed data. Strongly correlated levels may indicate emissions from a common source.

Measurements of a variety of elements from the fixed-site sampling were further analyzed by principal component analysis. In this analysis various species are grouped according to how their levels tend to increase and decrease together over time, possibly indicating a common source or sources. Spengler's team used principal component analysis to evaluate the levels of groups of measured elements in relation to traffic counts for passenger cars and diesel vehicles (trucks and buses) and to wind conditions during sampling. Industrial and residential combustion are other potential sources for groups of elements measured at the three fixed sampling sites. The results of principal component analyses were compared between sites to explore the differences in source profiles and wind conditions. The team also employed a statistical procedure called positive matrix factorization (PMF) to examine the patterns in measured levels of different groups of PAHs, NPAHs, and elements relative to a source measurement (traffic counts at the Peace Bridge). PMF analysis of the elemental data sets did not yield additional information beyond that provided by the principal component analysis.

Spengler's team used the real-time mobile monitoring data to assess the distribution of pollutants on four routes: three along streets in the neighborhood adjacent to and downwind of the Peace Bridge plaza, and one along Bird Island Pier to the west and upwind of the plaza. GPS coordinates were converted to spatial data sets using geographic information system (GIS) software, merged with a standard data set of streets, then linked to measurements made by study staff during the summer and winter campaigns, to determine levels of criteria air pollutants and MSATs at specific times and locations on the routes. They were thus able to map pollutant levels along the routes.

Commentary Tuble 2. Overview	or oumpring	includes and includes a second s
Monitoring Type / Equipment	Pollutant	Analysis Method
Fixed-Site, Integrated		
Harvard impactor	PM_{10}	Gravimetric analysis
Modified Harvard impactor with 2-stage PUF impaction heads, Teflon filters	PM _{2.5} EC-r Elements	Gravimetric analysis EEL smoke stain reflectometer Magnetic sector high-resolution inductively-coupled-plasma mass spectrometry (HR-ICP-MS)
Stainless steel, multibed thermal desorption tubes with Carbopack B, Carbopack X, and Carboxen 1001	VOCs	Gas chromatography with automatic thermal desorber (EPA Method TO-17)
DNPH-coated silica cartridges	Carbonyls	High-performance liquid chromatography with ultraviolet detection
Mist chamber	Acrolein	Gas chromatography using OSHA Method 52 for acrolein
ChemComb Organic Sampler with 2.5-µm inlet, prefired quartz filter, and glass sleeve with Supelpak-2B between two PUF pads	PAHs NPAHs	Concentration in hexane; identification and quantification using gas chromatography with mass spectroscopy in electron ionization mode Extraction from PAH concentrate using aminopropyl solid-phase extraction cartridge and liquid chromatography; gas chromatography with mass spectroscopy in negative chemical ionization mode
Fixed-Site, Continuous		
DustTrak Aerosol Monitor	$PM_{2.5}$	Laser-photometer
TSI P-Trak Model 8525	UFPs	Laser-photometer with isopropyl alcohol saturation and condensation
EchoChem PAS 2000CE	pPAHs	Photoelectric aerosol sensor with krypton-bromide excimer laser
2B Technologies Model 202 Ozone Monitor	O ₃	Ultraviolet light absorption
2B Technologies Model 400 Nitric Oxide Monitor	NO	Ultraviolet light absorption of $\rm O_3$ (before and after reaction with NO in sample stream)
Mobile		
TSI P-Trak	UFPs	Laser-photometer with isopropyl alcohol saturation and condensation
EchoChem PAS 2000CE	pPAHs	Photoelectric aerosol sensor with krypton-bromide excimer laser

Commentary Table 2. Overview of Sampling Methods

SUMMARY OF RESULTS

Spengler and his team discuss most of their results by drawing comparisons between measurements at sites that were predominantly upwind and downwind relative to the Peace Bridge plaza. Accounting for wind direction, they drew inferences about the likelihood that these measurements were related to the volume and composition of traffic traversing the Peace Bridge plaza. When comparing measurements around the study area, they also note which of the measured species are typically associated with traffic emissions, particularly diesel emissions. Notable sampling results are discussed here, and specific summary statistics for these results appear in Commentary Table 3. The authors provide further comparative analyses of differences related to the individual sampling campaign, season, time of day, and wind direction, as warranted, in the text of the Investigators' Report.

