

# Exposures to Multiple Air Toxics in New York City

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Efforts to assess health risks associated with exposures to multiple urban air toxics have been hampered by the lack of exposure data for people living in urban areas. The TEACH (Toxic Exposure Assessment, a Columbia/Harvard) study was designed to characterize levels of and factors influencing personal exposures to urban air toxics among high school students living in inner-city neighborhoods of New York City and Los Angeles, California. This present article reports methods and data for the New York City phase of TEACH, focusing on the relationships between personal, indoor, and outdoor concentrations in winter and summer among a group of 46 high school students from the A. Philip Randolph Academy, a public high school located in the West Central Harlem section of New York City. Air pollutants monitored included a suite of 17 volatile organic compounds (VOCs) and aldehydes, particulate matter with a mass median aerodynamic diameter  $\leq 2.5 \mu\text{m}$  ( $\text{PM}_{2.5}$ ), black carbon, and a suite of 28 particle-associated trace elements. Sequential 48-hr ambient samples also were collected over 8 weeks in each season at an urban fixed site and an upwind, nonurban fixed site. Personal, indoor, and outdoor concentrations of particle elements were generally similar, suggesting that ambient sources may have driven indoor and personal exposures for most elements. More varied relationships among personal, home indoor, and home outdoor concentrations were observed for VOCs and aldehydes. For formaldehyde and acetaldehyde, and several VOCs, indoor concentrations far exceeded outdoor levels and appeared to dominate personal exposures. Strong seasonal differences in indoor to outdoor concentration ratios were observed for these compounds, reflecting the influence of home air exchange rates. For other VOCs, especially those related to motor vehicle exhaust, more consistent indoor, outdoor, and personal concentrations were observed, suggesting that ambient concentrations may have been the driving force for personal exposures to some VOCs. These results demonstrate exposures to a wide range of air toxic pollutants among young people attending school in inner-city New York. **Key words:** adolescents, air toxics, exposure assessment, hazardous air pollutants, urban. *Environ Health Perspect* 110(suppl 4):539–546 (2002).

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Considerable progress has been achieved in reducing ambient concentrations of certain criteria air pollutants in the United States over the past 30 years, including lead, sulfur dioxide, carbon monoxide, and the coarse particle fraction of particulate matter. Over the same period there have been striking upward trends in asthma morbidity, especially in urban areas. At face value these opposing trends imply little or no relationship between air pollution and asthma. On the other hand considerable evidence exists that acute exacerbations of asthma can be triggered by ambient ozone and fine particles, two pollutants for which less progress has been achieved. Furthermore, little is known about temporal or spatial trends in ambient concentrations of the noncriteria “air toxic” pollutants. Air toxics include particulate metals, diesel exhaust, and a range of volatile organic compounds (VOCs), many of which could, at elevated concentrations, have adverse impacts on the respiratory system. Little is known about the health risks posed by ambient concentrations of air toxic pollutants, and even less is known about the potential cumulative impacts of exposures to multiple air toxics.

The potential risks associated with exposures to multiple air toxics may be greatest for residents of central urban neighborhoods, where the pollutant mix often represents the sum of regional, citywide, and local source pollutants. Further, evidence suggests that there is disproportionately high exposure of minority and disadvantaged populations to air pollutants (1–3). In the United States, 60% of Hispanics, and 50% of African Americans, compared with 33% of Caucasians, live in areas failing to meet two or more of the national ambient air quality standards (NAAQS) (3,4). These patterns may be due in part to the concentration of minority and low socioeconomic-status populations in cities, along with the tendency for some air pollution concentrations to be higher in urban, versus suburban and rural, areas.

An additional factor enhancing potential exposure risks related to air toxics in inner cities is the strong association between socioeconomic disadvantage and compromised health status. Of special concern are the high rates of asthma morbidity and mortality among disadvantaged urban residents. To date, little information has been available to characterize the cumulative air toxic exposure

burdens of inner-city residents, hampering efforts to assess and mitigate health risks.

The TEACH (Toxic Exposure Assessment, a Columbia/Harvard) study was designed to characterize levels of and factors influencing personal exposures to urban air toxics among high school students living in inner-city neighborhoods of New York City (NYC) and Los Angeles. The study included measurements of a wide range of air toxics, including VOCs, particulate matter with a mass median aerodynamic diameter  $\leq 2.5 \mu\text{m}$  ( $\text{PM}_{2.5}$ ), and associated metals and elements, and aldehydes. In this article, we report methods and data for the NYC phase of TEACH, focusing on the relationships between personal, indoor, and outdoor concentrations.

## Methods

### Study Design

Exposures to air toxics were assessed in a group of 46 high school students from the A. Philip Randolph Academy, a public high school located in the West Central Harlem section of NYC (Figure 1). Each of two field campaigns (winter and summer, 1999) involved 8 weeks of fixed-site ambient monitoring on the school roof and on a roof at the Lamont Doherty Earth Observatory (LDEO) in Palisades, New York. The school roof site was seven stories high and located on a ridge with one of the highest elevations in Manhattan, thus representing areawide urban concentrations. The LDEO roof site was on a three-story building near the Palisades cliffs overlooking the Hudson River, 13 miles northwest of Manhattan. The predominant winds are from the west, resulting in the

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LDEO rooftop usually being a representative site of the upwind air masses. However, it should be noted that, especially during the summer, sea breezes may sometimes cause winds to flow up the Hudson River Valley from NYC toward LDEO. Here we refer to these two outdoor monitoring locations as the urban fixed site and the upwind fixed site.

The fixed-site monitoring covered three consecutive 48-hr periods each week. Concurrent with the first of these ambient samples each week (Tuesday–Thursday), subject-based monitoring of personal, home indoor, and home outdoor samples were collected for 48 hr. Five subjects were typically monitored simultaneously each week. As shown in Table 1, pollutants monitored at every sampling event included a suite of 15 VOCs, PM<sub>2.5</sub>, black carbon, a suite of 28 particle trace elements, and two aldehydes. Air exchange rate (AER) was monitored in each home during the air pollution measurement period.

