Final Report

Air Toxics in Allegheny County: Sources, Airborne Concentrations, and Human Exposure

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EXECUTIVE SUMMARY

In January 2002, the Allegheny County Health Department (ACHD) in collaboration with Carnegie Mellon University embarked on a project to investigate air toxics in Allegheny County. The project involved both baseline and intensive sampling a suite of gas-phase organic air toxics. Measurements were made at multiple sites that represent different source/exposure regimes. A risk model was used to estimate chronic and acute cancer and non-cancer health risk. Statistical and deterministic modeling tools were used for the source-apportionment analysis.

The study sites were chosen to compare air toxic concentrations and health risks among areas dominated by different sources. Two of the sites were in residential areas adjacent to Neville Island, which is heavily industrialized. Sites were also located in downtown Pittsburgh, which has substantial mobile source emissions. A final site was located to measure regional background air toxic concentrations.

Ambient concentrations of twelve of the air toxics exhibited little spatial variability in Allegheny County. These twelve are 1,2-dichloropropane, 1,2-dibromomethane, bromoform, hexachlorobutadiene, chlorobenzene, bromomethane, 1,2-dichloroethane, 1,2,4-trichlorobenzene, chloromethane, carbon tetrachloride, formaldehyde and propionaldehyde. Urban concentrations of twelve air toxics were 1.25 to 2 times greater than the regional background site. These include 1,1 dichloroethane, 1,1,2-trichloroethane, 1,1,-dichloroethene, 1,1,2,2-tetrachloroethane, MTBE, 1,1,1-trichloroethane, benzyl chloride, chloroform, methyl isobutyl ketone, acetaldehyde, toluene and benzene. Fifteen of the thirty-nine measured pollutants exhibited significant site-to-site variable (at least a factor of 2), indicating important local sources. These fifteen are vinyl chloride, chloroethane, acrolein, hexane, 1,3-butadiene, carbon disulfide, m/p-xylene, o-xylene, tetrachloroethene, ethyl benzene, methylene chloride, styrene, 1,4-dichlorobenzene, trichloroethene, and hydrogen sulfide. The greatest spatial variability was seen for chlorinated compounds, which were highest at the Flag Plaza site in downtown Pittsburgh.

Study-average concentrations of twenty air toxics were above the national 50th percentile at at least one of the sites. Of these, twelve appear to be strongly influenced by local emissions with urban concentrations a factor of two or more greater than the regional background. Concentrations of benzene, toluene, propionaldehyde, tetrachloroethene, ethyl benzene, methylene chloride, styrene, 1,4-dichlorobenzene, trichloroethene, and hydrogen sulfide were greater than the national 75th percentile at all of the sites. This indicates a problem with regional emissions in southwestern Pennsylvania.

Lifetime cancer risks and non-cancer hazard quotients were determined for each compound. Historically been concern that spatial variation in air toxics sources and emissions rates may dominate risks and the estimated cancer risks across these four very different sites varied by less than a factor of two. In addition, the same pollutants contributed the majority of the cancer risks at all sites: formaldehyde, benzene and carbon tetrachloride. Two of these three pollutants, formaldehyde and carbon tetrachloride, are regional distributed which limited the site to site variability in health risks. Trichloroethene and 1,4-dichlorobenzene also added substantial risks at the downtown site. Only acrolein is predicted to pose a non-cancer health risk.

A mixture-interactions model was used as a first-cut screening tool to prioritize pollutant pairs for further study based on their plausible synergistic/antagonistic impacts on the toxicity of mixtures of gas phase air toxics for both cancer and non-cancer risks.
The greatest potential for interactions was predicted for acrolein and formaldehyde for respiratory non-cancer effects and formaldehyde and acetaldehyde for respiratory cancers. The method presented here for analyzing potential mixture can provide an informed basis for prioritizing particular interactions effects based on observed co-occurrence data.

The time series at each site are characterized by relatively stable background concentrations with short periods of higher concentrations. These short-duration, high-concentration events are likely associated with plumes from local sources influencing the site. The frequency and magnitude of these events varied from site to site and as a function of wind direction.

Preliminary source apportionment analysis has been performed using Positive Matrix Factorization (PMF). The goal of the analysis is to identify the sources of the air toxics posing the greatest health risk. The analysis indicates the importance of emissions from metallurgical coke production to benzene concentrations at the residential sites adjacent to Neville Island. Concentrations of 1,4-dichlorobenzene and trichloroethene were 12 and 26 times higher downtown compared to the regional background. This indicates an important local source(s) of these compounds, but the nature of these sources is not known. Only minor sources of these chlorinated toxics are contained in the Allegheny County Point Source Emissions Inventory and they are not emitted by mobile sources.

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INTRODUCTION

Title III of the 1990 Clean Air Act established 189 chemicals as air toxics or hazardous air pollutants (HAPs) of which 187 are still considered HAPs. Air toxics are pollutants that are known or suspected to cause serious health effects. Some of these species also play an important role in secondary aerosol and ground level ozone formation (Luecken, 2005). In the 1990s the Environmental Protection Agency (EPA) began the National Air Toxics Assessment (NATA) to determine the air toxics that pose the greatest risk to human health. NATA began with the 1996 assessment of 33 HAPs using a dispersion model and state and local emissions inventories to estimate nation wide exposure levels. The 33 compounds analyzed by NATA were those thought to pose the greatest risks. In 1999, the assessment was expanded to include 177 compounds. NATA determined that benzene presented the greatest potential cancer risk predominately from on road emissions, but that the total cancer risk associated with air toxics (1 to 25 in a million) was significantly smaller than the lifetime cancer rate in the US (1 in 3) (USEPA 2001). The greatest non-cancer risk was found to be respiratory issues. However large uncertainties still exist regarding sources, exposure and health risks mostly due to a lack of actual concentration measurements. Data is needed to evaluate predicted concentrations and to determine actual exposure.

Allegheny County has historically been the home of heavy industry. Though Pittsburgh's steel days are over, there are still 186 point sources in the county, 87 of which are large enough to be required to report air toxics emissions (ACHD 2004). There are still several large clusters of industrial activity, potentially creating concerns with environmental inequality.

In January 2002, the Allegheny County Health Department (ACHD) in collaboration with Carnegie Mellon University embarked on a project to investigate air toxics in Allegheny County. The project involved both baseline and intensive sampling a suite of gas-phase organic air toxics. Measurements were made at multiple sites that represent different source/exposure regimes. A risk model was used to estimate chronic and acute cancer and non-cancer health risk. Statistical and deterministic modeling tools were used for the source-apportionment analysis.

OVERVIEW AND OBJECTIVES OF RESEARCH

The overall project had five primary objectives:

1. Measure airborne concentrations of a large number of gas and particulate air toxics around Neville Island, in downtown Pittsburgh, and at a background site,
2. Estimate human exposure and health risks in the vicinity of sources and at the background location,
3. Quantify the contribution of different sources (regional background, industrial, mobile) to airborne concentrations and estimated health risks,
4. Establish the relative importance of regional transport versus local sources to air toxics exposures in the County, and
5. Compare air toxic concentrations and estimated health risks in Allegheny County to other areas of the country where adequate data exist.

APPROACH AND STUDY DESIGN

Measurement Locations

Air toxics concentrations were measured at the six monitoring sites in and around Pittsburgh, PA (Figure 1). Four of these sites are operated by the Allegheny County Health Department (ACHD) for compliance monitoring: Avalon (AIRS# 42-003-0002, Latitude (N) 40 29 59, Longitude (W) 80 04 17), Stowe (AIRS# 42-003-0116, Latitude (N) 40 29 07, Longitude (W) 80 04 38), South Fayette (AIRS# 42-003-0067, Latitude (N) 40 22 34, Longitude (W) 80 10 14), and Flag Plaza (AIRS# 42-003-0031, Latitude (N) 40 26 36, Longitude (W) 79 59 25). The Avalon and Stowe sites are located in two residential neighborhoods about 0.8 km from the same heavily industrialized area, Neville Island. Neville Island is home to many chemical and manufacturing facilities including a large metallurgical coke production plant; many of these facilities are old and poorly controlled. Historically there have been concerns about the environmental burden caused by emissions from these facilities on the residents of nearby communities (Wittig 1995). Mobile sources are expected to be the dominate source class in the downtown area (Flag Plaza site). South Fayette is not located near any major sources and is therefore representative of the regional background concentration.

The Allegheny County Health Department measured 24 hour averaged concentrations at each of these sites on a 1 in 6 day schedule during 2006 to provide baseline concentration data. These data were used to determine spatial variations throughout the county and to provide annual data for use in the risk analysis.

Intensives were at conducted at Avalon, downtown at the Diamond Building, and at the Carnegie Mellon University Campus. These intensives featured hourly measurements of gas-phase organic air toxics. The Diamond Building is located on the corner of Fifth and Liberty Avenues in downtown Pittsburgh, about one mile west of the Flag Plaza site. The Flag Plaza site could not be used for the hourly measurements because it lacked the necessary infrastructure. The Diamond Building and Avalon sites were chosen for hourly measurements to further understand the sources and prosperities of air toxics in heavily urbanized areas. The Carnegie Mellon University site was located adjacent to a large construction site and measurements were taken there to explore the effect of a source that is not routinely included in inventories or health analyses. High time resolved data collected at an urban background site in 2002 were also considered to further investigate explore air toxics exposure variations. A summary of the measurements taken during this project is shown in Table 1.

Table 1 Summary of measurements taken during project

Meaurement Site	24 hr Measurements	Hourly Measurements
Neville Island Influenced		
Avalon	1in 6 for 2006	Oct. 2006 - Jan. 2007
Stowe	1in 6 for 2006	-----
Downtown		
Flag Plaza	1in 6 for 2006	-----
Diamond Bldg.	-----	Feb. 2008 -May 2008
Carnegie Mellon University		
Constrution Site	-----	Jun. 2007 - Nov. 2007
Urban Background	-----	Jan. 2002 - Feb. 2002
Regional Background		
South Fayette	1in 6 for 2006	-----

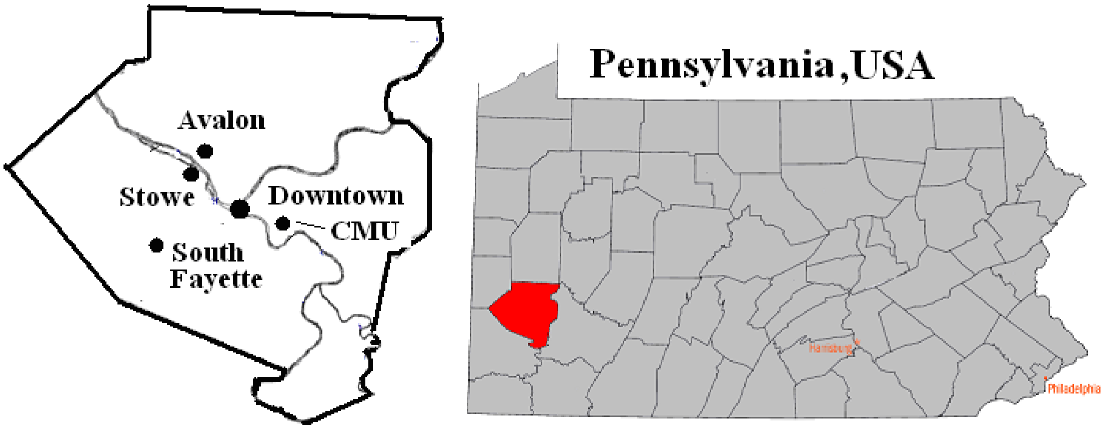


Figure 1 Location of air toxics monitoring sites.

Target Compounds

This study investigate ambient concentrations, health risks, and sources of anthropogenic volatile organic pollutants which with a special emphasis on those with high annual emissions in Allegheny County. Table 2 lists the 58 pollutants with the highest reported annual emissions for point sources in Allegheny County. The pollutants measured in this study are indicated by an "X" under the detector used to measure the pollutant, MSD or FID. Twenty-five of the fifty-one mobile source air toxics (MSAT) were also measured.

Instrumentation

Integrated Measurements

Twenty-four average concentrations were measured at the four ACHD air monitoring sites shown in Figure 1. These measurements were taken on a 1 in 6 day schedule following standard EPA standard protocols (TO-15 and TO-11a). These measurements were used to determine the spatial variation in air toxic levels and estimate chronic health risks.

High Time Resolved Measurements of Gas Phase Air Toxics

An automated GC/MS/FID (gas chromatograph/ mass spectrometer/ flame ionization detector) system was developed to measure gas phased concentrations of target air toxics as well as other volatile organic compounds (VOCs). The instrument consisted of an automated inlet fabricated at CMU, shown in Figure 2, connected to an Agilent 6890N GC/ 5975B MS/FID (6890N gas chromatograph/5975B mass spectrometer/flame ionization detector). The inlet was based on the design of Millet et al (2005) with different sorbent traps, GC columns, and analysis protocols.

The automated inlet consists of a main sampling line that drew ambient air through a 2 micron particle filter and a Nafion dryer (Perkin Elmer) to remove moisture at a flow rate of 2.5±.3 slpm. Two 30±.2 ml/min sample lines were drawn off of the main line to a heated automated valve assembly box containing three 12 port, 2-way switching valves (Vici Valco). The valves changed positions during runs to switch between trapping analyte and desorbing analyte onto the head of the GC columns. For 45 minutes of every hour the valves were positioned to flow across two OI Analytical #10 compound traps. After trapping, the valve positions changed and analyte was desorbed onto the head of one of two GC columns. The temperature of the GC oven was ramped from 40 to 200 ^{o}C using a specified protocol so that different compounds were sent to the detectors at different retention times for quantification by either MS or FID. The inlet was designed \so that the trapping period for a sample coincides with the analysis of the previous sample allowing for continuous sampling and analysis.

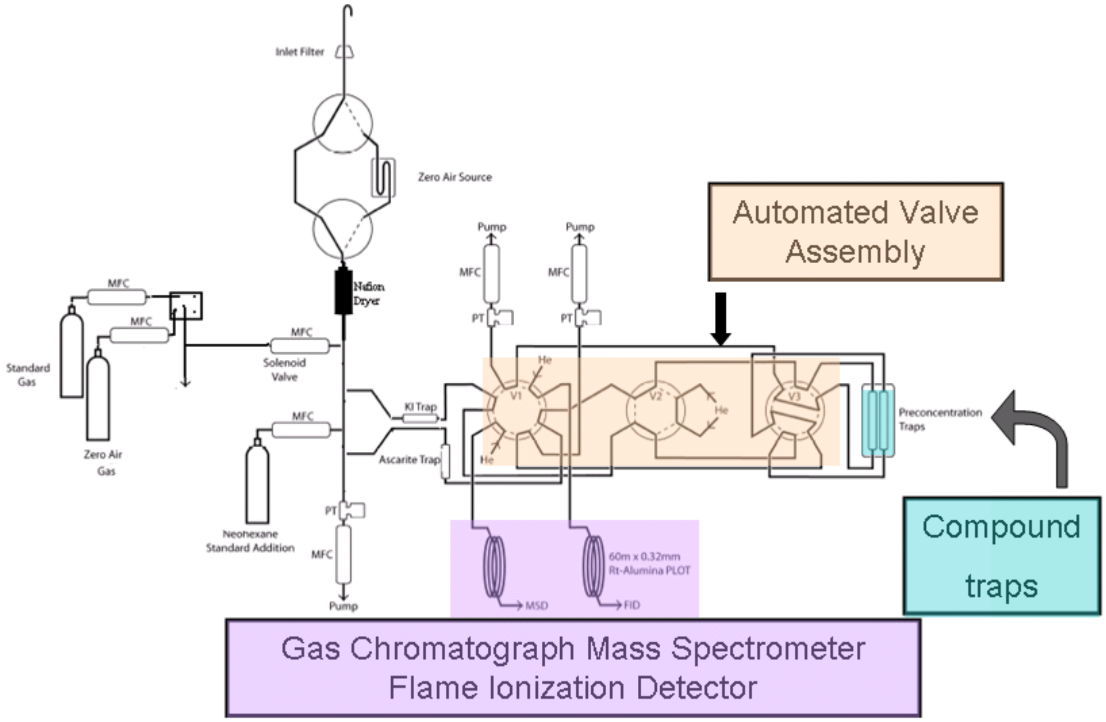
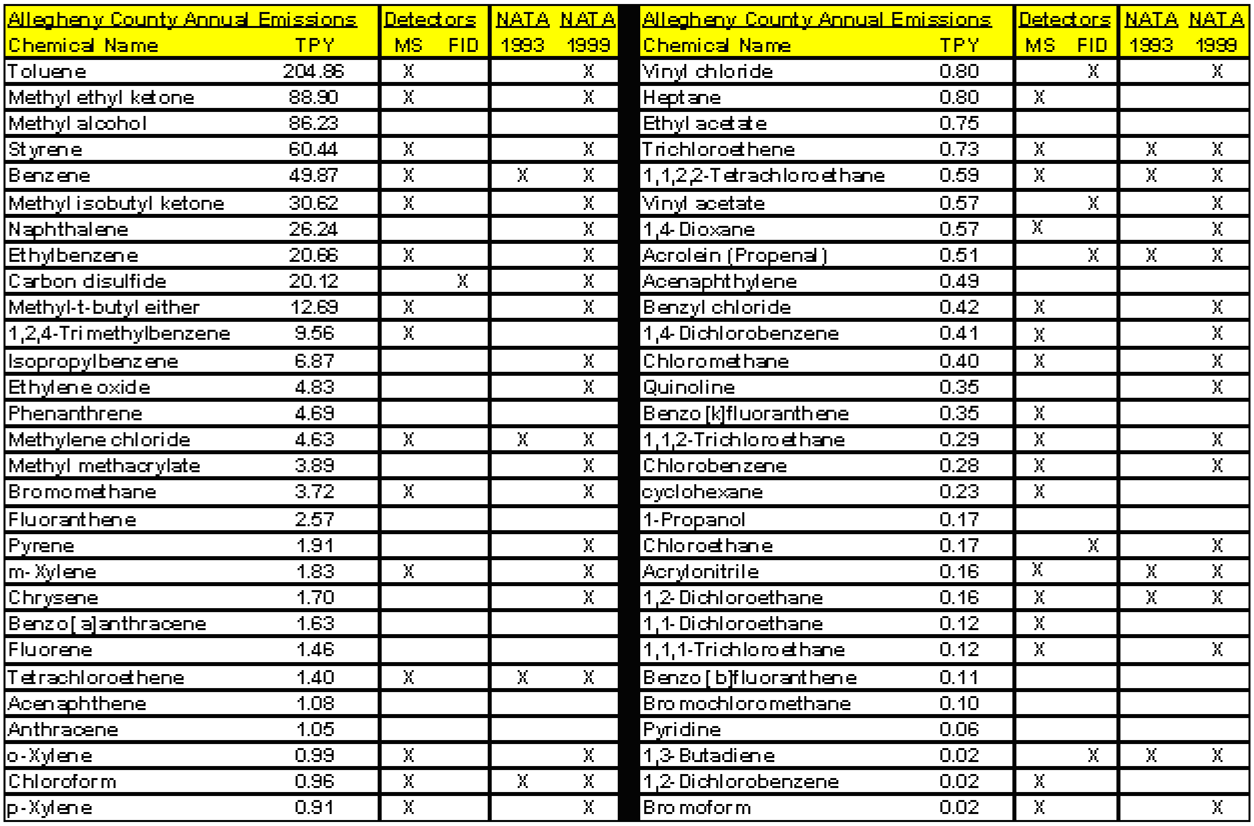


Figure 2 Schematic of automated GC/MS/FID (Millet, 2005)

Calibration and Data Validation

Calibration involved determining retention times and quantifying the MS response to varying amounts of analyte. The main line could be switched between outside air during sampling and zero air from a zero air generator (AADCO 737-series Pure Air Generator) during standard or zero-air runs. During standard runs, calibration gas is added to the mainline to achieve a wide range of concentration levels to test instrument performance. In order to quantify the response of the MS to different concentrations of VOCs in the air, the 1ppm TO-15/TO-17 gas standard from Spectra Chemicals was used as well as a 1ppm mixture of light VOCs from Scott Specialty Gas. The compound retention times were first identified for each peak using the mass spectra for identification. Once the retention times were known, a SIM (single-ion mode) method was developed to maximize MS sensitivity to the chemical compounds in the standard. The standard was dynamically diluted over concentrations ranging from 1ppt to 146 ppb to span the expected range of ambient concentrations. Each calibration point was repeated 3 to 5 times. The relationship between the response area and the analyte mass was determined and used to find airborne concentrations during measurement runs. Variance in MS response to repeated runs with constant concentration was used to determine measurement uncertainty. Table 3 lists the detection limits for the automated instrument.

Table 2 Annual emissions of important volatile organic compounds in the ACHD Point Source Inventory (ACHD 2004).



Allegheny County Annual Emissions		Detectors		NATA	NATA
Chemical Name	TPY	MS	FID	1993	1999
Toluene	204.86	X			X
Methyl ethyl ketone	88.90	X			X
Methyl alcohol	86.23				
Styrene	60.44	X			X
Benzene	49.87	X		X	X
Methyl isobutyl ketone	30.62	X			X
Naphthalene	26.24				X
Ethylbenzene	20.66	X			X
Carbon disulfide	20.12		X		X
Methyl-t-butyl either	12.69	X			X
1,2,4-Trimethylbenzene	9.56	X			
Isopropylbenzene	6.87				X
Ethylene oxide	4.83				X
Phenanthrene	4.69				
Methylene chloride	4.63	X		X	X
Methyl methacrylate	3.89				X
Bromomethane	3.72	X			X
Fluoranthene	2.57				
Pyrene	1.91				X
m-Xylene	1.83	X			X
Chrysene	1.70				X
Benzo[a]anthracene	1.63				
Fluorene	1.46				
Tetrachloroethene	1.40	X		X	X
Acenaphthene	1.08				
Anthracene	1.05				
o-Xylene	0.99	X			X
Chloroform	0.96	X		X	X
p-Xylene	0.91	X			X
Vinyl chloride	0.80		X		X
Heptane	0.80	X			
Ethyl acetate	0.75				
Trichloroethene	0.73	X		X	X
1,1,2,2-Tetrachloroethane	0.59	X		X	X
Vinyl acetate	0.57		X		X
1,4-Dioxane	0.57	X			X
Acrolein (Propenal)	0.51		X	X	X
Acenaphthylene	0.49				
Benzyl chloride	0.42	X			X
1,4-Dichlorobenzene	0.41	X			X
Chloromethane	0.40	X			X
Quinoline	0.35				X
Benzo[k]fluoranthene	0.35	X			
1,1,2-Trichloroethane	0.29	X			X
Chlorobenzene	0.28	X			X
cyclohexane	0.23	X			
1-Propanol	0.17				
Chloroethane	0.17		X		X
Acrylonitrile	0.16	X		X	X
1,2-Dichloroethane	0.16	X		X	X
1,1-Dichloroethane	0.12	X			
1,1,1-Trichloroethane	0.12	X			X
Benzo[b]fluoranthene	0.11				
Bromochloromethane	0.10				
Pyridine	0.06				
1,3-Butadiene	0.02		X	X	X
1,2-Dichlorobenzene	0.02	X			
Bromoform	0.02	X			X

Table 3 Compounds measured by automated GCMS/FID and detection limits in $\mu g/m^3$

Chemical Name	Chemical Class	Detection Limit
methylene chloride	Air Toxic	0.35
1,1-dichloroethane	Air Toxic	0.08
chloroform	Air Toxic	0.05
carbon tetrachloride	Air Toxic	0.06
benzene	Air Toxic	0.16
trichloroethene	Air Toxic	0.05
1,2-dichloroethane	Air Toxic	0.04
1,2-dichloropropane	Air Toxic	0.23
toluene	Air Toxic	0.19
1,1,2-trichloroethane	Air Toxic	0.05
1,2-dibromoethane	Air Toxic	0.08
bromoform	Air Toxic	0.10
chlorobenzene	Air Toxic	0.09
ethylbenzene	Air Toxic	0.09
m-xylene/p-xylene	Air Toxic	0.09
o-xylene	Air Toxic	0.09
styrene	Air Toxic	0.09
1,1,2,2-tetrachloroethane	Air Toxic	0.14
benzyl chloride	Air Toxic	0.26
hexachloro-1,3-butadiene	Air Toxic	0.53
1,2,4-trichlorobenzene	Air Toxic	7.42
methyl isobutyl ketone	Air Toxic	2.05
freon11	VOC	0.56
freon 113	VOC	0.38
trans-1,2-dichloroethene	VOC	0.40
cyclohexane	VOC	0.03
cis-1,2-dichloroethene	VOC	0.04
heptane	VOC	0.08
1,1,1-trichloroethane	VOC	0.03
bromodichloromethane	VOC	0.07
methyl ethyl keton	VOC	0.29
cis-1,3-dichloropropene	VOC	0.09
dibromochloromethane	VOC	0.09
tetrachloroethene	VOC	0.14
trans-1,3-dichloropropene	VOC	0.02
methyl butyl ketone	VOC	0.20
4-ethyltoluene	VOC	0.74
1,3,5-trimethylbenzene	VOC	0.25
1,2,4-trimethylbenzene	VOC	0.25
1,3-dichlorobenzene	VOC	0.30
1,2-dichlorobenzene	VOC	0.30

The performance of the automated GC/MS/FID based instrument was evaluated by comparing results to 24-hr canister samples taken following the TO-15 protocols. The comparisons were made using data collected at the Avalon site. For a given inter-comparison day, the canister concentrations were compared to the average concentration of the 24 hourly measurements taken during the same period. Good agreement was found with most compounds and those that exhibited poor inter-comparison where removed from analysis. Figure 3 shows results for the inter-comparison for toluene and benzene.