CHARACTERIZATION OF POLLUTANTS IN THE PEACE BRIDGE PLAZA AREA

Spengler and his team made extensive measurements during this study. Of greatest interest are the comparative summary statistics for measurements of several different

		Value for Fixed-Site Sampling Location ^b		
Pollutant	Summary Statistic	Chapel	School	GLC
PM ₁₀ (μg/m ³)	Mean	23.8	22.6	19.1
$PM_{2.5} (\mu g/m^3)$	Mean	15.7	14.6	13.4
EC-r (% in PM _{2.5})	Mean	17.0	7.6	5.4
VOCs (µg/m³)				
BTEX	Median	6.2	7.1	2.6
BTEX plus	Median	6.4	7.3	2.8
Benzene	Median	1.1	1.1	0.62
Chlorinated compounds	Median	0.99	1.2	0.85
Formaldehyde	Median	0.64	0.85	0.50
Acetaldehyde	Median	1.1	1.5	1.6
Acetone	Median	1.5	1.9	2.4
Elements (ng/m ³)				
Ca	Mean	79.0	40.0	47.0
Cr	Mean	0.72	1.1	0.19
Mn	Mean	2.3	1.9	1.9
Fe	Mean	88.0	55.0	57.0
Cu	Mean	5.6	3.4	1.7
Sb	Mean	0.79	0.45	0.52

Commentary Table 3. Summary of Selected Fixed-Site 12-Hour Daytime Integrated Sampling Results^a

a All summary statistics in this table were calculated using the combined results of sampling campaigns in winter 2005, summer 2005, and winter 2006.

^b Values appear in Appendix B of the Investigators' Report (available on the HEI Web site): PM_{10} and $PM_{2.5}$ in Table B.1, VOCs in Table B.5, and elements in Table B.7. The mean percentages of EC-r in $PM_{2.5}$ appear in the Investigators' Report Results.

classes of MSATs - particulate matter, VOCs and carbonyls, elements, PAHs, and NPAHs - and measurements from continuous sampling of PM, UFPs, pPAHs, and gaseous pollutants. They report and compare mean 12-hour daytime levels for each fixed sampling site for the winter 2005, summer 2005, and winter 2006 campaigns combined. For both PM_{10} and $PM_{2.5}$, the mean daytime levels were highest at the Chapel site (typically downwind of the plaza), and higher at the residential School site than at the upwind GLC site. The fraction of elemental carbon (EC) present in the collected PM_{2.5} followed the same pattern as the PM_{2.5} concentrations, with the median EC fraction at the Chapel site exceeding those at the School and GLC sites by a large margin (Commentary Table 3). The authors note that these results are consistent with motor vehicle emissions, and with their hypothesis that traffic at the Peace Bridge plaza is a significant source of pollution in the study area.

The investigators combined measurements for classes of VOCs, carbonyls, and aldehydes into composite variables for a comparative analysis of study results. These summary categories are presented in Table 13 of the Investigators' Report. Approximately two thirds of the sampling days were classified as having lake-wind conditions that resulted in the GLC site being directly upwind, the Chapel site being directly downwind, and the School site being less directly downwind of the Peace Bridge plaza. The investigators propose, therefore, that the higher levels of compounds measured at the Chapel site relative to the other sites in summary comparisons indicate that traffic at the plaza was a source for these pollutants.