### Study Communities

The study school was located at 135<sup>th</sup> Street and Convent Avenue in Harlem, a low-income neighborhood of mainly African-American and Hispanic (Dominican) residents. Students attending the school lived primarily in northern Manhattan and the South Bronx, with additional students coming from the boroughs of Queens and Brooklyn. From an environmental perspective, Harlem is at the center of the metropolitan New York region that in recent years has been out of compliance with the NAAQS for

particulate matter with a mass median aerodynamic diameter  $\leq 10 \mu\text{m}$  (PM<sub>10</sub>). Ambient air toxic levels in northern Manhattan and the South Bronx result from regionwide emissions as well as from local sources such as diesel bus depots, waste incinerators, industrial operations, and the network of commuter highways, commercial truck routes, and bus routes surrounding and interlacing these communities.

### Subject Recruitment

Initial contact with potential study subjects took place in school with the assistance of science teachers. Study staff visited classrooms to describe the goals and methods of the study and to distribute informational brochures and consent forms. At this stage, the school teachers also distributed and collected a brief student survey form on demographics, parental education, student commuting patterns, and personal and passive smoking exposures for all students. To be eligible, students needed to be nonsmokers from nonsmoking families and to be available for sampling in both winter and summer. Students interested in participating in the monitoring study were instructed to have the consent forms signed by a parent/guardian at home and then to return the signed consent forms to the teacher. Consent forms and student surveys were collected in batches and forwarded to study staff, who identified nonsmoking households and then contacted students by telephone to invite their participation. The protocol was approved by the Columbia Health Sciences Institutional Review Board and the Harvard Human Subject Committee.

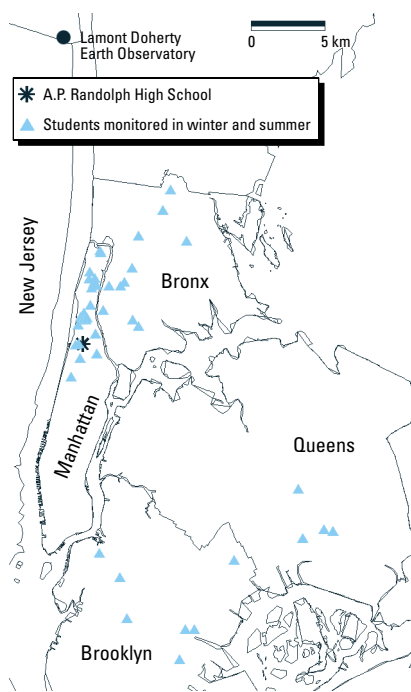
### Questionnaires

A detailed home characteristics questionnaire was administered to the subject or the parent/guardian in the home at the time of the initial sampling setup. This questionnaire

included information on home heating and cooking methods and habits, recent renovation work or hobbies that might result in VOC emissions, and other factors. Time-activity logs were completed by subjects during the 48-hr personal sampling period. In addition, at the completion of personal sampling, activity recall questionnaires were completed by the subjects.

### Air Sampling and Laboratory Analyses

Personal sampling was carried out using a portable, battery-operated pump (model 400S, BGI Inc., Waltham, MA, USA) housed in a customized daypack that the subjects carried over the shoulder. The pump flow was split three ways to collect one PM<sub>2.5</sub> filter at 4 L/min, one VOC thermal desorption tube at 1.8 standard cubic centimeters per minute (SCCM), and one C<sub>18</sub> aldehyde sampler at approximately 100 SCCM. Columbia black boxes (redesigned and rebuilt Harvard black boxes) containing three 7-L/min pumps (Medo, Inc., Hanover Park, IL, USA) were used to collect samples inside and outside of each subject's home and at the urban and upwind fixed sites. Two black boxes were used in each home, with one designated for indoor and the other for outdoor sampling. Duplicate indoor and outdoor PM<sub>2.5</sub> samples were collected onto Teflon filters, with one filter designated to be analyzed for PM<sub>2.5</sub>, reflectance, and total metals, and the second filter being archived for future analyses (placed in a petri dish wrapped in aluminum foil and stored in a freezer). The third pump in each black box had its flow split three ways to collect one VOC thermal desorption tube at approximately 1.8 SCCM, one C<sub>18</sub> aldehyde sampler at approximately 100 SCCM, and a vent line at approximately 4 L/min. Duplicate VOC and aldehyde samples were collected



**Figure 1.** Map of sampling locations for the NYC TEACH study.

**Table 1.** Target air toxics in the NYC TEACH study.

Particulate matter components		Volatile organic compounds	Aldehydes
PM <sub>2.5</sub>	Trace elements, cont.	1,1,1-Trichloroethane	Formaldehyde <sup>a</sup>
Black carbon	Magnesium (Mg)	1,4-Dichlorobenzene <sup>a</sup>	Acetaldehyde <sup>a</sup>
Trace elements	Manganese (Mn) <sup>a</sup>	Benzene <sup>a</sup>	
Aluminum (Al)	Nickel (Ni) <sup>a</sup>	1,3-Butadiene <sup>a</sup>	
Antimony (Sb) <sup>a</sup>	Platinum (Pt)	Carbon tetrachloride <sup>a</sup>	
Arsenic (As) <sup>a</sup>	Potassium (K)	Chloroform <sup>a</sup>	
Beryllium (Be) <sup>a</sup>	Scandium (Sc)	Ethylbenzene <sup>a</sup>	
Cadmium (Cd) <sup>a</sup>	Selenium (Se) <sup>a</sup>	<i>m,p</i> -Xylene <sup>a</sup>	
Calcium (Ca)	Silver (Ag)	<i>o</i> -Xylene <sup>a</sup>	
Cesium (Cs)	Sodium (Na)	Methylene chloride <sup>a</sup>	
Chromium (Cr) <sup>a</sup>	Sulfur (S)	MTBE <sup>a</sup>	
Cobalt (Co) <sup>a</sup>	Thallium (Tl)	Styrene <sup>a</sup>	
Copper (Cu)	Tin (Sn)	Tetrachloroethylene <sup>a</sup>	
Iron (Fe)	Titanium (Ti)	Toluene <sup>a</sup>	
Lanthanum (La)	Vanadium (V)	Trichloroethylene <sup>a</sup>	
Lead (Pb) <sup>a</sup>	Zinc (Zn)		

<sup>a</sup>These 26 pollutants were listed among 189 hazardous air pollutants in the 1990 Clean Air Act Amendments.

for at least 10% of sampling events. Flows were checked before and after all sampling events using calibrated flow meters. No sampling was carried out for particles larger than 2.5  $\mu\text{m}$  in diameter, nor did we analyze for biologic particles.