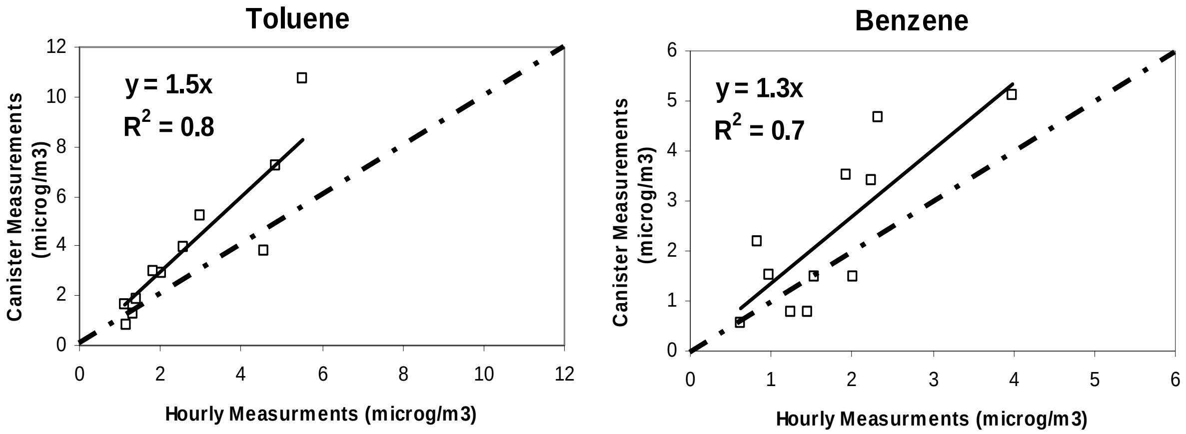


Figure 3 Comparison of averaged hourly concentrations from automated GC-MS/FID and 24-hr measurements from SUMMA canisters.

Thermal Desorption Aerosol GC-MS

A large suite of semivolatile organic molecular markers and air toxics were measured in downtown Pittsburgh with the Thermal Desorption Aerosol GC-MS based system (TAG). This suite covers several compound classes (n-alkanes, n-alkanoic acids, PAHs, triterpanes, etc.) and illustrates a spectrum of source contributions ranging from mostly local sources to mostly regional sources. A schematic of the TAG inlet is shown in Figure 4; the instrument is described in detail by Williams et al. (2006).

TAG has two modes of operation: ambient sampling with concurrent GC-MS analysis of the previously collected sample, and thermal desorption of the previously collected sample onto the GC column. All processes are completely automated and are controlled through Labview. During sampling, ambient air is pulled through a $PM_{2.5}$ cyclone and 3/8" copper tubing at 8.5 lpm into a custom collection inlet fabricated by Aerosol Dynamics, Inc. (Berkeley, CA). Particles are humidified to increase adhesion and minimize bounce before inertial impaction onto a collection cell, held at about 30-35°C during collection. Following collection, the cell is heated to 50°C for a couple minutes to purge water and volatile compounds from the sample. The cell and transfer lines are then ramped to a hold temperature of 300°C to thermally desorb the collected sample. Analytes are transferred to a six-port valve (Valco) held at 300°C, after which they are injected onto the head of the GC column at 45°C. During measurement campaigns, sampling was set on a 26-hour cycle that includes collection of twelve 90-minute ambient samples (along with thermal desorption, measurement resolution is 2 hours) as well as two 1-hour blanks. Analysis is ongoing for an additional set of measurements set on a 24-hour cycle that included three 4-hour daytime samples, two 1-hour blanks, and one overnight sample. Calibration standards used in this work are discussed in more detail below.

Online GC-MS analysis is performed using an Agilent 5890 GC coupled to a 5971 MSD. Chromatographic separation was performed using a Restek Rtx-5MS fused capillary column (30 m x 0.25 mm x 0.25 μm) with 1 mL/min flow in helium. The GC method takes one hour to complete and uses the following oven temperature protocol: initial temperature 80°C, ramp

50°C/min to 45°C, hold; ramp 8.6°C/min to 310°C, hold; ramp 70°C/min to 80°C final temperature for the start of the next run. The MS was operated in Selected Ion Monitoring (SIM) mode for the duration of this study; SIM windows used in this work is shown in Table 1. In addition to the analytes of interest, oxygen (m/z = 32) and CO_2 (m/z = 44) signals were monitored to ensure absence of major leaks, and polysiloxane ions (m/z = 207, 281) were monitored to ensure stability of the column stationary phase. Contaminant ions associated with Inertium that was applied to passivate all instrument parts contacting the sample (m/z = 211, 215, 289, 293, AMCX, Bellefonte, PA) were also monitored, but levels were usually low or absent from chromatograms.

TAG was calibrated using liquid standards that are manually injected directly into the collection cell. Standard #1 contained a mixture of nonpolar and polar analytes of interest (alkanes, alkanoic acids, PAHs, hopanes, and several of the marker compounds shown in Table 1), and was used to calibrate the MS response and stability via a multipoint calibration at the onset of measurements and a single-point calibration performed on most subsequent measurement days. Standard #2 contained a mixture of deuterated n-alkanes (C16, C20, C24, C30, C36), n-alkanoic acids (C16, C18), and cholesterol-d6. This mixture was injected into the collection cell almost daily on top of collected ambient samples, and instrument response to the deuterated analytes was compared to injections onto a blank cell in an effort to determine the extent of matrix effects and sample carryover into subsequent samples. Analysis of this data is ongoing, but the main findings thus far are (1) similar response for the n-alkanes when spiked in both blank and ambient samples, (2) much greater response for the alkanoic acids when spiked in ambient samples, suggesting the organic matrix may partially prevent decomposition of polar compounds during thermal desorption, and (3) small or negligible carryover (≈10%) into subsequent samples for the deuterated compounds.

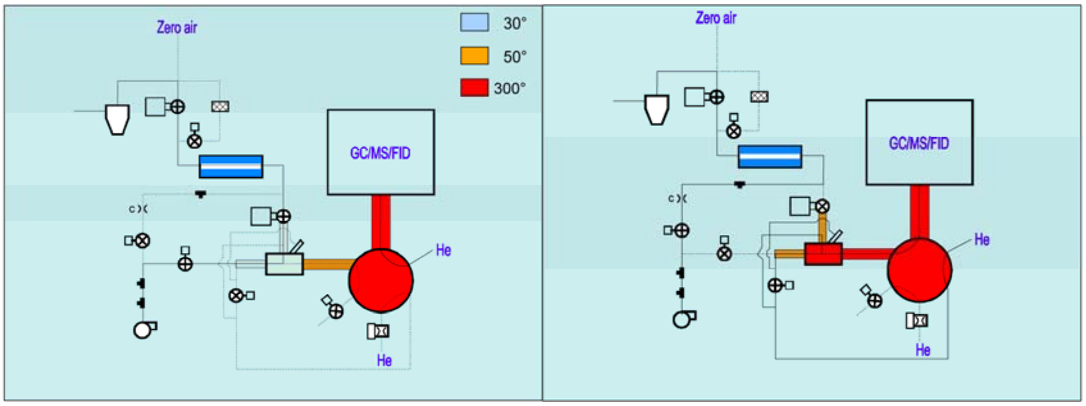


Figure 4. Schematic diagrams showing heated zones and flow paths during sampling/analysis mode (left) and thermal desorption mode (right). (From Dr. Nathan Kreisberg, Aerosol Dynamics Inc.)

RESULTS

Exposure

Tables 4 and 5 summarize the results from the 24-hr average measurements made at the four sites. The table lists mean, median, standard deviation, 95th, 75th, median, 25th, and 5th percentile concentrations. The annual average concentrations are plotted in Figures 5 and 6. Daily air toxics concentrations at the four main sites ranged from below detection limit to 24.4 ppb. Concentrations of some toxics exhibited little variation in time or space, but many exhibited significant site-to-site and day-to-day variation. Relative standard deviations ranged from zero to 6.8 times the mean. Concentrations of toluene, acetone, formaldehyde and benzene had the highest one-day concentration spikes at all sites except downtown where larges spikes in methylene chloride were observed.

One of the main goals of this work was to explore the spatial variability of air toxic concentrations throughout Allegheny County. Study-average concentrations at the ACHD sites are plotted in Figure 7. To simplify the discussion, we have averaged the data for the two residential sites adjacent to Neville Island (Stowe and Avalon), as the toxic concentrations at these two sites were similar. Figure 7 also separates pollutants into those dominated by regional and local sources based on comparisons with measurements at the regional background site. The air toxics sources were assumed to be regional when the concentrations at the two urban sites were within 25% of the regional background. Concentration ratios greater than this indicate significant contributions of local sources. The pollutants with elevated concentrations at the urban sites were further subdivided into those with concentrations ratios between 1.25 and 2 and those with concentration ratios greater than 2.

Figure 7 also compares air toxics concentrations around Pittsburgh, PA to data from urban areas throughout the United States. The national data are from the Air Quality System, AQS, a nationwide monitoring network located primarily in cities and towns to continuously monitor air toxics concentrations. Sonoma Technology, Inc. provided air toxic concentration distributions derived from national monitoring data for 2003 to 2005. The national data provide a bench mark for assessing the relative importance of air toxics at the different sites.

Ambient concentrations of twelve of the air toxics exhibited little spatial variability in Allegheny County. These twelve are 1,2-dichloropropane, 1,2-dibromomethane, bromoform, hexachlorobutadiene, chlorobenzene, bromomethane, 1,2-dichloroethane, 1,2,4-trichlorobenzene, chloromethane, carbon tetrachloride, formaldehyde and propionaldehyde. Figure 7 indicates that concentrations of only four of these regionally distributed toxics are above the national 50th percentile: chloromethane, carbon tetrachloride, formaldehyde, and propionaldehyde. Chloromethane concentrations in Allegheny County are roughly equivalent the national 75th percentile; chloromethane is emitted by natural sources through biomass burning/rotting (HSBD 2005). Propionaldehyde concentrations in Allegheny County are greater than the 95th percentile of the national data. There are many possible sources of propionaldehyde, including wood burning (HSDB 2003).

Table 4 Summary of air toxic concentrations in ppbv measured using SUMMA canisters and TO-15 method.

	FLAG PLAZA							SOUTH FAYETTE						
Chemical Name	**Mean**	**Median**	**5th percentile**	**25th percentile**	**75th percentile**	**95th Percentile**	**Stand. Dev.**	**Mean**	**Median**	**5th percentile**	**25th percentile**	**75th percentile**	**95th Percentile**	**Stand. Dev.**
Dichlorodifluoromethane	0.53	0.52	0.48	0.51	0.54	0.58	0.03	0.50	0.50	0.45	0.48	0.52	0.56	0.04
Chloromethane	0.64	0.63	0.54	0.58	0.69	0.76	0.07	0.57	0.56	0.49	0.53	0.61	0.69	0.07
1,2-Dichloro-1,1,2,2,tetrafluoroleth	0.02	0.02	0.01	0.01	0.02	0.02	0.00	0.02	0.02	0.01	0.01	0.02	0.02	0.01
Chloroethene	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,3-Butadiene	0.07	0.05	0.01	0.03	0.09	0.16	0.05	0.02	0.01	0.00	0.00	0.03	0.07	0.03
Bromomethane	0.01	0.01	0.00	0.01	0.01	0.02	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01
Chloroethane	0.01	0.00	0.00	0.00	0.01	0.02	0.02	0.00	0.00	0.00	0.00	0.01	0.01	0.00
Trichlorofluoromethane	0.31	0.31	0.26	0.29	0.33	0.38	0.04	0.27	0.27	0.24	0.25	0.28	0.33	0.03
Acetone	3.95	3.56	1.65	2.40	4.78	7.36	2.03	4.82	2.94	1.29	2.10	5.56	14.23	5.13
1,1-Dichloroethene	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Methylene Chloride	0.22	0.11	0.07	0.08	0.14	0.50	0.43	0.07	0.06	0.05	0.06	0.08	0.11	0.02
Carbon disulfide	0.07	0.02	0.01	0.02	0.04	0.26	0.18	0.03	0.02	0.01	0.02	0.06	0.07	0.03
Isopropyl Alcohol	0.72	0.55	0.22	0.35	0.94	1.75	0.57	0.28	0.22	0.10	0.17	0.34	0.65	0.18
1,1,2-Trichloro-1,2,2-trifluoroethane	0.12	0.12	0.10	0.11	0.13	0.14	0.01	0.08	0.08	0.06	0.08	0.08	0.09	0.01
Trans-1,2-Dichloroethene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,1-Dichloroethane	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MTBE	0.01	0.01	0.00	0.00	0.02	0.03	0.02	0.01	0.00	0.00	0.00	0.01	0.01	0.01
Methyl ethyl Ketone	0.53	0.46	0.25	0.34	0.66	0.96	0.30	0.53	0.36	0.16	0.21	0.74	1.44	0.49
Cis-1,2-Dichloroethene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hexane	0.20	0.14	0.06	0.10	0.25	0.50	0.17	0.10	0.09	0.04	0.06	0.12	0.18	0.05
Chloroform	0.03	0.02	0.01	0.02	0.03	0.04	0.01	0.02	0.02	0.01	0.01	0.02	0.02	0.01
Ethyl Acetate	0.04	0.01	0.00	0.01	0.03	0.11	0.09	0.01	0.01	0.00	0.00	0.02	0.04	0.01
Tetrahydrofuran	0.02	0.01	0.00	0.00	0.03	0.06	0.02	0.01	0.00	0.00	0.00	0.02	0.04	0.02
1,2-Dichloroethane	0.01	0.01	0.00	0.01	0.01	0.02	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.00
1,1,1-Trichloroethane	0.02	0.02	0.02	0.02	0.03	0.04	0.01	0.02	0.02	0.01	0.01	0.02	0.02	0.01
Benzene	0.42	0.34	0.16	0.22	0.55	0.85	0.27	0.33	0.22	0.08	0.15	0.34	0.60	0.47
Carbon tetrachloride	0.08	0.08	0.07	0.08	0.09	0.11	0.01	0.08	0.08	0.07	0.08	0.09	0.10	0.01
Cyclohexane	0.05	0.03	0.01	0.02	0.05	0.09	0.11	0.02	0.02	0.01	0.02	0.03	0.05	0.02
1,2-Dichloropropane	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Bromodichloromethane	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Trichloroethene	0.11	0.02	0.00	0.01	0.09	0.62	0.19	0.00	0.00	0.00	0.00	0.01	0.01	0.01
Heptane	0.09	0.07	0.03	0.05	0.12	0.22	0.07	0.06	0.05	0.03	0.04	0.07	0.12	0.03
Cis-1,3-Dichloro-1-Propene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Methyl Isobutyl Ketone	0.03	0.02	0.00	0.00	0.04	0.08	0.04	0.03	0.02	0.00	0.00	0.04	0.06	0.03
Trans-1,3-Dichloro-1-Propene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,1,2-Trichloroethane	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Toluene	0.85	0.52	0.23	0.38	0.97	1.92	1.08	0.51	0.41	0.09	0.24	0.59	0.99	0.62
Dibromochloromethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Methyl butyl Ketone	0.03	0.03	0.00	0.02	0.04	0.05	0.02	0.03	0.01	0.00	0.00	0.05	0.07	0.04
1,2-Dibromoethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Tetrachloroethylene	0.04	0.03	0.01	0.02	0.05	0.10	0.03	0.01	0.01	0.00	0.01	0.02	0.03	0.01
Chlorobenzene	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00
Ethylbenzene	0.10	0.07	0.04	0.05	0.13	0.26	0.07	0.04	0.03	0.01	0.02	0.04	0.08	0.03
m & p- Xylene	0.30	0.23	0.10	0.14	0.43	0.71	0.22	0.10	0.08	0.03	0.06	0.11	0.25	0.09
Bromoform	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Styrene	0.03	0.02	0.01	0.01	0.04	0.10	0.04	0.02	0.02	0.00	0.01	0.02	0.04	0.02
1,1,2,2-Tetrachloroethane	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
o-Xylene	0.11	0.08	0.04	0.05	0.15	0.27	0.08	0.04	0.03	0.01	0.02	0.05	0.10	0.03
1-Ethyl-4-Methylbenzene	0.05	0.04	0.01	0.02	0.06	0.09	0.04	0.02	0.01	0.01	0.01	0.02	0.06	0.02
1,3,5-Trimethylbenzene	0.03	0.03	0.01	0.02	0.04	0.07	0.02	0.02	0.01	0.00	0.01	0.02	0.05	0.02
1,2,4-Trimethylbenzene	0.12	0.08	0.03	0.06	0.15	0.25	0.08	0.05	0.03	0.01	0.02	0.05	0.11	0.04
Benzyl Chloride	0.00	0.00	0.00	0.00	0.01	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.01
1,3-dichlorobenzene	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,4-Dichlorobenzene	0.13	0.11	0.06	0.08	0.15	0.24	0.06	0.01	0.01	0.00	0.01	0.01	0.02	0.01
1,2-Dichlorobenzene	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01
1,2,4-Trichlorobenzene	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.01
Hexachloro-1,3-Butadiene	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01

	STOWE							AVALON						
Chemical Name	Mean	Median	5th percentile	25th percentile	75th percentile	95th Percentile	Stand. Dev.	Mean	Median	5th percentile	25th percentile	75th percentile	95th Percentile	Stand. Dev.
Dichlorodifluoromethane	0.51	0.50	0.46	0.48	0.53	0.55	0.04	0.51	0.50	0.46	0.49	0.53	0.57	0.03
Chloromethane	0.59	0.56	0.50	0.53	0.66	0.70	0.08	0.58	0.57	0.48	0.54	0.62	0.68	0.06
1,2-Dichloro-1,1,2,2,tetrafluoroleth	0.02	0.02	0.01	0.01	0.02	0.02	0.01	0.02	0.02	0.01	0.01	0.02	0.02	0.00
Chloroethene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,3-Butadiene	0.04	0.03	0.01	0.02	0.05	0.11	0.04	0.07	0.05	0.01	0.03	0.08	0.15	0.07
Bromomethane	0.01	0.01	0.00	0.01	0.01	0.02	0.01	0.01	0.01	0.00	0.01	0.01	0.02	0.01
Chloroethane	0.01	0.01	0.00	0.00	0.01	0.03	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.00
Trichlorofluoromethane	0.27	0.27	0.24	0.25	0.29	0.31	0.03	0.29	0.28	0.25	0.26	0.30	0.37	0.04
Acetone	5.12	3.89	2.04	2.91	5.67	11.38	3.64	5.59	3.64	1.73	2.72	7.27	15.06	4.61
1,1-Dichloroethene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Methylene Chloride	0.10	0.08	0.06	0.07	0.10	0.17	0.04	0.10	0.09	0.06	0.07	0.12	0.21	0.05
Carbon disulfide	0.03	0.02	0.01	0.02	0.03	0.07	0.02	0.03	0.02	0.01	0.02	0.04	0.09	0.03
Isopropyl Alcohol	0.33	0.31	0.14	0.19	0.41	0.71	0.18	0.46	0.37	0.14	0.26	0.59	1.18	0.31
1,1,2-Trichloro-1,2,2-trifluoroethane	0.08	0.08	0.07	0.07	0.08	0.09	0.01	0.08	0.08	0.07	0.08	0.08	0.09	0.01
Trans-1,2-Dichloroethene	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,1-Dichloroethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MTBE	0.01	0.00	0.00	0.00	0.01	0.03	0.01	0.01	0.01	0.00	0.00	0.02	0.03	0.01
Methyl ethyl Ketone	0.58	0.46	0.24	0.35	0.76	1.10	0.31	0.65	0.56	0.25	0.38	0.89	1.30	0.35
Cis-1,2-Dichloroethene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hexane	0.15	0.11	0.05	0.07	0.18	0.37	0.12	0.20	0.18	0.07	0.11	0.22	0.39	0.13
Chloroform	0.02	0.02	0.01	0.01	0.02	0.03	0.01	0.03	0.02	0.01	0.02	0.03	0.05	0.01
Ethyl Acetate	0.03	0.02	0.00	0.01	0.04	0.08	0.03	0.04	0.03	0.00	0.01	0.07	0.12	0.04
Tetrahydrofuran	0.02	0.01	0.00	0.00	0.03	0.05	0.02	0.02	0.01	0.00	0.00	0.02	0.08	0.02
1,2-Dichloroethane	0.01	0.01	0.00	0.01	0.01	0.01	0.00	0.01	0.01	0.00	0.01	0.01	0.01	0.00
1,1,1-Trichloroethane	0.02	0.02	0.01	0.01	0.02	0.02	0.01	0.02	0.02	0.01	0.01	0.02	0.02	0.01
Benzene	0.52	0.36	0.13	0.23	0.54	1.33	0.47	0.73	0.62	0.18	0.33	1.01	1.46	0.58
Carbon tetrachloride	0.08	0.08	0.07	0.08	0.09	0.10	0.01	0.08	0.08	0.07	0.08	0.09	0.10	0.01
Cyclohexane	0.03	0.02	0.01	0.02	0.04	0.09	0.03	0.05	0.04	0.02	0.02	0.05	0.10	0.03
1,2-Dichloropropane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Bromodichloromethane	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Trichloroethene	0.01	0.00	0.00	0.00	0.01	0.02	0.01	0.01	0.01	0.00	0.00	0.01	0.02	0.01
Heptane	0.07	0.05	0.03	0.04	0.10	0.17	0.05	0.09	0.07	0.04	0.05	0.10	0.22	0.06
Cis-1,3-Dichloro-1-Propene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Methyl Isobutyl Ketone	0.03	0.03	0.00	0.01	0.05	0.08	0.03	0.05	0.04	0.00	0.00	0.08	0.19	0.06
Trans-1,3-Dichloro-1-Propene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,1,2-Trichloroethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Toluene	0.68	0.54	0.21	0.39	0.89	1.71	0.45	0.98	0.78	0.39	0.56	1.29	2.13	0.58
Dibromochloromethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Methyl butyl Ketone	0.05	0.04	0.00	0.02	0.06	0.11	0.03	0.04	0.02	0.00	0.01	0.07	0.14	0.05
1,2-Dibromoethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Tetrachloroethylene	0.03	0.02	0.01	0.01	0.04	0.09	0.03	0.06	0.03	0.01	0.02	0.04	0.13	0.11
Chlorobenzene	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Ethylbenzene	0.13	0.06	0.03	0.04	0.11	0.44	0.21	0.12	0.10	0.04	0.08	0.13	0.26	0.07
m & p- Xylene	0.27	0.17	0.06	0.11	0.33	0.78	0.26	0.36	0.29	0.12	0.20	0.40	0.87	0.25
Bromoform	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Styrene	0.08	0.05	0.02	0.03	0.08	0.22	0.10	0.11	0.10	0.02	0.06	0.16	0.24	0.07
1,1,2,2-Tetrachloroethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
o-Xylene	0.12	0.08	0.02	0.05	0.14	0.31	0.11	0.15	0.13	0.05	0.09	0.18	0.34	0.09
1-Ethyl-4-Methylbenzene	0.04	0.03	0.01	0.02	0.05	0.11	0.04	0.07	0.06	0.02	0.04	0.09	0.13	0.04
1,3,5-Trimethylbenzene	0.03	0.02	0.01	0.01	0.04	0.08	0.02	0.04	0.03	0.01	0.02	0.05	0.11	0.03
1,2,4-Trimethylbenzene	0.11	0.07	0.03	0.06	0.11	0.31	0.09	0.16	0.13	0.05	0.11	0.18	0.38	0.10
Benzyl Chloride	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01
1,3-dichlorobenzene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
1,4-Dichlorobenzene	0.02	0.02	0.00	0.01	0.03	0.04	0.01	0.02	0.02	0.01	0.01	0.03	0.05	0.02
1,2-Dichlorobenzene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01
1,2,4-Trichlorobenzene	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.01	0.01	0.01
Hexachloro-1,3-Butadiene	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01

Table 5 Summary of air toxic concentrations in ppbv measured using cartridge and TO-11a method.