BTEX, BTEX Plus, and Chlorinated Compounds

The authors created composite variables to represent benzene, toluene, ethylbenzene, and xylenes (BTEX), the BTEX compounds plus 1,3-butadiene, MTBE, and styrene (BTEX plus), and the sum of five chlorinated compounds. Overall mean and median levels of BTEX in weekday 12-hour samples were highest at the School site, followed by the Chapel site, and then the GLC site (Table B.5 in Appendix B, available on the HEI Web site). The mean and median levels of BTEX plus were similar to the BTEX levels. Overall mean and median levels of the chlorinated compounds category were similar across all three fixed sampling sites, indicating, as the authors suggest, that the composition of the regional air mass, and not local sources, was predominantly responsible for the levels of these compounds.

Benzene, Formaldehyde, and Acetaldehyde

Median davtime benzene levels were lowest by far at the GLC site, with measurements at the School and Chapel sites demonstrating similar and higher levels. Overall mean and median daytime formaldehyde levels were highest at the School site, followed by the Chapel site, and then the GLC site. The authors note also that formaldehyde levels at the School site were five times as high in the summer as they were in the winter, while at the GLC site, winter levels were twice as high as summer levels. This seasonal variation highlights the importance of photochemical reactions for pollutant levels, as was noted in HEI's report on Mobile-Source Air Toxics (HEI Air Toxics Review Panel 2007). Acetaldehyde levels were highest at the GLC site, nearly as high at the School site, and much lower at the Chapel site. The authors note that wind patterns and urban area emissions likely resulted in the higher measured levels of acetaldehydes at the GLC site than at the other two sites in the winter, but not in the summer. Acetone levels for all daytime samples were fairly similar across all three sites, although they were slightly elevated at the GLC site. Overall, the patterns of measured levels for these VOCs present a mixed picture of potential sources, with downwind benzene and formaldehyde levels appearing to be associated with activities at the Peace Bridge plaza, and with acetone and acetaldehyde levels deriving from other urban sources.

Elements

Spengler's team analyzed fixed-site PM_{2.5} samples for 28 different elements. Of the elements detected, the summary levels of 22 elements did not vary importantly across the three fixed sampling sites, implying either regional emissions or natural sources. Elements with little or no variation in their concentrations between sites included the crustal elements sodium, magnesium, aluminum, potassium, titanium, and zinc; elements associated with fossil fuel (coal and oil) combustion, sulfur, arsenic, selenium, vanadium, and nickel; and the elements beryllium, silver, cadmium, tin, cesium, and thallium. Summary levels for the 12-hour weekday daytime samples of these elements are found in Table B.7 (Appendix B). Although the elements related to fossil fuel combustion could be derived from the

diesel emissions of truck traffic, the authors hypothesize that in this study the dominant sources for these elements may have been regional, such as electrical power plants and emissions from the New York City area.

Mean daytime weekday levels of elements that were, on average, present at higher levels at the Chapel site than at the other sites are presented in Commentary Table 3. These elements are calcium, chromium, manganese, iron, copper, and antimony. As antimony, manganese, and hexavalent chromium are MSATs, and iron and copper could also be derived from mobile sources, the authors suggest that the higher levels at the downwind Chapel site appear to be related to emissions from traffic transiting the Peace Bridge plaza during the sampling campaigns (although iron is also present in particulate matter from crustal sources). Levels of these elements at the School site were either similar to those at the GLC site, or intermediate between those at the Chapel and GLC sites, further implicating traffic emissions at the plaza as a possible source of these elements given predominant wind patterns during the sampling campaigns. Thus the overall results for analysis of elements in PM_{2.5} samples are suggestive of possible traffic sources, but not conclusive.

PAHs

Spengler's team noted important contrasts in levels of PAHs and NPAHs across the three fixed sampling sites, as well as some important seasonal differences. They divided the 38 detected PAH compounds included in the PMF analysis into three groups by molecular weight: lightweight compounds, such as fluorene; medium-molecular-weight compounds, including many methylated PAHs; and PAHs heavier than benzo[k]fluoranthene, including pyrene. Results for the 12-hour weekday daytime sampling for PAHs are presented in Table B.11 (Appendix B).