During each sampling week, a total of three 48-hr sample sets were collected at the urban and upwind fixed sites. The first of these samples was taken at the same time as the individual indoor and outdoor samples; two additional consecutive 48-hr samples were taken thereafter. The objectives for obtaining these additional rooftop samples were 2-fold: *a*) to place the individual personal, indoor, and outdoor sampling in context of the temporal variability, and *b*) to provide additional outdoor samples for source apportionment purposes.

VOC samples were collected on multi-sorbent "Air Toxics" tubes (Perkin-Elmer, Inc., Shelton, CT, USA) using the U.S. Environmental Protection Agency Compendium Method TO-17. The tubes were stainless steel and approximately 90 mm (3.5 inches) long and 6.35 mm (0.25 inches) in diameter containing 35 mm of Carboxen B (a medium-strength hydrophobic sorbent) and 10 mm of Carboxen 1000 (a strong sorbent, slightly hydrophilic). The mixture of sorbent strengths allowed for collection of VOCs from *n*-C<sub>3</sub> to *n*-C<sub>12</sub>. The low sampling rate prevented breakthrough and loss of collected VOCs. A diffusion barrier was developed to prevent sampling by diffusion during the lag time before and after active sampling in the home-based and fixed-site monitors, where sampling was activated and deactivated by automatic timers. The diffusion barrier consisted of a small-inner-diameter (0.02 mm) stainless steel tube 200 mm in length. A similar diffusion barrier was tested and used in a recent European study (5). Analysis of VOC tubes was carried out using a Perkin-Elmer automatic thermal desorber (model 400) connected to a Hewlett Packard 5890II gas chromatograph /5971 mass spectrometer with quantification software (Hewlett Packard, Palo Alto, CA, USA). 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. Vapor-phase internal standard was injected into the device and the tube was kept in place 5 min. The vapor-phase internal standard is 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 is drawn up with a gas-tight syringe and injected into the injector-port/spiking device with flow onto the sample tube. Drawing different volumes yields different masses of analytes on tube and thus different levels of calibration.

Teflon filter samples were collected in plastic cassettes attached downstream from a cyclone with a 2.5  $\mu\text{m}$  aerodynamic-diameter cut point (model KTL, BGI, Inc.) when operated at 4 L/min  $\pm$  10%. Flows were checked before and after sampling. Filters were weighed pre- and postsampling on a microbalance at the Harvard School of Public Health Laboratory after being conditioned in a temperature-humidity-controlled environment for at least 24 hr (by cracking the petri dish cover) and statically discharged via a polonium source.

After PM<sub>2.5</sub> analyses were complete, filters were returned to Columbia, where they were analyzed inside a class-100 flow bench for reflectance using a smoke stain reflectometer (model 43D; Diffusion Systems Ltd., London, UK). Prior work (6,7) has demonstrated that reflectance can be a good proxy for elemental carbon concentrations in outdoor filters. Measurements of five separate locations are made on each filter. However, because in this method the reflectometer head may touch the active filter area (potentially resulting in metals contamination), we designed and built a new filter holder that touches only the outer plastic ring, holding the filter in a fixed flat geometry. This modification enables reflectance measurements to be made without a significant risk of contaminating the filter for later multielement analysis. However, the reflectance measurement is sensitive to the distance between the reflectometer head and the filter (which is an additional 2.5 mm with our filter holder); consequently, to help distinguish our measurements from those of others, we will report our reflectance measurements as "modified" absorption coefficients (Abs\*). Reflectance measurements are expressed as the absorption coefficient in reciprocal meters times 100,000.

After reflectance measurements, filters were prepared for multielement analysis by magnetic-sector high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). Filters (with supporting ring removed) were microwave extracted in two steps inside 7-mL Teflon vials, which were placed inside microwave vessels containing 10 mL 65% HNO<sub>3</sub>. For winter samples, reagents in step 1 were 60  $\mu\text{L}$  water and 200  $\mu\text{L}$  concentrated HNO<sub>3</sub>; in step 2 reagents were 100  $\mu\text{L}$  HNO<sub>3</sub> and 40  $\mu\text{L}$  hydrofluoric acid. After extraction, the mass of remaining digest solution was calculated gravimetrically and brought up to 5 mL to approximately 5% acid strength. The filter was removed, transferred to a clean vial, and redigested in the same manner. Both the first and second digests were analyzed. Reagents for summer filters were 20  $\mu\text{L}$  ethanol, 60  $\mu\text{L}$  water, and 225  $\mu\text{L}$  concentrated HNO<sub>3</sub> in step 1, and 10  $\mu\text{L}$  ethanol, 40  $\mu\text{L}$  hydrofluoric acid, and 100  $\mu\text{L}$

HNO<sub>3</sub> in step 2. The addition of ethanol eliminated the need for redigestion of the filter, so it was not done for summer samples. This streamlining of the analytical procedure had no significant impact on the measurements. Recoveries of standards and duplicate precisions were very good in both seasons.

Diluted digests were analyzed by HR-ICP-MS. Winter New York samples were run on the Element (Finnigan-Mat, Bremen, Germany) at Rutgers University; summer New York digests were run on the newly purchased Axiom (VG-Elemental, Franklin, MA, USA) at LDEO. Data were collected for all isotopes of interest at the appropriate resolving power (RP) to avoid isobaric interferences. Be, Ag, Cd, Sn, Sb, Cs, La, Pt, Tl, and Pb, for which interferences are not a problem, were run at RP 400; Na, Mg, Al, S, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn, at RP 3,000–4,300; and K, As, and Se, at RP  $\geq$  9,300. Indium was added to all samples, blanks, and standards as an internal drift corrector and run in all resolving powers. Quantification is done by external and internal standardization.

HR-ICP-MS data were drift corrected with indium, quantified, converted to a mass, and corrected for blanks. Samples that were below the limit of quantification (LOQ) based on daily procedural blanks were flagged. For New York winter samples, analyte mass of the first and second digests was combined. All sulfur mass concentrations are reported as sulfate concentrations, which is assumed to be the predominant sulfur species on the PM<sub>2.5</sub> filters.