	FLAG PLAZA							SOUTH FAYETTE						
Chemical Name	**Mean**	**Median**	**5th percentile**	**25th percentile**	**75th percentile**	**95th Percentile**	**Stand. Dev.**	**Mean**	**Median**	**5th percentile**	**25th percentile**	**75th percentile**	**95th Percentile**	**Stand. Dev.**
Formaldehyde	1.69	1.26	0.48	0.84	2.46	3.59	1.13	1.68	1.30	0.57	0.99	2.22	3.50	1.16
Acetaldehyde	1.00	0.95	0.37	0.62	1.25	1.99	0.47	0.80	0.79	0.44	0.63	0.94	1.26	0.27
Acrolein	0.05	0.04	0.00	0.02	0.06	0.17	0.06	0.04	0.03	0.01	0.02	0.05	0.07	0.02
Acetone	1.63	1.48	0.83	1.18	2.20	2.72	0.70	1.15	1.05	0.58	0.83	1.46	1.82	0.48
Propionaldehyde	0.31	0.25	0.08	0.16	0.37	0.79	0.22	0.27	0.21	0.13	0.17	0.35	0.56	0.15
Methyl Ethyl Ketone	0.29	0.27	0.14	0.19	0.35	0.52	0.13	0.20	0.19	0.11	0.14	0.27	0.29	0.07
Methyl Isobutyl Ketone	0.02	0.01	0.00	0.00	0.02	0.07	0.02	0.01	0.00	0.00	0.00	0.00	0.05	0.03

	STOWE							AVALON						
Chemical Name	**Mean**	**Median**	**5th percentile**	**25th percentile**	**75th percentile**	**95th Percentile**	**Stand. Dev.**	**Mean**	**Median**	**5th percentile**	**25th percentile**	**75th percentile**	**95th Percentile**	**Stand. Dev.**
Formaldehyde	1.67	1.25	0.43	0.92	2.46	3.30	1.07	2.11	1.72	0.95	1.20	2.78	4.13	1.18
Acetaldehyde	1.02	0.85	0.40	0.66	1.28	1.96	0.55	1.11	0.97	0.60	0.73	1.29	2.18	0.50
Acrolein	0.06	0.06	0.01	0.03	0.08	0.14	0.06	0.07	0.06	0.02	0.05	0.09	0.15	0.04
Acetone	1.73	1.47	0.53	1.03	2.01	3.73	1.02	1.59	1.38	0.76	0.99	1.95	3.16	0.76
Propionaldehyde	0.32	0.23	0.12	0.17	0.41	0.70	0.21	0.34	0.27	0.14	0.21	0.43	0.69	0.17
Methyl Ethyl Ketone	0.29	0.25	0.10	0.17	0.35	0.59	0.16	0.49	0.27	0.16	0.22	0.41	0.96	0.96
Methyl Isobutyl Ketone	0.02	0.02	0.00	0.00	0.03	0.04	0.02	0.03	0.02	0.00	0.01	0.03	0.09	0.03

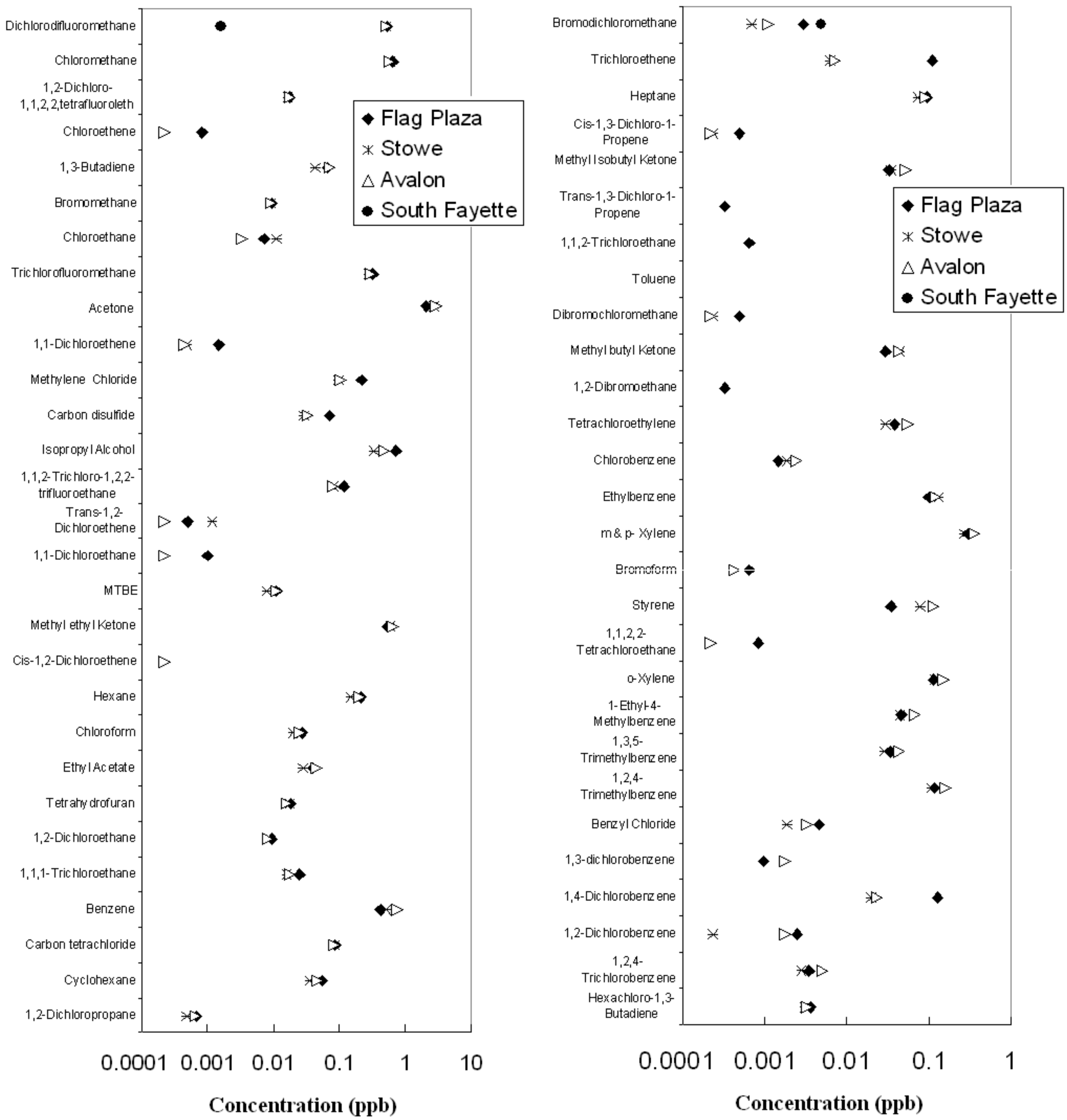


Figure 5 Study average air toxic concentrations measured at four ACHD sites measured using the TO-15 method.

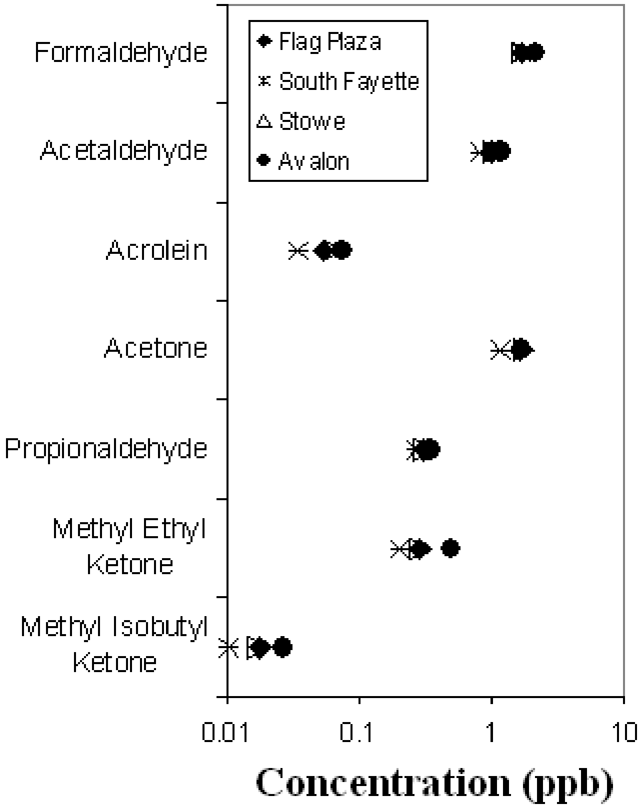


Figure 6 Study-average air toxic concentrations measured at four ACHD sites using the TO-11a method.

Urban concentrations of twelve air toxics appear to be moderately influenced by local sources (concentrations ratios of 1.25 to 2). These include 1,1 dichloroethane, 1,1,2-trichloroethane, 1,1,-dichloroethene, 1,1,2,2-tetrachloroethane, MTBE, 1,1,1-trichloroethane, benzyl chloride, chloroform, methyl isobutyl ketone, acetaldehyde, toluene and benzene. Figure 7 also indicates that even a modest increase (less than a factor of 2) in concentration can result in substantial shifts in exposure relative to the national data. For example, toluene concentrations are only 1.5 times higher at the urban sites, but this shift the exposure from the 50th percentile to the 75th relative to the national data. Benzene concentrations at the industrial influenced site are 1.6 times the regional background, which shifts concentrations from the 75th to almost the 95th percentile.

Fifteen of the thirty-nine measured pollutants exhibited large site-to-site variable (at least a factor of 2). These fifteen are vinyl chloride, chloroethane, acrolein, hexane, 1,3-butadiene, carbon disulfide, m/p-xylene, o-xylene, tetrachloroethene, ethyl benzene, methylene chloride, styrene, 1,4-dichlorobenzene, trichloroethene, and hydrogen sulfide. The greatest spatial variability was seen for chlorinated compounds, which were highest at the Flag Plaza site. For example, 1,4-dichlorobenzene and trichloroethene were 12 and 26 times higher downtown compared to the regional background. This indicates an important local source(s) of these compounds, but the nature of these sources is not known. Relative to the national data, these local emissions substantially influence exposure; for example, the average concentration of trichloroethene is below the 5th national percentile at the regional background site versus greater than the national 95th percentile at the downtown site. 4-Dichlorobenzene is used as an insecticide, deodorant, and a chemical intermediate for polymers(HSBD, 2008). Trichloroethene is used as a degreaser and in several industries including printing, automotive, and plastics (HSBD, 2008). Only minor sources of these chlorinated toxics are contained in the Allegheny County Point Source Emissions Inventory (ACHD 2006) and they are not emitted by mobile sources (USEPA 2007).

Figure 8 shows concentration ratios of study-average concentrations measured at the three ACHD urban sites (Avalon, Stowe, and Flag Plaza) versus those measured at the regional background site (South Fayette). In this figure we have divided the data into two groups: air toxics with peak concentrations at the industrial-influenced sites (Avalon and Stowe) and those that were highest at the downtown site.

Concentrations of styrene, tetrachloroethene, methyl isobutyl ketone, benzene and ethylbenzene were highest at the two industrial-influenced sites. Concentration ratios of these compounds versus the regional background ranged from 1.6 to 4.8. The largest concentrations ratios were observed for tetrachloroethene and styrene. The Allegheny County Point Source Emissions Inventory (ACHD 2006) indicates that the industrial facilities located on Neville Island are major sources of many of these toxics.

Concentrations of trichloroethene, 1,4 dichlrobenzene, methylene chloride, carbon disulfide, vinyl chloride, and 1,1,1-trichloroethene were highest at the Flag Plaza site (downtown). Concentration ratios of these compounds at downtown site versus the regional background ranged from 1.1 to 24.

Although it is no longer classified as an air toxic, hydrogen sulfide is also included in Figure 7. Concentrations in Avalon were a factor of 1000 over the 95th percentile of the national data. Hydrogen sulfide is a by product of coke production; there is a metallurgical coke works on Neville Island.

The comparisons with the national data shown in Figure 7 provide one measure of which air toxics are most problematic in Allegheny County. Study-average concentrations of twenty air toxics were above the national 50th percentile at one of the four ACHD sites. Of these, 12 appear to be strongly influenced by local emissions; concentration ratios greater than 2 relative to the background site. Concentrations of benzene, toluene, propionaldehyde, tetrachloroethene, ethyl benzene, methylene chloride, styrene, 1,4-dichlorobenzene, trichloroethene, and hydrogen sulfide were greater than the national 75th percentile at all of the sites. This indicates a problem with regional emissions in southwestern Pennsylvania.

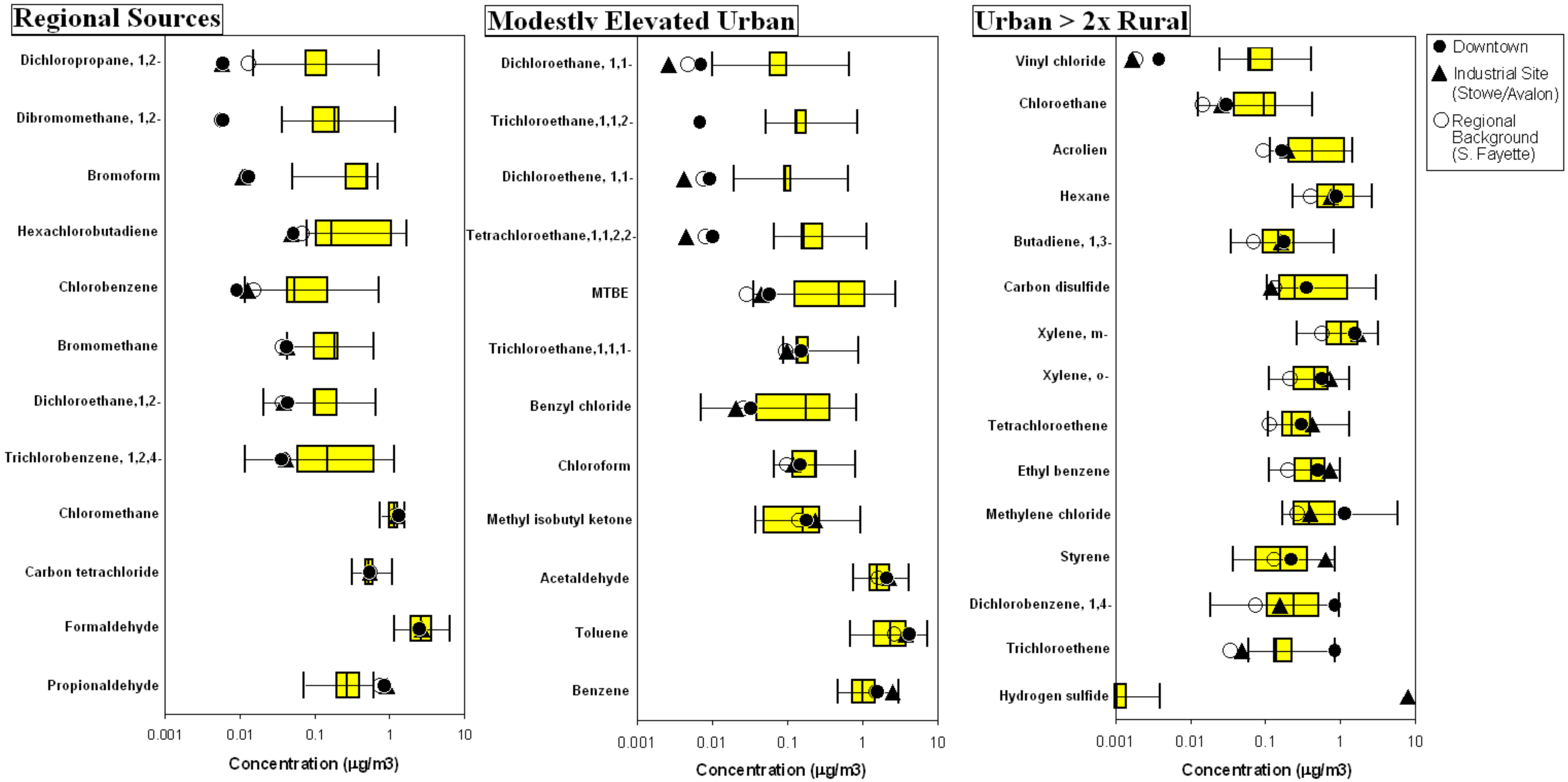


Figure 7 Comparison of Allegheny County annual average air toxics concentrations (symbols) to national data . The national data are presented using a box plot: the box extends from 25th percentile to the 75th percentile of the national data with the center line representing the 50th percentile national concentration. Whiskers extend to the 5th and 95th percentiles of the national data.

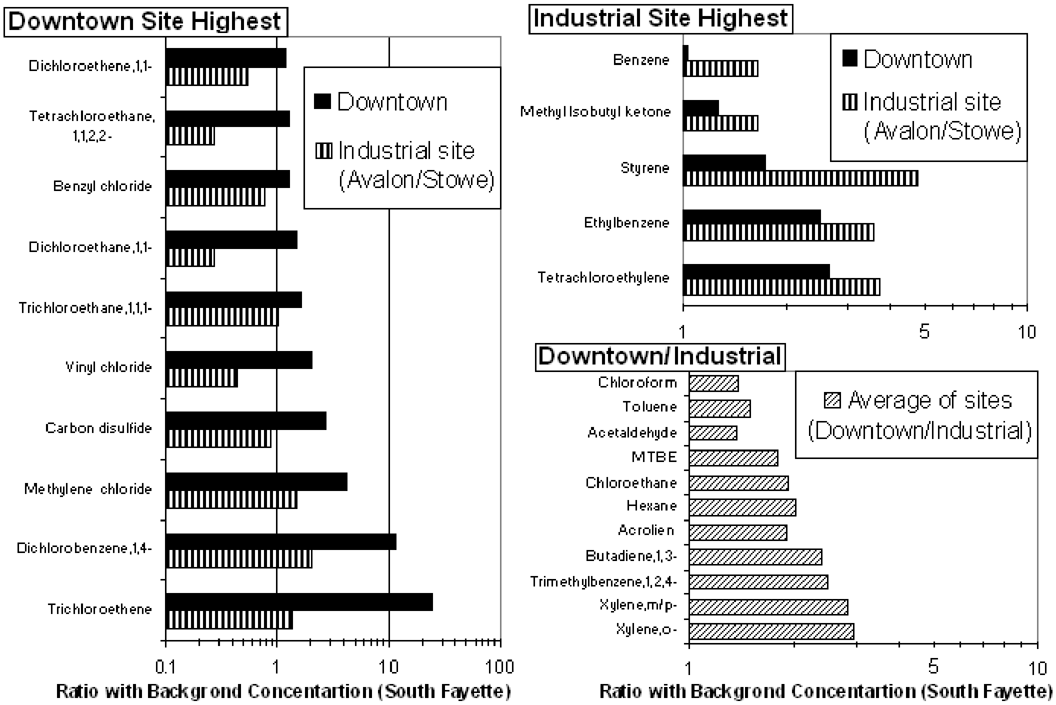


Figure 8 Ratio of the measured annual air toxic concentrations at Avalon/Stowe and Flag Plaza to those measured in South Fayette, the regional background site.

High Time Resolved Data

Figures 9-12 shows time series of hourly concentrations measurements of selected air toxics to illustrate the temporal variability of the data. Figure 9 plots of data from October 2006 measured at the Avalon site; Figure 10 shows a time series from January 2002 measured at an urban background site near Carnegie Mellon University; Figure 11 shows a time series from March/April 2008 measured at the Diamond Building; and Figure 12 shows a time series of measurements made in June 2007 next to a construction site on the Carnegie Mellon University campus.

The time series at each site are characterized by relatively stable background concentrations with short periods of higher concentrations. These short-duration, high-concentration events are likely associated with plumes from local sources influencing the site. The frequency and magnitude of these events varied from site to site and as a function of wind direction.

The plume events occurred most frequently and for longer durations at the Avalon site compared to the other sites. At this site, the characteristics of plumes were clearly a function of wind direction.

At the Diamond Building, large spikes in toluene concentrations were observed, but the plume events were less frequent than at the Avalon site. Baseline concentrations were also lower at the Diamond Building than at Avalon. Fewer plume events occurred at the urban background site compared to the Diamond Building or Avalon sites. This may have been due to traffic on a road adjacent to the site. Measurements taken adjacent to the construction site had lower concentrations and fewer plume events.

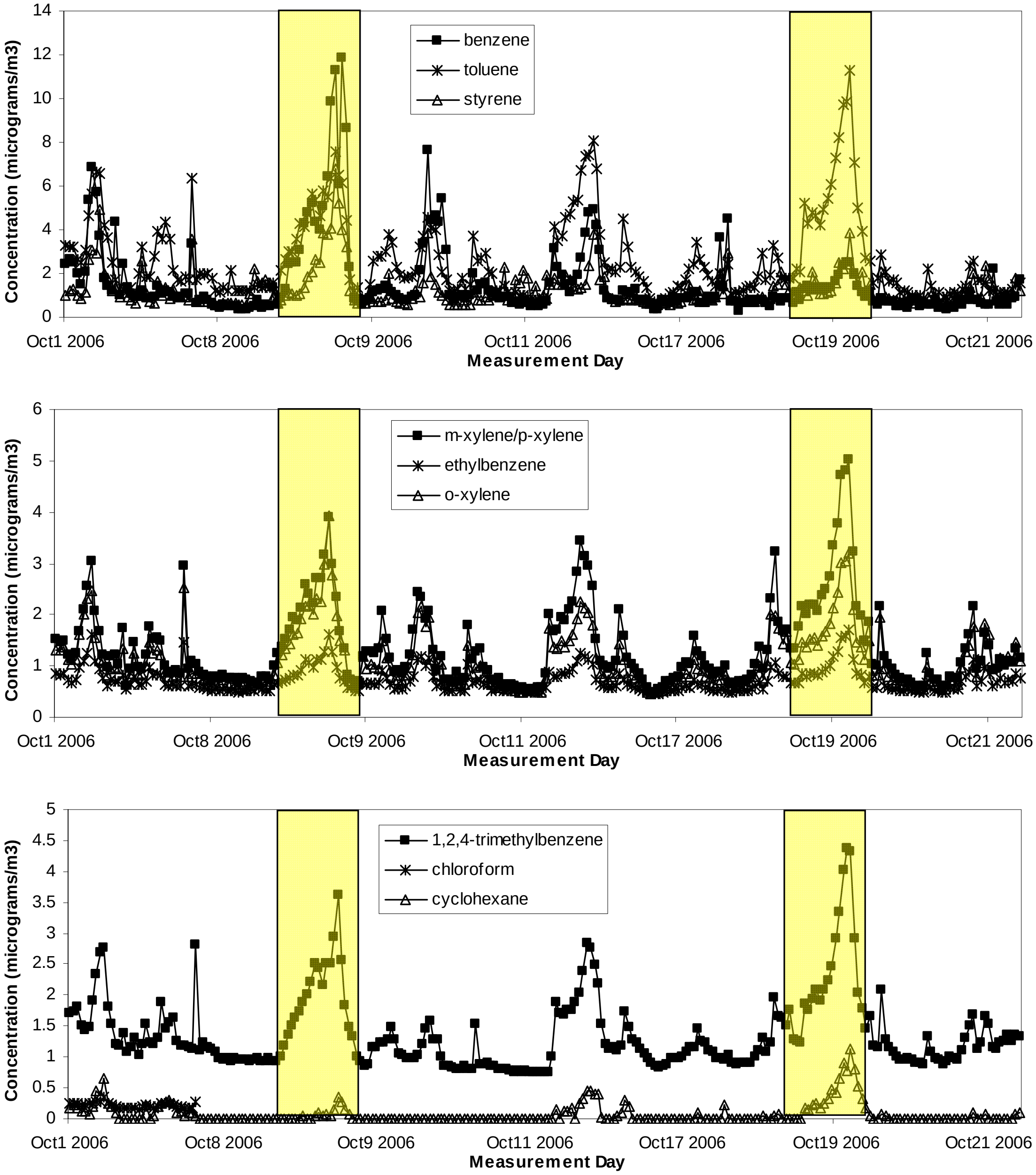


Figure 9 Time series of hourly concentration measured during October 2006 at the Avalon site. The shaded regions indicate two of the many plume that influenced this site.