The investigators found that for all but a few of the PAH compounds, concentrations at the Chapel site were highest when winds were classified as "city/other winds" — that is, when the site was downwind of the city of Buffalo and upwind of the Peace Bridge plaza (Figures 20–22 in the Investigators' Report). For compounds typically associated with combustion emissions, such as naphthalene and benzo[*a*]pyrene, city-wind conditions produced overall mean concentration ratios between the Chapel and GLC sites ranging from 1.1 to 1.4 (although the authors note that under lake-wind conditions concentrations of light PAHs like naphthalene were up to ten times as high at the Chapel site). These findings imply that regional traffic emissions, fossil fuel combustion, and such urban infrastructural features as asphalt surfaces and tar-based roofing materials

could contribute nearly as much PAH to the ambient air as traffic emissions from the Peace Bridge plaza itself under common wind and weather conditions in the area.

The light PAHs, such as naphthalene and methylated naphthalene compounds, were consistently highest at the Chapel site, followed by the School site and GLC site (Table B.11 in Appendix B). This pattern of downwind enrichment, which indicates that traffic emissions at the plaza were a source, was more pronounced in the summer, when traffic levels were higher and temperatures were warmer. Other areal sources of PAH, such as emissions from roofing materials and roadway asphalt, coal and biomass combustion, and tars and lubricants, may have complicated these interpretations.

NPAHs

Overall concentrations of 14 NPAHs at the GLC and Chapel sites under lake-wind conditions are compared in Investigators' Report Figure 25. Median ratios for measurements at these sites demonstrate that the levels of some of the NPAHs at the Chapel site were nearly tenfold those at the GLC site. This enrichment, along with the known relationship between diesel combustion and these compounds, indicates that traffic at the Peace Bridge plaza may be a major local source for these compounds. 3-Nitrofluoranthene is the sole exception since it was detected at both sites only during winds classified as city/other, implying a city-based source for this compound.

Daytime and nighttime mean PAH and NPAH concentrations measured during one week in summer 2005 using Graseby Andersen high-volume samplers revealed some important contrasts, as shown in Investigators' Report Table 21. For all PAHs combined and for all NPAHs combined, concentrations were highest at the neighborhood School site, followed by the Chapel site adjacent to the Peace Bridge plaza. At the School site, the PAH concentrations were higher during the day, while the NPAH concentrations were higher at night. At both the Chapel and GLC sites, PAH concentrations lacked any consistent diurnal trends, while NPAH concentrations were consistently higher at night.

Continuous UFP Measurements

Results from 600 hours of 10-minute average UFP counts at each of the three fixed sampling sites in the winter 2005, summer 2005, and winter 2006 campaigns combined are presented in Investigators' Report Table 22. A seasonal comparison of measurements from the summer 2005 and winter 2006 campaigns is shown in Investigators' Report Table 23. The mean UFP count was substantially higher at the Chapel site, followed by the School and GLC sites. The relative differences between the

UFP counts at the sites were similar in winter and summer measurements, with all three sites recording higher UFP counts in the winter. As with any UFP measurements, the tendency for extremely small particles to combine into larger agglomerated particles at some distance from the source must be considered. Such agglomeration is known to result in lower number counts in smaller UFP size ranges and lower overall UFP number counts at increasing distances from the source, as discussed in the text. Therefore, overall UFP number counts would be expected to be higher at the Chapel site near the Peace Bridge plaza and lower at the more distant School and GLC sites, even if lake-wind and city/other-wind conditions were equally represented in the sampling campaigns. This pattern is apparent in the sampling data, since the nearest downwind site (Chapel) recorded the highest number counts of UFPs, followed by the more distant downwind site (School) and the upwind GLC site. The differences between UFP number counts measured at the Chapel and School sites could be due, in part, to this particle agglomeration phenomenon.