Aldehydes were sampled by the method of Fung and Grosjean (8), with air pumped through a cartridge packed with C<sub>18</sub> coated with acidified 2,4-dinitrophenylhydrazine (DNPH). Samplers were sealed and refrigerated before and after use and during shipping. Analyses were performed at the Harvard School of Public Health. The DNPH derivatives (hydrazones) were eluted with acetonitrile and then analyzed using high-pressure liquid chromatography (model 1100, Hewlett Packard) with an ultraviolet detector (360 nm). External standards were used to determine the concentration in the samples based on the peak area. Laboratory and field blanks were used for quality control purposes. The concentration of aldehydes found in blank cartridges was subtracted from the sample concentration. The variability of the blank levels was used to determine the limit of detection.

AERs were measured using the perfluorocarbon technique, which is based on diffusional sources (continually release of tracer gas) and diffusional samplers [capillary absorption tubes (CATs)]. The sources were placed in the subject's home 24–72 hr before

placement of CATs to allow equilibrium to develop between source release rate and the AER of the home. Two or three CATs were placed per home, typically in the main living area and in the subject's bedroom.

### Data Analysis

To describe overall air toxic exposures in the NYC study, we computed means and standard deviations of concentrations for each pollutant measured in personal, home outdoor, and home indoor samples. Results are presented separately for winter and summer. To identify and distinguish pollutants for which exposures were dominated by outdoor concentrations as opposed to indoor concentrations, we plotted median indoor/outdoor (I/O) ratios. To examine spatial and temporal patterns in traffic-related VOC concentrations, home outdoor, urban fixed-site, and upwind fixed-site methyl *tert*-butyl ether (MTBE) concentrations were plotted for the winter monitoring season.

### Results

The full list of 47 air pollutants we quantified is shown in Table 1. These included PM<sub>2.5</sub> and 29 particulate matter elemental components, 15 VOCs, and 2 aldehydes. Twenty-six of these pollutants were listed among 189

hazardous air pollutants in the 1990 Clean Air Act amendments.

A total of 46 students who self-reported not smoking and not being exposed to environmental tobacco smoke were enrolled in the NYC TEACH project, including 33 who completed both winter and summer phases. Five students in winter and eight students in summer participated in only one season. Subjects ranged from 14 to 19 years of age, with 31 (67%) female and 15 (33%) male (Table 2). The racial distribution was 43% African American, 50% Hispanic, and the remaining 7% either Asian or not reported. Most students lived in apartment buildings (76%). These and other characteristics were similar to a larger group of 611 students surveyed at the school (Table 2).

Figure 1 shows a map of the study area, with symbols indicating the locations of the school and subject homes. The majority of the students lived in the upper Manhattan (63% in the winter and 46% in the summer) and Bronx (24% in winter and 27% in summer) boroughs of NYC, with only a few in Brooklyn (8% for winter and 10% for summer) and Queens (5% for winter and 17% for summer).

Table 3 displays means and standard deviations of PM<sub>2.5</sub> and associated component

concentrations measured on personal, home indoor, and home outdoor filter samples in winter and summer. Also listed are the limits of detection for each analyte. Most particle components, even those having the lowest concentrations, were detected at levels at least one order of magnitude above the limit of detection, reflecting the high sensitivity of HR-ICP-MS for elemental analyses of air samples. Most concentrations fell in the range from <1 to 100 ng/m<sup>3</sup>, with PM<sub>2.5</sub>, sulfate, and iron extending into the 1–20 µg/m<sup>3</sup> range. Many elements had very skewed distributions, with standard deviations exceeding the means. For most elements, indoor, outdoor, and personal concentrations were rather consistent, suggesting that ambient air may have been the driving force for both indoor and personal exposures for most elements. However, there were several elements, including iron and manganese in both seasons, aluminum in winter only, and antimony, chromium, and lead in summer only, for which personal exposures exceeded both indoor and outdoor concentrations by at least a factor of two. For iron, the increase was a factor of five or six. This suggests the existence of one or more personal activities or microenvironments outside the home in which high exposures to certain metals occur.

VOC and aldehyde concentrations are similarly displayed in Table 4 for winter and summer. For VOCs and aldehydes, mean concentrations ranged about two orders of magnitude, with many means falling in the range from less than 1 to about 20 µg/m<sup>3</sup>. For a few elements, detection limits were less than a factor of two below the lowest mean concentration (i.e., outdoors). This was the case for benzene in both seasons, chloroform in winter, and methylene chloride in summer. Indoor and personal concentrations were frequently higher than those outdoors (i.e., both indoor and personal two times higher than outdoors), especially in winter. This indicates that for many VOCs, indoor concentrations may dominate personal exposures in this population. On the other hand, somewhat more consistent indoor, outdoor, and personal concentrations were observed for the group of VOCs often associated with motor vehicle emissions, including benzene, toluene, ethylbenzene, xylenes, and especially MTBE. For these compounds, ambient air may be an important driver of personal concentrations in this community.

To further explore the relationships between indoor and outdoor concentrations for the full suite of air toxics measured, Figures 2 and 3 display box plots of I/O ratios for particle-associated elements and VOCs/aldehydes, respectively. From bottom to top, the box plots present the 5<sup>th</sup>, 25<sup>th</sup>,

**Table 2.** Subject characteristics for the NYC TEACH study.

	School survey (n = 611)		Study subjects (n = 46)	
	Frequency	%	Frequency	%
Sex				
Male	256	42.2	15	32.6
Female	351	57.8	31	67.4
Not answered	4	0.66	0	0
Race				
African American	280	45.8	20	43.5
Hispanic	286	46.8	23	50
White	8	1.31	0	0
Asian	10	1.64	1	2.17
Others	4	0.66	0	0
Don't know	15	2.45	2	4.35
Not answered	8	1.31	0	0
Father education level				
Did not graduate from high school	70	11.5	6	13.0
High school graduate	128	21.0	7	15.2
Technical trade school	18	2.95	3	6.52
Some college	71	11.6	8	17.7
College graduate	103	16.9	9	19.5
Graduate professional	38	6.22	4	8.7
Don't know	181	29.6	9	19.6
Not answered	2	0.33	0	0
Type of home				
Single-family home	49	8.02	4	8.7
2–3-family home	47	7.69	6	13.0
Apartment building	490	80.2	35	76.0
Office–apartment building	5	0.82	0	0
Others	16	2.62	1	2.17
Not answered	4	0.65	0	0
Age (years)				
Minimum		12.5		14.1
Maximum		19.6		18.7
Mean		16.1		16.8
Standard deviation		1.2		0.92



**Table 3.** Means and standard deviations of PM<sub>2.5</sub>, absorbance, and particle-associated elements for personal, home indoor, and home outdoor locations (and limits of detection).