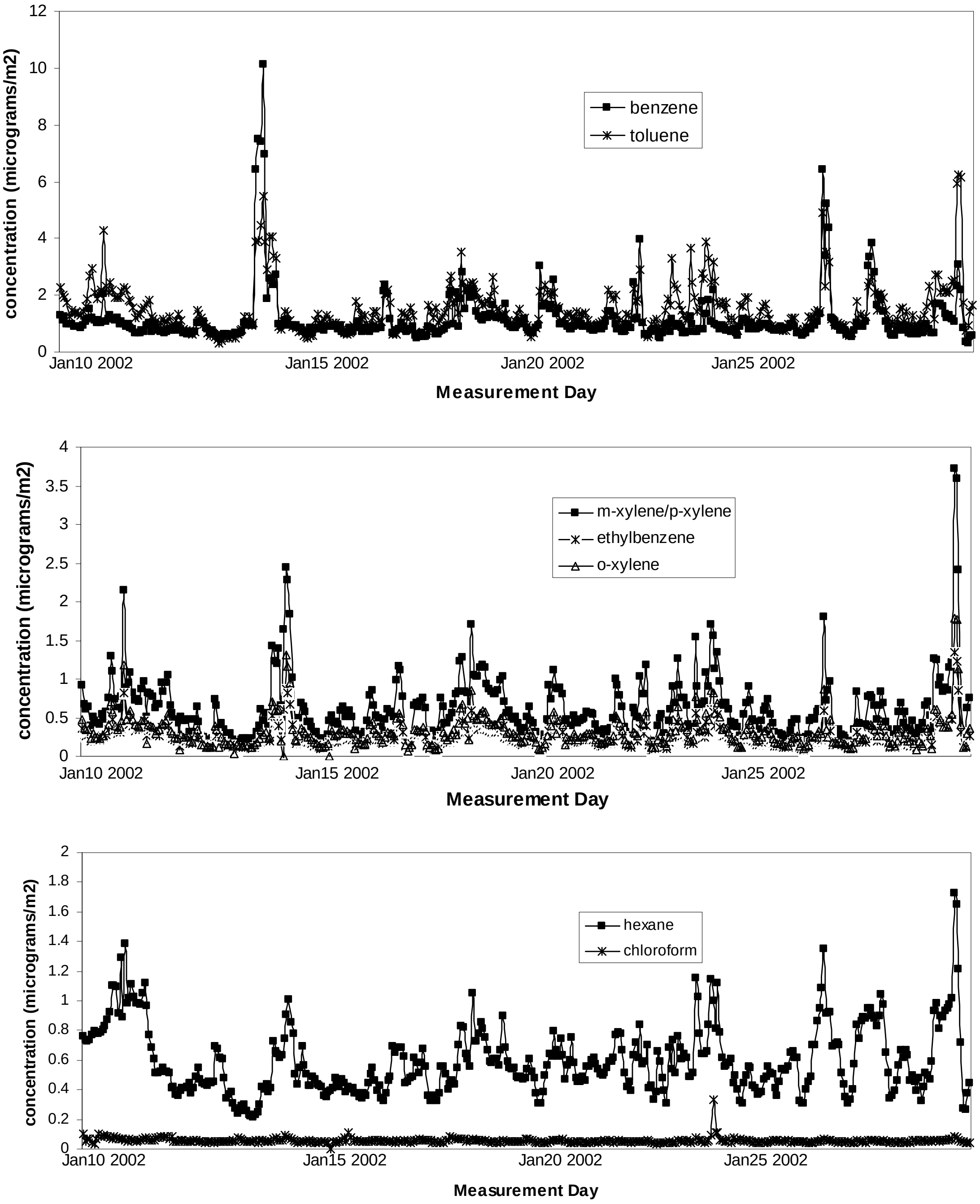


Figure 10 Time series concentration of hourly air toxic concentrations measured in January 2002 at CMU urban background site.

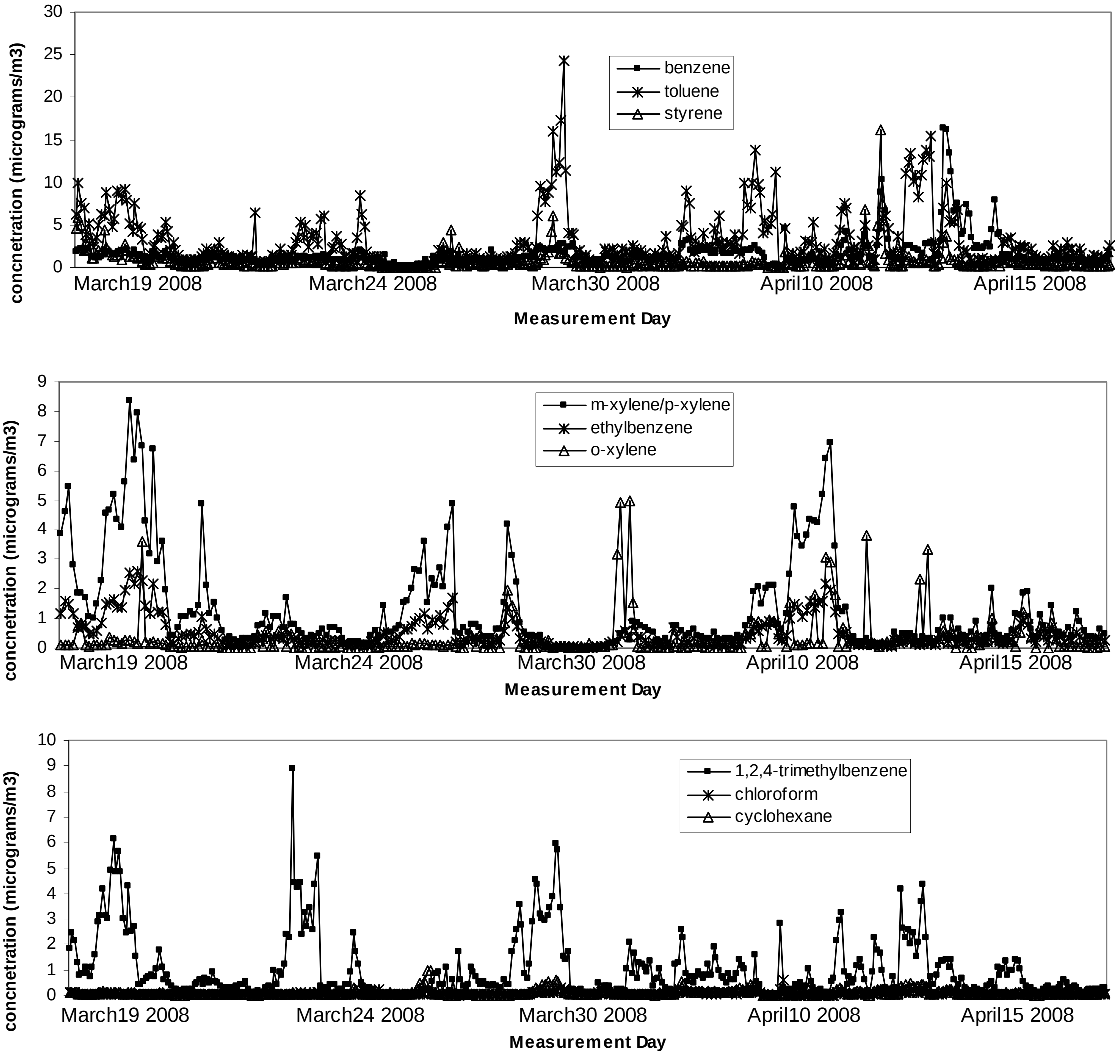


Figure 11 Time series of hourly air toxic concentrations measured during March-April 2008 at the downtown Diamond Building site.

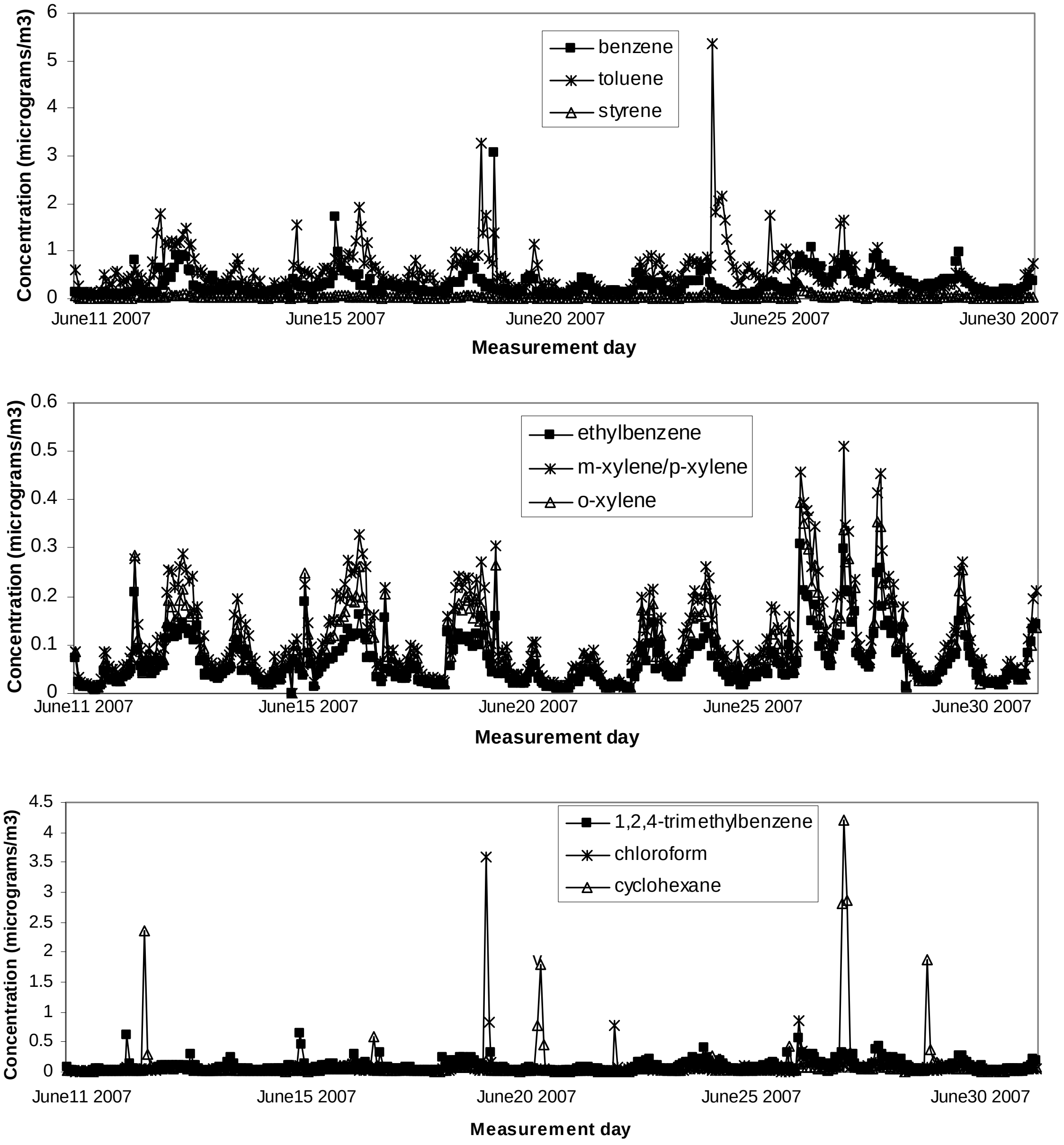


Figure 12 Time series of hourly air toxic concentrations measured during June2007 at the CMU construction site.

A set of condensed phase hopanes and steranes were monitored to track emissions from mobile sources. These compounds are naturally present in lubricating oil and have been extensively used as molecular markers for fossil fuel combustion. Figure 13 shows time series data measured that the Diamond Building site. The data show regular daily patterns on weekdays, and indicate contributions to hopane/sterane levels are almost entirely driven by local mobile sources – particularly during morning and evening rush hour periods and midday. Figure 1 shows time series data for those hopanes/steranes that were above detection limits most of the time during the day and sometimes at night. Heavier triterpanes (bis-, tris-, tetrakis-, and pentakishomohopanes) were occasionally detected when total marker concentrations were highest. In conjunction with black carbon data measured using an aethalometer (Magee Scientific AE31), these data will provide insight into contributions from gasoline and diesel (on- and off-road) vehicles to total hopane/sterane loadings in the downtown area.

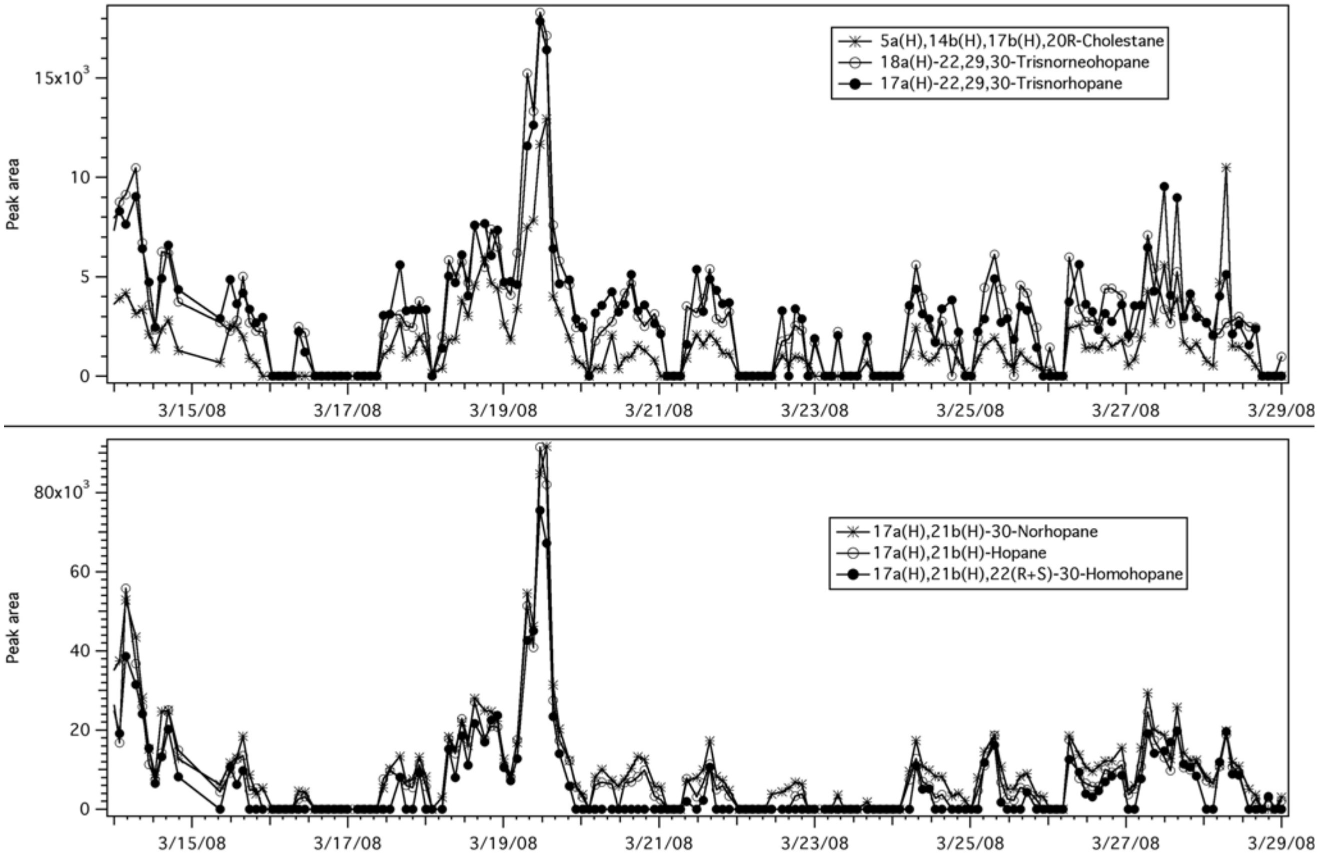


Figure 13 Time series data for a suite of hopanes and steranes measured with TAG. Data are 2-hour averages. Hopane/sterane levels ranged from less than the detection limit on nights and weekends to approximately 0.5 ng/m^3 for cholestane, trisnorneohopane and trisnorhopane and 2 ng/m^3 for norhopane and hopane.

Polycyclic organic matter was also measured during the study, including the EPA Priority PAHs, PAH ketones, and other PAH and hetero-PAH (e.g. retene, dibenzothiophene) used to apportion emissions from specific source classes. In general, POM levels were much less dynamic than hopanes and steranes, with background concentrations often within a factor of 2 of the highest measured concentrations during this campaign. This suggests appreciable contribution to PAH levels from regional combustion sources in addition to local sources. Heavier 4-,5-, and 6-ring PAHs were detected occasionally but were usually below detection limits (approximately 0.1 – 1 ng/m3 for chrysene, benzofluoranthenes, benzopyrenes, etc. at 90 min collection periods).

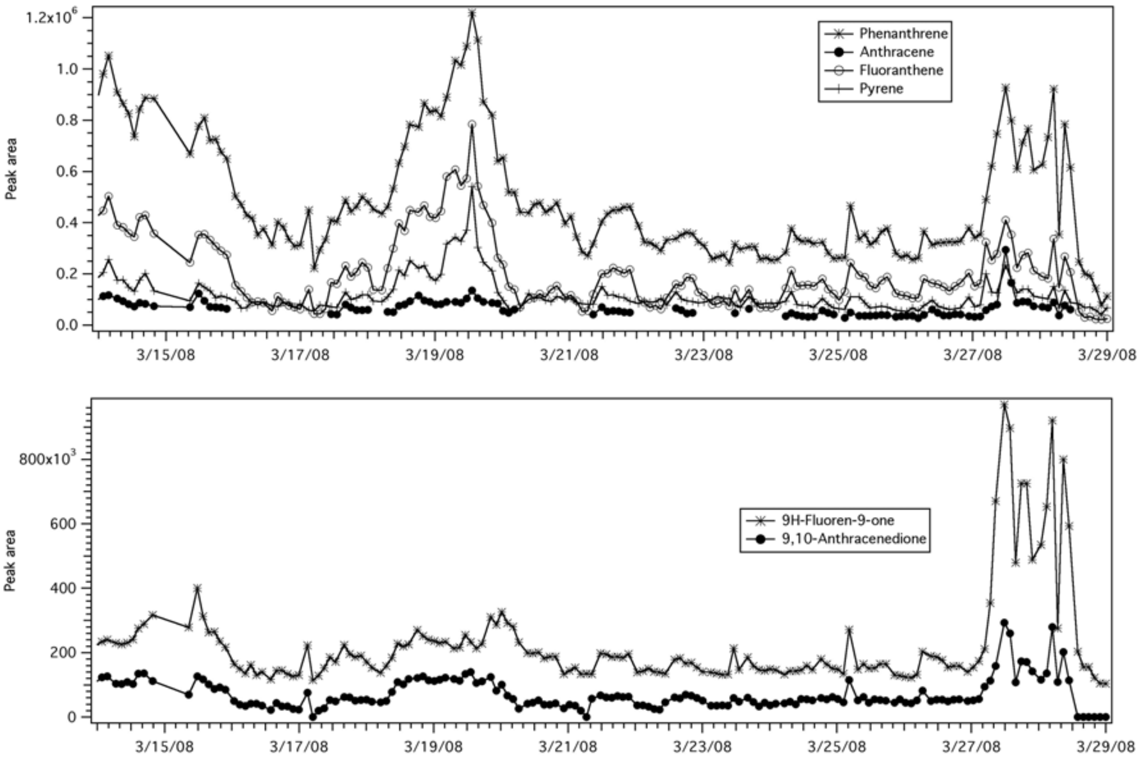


Figure 14. Time series data for several POM compounds measured with TAG. Data represent 2-hour averages. Concentrations for PAH and PAH ketones shown here are generally in the 0.5 – 5 ng/m^3 range, and indicate significant regional as well as local sources.

Effects of Wind Direction

The hourly measurements allowed us to analyze the effect of wind direction on concentrations, which aids in the identification of local sources. To illustrate the approach we show some of the high time resolved data from the Avalon site. Wind direction had a very noticeable effect on air toxic concentrations and plume event characteristics, indicating the contribution of different sources. Figure 15 shows the hourly concentration of two compounds, benzene and toluene, as function of wind direction. High benzene concentrations occur when the wind was blowing off of Neville Island (180°-270°). The industrial sites adjacent to Avalon were not the only source of plumes. Winds from downtown Pittsburgh also elevated air toxics concentrations at Avalon. Toluene concentrations increase when the wind comes from the downtown direction (90°-180°). There are substantial emissions of mobile sources in the downtown area; toluene is a marker for gasoline vehicle emissions.

Air toxic concentrations were not always elevated when the wind was blowing from these directions due to the effects of varying meteorological conditions on pollutant dispersion, but plume event characteristics do seem to be wind direction dependent, and Pittsburgh and Neville Island appear to be the two main areas causing the higher concentration events at Avalon. Figure 16 shows how the ratio of benzene/toluene varied for different wind angles.

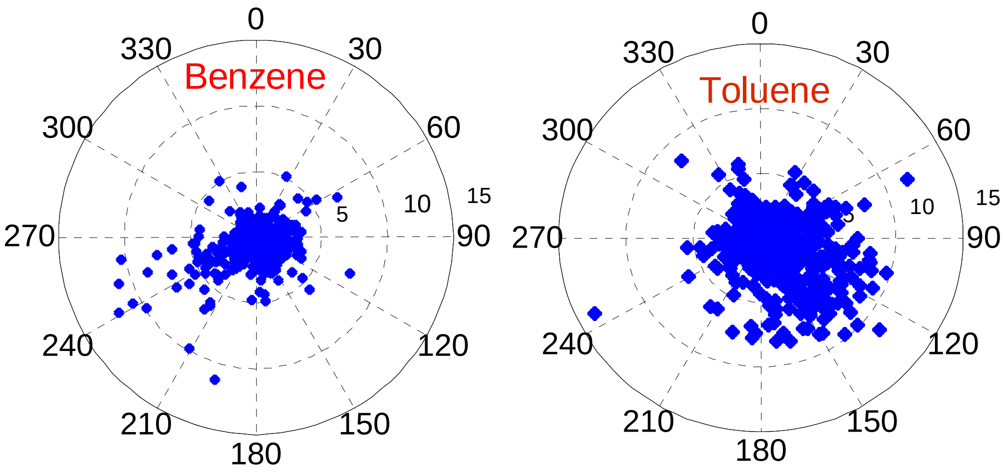


Figure 15 Measured hourly air toxic concentrations (μg/m^3) as a function of wind direction. Benzene is elevated when wind is coming from Neville Island (180°-270°). Toluene is elevated when wind is coming from downtown (90°-180°).