Continuous PM_{2.5} Measurements

Concentrations of $PM_{2.5}$ are summarized as 10-minute averages in Investigators' Report Table 26. In contrast to the UFP count results, the mean $PM_{2.5}$ concentrations, as well as the percentile distributions and standard deviations for the data, are relatively uniform at the three sites. This pattern indicates that the $PM_{2.5}$ levels measured in the study area may be dominated by well-documented regional air pollution patterns and not the local sources associated with either the Peace Bridge plaza or the city of Buffalo.

Continuous pPAH Measurements

Ten-minute average concentrations of pPAHs in PM_{2.5} at the three sampling sites, shown in Investigators' Report Table 24, demonstrate a similar pattern to the UFP counts. Although the GLC site registered the highest maximum concentration, it had the lowest mean concentration, indicating that a few high readings dominated the summary statistics for pPAHs at the GLC site. The highest mean concentration was at the Chapel site, followed by the School and GLC sites. Twelve-hour average pPAH concentrations for daytime and nighttime sampling, displayed in Investigators' Report Table 25, demonstrate the same pattern, with substantially higher mean concentrations recorded both day and night at the Chapel site than at the School and GLC sites. It is important to note that these measurements are concentrations of pPAH in PM_{2.5} and reflect an enrichment of pPAH in those samples, since

 $\mathrm{PM}_{2.5}$ levels did not vary between the three sites. These results support the investigators' hypothesis that there is a relationship between diesel-engine traffic and downwind exposures, since pPAH concentrations in $\mathrm{PM}_{2.5}$ were highest at the site that was most frequently downwind of the expected sources.

Continuous Gaseous Pollutant Measurements

Spengler's team encountered difficulties with the continuous sampling equipment used to obtain NO_x and O₃ measurements. Owing to flawed software for O₃ data storage, which was not discovered until the end of the summer 2005 sampling campaign, most of the data were not reliable, and there were insufficient data for O₃ from the summer 2005 campaign for analysis. The O₃ data from the winter 2006 campaign were not reported because the levels were frequently at or near the limit of detection. The NO_x monitors were prototypes with serious reliability issues and did not provide reliable data.

RELATIONSHIP OF TRAFFIC AT THE PEACE BRIDGE TO POLLUTANT CONCENTRATIONS IN AMBIENT AIR

Spengler's team compared measurement data obtained with lake winds (the predominant wind direction) and with winds blowing over the city of Buffalo toward the lake, or from other directions, to assess the plausibility of a relationship between traffic at the Peace Bridge plaza and levels of airborne pollutants at the Chapel and GLC sites. They further applied models from principal component analysis for elements and PMF models for PAH and NPAH compounds in order to statistically assess this relationship. Out of a total of 24 possible 12-hour sampling periods, 15 samples were collected under lake-wind conditions, and 9 under city/other-wind conditions, consistent with historical prevailing wind patterns for the area. The investigators believe that the proportional number of samples in each wind-type category was sufficient for contrasting measured pollutant levels during different wind conditions at the three fixed sampling sites.

Pairing samples by sampling period and calculating the ratio of measured levels at the Chapel site to those at the GLC site, the authors ranked the results for EC reflectance (EC-r) and also plotted those for the total PAHs (sum of all PAH concentrations), for the 22 sampling periods with valid measurements in Investigators' Report Figure 15 (see also Table 12). The highest Chapel-to-GLC ratios for EC-r (right end of the *x* axis) are associated with lake-wind events, which would enrich levels of EC-r at the Chapel site if they were the result of mobile-source emissions at the plaza. The lower ratios are predominantly for city/other-wind events, which would enrich the levels of EC-r at the GLC site and

thus lower the Chapel-to-GLC ratios. In general, the measurements for the sum of PAHs show the same trend of higher Chapel-to-GLC ratios with lake winds. Ratios for the levels of elements measured at the Chapel and GLC sites, shown in Investigators' Report Figure 18, demonstrate a pattern of higher levels of calcium, iron, zinc, chromium, copper, aluminum, antimony, strontium, cobalt, titanium, manganese, magnesium, and EC-r at the Chapel site on lake-wind days, consistent with the investigators' hypothesis.