Analyte <sup>a</sup>	LOD	Home outdoor			Home indoor			Personal		
		<i>n</i>	Mean	SD	<i>n</i>	Mean	SD	<i>n</i>	Mean	SD
Winter										
PM <sub>2.5</sub> (µg/m <sup>3</sup> )	0.45	37	11.9	3.8	38	20.9	16.9	35	17.0	6.8
Abs (1/m × 10 <sup>5</sup> )	0.57	37	1.94	0.91	38	1.62	0.78	35	1.65	0.70
Aluminum (Al)	9	36	40	17	26	41	23	8	86	30
Antimony (Sb)	0.008	36	1.48	1.04	38	5.29	22.82	35	4.32	16.03
Arsenic (As)	—	0	—	—	0	—	—	0	—	—
Beryllium (Be)	—	0	—	—	0	—	—	0	—	—
Cadmium (Cd)	0.005	36	0.157	0.092	38	0.207	0.164	35	0.287	0.239
Calcium (Ca)	8	36	65	31	38	92	105	35	129	76
Cesium (Cs)	0.0004	36	0.0105	0.0052	38	0.0087	0.0057	35	0.0089	0.0043
Chromium (Cr)	2.50	0	—	—	0	—	—	0	—	—
Cobalt (Co)	0.004	36	1.59	0.78	38	1.76	3.39	35	1.26	0.77
Copper (Cu)	1.0	36	6.0	3.0	38	7.0	4.7	35	10.5	7.1
Iron (Fe)	05	36	107	41	38	84	40	35	633	588
Lanthanum (La)	0.004	36	0.81	0.49	38	0.72	0.56	35	0.62	0.31
Lead (Pb)	0.03	36	6.96	3.27	38	22.4	70.2	35	16.1	36.4
Magnesium (Mg)	0.6	36	30.0	14.0	38	30.7	17.4	35	44.4	65.7
Manganese (Mn)	0.20	36	2.35	0.94	38	2.20	1.15	35	7.35	5.15
Nickel (Ni)	0.09	36	32.3	22.4	38	31.6	54.5	35	49.6	114
Platinum (Pt)	0.0001	36	0.0008	0.0008	38	0.0010	0.0008	35	0.0008	0.0004
Potassium (K)	4	36	44	17	38	84	66	35	80	56
Scandium (Sc)	0.001	36	0.006	0.004	29	0.006	0.004	0	—	—
Selenium (Se)	—	0	—	—	0	—	—	0	—	—
Silver (Ag)	0.001	36	0.059	0.043	38	0.096	0.113	35	0.124	0.128
Sodium (Na)	5	22	117	70	30	153	135	27	142	79
Sulfur (S)	16	36	840	352	38	983	1,080	35	947	628
Thallium (Tl)	0.0002	27	0.0142	0.0094	38	0.0149	0.0099	35	0.0133	0.0081
Tin (Sn)	0.04	36	0.79	0.56	38	1.01	0.53	35	1.21	0.66
Titanium (Ti)	0.2	36	2.45	1.65	38	2.94	2.22	35	4.75	2.02
Vanadium (V)	0.02	36	7.68	3.14	38	9.49	20.66	35	6.56	3.67
Zinc (Zn)	0.2	36	35.8	29.0	38	120.7	370.6	35	80.3	143.7
Summer										
PM <sub>2.5</sub> (µg/m <sup>3</sup> )	0.90	38	13.6	4.5	40	19.0	21.5	40	18.5	17.7
Abs (1/m × 10 <sup>5</sup> )	0.23	38	1.79	0.71	40	1.66	0.62	40	1.71	0.61
Aluminum (Al)	2	36	37	18	39	39	31	40	50	20
Antimony (Sb)	0.01	36	1.05	0.45	39	0.90	0.40	40	2.87	12.68
Arsenic (As)	0.03	36	0.37	0.18	39	0.40	0.20	40	0.45	0.37
Beryllium (Be)	0.0003	15	0.0032	0.0025	18	0.0016	0.0007	33	0.0019	0.0008
Cadmium (Cd)	0.006	36	0.118	0.055	39	0.145	0.110	40	0.215	0.293
Calcium (Ca)	3	36	47	23	39	54	26	40	70	41
Cesium (Cs)	0.0002	36	0.0046	0.0018	39	0.0044	0.0020	40	0.0042	0.0018
Chromium (Cr)	0.40	34	0.46	0.41	39	0.55	0.29	39	1.99	1.98
Cobalt (Co)	0.004	36	0.78	0.46	39	0.72	0.48	40	0.68	0.42
Copper (Cu)	0.60	36	12.6	44.0	39	10.3	30.6	40	8.5	13.0
Iron (Fe)	22	36	114	56	39	95	47	40	519	556
Lanthanum (La)	0.0003	36	0.59	0.37	39	0.55	0.53	40	0.46	0.27
Lead (Pb)	0.03	36	6.61	5.08	39	5.83	4.38	40	88.85	525.56
Magnesium (Mg)	1	1	16.9	—	32	25.2	12.8	40	25.2	10.5
Manganese (Mn)	0.20	36	2.06	0.93	39	1.81	0.81	40	5.78	5.26
Nickel (Ni)	0.2	36	11.7	6.3	39	12.6	8.4	40	17.3	24.7
Platinum (Pt)	0.0001	36	0.0016	0.0008	39	0.0014	0.0010	40	0.0017	0.0014
Potassium (K)	3	0	—	—	32	64	58	40	59	34
Scandium (Sc)	0.001	33	0.007	0.004	39	0.005	0.003	40	0.006	0.003
Selenium (Se)	0.2	34	0.58	0.34	39	0.52	0.28	40	0.51	0.19
Silver (Ag)	0.001	36	0.043	0.031	39	0.062	0.041	40	0.098	0.074
Sodium (Na)	2	36	103	69	39	122	98	40	104	38
Sulfur (S)	2	36	1,760	1,160	39	1,230	687	40	1,100	498
Thallium (Tl)	0.00004	36	0.0064	0.0024	39	0.0079	0.0060	40	0.0081	0.0072
Tin (Sn)	0.01	20	0.90	0.48	39	1.42	1.92	40	1.59	1.98
Titanium (Ti)	0.3	36	3.54	1.28	39	3.46	1.36	40	4.14	2.13
Vanadium (V)	0.01	36	4.62	1.63	39	4.17	1.68	40	3.81	1.46
Zinc (Zn)	0.3	36	34.8	40.5	39	86.2	188	40	76.6	143

Abbreviations: LOD, limit of detection; SD, standard deviation. <sup>a</sup>Concentrations are ng/m<sup>3</sup> unless otherwise stated.