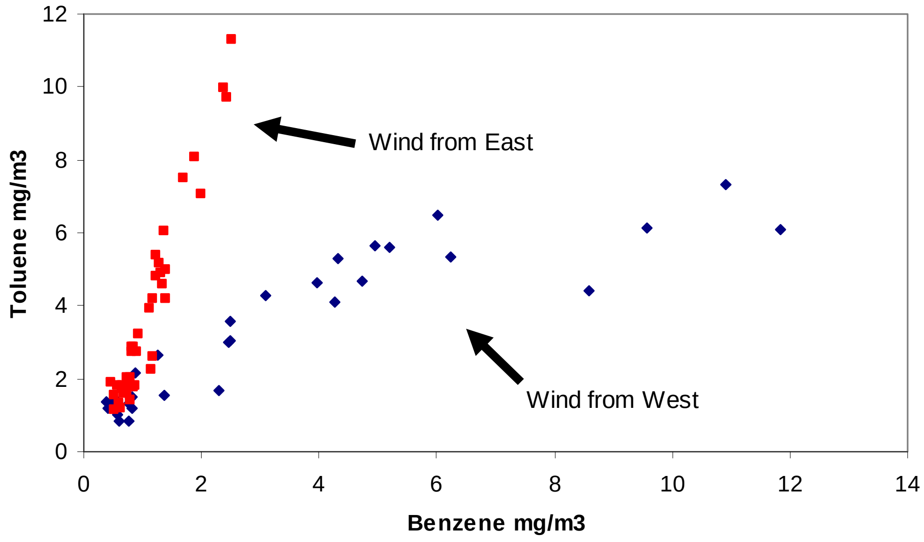


Figure 16 Effect of wind direction on concentration ratios of toluene and benzene as a function of wind direction for two plume events.

Temporal Patterns

Variations in pollutant concentrations based on day of the week, hour of the day, and seasonally were also explored. Two sources of interest in Allegheny County are metallurgical coke production and mobile sources. Benzene is emitted by both coke production and mobile source emissions. Toluene is emitted by gasoline powered vehicles. Figures 17-20 plot day of the week data for benzene and toluene concentrations at each of the 4 sites where hourly measurements were performed. No day stood out as particularly worse then the others.

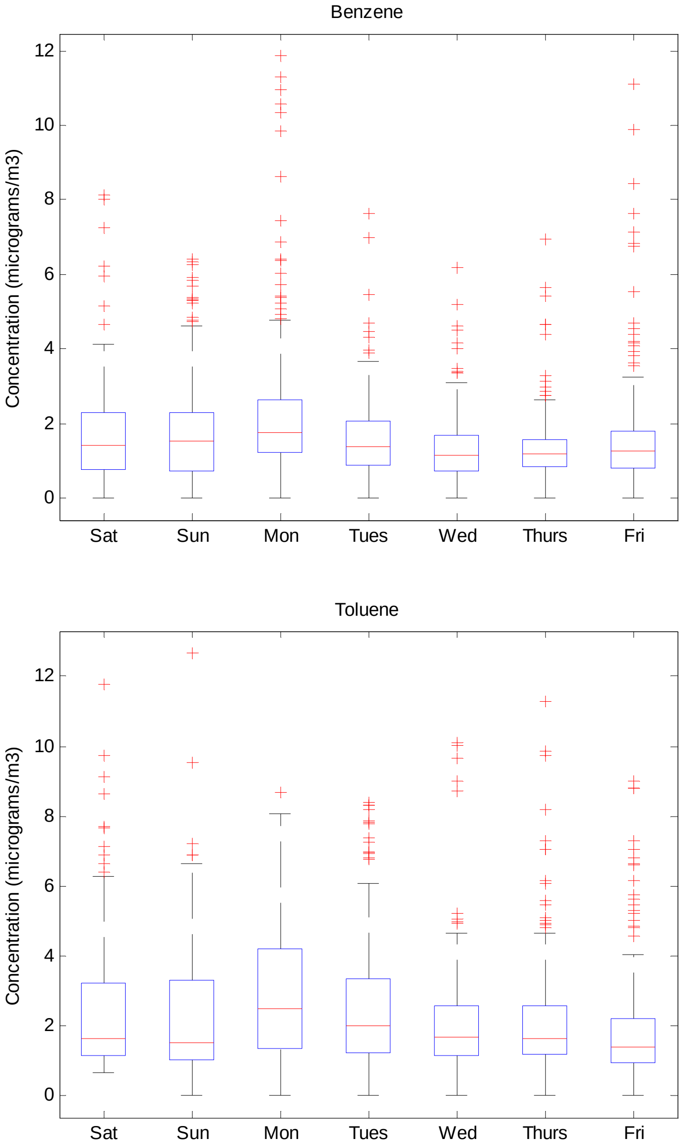


Figure 17 Box plot illustrating distribution of hourly concentrations of benzene and toluene as a function of the day of the week measured in Avalon during the fall of 2006. The box extends from 25th percentile to the 75th percentile of the hourly data with the center line representing the 50th percentile. Whiskers extend to the 5th and 95th percentiles of the national data. Crosses indicate concentrations greater than the 95th percentile.

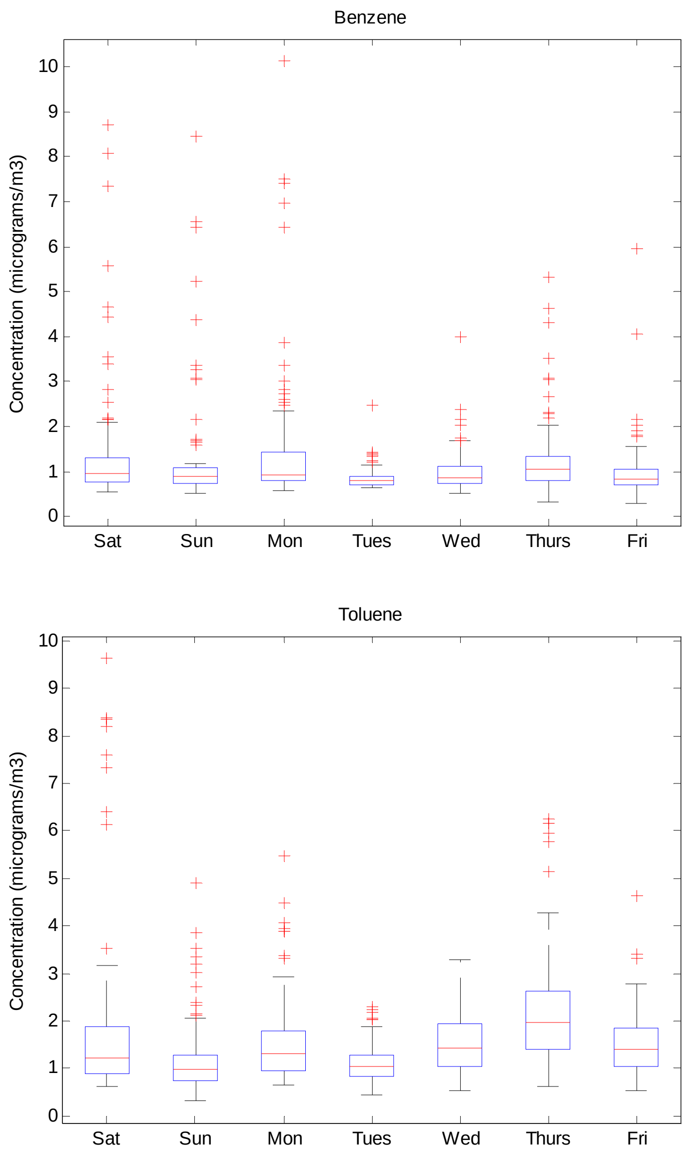


Figure 18 Box plot illustrating distribution of hourly concentrations of benzene and toluene as a function of the day of the week in the urban background measured adjacent to the Carnegie Mellon University campus in January 2002. The box extends from 25th percentile to the 75th percentile of the hourly data with the center line representing the 50th percentile. Whiskers extend to the 5th and 95th percentiles of the national data. Crosses indicate concentrations greater than the 95th percentile.

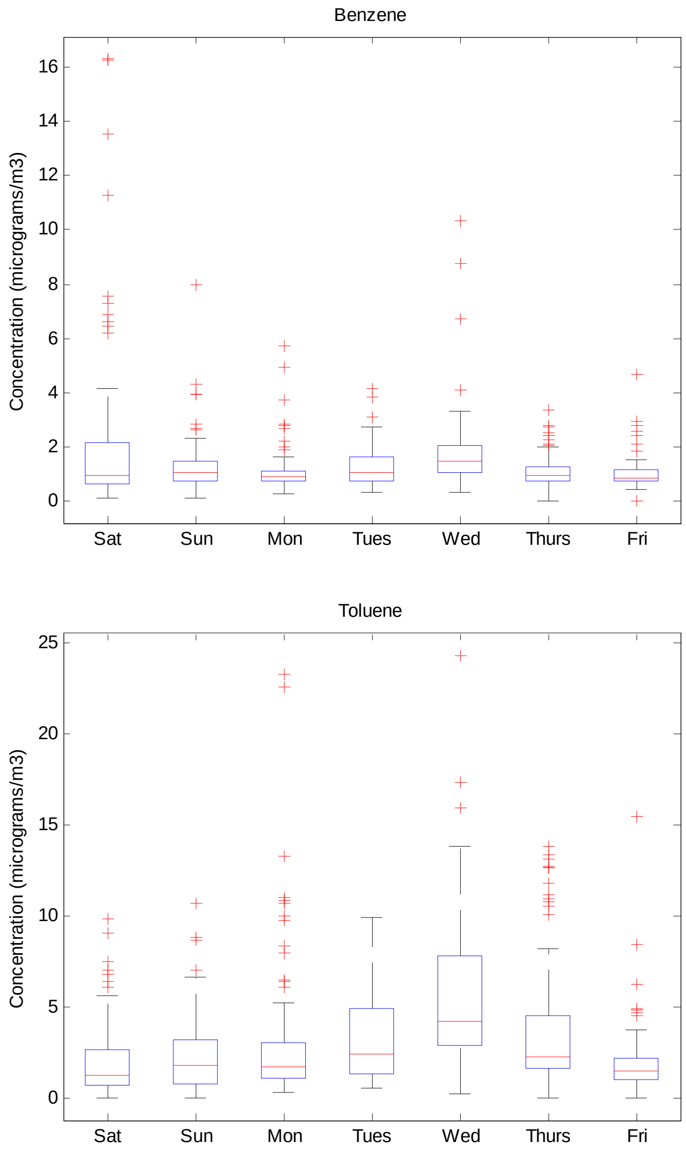


Figure 19 Box plot illustrating distribution of hourly concentrations of benzene and toluene as a function of the day of the week measured at the Diamond Building site during the winter for 2008. The box extends from 25th percentile to the 75th percentile of the hourly data with the center line representing the 50th percentile. Whiskers extend to the 5th and 95th percentiles of the national data. Crosses indicate concentrations greater than the 95th percentile.

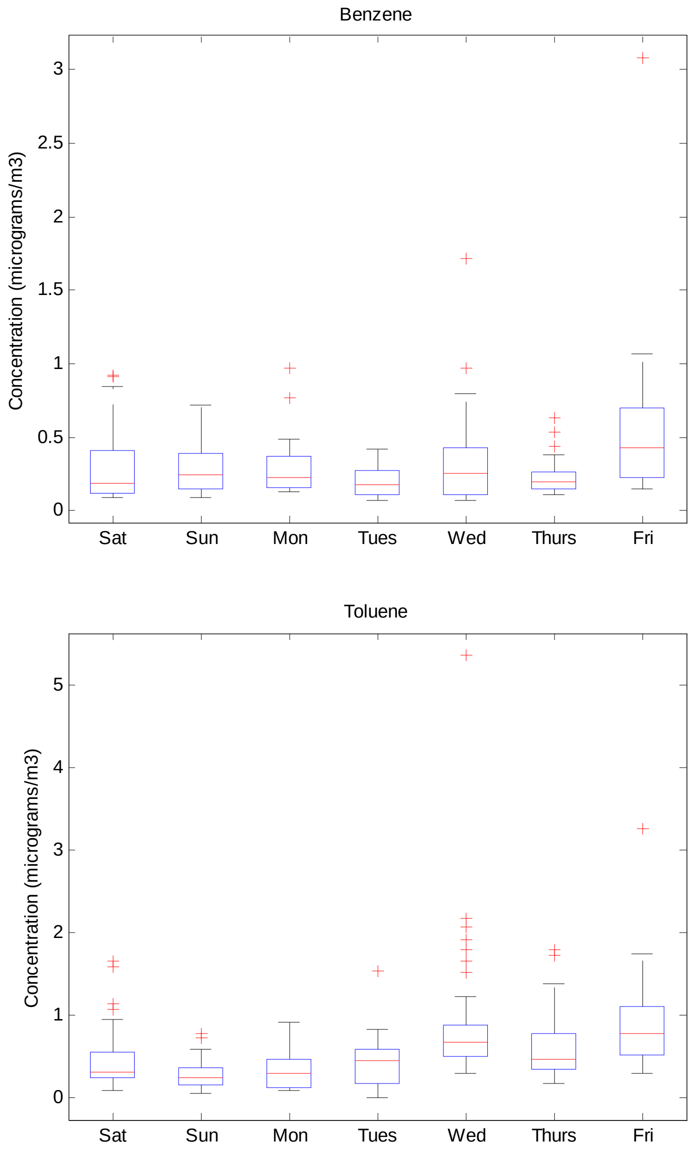


Figure 20 Box plot illustrating distribution of hourly concentrations of benzene and toluene as a function of the day of the week measured adjacent to a construction site on the Carnegie Mellon University campus. The box extends from 25th percentile to the 75th percentile of the hourly data with the center line representing the 50th percentile. Whiskers extend to the 5th and 95th percentiles of the national data. Crosses indicate concentrations greater than the 95th percentile.

Figure 21-24 show the average diurnal pattern for selected air toxics at the four sites with hourly concentration data. There are no clear systematic patterns with day of the week. Each site exhibits somewhat different diurnal patterns. At the Avalon site, Figure 21 indicates that concentrations of most of the air toxics are higher at night when the boundary layer is lower. Figures 22 and 23 show early morning spikes in air toxic concentrations at the urban background site and the Diamond Building, associated with the morning rush hour. This underscores the strong influence that mobile source emissions have on air toxic concentrations in urban areas. A very different diurnal pattern for air toxics occurs adjacent to the construction site (Figure 24). Here the spikes occur during the day, presumably associated with specific activities at the site.

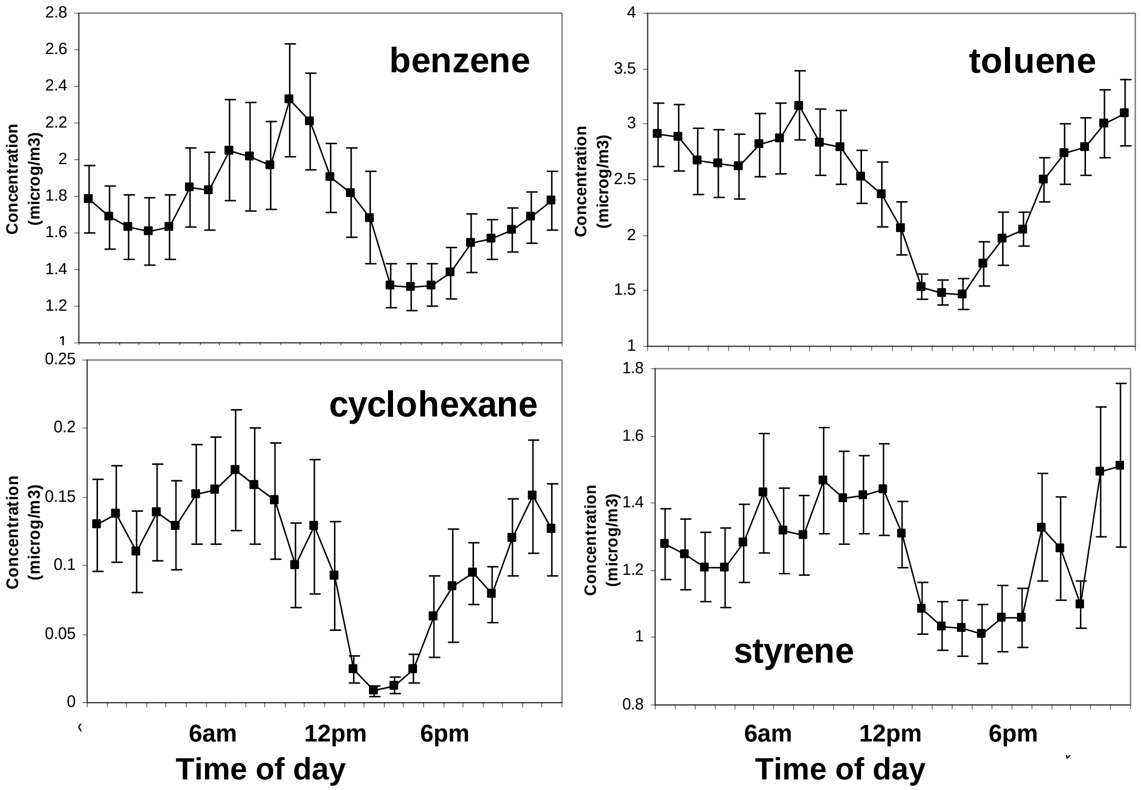


Figure 21 Average diurnal patterns of selected air toxics measured at Avalon.

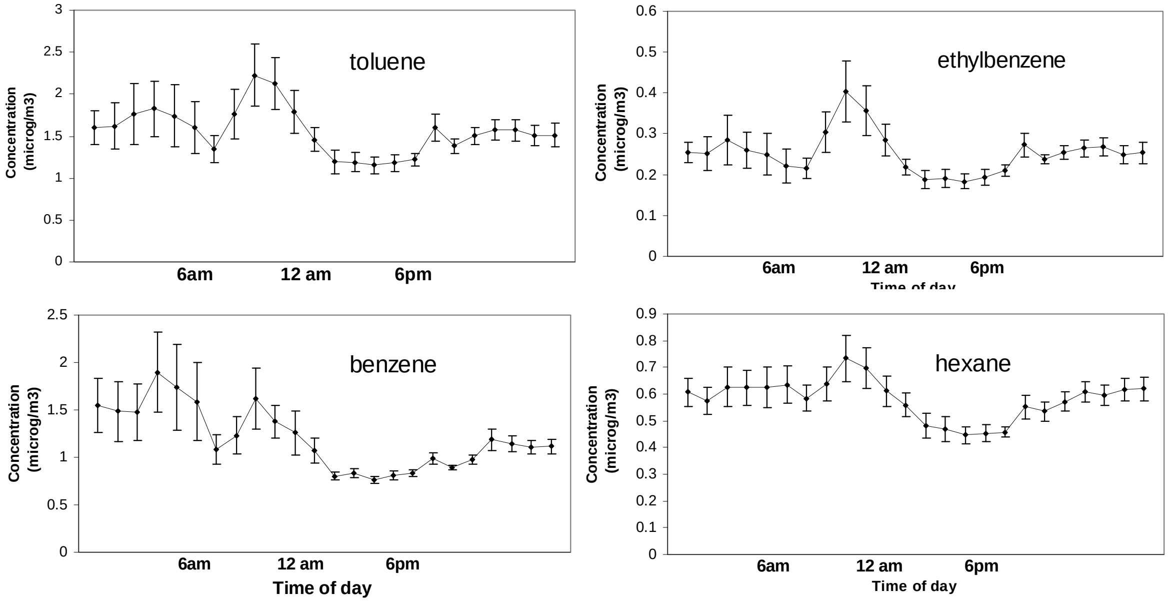


Figure 22 Average diurnal patterns of selected air toxics measured at urban background site adjacent to the Carnegie Mellon University campus.

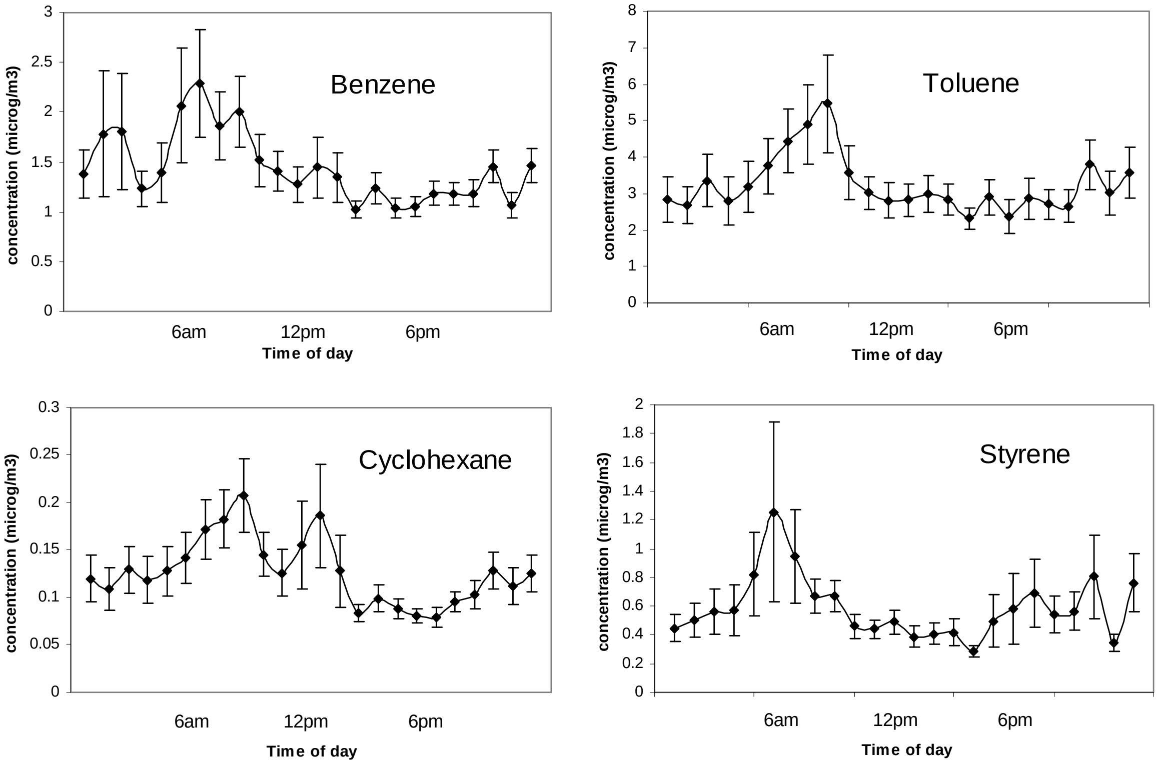


Figure 23 Average diurnal patterns of air toxics measured at the Diamond Building in downtown Pittsburgh.