An analysis of correlation between levels of VOCs, aldehydes, and chlorinated compounds for samples from the Chapel and GLC sites was less conclusive overall (Table 13 in the Investigators' Report). Levels of BTEX compounds at the two sites were not correlated for lakewind events, but highly correlated for city/other-wind events. Levels of the BTEX plus summary category at the two sites, and of all but one individual component of that category (MTBE), were strongly correlated with wind direction: higher levels at the Chapel site were associated with lake-wind events, and higher levels at the GLC site were associated with city/other-wind events. Comparisons between the two sites did not show any enrichment of chlorinated compounds or carbonyls downwind of the Peace Bridge.

Principal component analysis using measurements of 25 elements in the complete data set, classified by sampling site and wind direction, resulted in the grouping of elements with similarly varying levels into five factors or components. One component contained elements associated with both coal combustion and traffic-related emissions. Another component included, among other elements, nickel and vanadium, which are associated with residual fuel oil combustion. A third component contained magnesium, aluminum, and calcium, which are indicative of crustal material, while the fourth and fifth components were not easily associated with known sources. Specific results of this analysis for the Chapel site under lake-wind conditions are presented in Investigators' Report Table 18. The principal component analyses indicated that measured levels of a group of air toxics associated with traffic emissions are higher at the Chapel site when it is downwind of the Peace Bridge plaza (relative to levels measured when it is upwind and to levels of other components), suggesting that traffic emissions are a substantial source of air toxics in the study area.

PMF was applied to site-specific PAH results from the winter 2005, summer 2005, and winter 2006 sampling sessions. The analysis divided the PAHs into light, medium, and heavy profiles based on molecular weight (shown in Figures 29 and 30 of the Investigators' Report). The light PAH profile was more abundant at the GLC site than at the School or Chapel sites. The medium PAH profile was not common at the GLC site, but was dominant at the School and Chapel sites in the summer and about five times higher at the School site. Heavy PAHs were relatively abundant at all sites in the winter and could be associated with traffic sources or with the combined effects of low temperature (lack of volatilization of PAHs to lighter profiles) and increased coal and oil combustion for industrial and residential heating. These patterns of PAH concentrations across sites that vary with PAH weight class and sampling campaign season indicate the presence of a complex mixture of PAH sources in the urban environment, seasonal changes in sources, and varying interactions of PAHs with weather conditions.

SPATIAL PATTERNS OF POLLUTANTS IN A NEIGHBORHOOD NEAR THE PEACE BRIDGE PLAZA

Spengler's team developed an innovative mobile monitoring scheme for measuring neighborhood exposures. The UFP and pPAH levels, measured under different wind conditions at different times of day, are depicted on maps of the neighborhood study area in Investigators' Report Figures 53 through 61. Busy intersections and possible combustion sources in the neighborhood probably contributed to the UFP and pPAH levels, as indicated by sampling results under city-wind conditions. The investigators suggest that the maps showing UFP and pPAH levels verify the general association between higher concentrations and distance from the Peace Bridge plaza under lake-wind conditions (pPAH levels on winter mornings being one exception).

HEI HEALTH REVIEW COMMITTEE EVALUATION

The HEI Health Review Committee undertook an independent and detailed review of the final report by Spengler and colleagues and noted the following points.

METHODS

The Review Committee considered the methods that Spengler and his research team used to measure pollutants in a variety of ways to be sound and generally well implemented, and they were satisfied with the large number of elements and compounds that were measured. The pilot studies provided valuable background for designing an effective sampling campaign for the main study. The Review Committee noted that the sampling campaigns were well designed and conducted, and the data were of high quality overall. They also commented that the mobile monitoring scheme using GPS units and real-time measuring equipment carried in backpacks to study spatial distributions of pollutants near the Peace Bridge plaza was innovative and successful. This effort complemented the fixed-site sampling campaigns by more finely evaluating potential source impacts on local variations in pollutant levels, particularly within a residential neighborhood adjacent to the Peace Bridge plaza.