**Table 4.** Means and standard deviations ( $\mu\text{g}/\text{m}^3$ ) of VOCs and aldehydes for personal, home indoor, and home outdoor locations (and limits of detection).

Analyte	LOD	Home outdoor			Home indoor			Personal		
		<i>n</i>	Mean	SD	<i>n</i>	Mean	SD	<i>n</i>	Mean	SD
Winter										
1,1,1-Trichloroethane	0.13	36	0.51	0.29	36	5.43	22.78	36	2.01	4.18
1,3-Butadiene	0.06	36	0.13	0.28	36	1.18	1.54	36	0.87	1.29
1,4-Dichlorobenzene	1.29	36	5.03	7.11	36	54.9	105	36	43.4	77.4
Acetaldehyde	1.27	36	2.78	0.87	38	15.6	9.7	38	13.0	7.7
Benzene	1.66	36	2.55	1.40	36	5.97	7.29	36	4.70	3.33
Carbon tetrachloride	0.1	36	0.75	0.16	36	0.75	0.16	36	0.67	0.13
Chloroform	0.12	36	0.23	0.21	36	3.83	3.12	36	3.00	2.74
Ethylbenzene	0.22	36	1.27	0.57	36	3.57	6.91	36	2.24	2.37
Formaldehyde	0.96	36	2.11	0.85	38	12.1	5.0	38	11.5	4.9
Methylene chloride	0.25	36	1.96	3.68	36	6.19	13.8	36	3.80	5.95
MTBE	0.46	36	11.9	6.0	36	21.0	32.6	36	15.5	11.7
Styrene	0.17	36	0.43	0.25	36	1.25	0.70	36	1.01	0.46
Tetrachloroethylene	0.12	36	2.42	1.93	36	7.53	14.71	36	7.98	19.28
Toluene	1.98	36	6.50	3.08	36	17.7	14.4	36	15.5	12.9
Trichloroethylene	0.15	36	0.36	0.26	36	1.26	3.59	36	2.62	8.30
<i>o</i> -Xylene	0.29	36	1.52	0.81	36	3.36	6.09	36	2.24	2.09
<i>m,p</i> -Xylene	0.78	36	4.46	2.16	36	10.4	20.1	36	6.71	5.69
Summer										
1,1,1-Trichloroethane	0.13	35	0.76	1.84	40	1.21	3.03	41	1.11	1.37
1,3-Butadiene	0.06	35	0.14	0.41	40	1.01	2.56	41	1.16	1.95
1,4-Dichlorobenzene	0.14	29	4.31	6.04	36	108	503	40	41.1	88.2
Acetaldehyde	0.33	36	4.15	1.53	41	14.98	16.70	42	20.2	15.9
Benzene	1.9	35	1.31	1.01	41	1.75	1.17	41	3.09	1.94
Carbon tetrachloride	0.1	33	0.49	0.25	39	0.53	0.24	41	0.59	0.29
Chloroform	0.12	33	0.33	0.73	40	2.01	2.02	41	2.80	2.73
Ethylbenzene	0.17	29	1.88	1.75	36	1.99	1.08	40	3.37	2.02
Formaldehyde	0.15	36	5.28	2.27	41	20.9	11.0	42	28.5	13.8
Methylene chloride	1.84	35	1.10	1.33	40	8.80	32.32	41	9.3	29.1
MTBE	0.13	35	12.7	14.0	40	21.1	50.9	41	29.5	67.7
Styrene	0.08	30	0.32	0.25	37	0.80	0.70	40	1.68	1.76
Tetrachloroethylene	0.17	30	9.46	34.33	36	6.45	11.69	40	9.18	15.49
Toluene	0.28	31	7.48	3.84	37	14.9	19.8	40	37.4	60.5
Trichloroethylene	0.15	31	0.24	0.31	38	0.32	0.52	40	0.51	0.93
<i>o</i> -Xylene	0.37	30	2.00	1.99	36	2.27	1.38	40	3.93	2.33
<i>m,p</i> -Xylene	0.94	30	5.77	6.18	36	6.44	4.11	40	10.9	6.8

Abbreviations: LOD, limit of detection; SD, standard deviation.