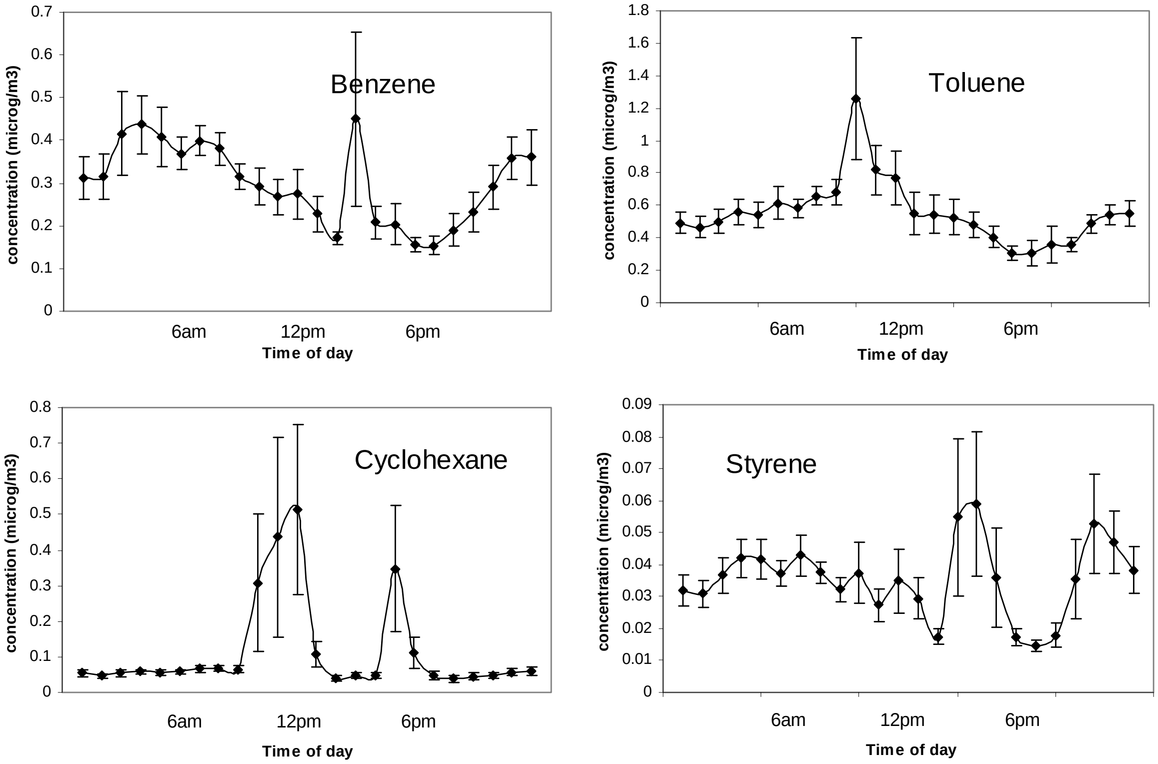


Figure 24 Average diurnal patterns of air toxics measured adjacent to a construction site on the Carnegie Mellon University campus.

Seasonal average concentrations where calculated for each of the compounds measured at the four ACHD sites. The means were then compared between seasons using a student t test (Navidi 2006). Propionaldehyde, acetaldehyde, formaldehyde, and acrolein all had statistically significant seasonal variations for at least one measurement location. The seasonal patterns for these compounds are shown in Figure 25. Propionaldehyde concentrations were highest in the fall with the seasonal variations being somewhat more pronounced at the industrial influenced and regional background sites. Previous work has shown that highest biomass smoke levels occur in the fall in Allegheny County, presumably associated with open burning of yard wastes (Robinson et al. 2006). Formaldehyde concentrations are highest in the summer since it is a secondary product of VOC photolysis (HSDB 2008). Acrolein concentrations are highest in the summer downtown, Flag Plaza, but lowest in the summer elsewhere. Acrolein is emitted by automobiles, coal power plants, and smoking; it is also produced in the atmosphere from VOC photolysis or photo-oxidation (HSBD 2008).

Benzene, acetone, 1,3 butadiene, and methyl ethyl ketone had statistically significant seasonal variations for at least one measured site, Figure 26. As expected, acetone and methyl ethyl ketone concentrations were highest in the summer. These species are secondary products of VOC photolysis or photo-oxidation. Benzene shows the highest seasonal variation at Avalon possibly due to increased inversions in the winter.

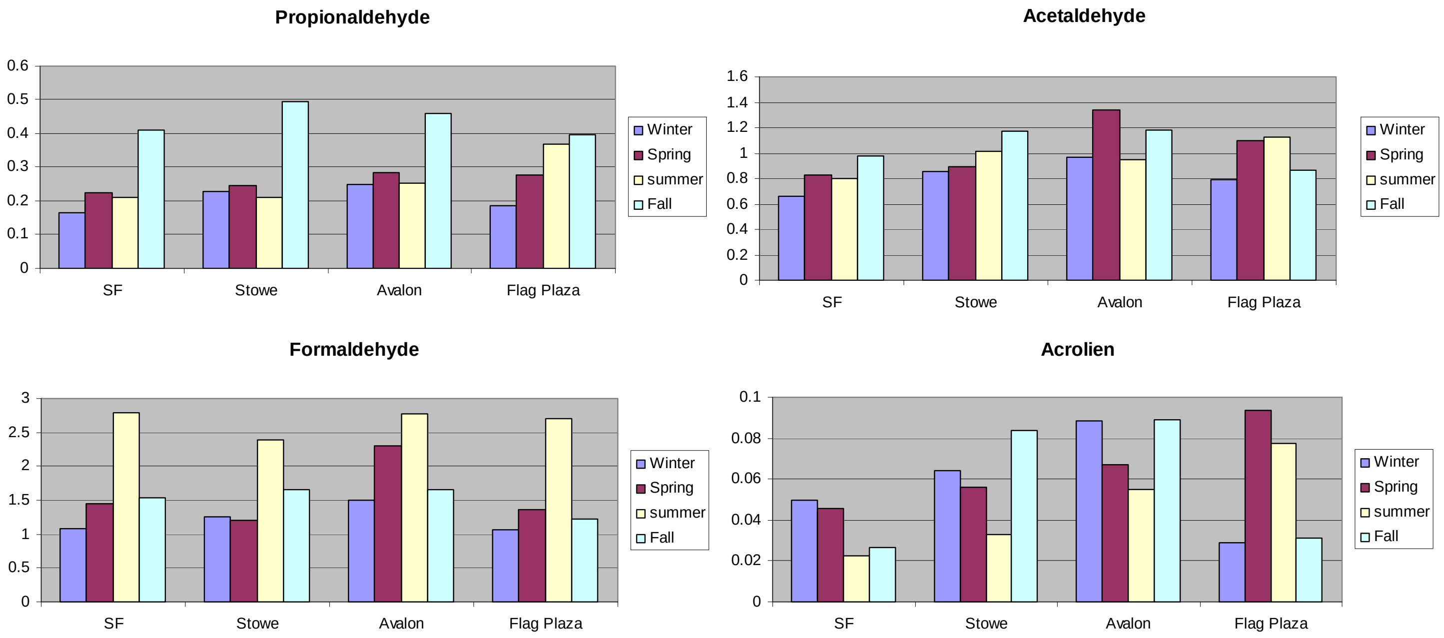


Figure 25 Compounds measured with TO-11a method that had statistically significant seasonal variations for at least one site (concentrations in µg/m^3). SF = South Fayette

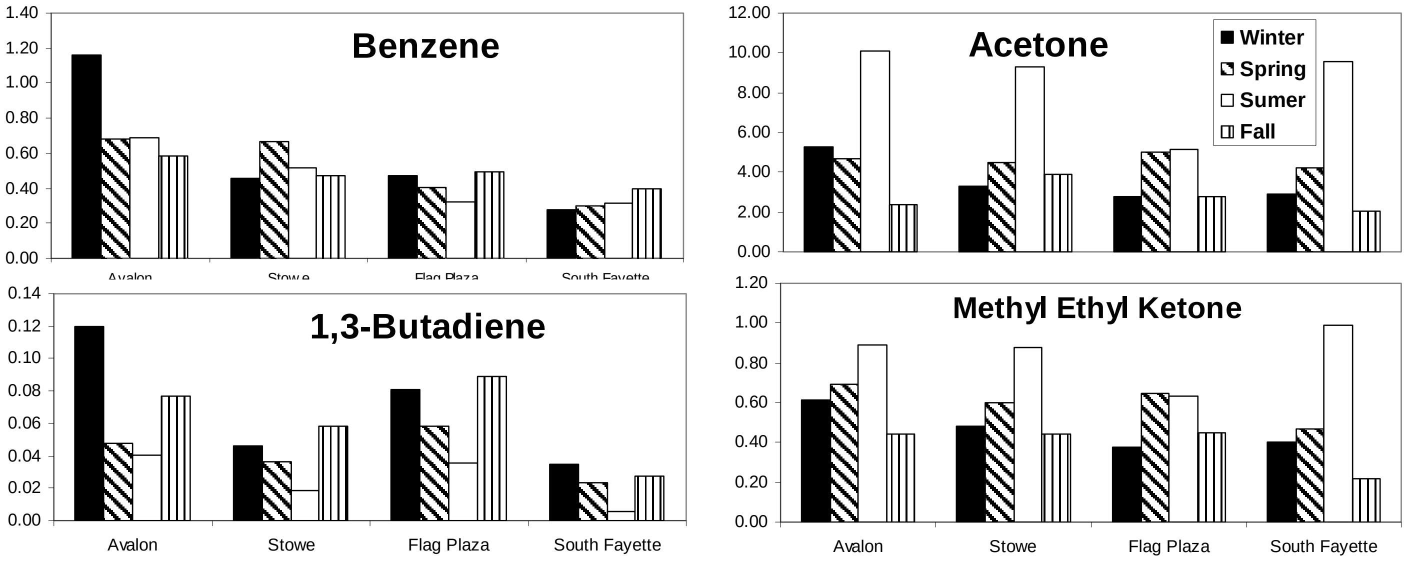


Figure 26 Compounds measured using the TO-15 method that had statistically significant seasonal variations for at least one site (concentrations in µg/m^3)

Risk Analysis

Although air toxic concentration data are useful for identifying hot spots, the variations in human health risks are ultimately a more important concern. In fact, since the toxicity of air toxics varies widely, one can draw misleading conclusions if one only considers the concentration data.

In this section we present results from health risk analysis performed using both the high time resolved and 24-hour average data using both traditional and advanced health risk models. Chronic health risks were calculated using estimated annual average concentrations. Since measurements were taken on a one-in-six day schedule, the sample mean is not necessarily the same as the annual average concentration. Therefore, we assumed that the concentrations were normally distributed and the confidence interval for the annual mean concentration was estimated for each pollutant. To be conservative, the concentrations used in the chronic risk analysis were the upper limit of the 95% confidence interval of the mean.

Table 6 Air toxics considered in risk analysis.

Chemical Name	CAS	Cancer URE (Unit Risk) (1/(µg/m3))	Source	Chronic Inhalation RFC (1/(µg/m3))	Source	Systems Targeted by Cancer effects	Systems targeted by non-cancer effects	Modeled in 1996 NATA
Acetaldehyde	75070	2.2E-06	IRIS	9	IRIS	Hem,Res		X
Acetone	67641			310	ATSDR		N	
Acrolien	107028			0.02	IRIS		Res	X
Benzene	71432	7.8E-06	IRIS	60	CAL EPA	Hem	N	X
Benzyl chloride	100447	4.9E-05	IRIS			Res		
Bromoform	75252	1.1E-06	IRIS	70	Calc		Ren,Hep	
Bromomethane	74839			5	IRIS		Res,N	
Butadiene, 1,3-	106990	3.0E-05	IRIS	2	IRIS	Hem	Res	X
Carbon disulfide	75150			710	IRIS			
Carbon tetrachloride	56235	1.5E-05	IRIS	40	CAL EPA	Hep		X
Chlorobenzene	108907			1000	CAL EPA			
Chloroethane	75003			10000	IRIS			
Chloroform	67663	2.3E-05	IRIS	98	ATSDR	Hep,Ren	Hep	X
Chloromethane	74873			90	IRIS		N	
Dibromoethane, 1,2-	106934							X
Dichlorobenzene, 1,4-	106467	1.1E-05	CAL EPA	800	IRIS	Ren		
Dichloroethane, 1,1-	75343	1.6E-05	CAL	500	HEARST	Hep,Rep		
Dichloroethane,1,2-	107062	2.6E-05	IRIS	2400	ATSDR	Rep,Hem,Res		X
Dichloroethene, 1,1-	75354			200	IRIS		Ren,Hep	
Dichloropropane, 1,2-	78875	1.9E-05	Calc	4	IRIS	Hep	Hep	X
Ethyl benzene	100414			1000	IRIS		Res,Ren,Hep	
Formaldehyde	50000	1.3E-05	IRIS	9.8	IRIS	Hem	Res	X
Hexachlorobutadiene	87683	2.2E-05	IRIS	0.7	Calc	Ren		X
Hexane	110543			200	IRIS		N	
Methyl isobutyl ketone	108101			280	Calc			
Methylene chloride	75092	4.7E-07	IRIS	1000	ATSDR	Hep	Hep	X
MTBE	1634044			3000	IRIS		Ren	
Propionaldehyde	123386							
Styrene	100425			1000	IRIS		N	
Tetrachloroethane, 1,1,2,2-	79345	5.8E-05	IRIS&Cal			Hep		X
Tetrachloroethene	127184	5.9E-06	CAL EPA	270	ATSDR	Hep,Ren,Rep,Res	N	
Toluene	108883			400	IRIS		Res,N	
Trichlorobenzene, 1,2,4-	120821			200	HEARST			
Trichloroethane, 1,1,1-	71556							
Trichloroethane,1,1,2-	79005	1.6E-05	IRIS	14	Calc	Hep,Ren		
Trichloroethene	79016	2.0E-05	CAL EPA	600	CAL EPA	Hep,Ren,Rep,Hem	N	X
Vinyl chloride	75014	8.8E-06	IRIS	100	IRIS	Hep,Hem,Res	Hep	X
Xylene, m/p	108383			100	IRIS		N	
Xylene, o-	95476			100	IRIS		N	
Hydrogen Sulfide	647783			2	IRIS		Res,N	

This study measured outdoor concentrations and the risk analysis was performed directly on these data. Outdoor exposure levels provide an estimate of the maximum risks associated with outdoor sources.

The toxicity data used in this work are taken from the EPA, CAL EPA, the Agency for Toxic Substances and Disease Registry, and the DOE Risk Assessment Information System (ATSDR 2002, CalEPA 2002, USEPA 2002, DOE 2006). The toxicity data are summarized in Table 6.

Traditional Health Risk Models

Cancer Risk

A linear no-threshold model was used to asses the lifetime cancer risk for 50 pollutants. This is the standard first-order method of assessing cancer risk (Ramaswami, 2005). To be conservative, the 95th upper confidence level of the mean annual concentration was used to calculate total risks (Sciences International, 2003). The lifetime cancer risk, LIR, for individual air toxics was determined by

$$LIR = URE * C$$

where C is the 95th upper confidence level of the mean annual concentration and URE is the unit risk estimate for the target species.

A LIR of 1 x 10^{-6} or less is considered acceptable according to the 1990 Clean Air Act. Compounds with LIR greater than this represent an elevated risk. If URE data were not available, an estimate was calculated form the oral carcinogenic potency slope factor as was done in the West Louisville Air Toxics Risk Assessment (Sciences International, 2003):

$$URE = \frac{OSF * IR}{BW}$$

where OSF is the oral carcinogenic slope factor (mg/kg-day), IR is the inhalation rate ($20m^3$/day) and BW is the assumed body weight (70 kg).

The LIR calculated for each site is shown in Figure 6. Of the compounds studied 11 present elevated cancer risks. All of the sites have elevated benzene and formaldehyde risks above 10^{-6} threshold. These compounds pose the greatest risk at the two sites adjacent to Neville Island (Avalon and Stowe). Acetaldehyde concentrations were also elevated through out the county. Carbon tetrachloride risk is relatively constant throughout the county. Chloroform and 1,3 butadiene cause an elevated risk at all four sites with the highest risks seen at Avalon and downtown. Trichloroethene and 1,4 dichlorobenzene considerably elevate risks downtown, but do not play as significant of a role in other areas of the county.

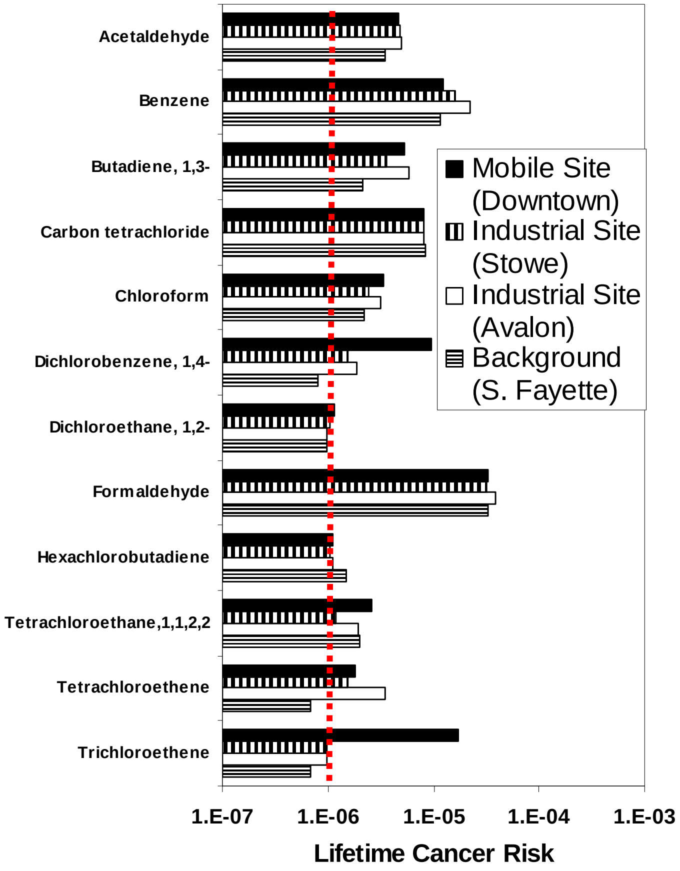


Figure 27 Estimated lifetime cancer risks for the four study sites.

Figure 28 shows the additive cancer risk at each site, showing the relative contribution of each toxic. Given the large differences in toxicities, the risks are largely associated with specific compounds and not specific sites. In other words, the cancer risks were driven by the essentially the same set of compounds at all of the sites. The pollutants that pose the most cancer risks across the county, from largest to smallest, are formaldehyde, benzene, carbon tetrachloride, acetaldehyde, and 1,3-butadiene. Formaldehyde and carbon tetrachloride are both regional toxics. Carbon tetrachloride is no longer widely used, but it has a long atmospheric lifetime (HSBD 2005). Formaldehyde is formed in the atmosphere from the oxidation of hydrocarbons (HSBD 2006). The other toxics that post substantial risk throughout the county (benzene, carbon tetrachloride, and 1,3-butadiene) are associated with mobile and industrial source emissions. For example, benzene is emitted from coke production facilities. Figure 7 indicates that benzene concentrations are elevated throughout the region relative to national data. This likely is associated with the emissions from coke production.

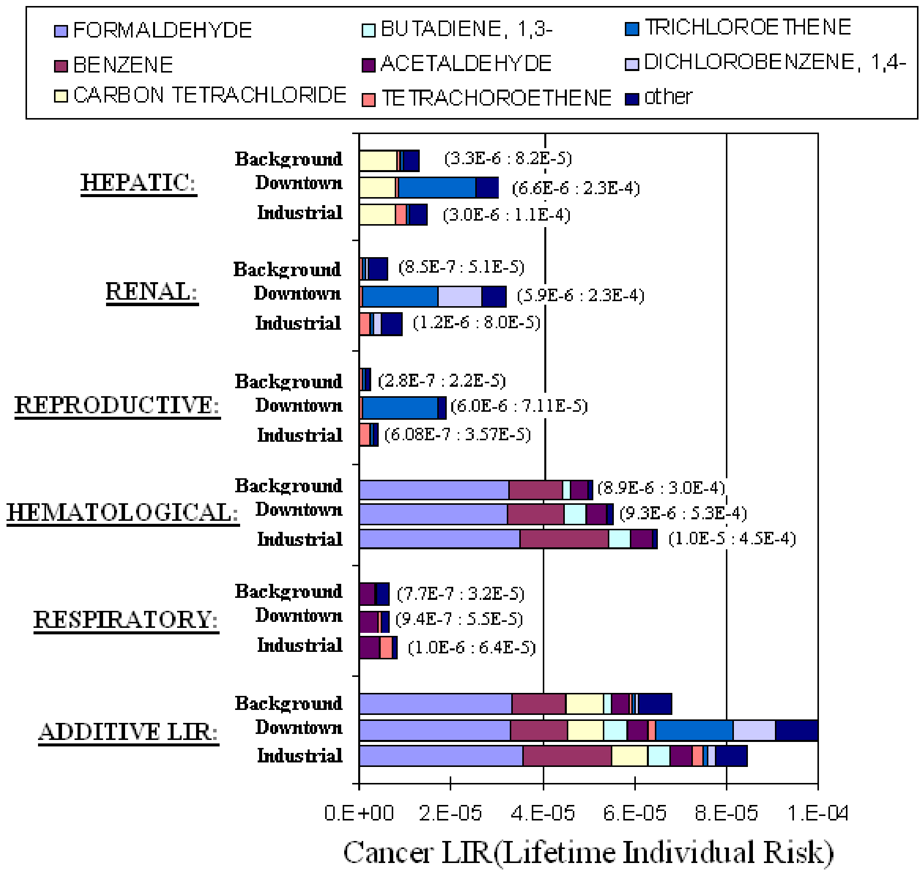


Figure 28 Additive cancer lifetime incidence rate, LIR, and additive cancer lifetime incidence rates for target systems with risks greater than 10^{-6}. The number in parenthesis indicate the risk for maximum antagonistic and synergistic interactions (B_{jk}=-1 or 1, M_{jk} =10).

At the downtown site, trichloroethene and 1,4 dichlorobenzene significantly contribute to the cancer risk. At this site they accounted for 26% of the estimated cancer risk but only 2-3% of the risks elsewhere.

Figure 28 also shows the additive *LIR* for each of the target systems with a risk larger than 10^{-6}. The greatest cancer risks for each site were found to be for the hematological systems. The chlorinated compounds increased risks of renal, hepatic and reproductive cancer at the downtown site.

Environmental justice studies often use the spatial variation in emissions as an indicator for risks. Except for chlorinated compounds downtown, air toxics concentrations varied by less then a factor of 4 across the ACHD sites, which represent very different exposure regimes. A factor of four is much less than the compound-to-compound differences in toxicity. Although concentrations of six air toxics were a factor of two or more higher at the two residential sites located close to Neville Island. The estimated cancer risk was only 25% higher at these sites than the regional background site. This underscores the regional nature of the air toxics problem in Allegheny County. Most of the increased risk was due to modestly higher benzene concentrations. Larger variations in toxics concentrations are seen downtown where 8 toxics are greater than a factor of 2 higher and 2 toxics are more than a factor of 10 higher than the regional background. The estimated lifetime cancer risk at downtown was 50% higher than at the regional site.

Non-Cancer Risks

To quantify non-cancer health risks, the hazard quotient, HQ, was determined for the compounds measured (Ramaswami 2005)

$$HQ = \frac{C}{RFC}$$

by dividing the 95th percentile upper confidence limit of the study average concentration by the reference concentration, RFC, for each species. The hazard index was also determined for each site by adding all of the HQ values for species at the same location.

The hazard quotient is thought to be proportional to risk, but is not a direct measure of the probability of disease like the *LIR* (USEPA 2005). Therefore *HQ* provides a binary indication of risk: values less then 1 are considered non-hazardous, while values of 1 or greater indicate that there is potential for an elevated non-cancer risk. It also indicates the how much ambient concentrations must be reduced achieve a “safe” level.

The non-cancer HQ are shown in Figures 29. The only air toxic that poses a non-cancer risk is acrolein. The HQ for acrolein exceeds one at all of the sites. We used maximum value from the hourly measurements to assess acute health risks. There were no acute health risks found at any of the sites.

Health Risks of other Air Toxics

This study focused on thirty nine organic air toxics. The risk estimates for these compounds were compared to estimates derived from archived data for metals and polycyclic aromatic hydrocarbons (PAHs) collected in 2002 as part of the Pittsburgh Supersite (Wittig 2004). This urban background site was not strongly influence by local sources and therefore provides a measure of the regional exposure. *RfC* and *URE* values from the literature were used to calculate non-cancer and cancer chronic risks for the airborne metals and PAHs.

At the Avalon site hydrogen sulfide was also compared to risks from other pollutants. Hydrogen sulfide is associated with industrial processes, such as coke works. The Allegheny County Health Department monitors hydrogen sulfide at 2 locations in the county adjacent to coke plants (ACHD, 2008). Although hydrogen sulfide is not classified as an air toxic, the EPA IRIS database has provided an *RfC* for the calculation of non-cancer risk. Hydrogen sulfide affects the respiratory, reproductive, neurological, and cardiovascular systems (HSDB 2005).