STATISTICAL ANALYSIS METHODS

The Review Committee found that the investigators' team used appropriate methods to compare and contrast ambient pollutant levels at the three sites. However, the Committee viewed the investigators' source apportionment analysis as largely exploratory, given the relatively small number of samples available for analysis. They expressed concern that the investigators provided little justification for the choice of principal component analysis for the elemental data and PMF for the PAH and NPAH data, as opposed to using other available methods.

STUDY DESIGN

The sampling campaigns and data sets were thorough and comprehensive. The Committee felt, however, that the overall quantity of data for any given element or compound or sampled species was still too limited to produce adequate statistical power for more advanced analyses such as complicated regressions or source apportionment studies. It was also difficult to fully combine data sets between the pilot studies and the main sampling campaigns because the Peace Bridge plaza was under construction and the tollbooth area was relocated to the Canadian side of the bridge before the summer 2005 campaign. This further reduced the size of the data set for any given statistical analysis, limiting the investigators' ability to make statistically sophisticated comparisons that would supplement their characterization of the air quality around the plaza.

Aside from these concerns, the Review Committee felt that the study design was sound and that the study was well conducted. Moreover, they noted that the study made some important innovations and contributions to study design for research intended to identify potential hot spots of emissions, particularly from traffic and roadway sources. Innovations included the use of multiple years of data on prevailing wind patterns to determine the location of fixed sampling sites relative to the Peace Bridge plaza before the study began (instead of sampling in convenient locations and recording wind directions post hoc), and the use of study staff walking fixed routes for intensive local monitoring of specific air pollutants in the adjacent neighborhood. Collection of both continuous and integrated samples at the same location was another strength of the study.

RESULTS

The Review Committee believed that Spengler's team made a thorough assessment of the concentrations of MSATs surrounding the Peace Bridge plaza. They felt that the resulting measurements were sound and that the summary measurements by season and sampling campaign adequately described the air quality in the area. The summary results for upwind and downwind locations, as well as for the individual sites, are therefore the best indicators of relationships between traffic at the plaza and downwind exposure and are the most important results from this study. The movement of the tollbooths, however, potentially reduced the overall mean MSAT levels that were calculated across the time period before and after the plaza reconstruction. The Review Committee noted that any conclusions about the relationship between traffic and pollutant levels beyond exploration of patterns of wind direction, traffic composition, and measured levels of selected traffic-related elements and compounds should be interpreted with caution.

The innovative mobile monitoring program provided an assessment of pollutant levels in the nearby neighborhood, and the Committee generally supported the value of these GIS-based results. The Committee did express some concern that local traffic on the streets, particularly the busy thoroughfares that had the highest pollutant concentrations, may have had a greater influence on exposure levels measured by the study staff than the Peace Bridge plaza traffic itself, especially for species known to decay at a short distance from the emission source. Nonetheless, this assessment of traffic and pollutant concentrations is important to understanding the air quality in neighborhoods that are usually downwind of the Peace Bridge plaza, where local residents have reported adverse health effects (Lwebuga-Mukasa et al. 2004). The measurement data set that Spengler and his team developed for this study is important to understanding local contributions to selected MSATs in areas where people live and work compared with exposures in an area primarily used for recreation (the Bird Island Pier route). This study also demonstrated that a concentration of mobile-source emissions, combined with relatively consistent meteorology, could result in areas with elevated concentrations that are dependent on wind conditions. Thus the results of this study indicate that wind speed and direction should be considered in any study characterizing a putative hot spot.