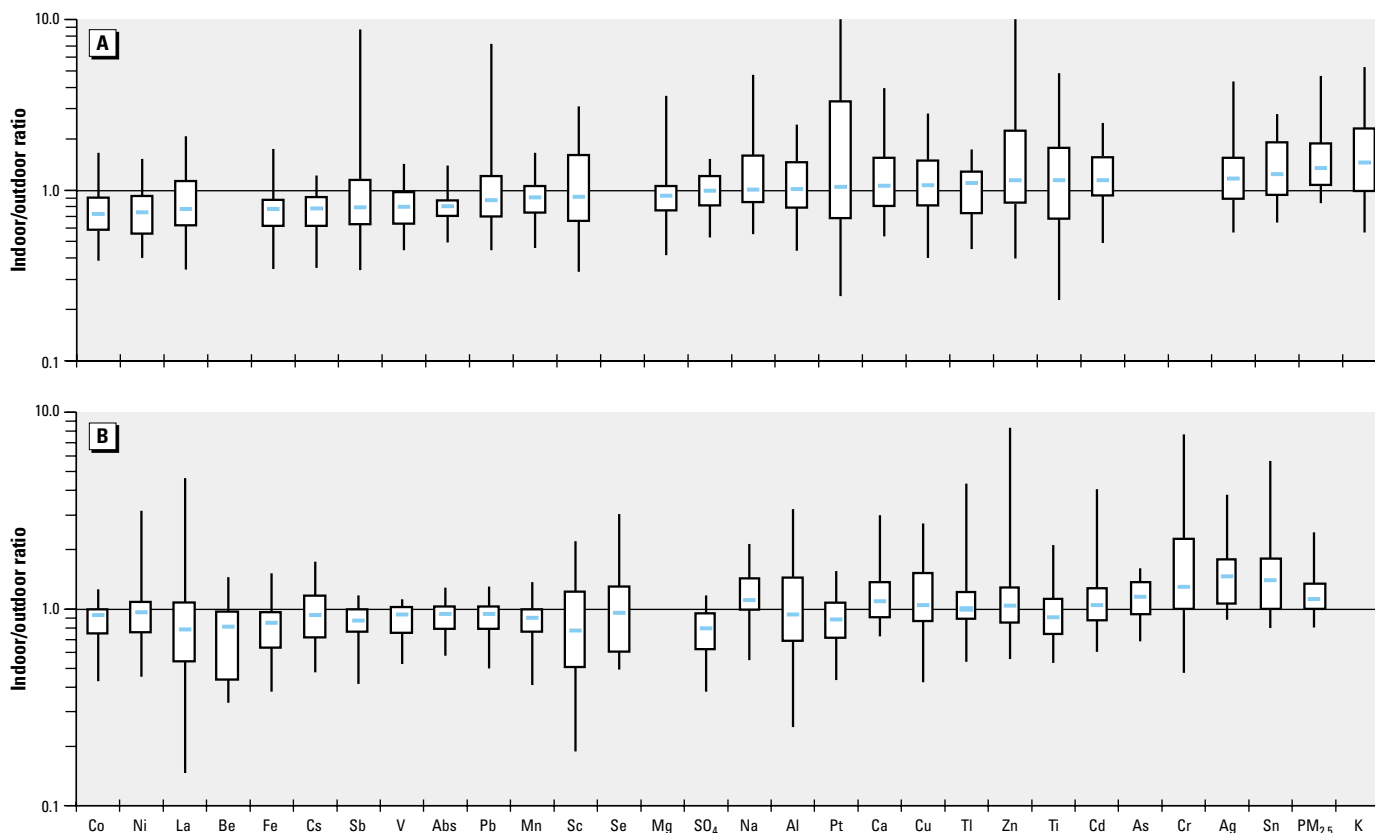
50<sup>th</sup> (i.e., median), 75<sup>th</sup>, and 95<sup>th</sup> percentiles of each distribution. Winter and summer I/O ratios are plotted together in each figure. Median I/O ratios for most particle-associated elements were close to or less than 1.0 in both winter and summer, consistent with the notion that ambient levels were the driving force for indoor concentrations for most elements. However, there was a subset of elements that exhibited median I/O ratios greater than 1. Particle components with elevated I/O ratios included zinc, titanium, cadmium, silver, tin, PM<sub>2.5</sub>, and potassium in winter and arsenic, chromium, silver, and tin in summer (note that arsenic and chromium were analyzed only in summer). For elements with higher outdoor than indoor concentrations, I/O ratios were slightly lower in winter than in summer, consistent with decreased winter AERs and resulting diminished penetration of outdoor particles. There was a weak tendency for this relationship to reverse for those elements with evidence of indoor sources (i.e., I/O ratios >1), where I/O ratios were often slightly higher in winter than in summer. This is consistent with increased

trapping of indoor-generated pollutants in winter when home AER was lower.

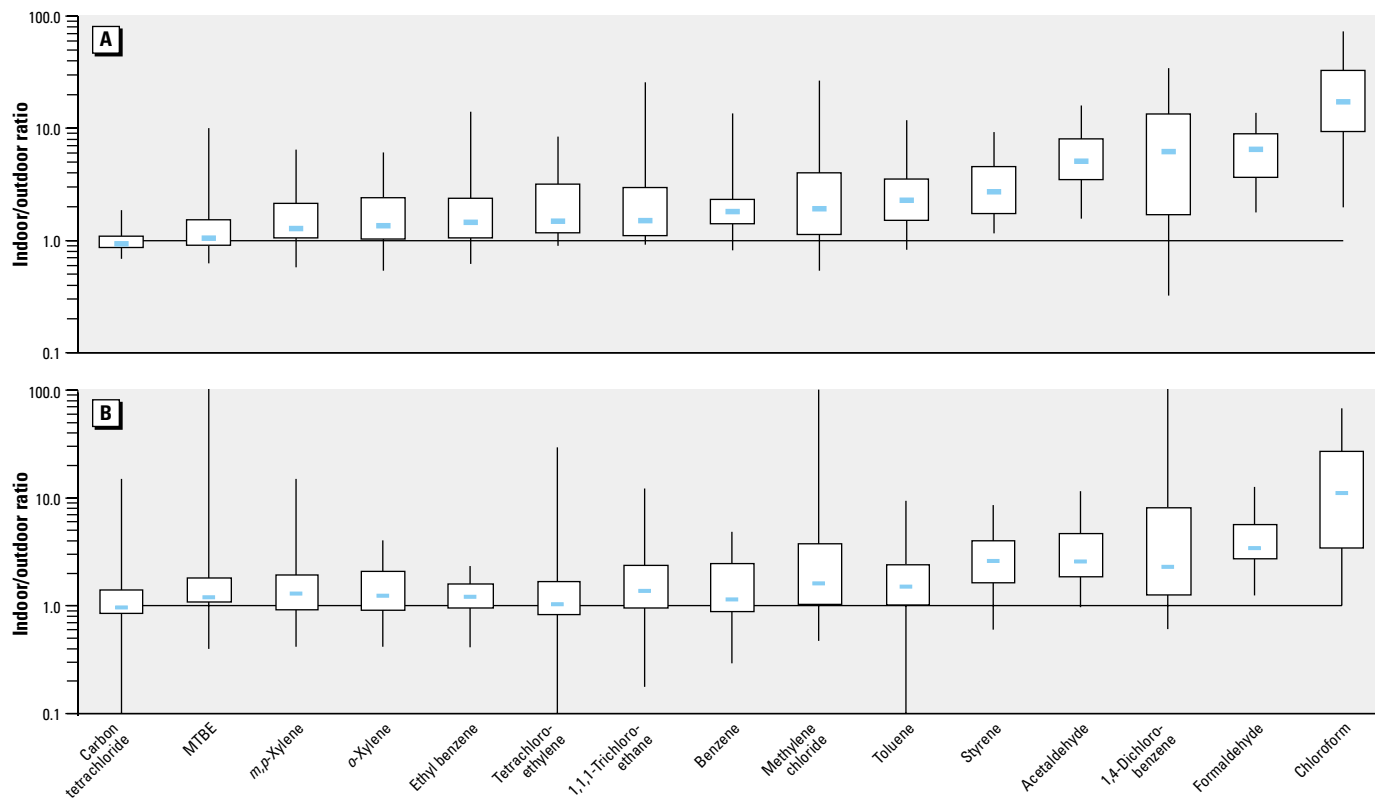
I/O ratios for VOCs and aldehydes were generally much higher than those seen for the elements, with nearly half the compounds exhibiting median I/O ratios of 2 or greater (Figure 3). There was a tendency for I/O ratios to be lower (i.e., closer to 1) in summer than in winter, reflecting enhanced AER and clearance of indoor-generated pollutants. Indoor concentrations far exceeded outdoor levels (I/O ratio > 4) for chloroform in both seasons and for the two aldehydes and 1,4-dichlorobenzene in winter. These findings are consistent with more significant and widespread indoor sources for these compounds. As suggested by the results in Table 4, there also were several VOCs for which I/O ratios clustered close to 1, including the traffic-related compounds such as MTBE.