Figures 30a and 30b compare the cancer and non-cancers risks from measured gas-phase air toxics to metals and PAHs, and to hydrogen sulfide at the industrial site (Avalon). The additive *LIR* at all of these sites due to target organic air toxics is higher then the risk from metals or

PAHs at an urban background site. The regional background additive gas phase air toxics *LIR* is 2 times higher than the additive metals *LIR* at the urban background and 25 times higher then the additive PAH *LIR* at the urban background. For non-cancer risks, acrolein has the highest hazard quotient at all sites. At the Avalon site, hydrogen sulfide presents an added risk with a HQ>1.

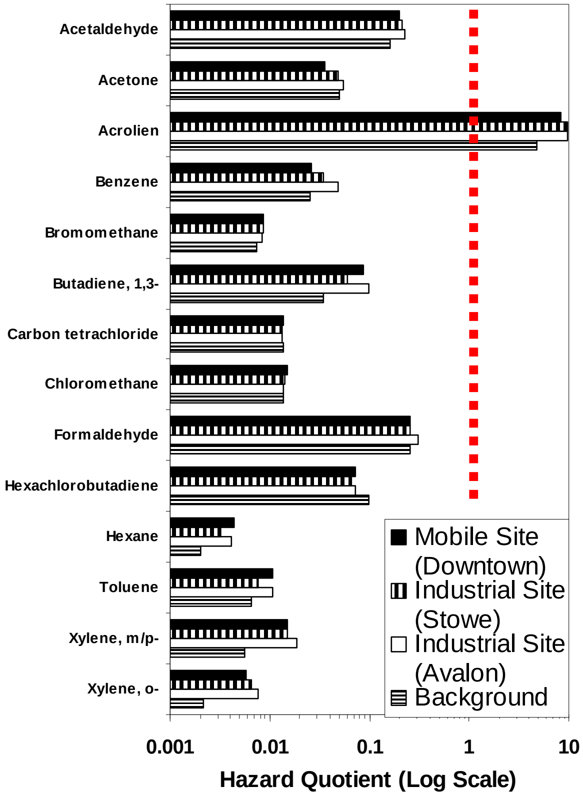


Figure 29 Hazard quotient for non-cancer chronic health effects.

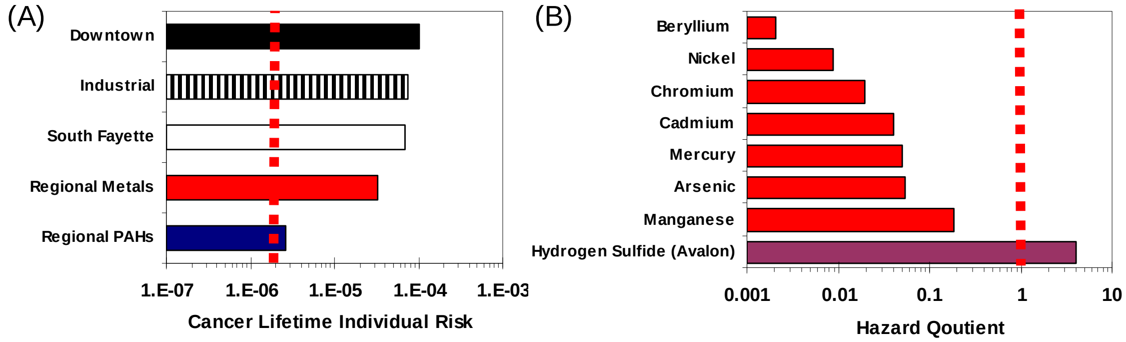


Figure 30 A) Comparison of additive cancer risk from gas-phase air toxics to PAHs and metals B) comparison of non-cancer gas-phase air toxic hazard quotients to metals and hydrogen sulfide (Industrial site only). The dashed line represents a baseline level of risk, 1 in a million for cancer or 1 for hazard quotient.

Health Risk Analysis with Advance Models

Traditional risk analysis does not account for interaction of pollutants. The EPA (2000) has proposed a model for determining interactive risks based on the work of Mumtaz and Durkin (Mumtaz and Durkin 1992). The EPA model modifies each pollutant's individual *HQ* according to its interaction with each other pollutant in the mixture to define the total interactive hazard for target system/organ *p* as (USEPA 2000):

$$
\begin{aligned}
HI_{\text{int},p} &= \sum_{j=1}^{n} HQ_{pj} \left(\sum_{k \neq j}^{n} f_{pjk} (M_{jk})^{Bjk*gpjk} \right) \\
f_{pjk} &= \frac{HQ_{pk}}{HI_{add,p} - HQ_{pj}} \\
HI_{add,p} &= \sum_{j=1}^{n} HQ_{pj} \\
g_{pjk} &= \frac{\sqrt{HQ_{pj} * HQ_{pk}}}{(HQ_{pj} + HQ_{pk})/2}
\end{aligned}
\tag{1}
$$

Where:

HQ_{pj} = hazard quotient for pollutant *j* for system *p* (equation S.3)
f_{jk} = hazard of the k^{th} pollutant relative to the total additive hazard of all of the chemicals interacting with pollutant *j*.
M_{jk} = interaction magnitude, the EPA has suggested a default of M_{jk} =5, but M_{jk} has been shown to be up to 10 for low dose mixtures (Ryker and Small 2008)
B_{jk} = weight of evidence that chemical *k* will effect chemical *j*'s toxicity. B_{jk} ranges from -1 to 0 for antagonistic effects and from 0 to 1 to synergistic effects.
g_{pik} = the degree to which *j* and *k* are present in equi-toxic amounts.

The main assumptions of the model are that interactions between pairs of chemicals contribute the majority of the mixture effect, that synergistic/antagonistic effects are maximized when two pollutants are present in equal toxicity, the equation reduces to the additive model when interactions are minimized, and adverse health effects of chemical mixtures are limited to the effects of the individual pollutants. This model also allows for non-symmetric interactions between compounds. For instance, chemical A may have a synergistic effect on chemical B's toxicity, but chemical B may have an antagonistic or additive effect on chemical A's toxicity. $HI_{int,p}$ values can range from $M_{jk}*HI_{add,p}$ to $HI_{add,p}/ M_{jk}$ due to the mathematical constraints of the model.

This interaction model was recently applied by Ryker and Small (2008) to evaluate the potential for interaction among inorganic contaminates in US drinking water. In this paper, the model is used to explore the levels of interaction of air toxics. Since there are essentially no interactions data, this analysis provides an initial screening to identify potentially important interactions for further research.

To apply the model, pollutants were subdivided into groups based on target systems: neurological, respiratory, cardiovascular, developmental, skin, hematological, immunological, reproductive, renal, and hepatic. Three limiting cases were explored for each target system, the no-interaction condition, the total synergism condition and the total antagonism condition. The no-interaction condition assumes that all risks are additive (B_{jk}=0). The total synergism model assumes that all of the chemicals are interacting to enhance toxicity at the upper limit of interaction seen in other low-dose mixtures (M_{jk} =10 and B_{jk}= 1 for all compounds). This condition represents a worst case scenario for potential health risk. The total antagonism model assumes that all of the chemicals are interacting to reduce toxicity with the upper limit of antagonistic interaction magnitude seen in low-dose mixtures (M_{jk} =10 and B_{jk}= -1 for all compounds). This condition represents a best case scenario for potential health risks from mixtures.

Similar to previous applications, we use *HQ* as a measure of non-cancer equi-toxicity. As previously stated, non-cancer *HQ* values are not directly comparable between pollutants because the *RfC* is related to differing levels of toxicity. The differences in toxicity associated with *HQ* values add a level of uncertainty to the interactive analysis but should not greatly affect the prioritizing of interactions for research priorities.

Although the interaction model was developed to explore non-cancer risks, it can be adapted to be applied to cancer risks as well. EPA proposed a method for translating the LIR to a hazard quotient for a given cancer risk threshold by normalizing exposure, *E*, by a dose associated with a given risk level, *DR*, which is equivalent to the previously calculated *LIR* normalized by a cancer risk threshold, *RT*. The equivalent cancer hazard quotient of a pollutant n would be (USEPA 2000):

$$HQ_n = \sum E_n / DR_n = \sum LIR_n / RT \qquad (5)$$

When the cancer HQ_n is used in the interactive model, equation 4, the *RT* factors out due to algebra allowing for the use of the *LIR* values in the equation to determine cancer interactions.

The potential synergistic/antagonistic hazard indices and cancer *LIR* for each of the target systems were calculated for systems that had two or more measured pollutants that affected it. In addition to the volatile organic air toxics, non-cancer interactions with manganese hydrogen sulfide were also explored. The manganese data were from an urban background site, and the hydrogen sulfide analysis was performed using the data from the Avalon site.

Figure 31 shows the best and worst case scenario for non-cancer and cancer risks. For both the cancer and non-cancer interaction risk calculations compounds were subdivided into target systems: neurological (N), respiratory (Res), cardiovascular, developmental (D), skin (S), hematological (Hem), immunological (I), reproductive (Rep), renal (Ren), and hepatic (Hep). Compounds may affect more then one system. Each symbol is the non-interactive hazard index or cancer risk and the error bars extend to the calculated best and worst case interactive risk levels. For the non-cancer risks, the greatest potential for adverse interactive effects is in the respiratory and neurological systems. For cancer risks all of the additive risks are already greater than 1 x 10^{-6}, but respirator, renal and hepatic systems may face a risk greater than 1 x 10^{-4}. The next step for this work will be to identify the compounds that drive interactive effects and to explore the available literature to see what interactions are possible.

Figure 32 plots the risk enhancement ratio, $HI_{int,p}$/$\mathrm{HI}_{\mathrm{add,p}}$ or $LIR_{int,p}$/$LIR_{add,p}$, for the total synergism case (M_{jk} =10 and B_{jk}= 1) for systems that could present a non-cancer $HI_{int,p}$>1 or a cancer $LIR_{int,p}$>1E-4. Non-cancer risks for four organ systems were investigated using the interactive risk model. Of the four, pollutant interactions could cause elevated non-cancer risks for both the neurological and respiratory systems. The pollutants that drive these interactions are shown in Figure 32a. The interactions driving non-cancer risk enhancement were independent of source regime. The estimated risk enhancement for these systems ranged from 2-8 times the additive hazard index. If one only considers air toxics, the possible synergistic interaction of 1,3-butdaiene, toluene, and formaldehyde on acrolein as well as the possible effect of acrolein on formaldehyde have the greatest potential for increasing respiratory risks. Acrolein/formaldehyde interactions may be especially important to consider since in many areas acrolein concentrations are higher than in Allegheny County (Figure 7).

Hydrogen sulfide targets the respiratory system and manganese targets the respiratory and neurological systems (USEPA 2002). Including these two pollutants in the non-cancer interactive risk analysis suggested additional potentially important interactions, Figure 5a. For example, acrolein/hydrogen sulfide may be important. This analysis only includes a subset of air toxics, adding in additional pollutants may substantially alter results making identifying important pollutants a priority.

For cancer risks, the hematological, renal and hepatic systems have the potential for $LIR_{int,p}$ greater than 1×10^{-4}. The pollutants that drive these interactions are shown in Figure 32a. The air toxics dominating the enhancement factor varied from site to site for cancer risks. Although trichloroethene and 1,4-dichlorobenzene downtown alter hematological priorities, benzene/formaldehyde interactions are the most significant potential contributor to risks in Allegheny County and presumably elsewhere since formaldehyde and benzene dominate cancer risk throughout the nation (USEPA 2001). For the hepatic risks, interactions of chlorinated compound with carbon tetrachloride drive risks at all sites. Downtown the renal system has the potential for elevated risks due to trichloroethene and 1,4-dichlorobenzene.

The interaction model has identified several pollutant pairs that could potentially interact to substantially enhance health risks. This model may be used to prioritize future interactions research.

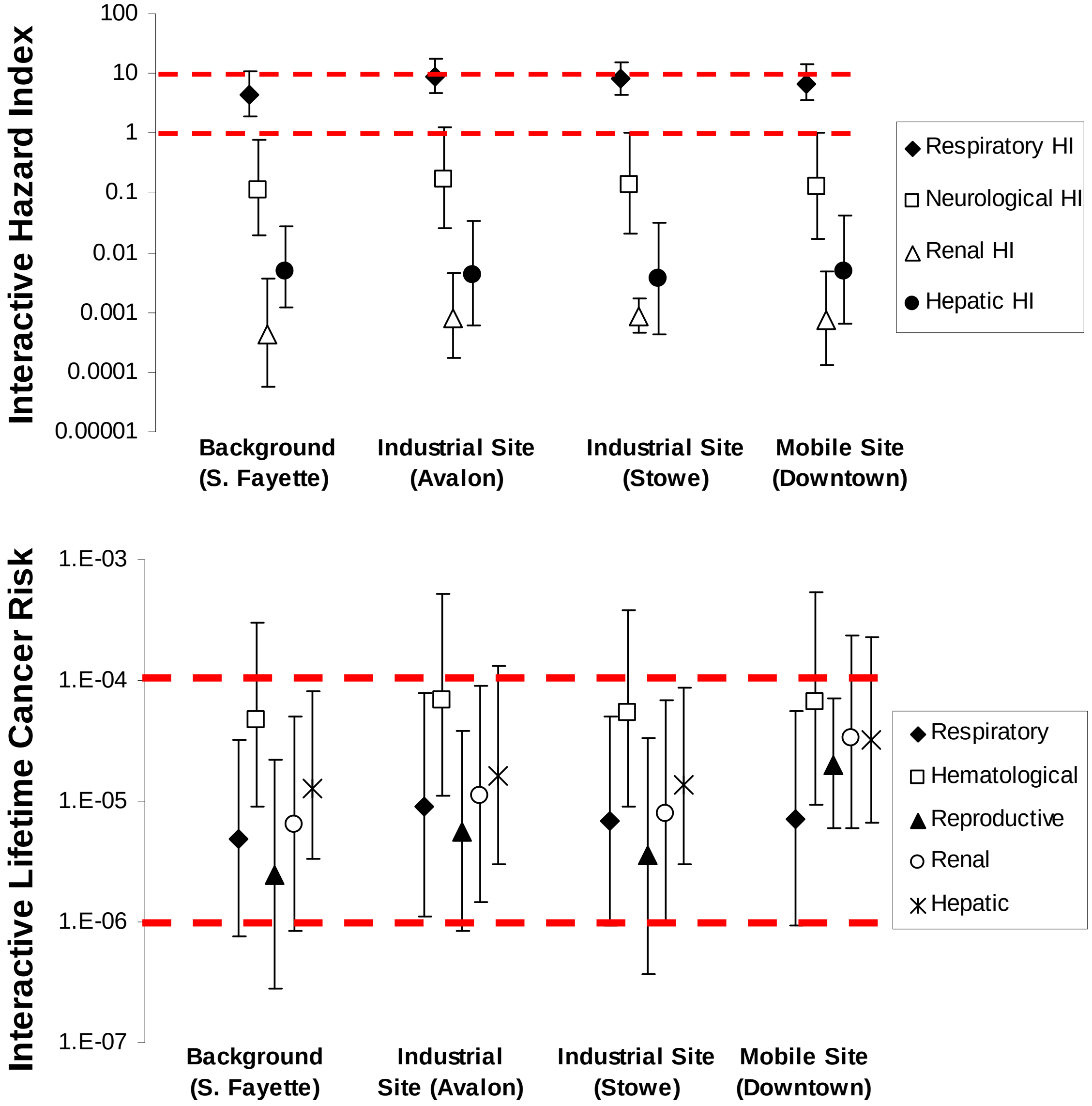
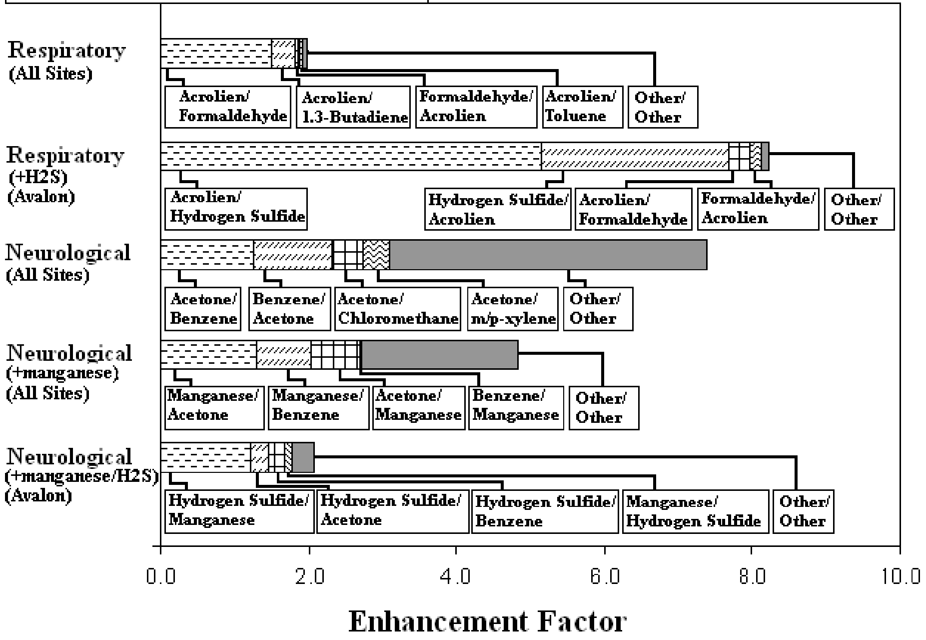


Figure 31 Best and worst case scenarios for synergistic/antagonistic non-cancer health effects. Symbols represent the additive hazard index; the error bars extend to the best and worse possible values for the hazard index.

a) Non-Cancer Interactions



b) Cancer Interactions

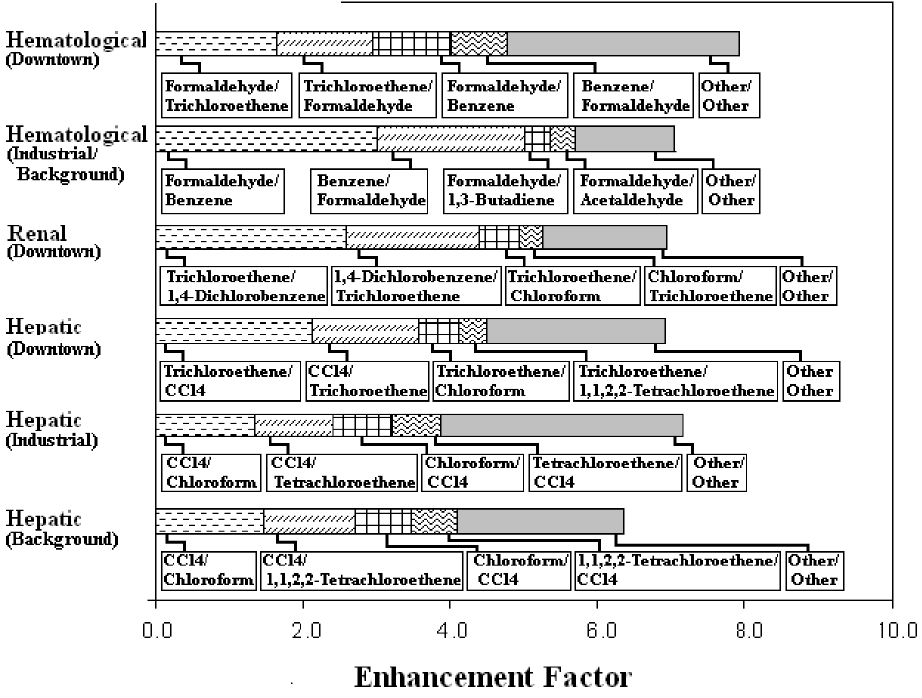


Figure 32 Enhancement factors for each target system that has a potential for risk above threshold. ($HI_{int,p}$ greater than 1, $LIR_{int,p}$ greater than 1 x 10^{-4}). The maximum possible enhancement is 10, the assumed value of M_{jk} in the interactive risk model. Format for listing interaction pairs is A/B where A is the pollutant being affected by pollutant B.

Source apportionment

A goal of this overall project is to connect ambient concentrations and health risks to sources. This is being done using a combination of statistical and deterministic modeling tools. The source apportionment analysis is being performed by Carnegie Mellon University with support from the Allegheny County Health Department Clean Air Fund. This work is still ongoing with final results expected in December 2008. In this report we present selected preliminary results from this analysis.

Local versus Regional Sources

Plume events caused by emissions of local sources have a large effect on air toxic concentrations and can be used to determine contributions of local sources and the regional background to individual air toxics concentrations. Figure 13 shows how highly time resolved data can be used to divide outdoor exposure into contribution of the regional background versus plumes. This involved extrapolating between plume events to estimate background concentration, as shown in Figure 13, and then calculating the fraction of the total exposure due to the background versus plume events. For compounds that were sometimes below detection limits, the background concentration was assumed to be the detection limit in order to be conservative about the effect of plume events.

Figure 14 shows results from this analysis for data collected at Avalon. Benzene and methylene chloride outdoor exposure was mostly from plume events while ethylbenzene and chloroform exposures were mostly from background contributions.

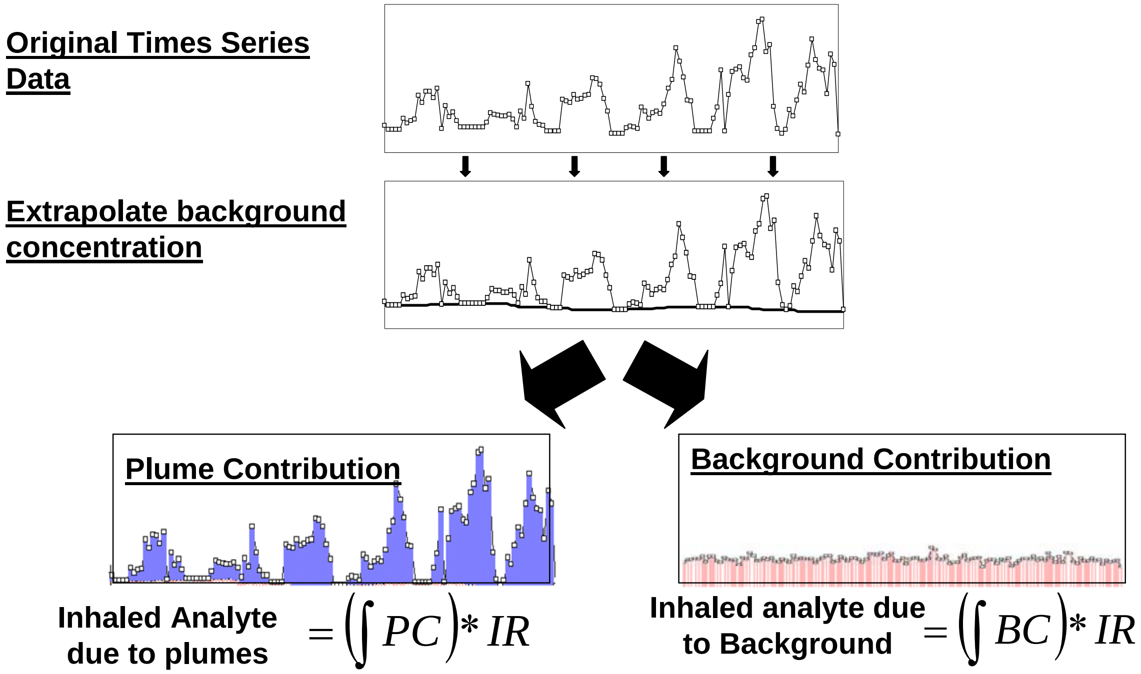


Figure 33 Quantifying the effect of plume events on outdoor exposure

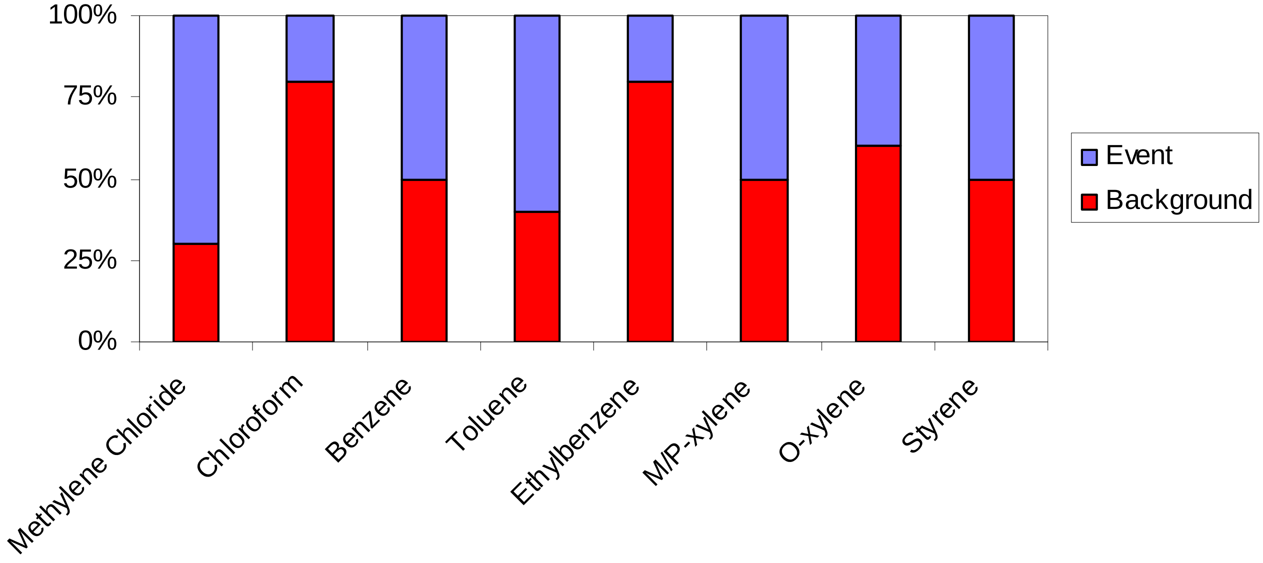


Figure 34 Estimate of relative contribution of plume events to air toxic exposure at the Avalon site.