In the final analysis, the Review Committee and the investigators were somewhat at odds about whether the Peace Bridge plaza constituted a hot spot of MSAT emissions and potentially high community exposure. According to Spengler and his colleagues, the Peace Bridge plaza, at the time the study was conducted, met the definition of a hot spot as a location with pollutant concentrations higher than those of the surrounding area. The conclusions to the Investigators' Report state that "The Peace Bridge plaza and the adjacent neighborhood represent a classic mobile-source hot spot. Congestion of car, bus, and truck traffic results in a persistent source of emissions. Persistent southwest to northwest winds increase PM and EC. We have presented evidence that many compounds emitted directly from cars and heavy-duty vehicles were substantially elevated immediately downwind of the plaza."

While the Review Committee took note of the authors' interpretation, it had two reservations regarding this conclusion. First, although differences in methods, instruments, and other conditions make it difficult to compare results across studies, the levels of MSATs reported in this study were not high relative to levels of MSATs measured at other congested U.S. locations. The authors note this in their comparison of the measurements for a variety of elements and compounds with those in the TEACH (Toxics Exposure Assessment Columbia and Harvard) studies in New York City and Los Angeles (Sax et al. 2006) and the RIOPA (Relationships of Indoor, Outdoor, and Personal Air) study in Houston and Los Angeles (Weisel et al. 2005). Second, though meteorologic conditions will affect pollutant levels at any location, the Committee noted that the elevated concentrations near the Peace Bridge were particularly dependent on wind direction: because the wind direction was from Lake Erie and the Niagara River 45% of the time (60% in the summer), the community did not experience higher levels of pollutants the other 55% of the time (40% in the summer) when the wind direction changed. Thus, in view of the relatively low elevations of MSAT pollutants, and varying meteorologic conditions at different times of the year, the Committee did not agree with designating the Peace Bridge site an unqualified hot spot.

The Committee ultimately concluded that determining whether an area is a hot spot is difficult. The subtle differences of opinion on the characterization of an air toxics hot spot notwithstanding, Spengler and his team have done an excellent job of characterizing and investigating an area with potentially elevated emissions of MSATs.



CONCLUSIONS

The Review Committee noted that the Buffalo Peace Bridge Study by Spengler and his colleagues makes valuable contributions to HEI's hot-spot assessment program in several areas. First and foremost, their presentation of how to thoroughly characterize levels of air toxics surrounding a putative hot spot for mobile-source air pollution emissions is exemplary.

Spengler's team devised a study design and sampling scheme for characterizing air pollutant levels in an area of potentially high emissions that included important and innovative features. Their scheme for selecting sampling sites based on historic prevailing wind conditions relative to a putative pollution source strengthened their overall ability to attribute measured MSAT levels to traffic at the Peace Bridge plaza. They also selected an appropriate study location for a traffic-related emissions study by targeting a somewhat geographically isolated source of potentially high emissions for intensive analysis.

Although the overall levels of MSATs in this study area do not seem to be high relative to other locations in the United States, the investigators' data sets do contribute to our understanding of how traffic emissions may result in elevated levels of airborne MSATs in a local area. Finally, their mobile monitoring program for evaluating air toxics levels in a local neighborhood was both innovative and potentially valuable for future studies of variability in levels of air toxics at small geographic scales in inhabited areas, and it further adds to the field by demonstrating economical methods for such assessments.

Relocation of the tollbooths to the Canadian side of the Peace Bridge and other changes that altered the traffic and idling patterns in the plaza made comparisons between the individual sampling campaigns in this study difficult. Subsequent construction to move the traffic away from the residential neighborhood and increase capacity for truck inspections has likely altered the present-day patterns of MSAT concentrations in the study area relative to those reported in this study. Furthermore, emissions from motor vehicles are changing as a result of new fuels and new emission-control technologies. Meanwhile, the Peace Bridge remains one of the most heavily traveled border crossings in the United States. The data collected in this study may provide important baseline information for assessing the effects of changes in infrastructure and traffic patterns on MSAT concentrations in the Peace Bridge plaza area.

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