As an example of how the data set can be used to explore the relative magnitudes of temporal and spatial variability for traffic-related VOCs, Figure 4 displays a plot of MTBE concentrations measured at all of the outdoor sites throughout the winter monitoring season, including home

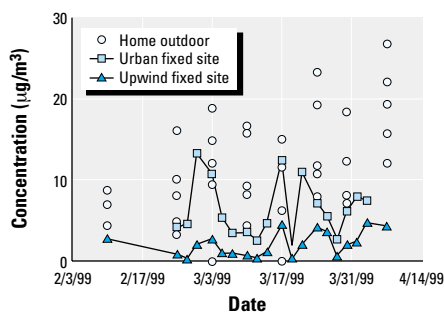
outdoors (three to five homes simultaneously each week), the urban fixed site (on the school roof), and the upwind fixed site. Temporal cycles with roughly weekly periods were evident in both the upwind and urban concentrations, reflecting synoptic weather patterns influencing the larger region. A substantial "urban influence" was observed, with urban fixed-site concentrations ranging from 2 to 13  $\mu\text{g}/\text{m}^3$  compared with a range of 0–5  $\mu\text{g}/\text{m}^3$  at the upwind site. This difference was statistically significant at the 0.05 level using a two-sided paired *t*-test. A further increase in concentrations above those observed at the urban fixed site was seen at the home outdoor locations, perhaps reflecting greater influences of local traffic at sites closer to the ground (recall that the urban fixed site was on the roof of the seven-story school). Considerable interhome spatial variability also was evident, suggestive of differential impacts of local sources. This inference was supported by the monotonic relationship observed between home outdoor MTBE concentrations and self-reported truck and bus traffic near the home (data not shown).



**Figure 2.** Box plots of home I/O ratios for PM<sub>2.5</sub>, absorbance (Abs), and particle-associated elements: (A) winter, (B) summer. From bottom to top, each box presents the 5<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 95<sup>th</sup> percentiles.



**Figure 3.** Box plots of ratios of home indoor to home outdoor concentrations for VOCs and aldehydes: (A) winter, (B) summer. From bottom to top, each box presents the 5<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 95<sup>th</sup> percentiles.



**Figure 4.** Time series plot of winter outdoor MTBE concentrations measured at individual homes and at the urban and upwind fixed sites.

## Summary and Discussion

We presented methods and preliminary results of urban air toxic exposures of Harlem high school students measured in the NYC TEACH study. Median concentrations for personal, home outdoor, and home indoor samples were displayed to examine general ranges of concentrations, relationships among concentrations measured in the three locations, and analytical detection limits. Median I/O ratios were examined for all pollutants to determine the relative importance of indoor and outdoor sources. Finally, to explore spatial patterns in traffic-related VOCs, ambient concentrations of MTBE measured at the subject's homes, on the school roof, and at the upwind site were examined.

In general, personal, indoor, and outdoor median concentrations of most particle-associated elements were similar, suggesting that ambient sources may have driven indoor and personal exposures for most elements measured. Little evidence was seen for major indoor sources of particle-associated elements in this subject population, which excluded homes with smokers. Evidence for indoor and personal sources of particle-associated

elements did exist for a small number of elements, however. Seasonal differences in home AERs (lower in winter than in summer) appeared to influence I/O ratios.

In contrast, a more varied pattern of relationships among personal, home outdoor, and home indoor concentrations was observed for VOCs and aldehydes. For formaldehyde and acetaldehyde, and several VOCs, indoor concentrations far exceeded outdoor levels and appeared to dominate personal exposures. Strong seasonal differences in I/O ratios were observed for these compounds, reflecting the influence of home AERs. For other VOCs, more consistent indoor, outdoor, and personal concentrations were observed, suggesting that ambient concentrations may have been the driving force for personal exposures to VOCs in some cases. This was especially evident for the group of VOCs associated with motor vehicle emissions, including benzene, toluene, ethylbenzene, xylenes, and MTBE. Thus, there were two classes of VOCs apparent in this study, those related mainly to indoor sources and those related mainly to outdoor sources. Spatial and temporal patterns of winter MTBE concentrations demonstrated a strong urban influence on exposure levels, with spatial variability across homes that was consistent with differential traffic impacts.

Active or passive smoking can have a large impact on indoor and personal concentrations. For this reason, we excluded smokers and smoking families from the study based on self-report. We chose not to burden the subjects with urine sampling and thus were unable to use cotinine to verify nonexposure status. If smoking had occurred by subjects during the 48-hr sampling period, it is likely that personal  $PM_{2.5}$  concentrations would

have exceeded the indoor values. This was not observed (Table 2), which provides some measure of confidence that the self-reporting was valid.

These results demonstrate exposures to a wide range of air toxic pollutants among young people attending school in inner-city New York. Although exposures to some air toxics are clearly driven by indoor sources, exposures to many other pollutants appear to relate more to ambient sources. For several VOCs, urban motor vehicle emissions appear to play an important role in exposures.

The implications of multiple air toxic exposures to the health of young people in NYC are not known. However, given the multiple social, economic, and health stresses faced by many urban residents, the possible health impacts of these cumulative exposures should be a high priority for future research.

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