Receptor modeling

Positive Matrix Factorization (PMF), a FA program with a non-negativity constraint, was used to analyze the hourly data (Paatero 1994). This model has been widely applied to the analysis of air quality data. PMF solves the equation:

$$X = GF + E$$

where X represents the measured data matrix, the concentration of each compound vs. time. G represents the contribution from a given factor for each set of measurements. F represent the non-dimensional composition of each of the factors. PMF solves for the G and F that minimize the sum of squares, Q, of the error, e_{ij}, scaled by the measurement uncertainty, s_{ij}.

$$Q = \sum \sum (e_{ij} / s_{if})^2$$

The two main user inputs in PMF are the number of factors and the degree of matrix rotation. The major challenge with PMF is interpreting the factors extracted from the data as sources or source classes. To aid in associating factors with sources, event profiles were developed from the plume events in the data for Avalon and will be developed for other sites, inventory profiles were taken from the ACHD point source emission inventory, and mobile source profiles were taken from the EPA Mobile Source Air Toxics Website.

In addition to using emissions data to correctly identify the number of factors and the correct matrix rotation, further statistical analysis is being performed (Lanz et al. 2007). This include using the Q-value and goodness of fit measures (R^2). The goal is to find the solution that makes physical sense while minimizing Q as a function of the rotation and the number of factors. G space plotting (Paatero 2005) will also be used to identify unrealistic rotations. Similar analyses were performed on each of the high time resolved data sets.

Event Profiles

To help interpret the PMF results we are deriving event profiles directly from the high time resolved data. These events were associated with particular wind directions and therefore represented an aggregate source profile.

Two of the highest concentration events measured at the Avalon site are indicated by the shaded regions in Figure 9. One event occurred when the wind was blowing from downtown Pittsburgh and the second when the wind was from Neville Island. These two high concentration periods were used to define event profiles. The data were corrected for estimated background concentrations (the highest concentration events were used to minimize the effect of the background). Ratios of these background corrected concentration are used as event profiles. A characteristic profile for the regional background was also developed.

The event profile for Neville is dominated by benzene, while the Pittsburgh event profile is predominately methylene chloride and toluene. Methyl ethyl ketone (MEK) showed no wind direction dependence and was removed from the determined event profiles for Pittsburgh and Neville.

Emission Profiles from ACHD Inventory and EPA

Emissions of many of the compounds used in the PMF modeling are reported in the ACHD point source emission inventory, no sources reported emissions of 4-ethyltoluene. To determine potential wind direction based factors, the sources in the inventory where binned into 20^o sectors based on direction from Avalon. Since different sources are located at varying distances from Avalon, in order to estimate an aggregated emissions profile one needs to account for differences in emission rates and potential difference in pollutant dispersion. To account for differences in dispersion, the centerline plume concentration was calculated using a Gaussian plume dispersion model assuming all point sources had the same stack characteristics and that the wind is blowing directly from the source to Avalon. This provides a zeroeth order scaling of the relative importance of sources. The concentration ratios were used to determine the direction based inventory profiles. The determined inventory profiles were used to aid in identification of factors in the PMF solution. The relative pollutant concentration levels at Avalon for each inventory profile were also determined. Gasoline vehicles profiles were taken from the EPA (USEPA 2001).

PMF Results

PMF for the Avalon site are presented in Figure 35. An 8 factor solution with a 0.2 rotation best provided the most interpretable solution. The eight factors included:

Pittsburgh Factor: An acetone dominated unidentified factor with elevated concentrations when the wind is blowing from downtown Pittsburgh

Background Factor: This is a factor though to contain the background concentrations of several of the compounds measured.
Mobile Gasoline Factor: A toluene dominated factor that is thought to represent the contribution from mobile gasoline. It matches well to the EPA gasoline profile.
Neville Island Factor: A benzene dominated factor that is highly eleveated with wind coming off of Neville Island. The factor profile matches well with the coke works emissions profile.
MEK Factor: A methyl ethyl ketone dominated factor that is not a function of wind direction. There are several sources of MEK in the county and this may just be a grouping of those sources.
Secondary Factor: This factor is dominated by products that are formed from VOC photolysis and photo-oxidation, acetone and MEK, and may represent a more aged air mass.
ACSA Factor: This is a tetrachloroethene and trichloroethene dominated source that has a similar profile to the Allegheny County Sanitary Authority and has elevated contributions to ambient concentrations when the wind blows from the direction of the ACSA.
F8: This factor is as of yet unidentified

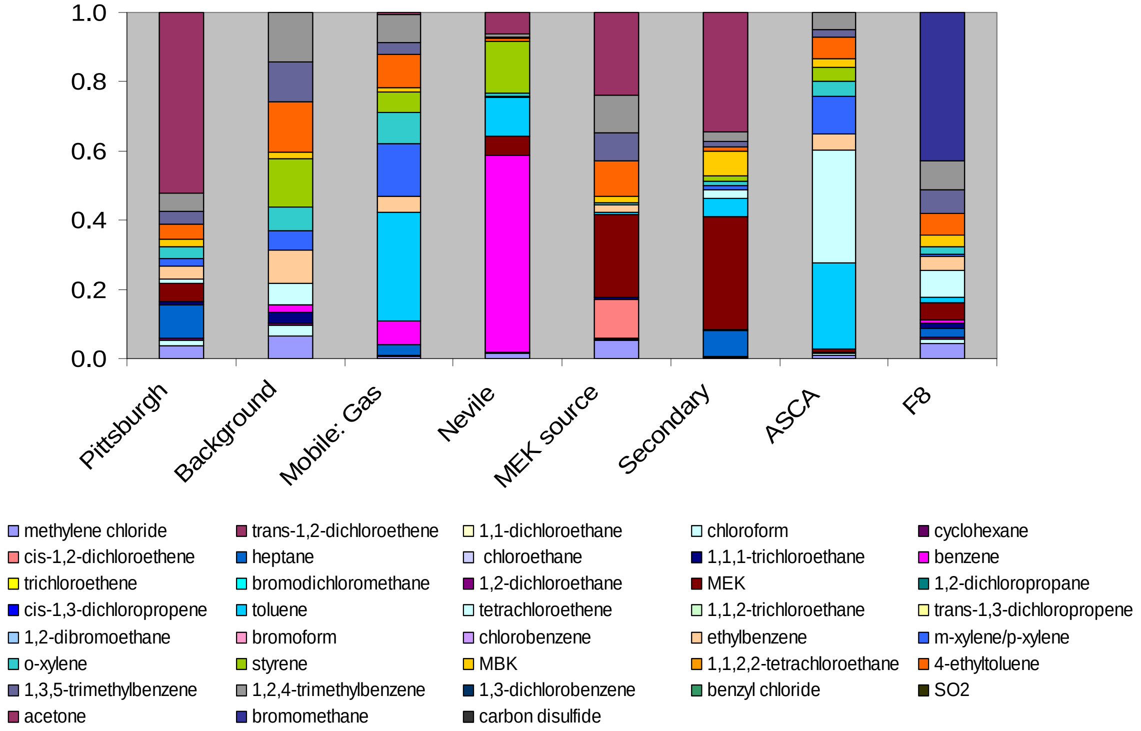


Figure 35 PMF solution for the hourly data collected at the Avalon site.

Three of the factors have been strongly linked to sources: gasoline mobile source factor, the Neville island factor, and the Allegheny County Sanitary Authority factor (ACSA). As an example, the ACSA factor is shown in Figure 36. The ACSA factor was identified by comparing the PMF determined factor profile to the emissions profile for ACSA to ACHD and by comparing the factor strength to wind direction. The ACSA factor contribution elevates greatly when wind is coming up river from ACSA.

Once the source contributions and source profiles are determined, we can estimate the contribution of each source to the total fraction of the risk. Figure 37 shows some preliminary results in our work to link health risks to sources. It presents the Neville Island factor profile and this factor's contribution to the cancer risk at Avalon. The Neville factor contributes almost 80% of the benzene exposure at Avalon and slightly more than 40% of the total lifetime cancer risk.

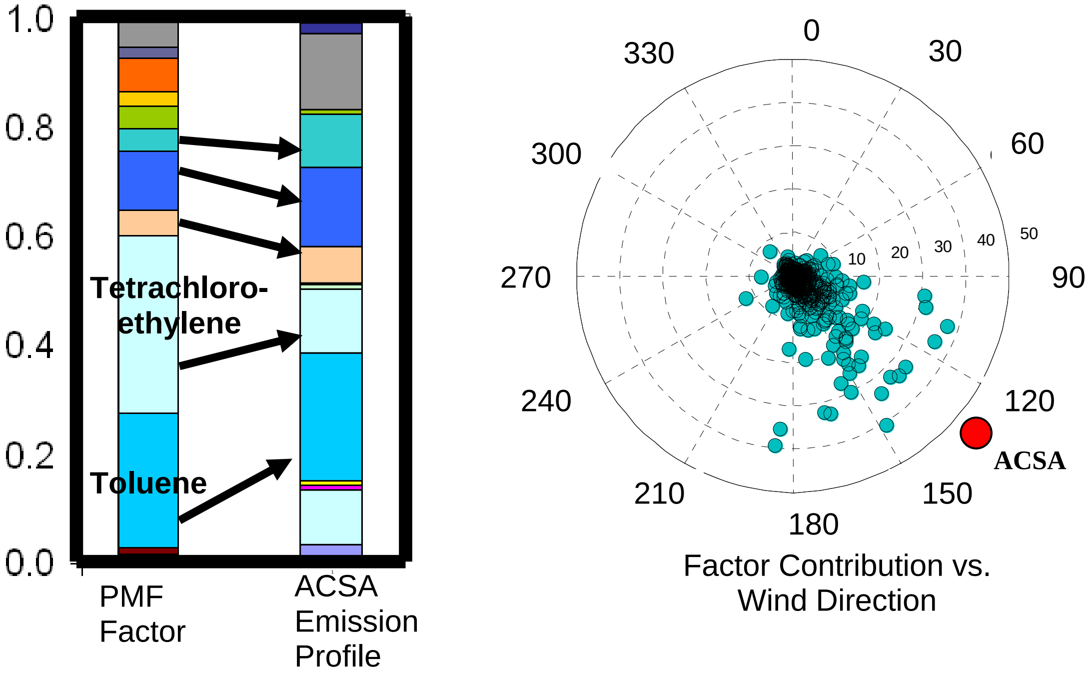


Figure 36 Allegheny County Sanitary Authority factor. PMF factor profile is very similar to reported emissions profile and factor contribution is greatly elevated when wind comes from the ACSA facility, indicated by the red dot on the wind rose.

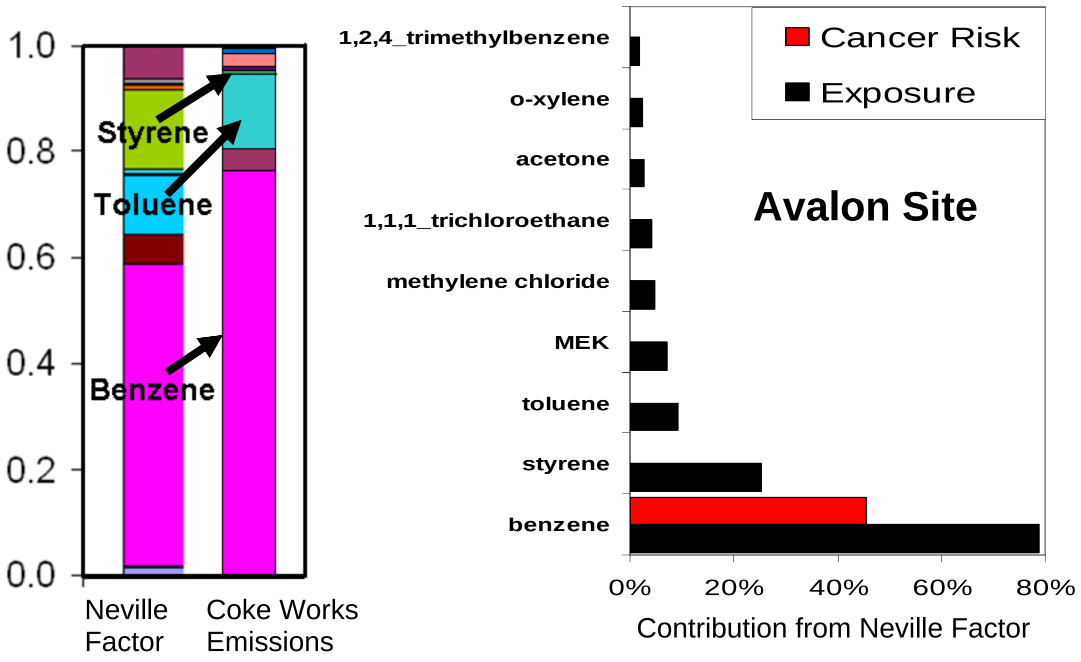


Figure 37 Neville Island factor is similar to coke production emission profile. The Neville Island factor is responsible for 45% of the cancer risk from the set of chemicals measured and for 78% of the benzene exposure. Similar analysis can be done to calculate factor contribution to hazard index.

Comparisons with Dispersion Model Predictions

We are also comparing the receptor modeling results to predictions of the National Air Toxics Assessment (NATA). NATA uses emissions data in conjunction with a dispersion model to estimate local level risks to air toxics. A few studies have compared predictions of the NATA modeling framework to measured concentrations (Wheeler 2004). For gas-phase primary emissions they found that the predicted concentrations were generally within a factor of 10. The study also found that the model is not a good predictor of concentrations more than 50 km from source or secondary compound concentrations. However, previous studies have not compared source resolved predictions.

Figure 38 shows an initial comparison between measured annual average air toxic concentrations at the four ACHD sites to the 1999 NATA predictions. Although predicted concentrations are mostly within a factor of 10 of the measured values, NATA systematically under predicts concentrations. The worst model performance is for styrene.

Figure 39 plots the ratio of the measured concentrations to the predictions for the 4 sites. NATA under predicts concentrations at the Avalon and Stowe, the point source dominated sites, more so than at downtown or South Fayette sites. This raises a concern about possible bias at certain sites, strongly influenced by local sources.

Figure 40 compares the NATA predicted source apportionment for each of the four sites as well as that calculated from the Avalon high-time resolved data. The NATA apportionment does not differ greatly for the four sites. However the PMF analysis of the high time resolved data, NATA appears to under-predict the contribution of point sources. These results indicate that NATA may not correctly predict the sources of exposure.

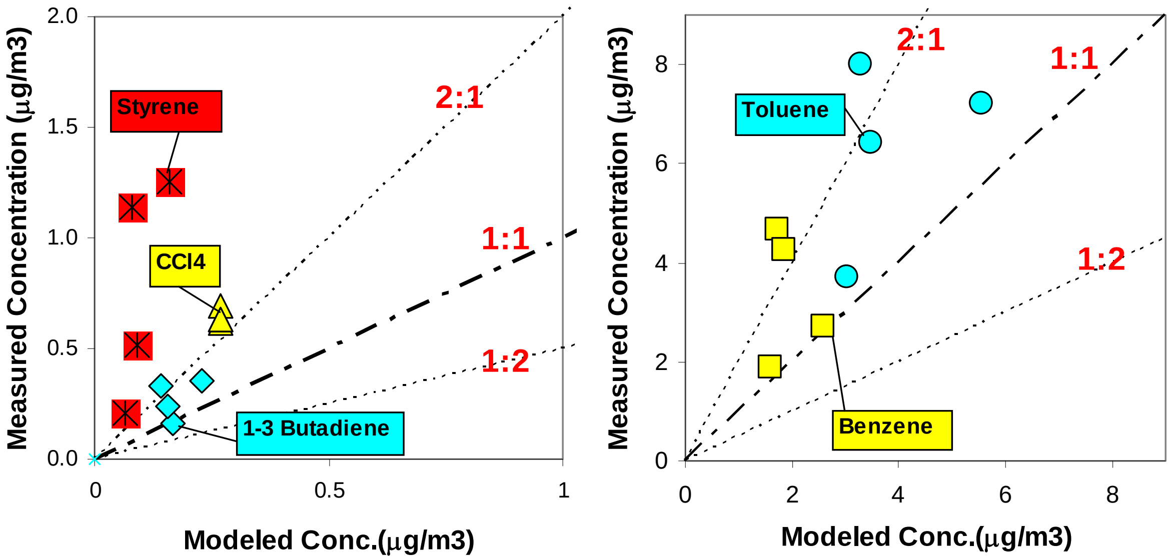


Figure 38 Comparison of measured and predicted annual average concentrations of four gas phase organic air toxics. Predictions are from the 1999 NATA for the census tracts in which the measurement site was located.

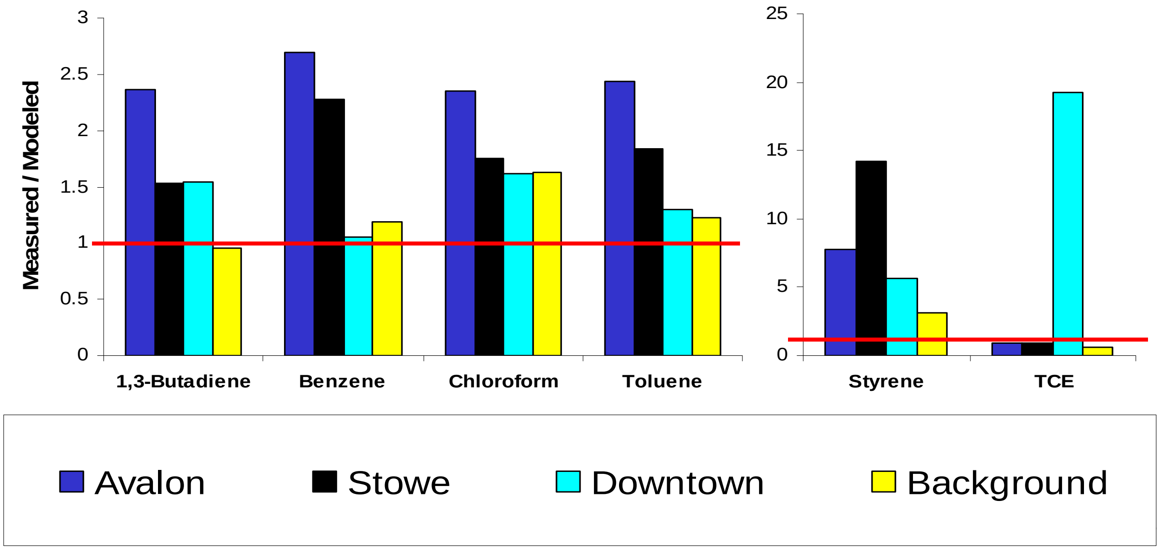


Figure 39 Ratio of measured-to-predicted air toxic concentrations at the four ACHD monitoring sites. NATA under-predicts concentrations at the point source dominated sites (Avalon and Stowe) more so than at the mobile (downtown) and background sites.

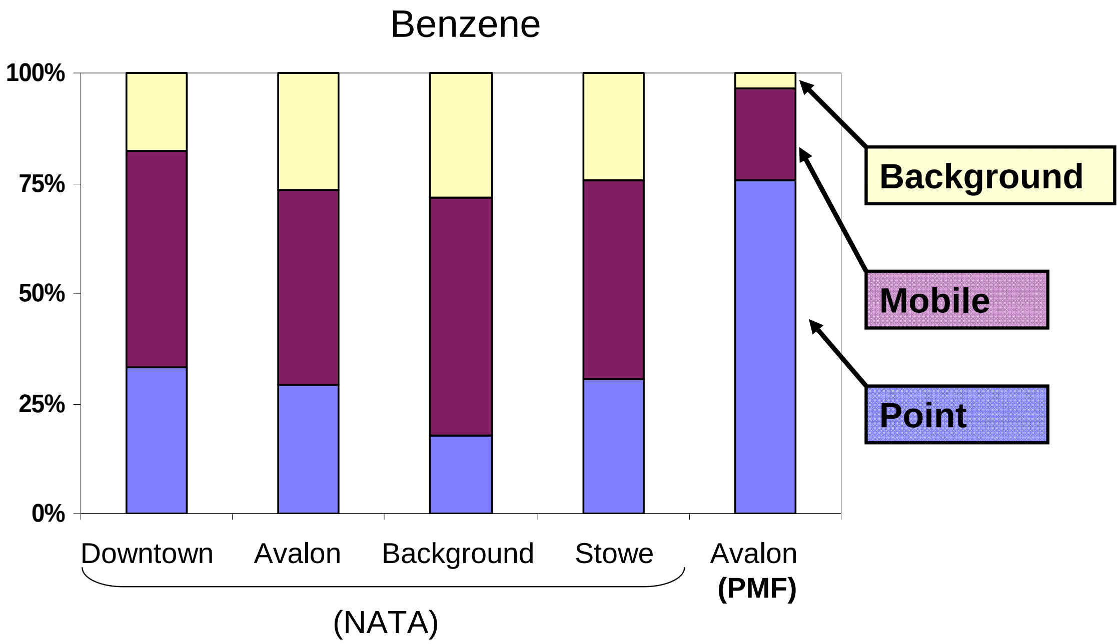


Figure 40 NATA source apportionment of Benzene for the four ACHD sites.

CONCLUSIONS

In January 2002, the Allegheny County Health Department (ACHD) in collaboration with Carnegie Mellon University embarked on a project to investigate air toxics in Allegheny County. The project involved both baseline and intensive sampling a suite of gas-phase organic air toxics. Measurements were made at multiple sites that represent different source/exposure regimes. A risk model was used to estimate chronic and acute cancer and non-cancer health risk. Statistical and deterministic modeling tools were used for the source-apportionment analysis.

The study sites were chosen to compare air toxic concentrations and health risks among areas dominated by different sources. Two of the sites were in residential areas adjacent to Neville Island, which is heavily industrialized. Sites were also located in downtown Pittsburgh, which has substantial mobile source emissions. A final site was located to measure regional background air toxic concentrations.

Ambient concentrations of twelve of the air toxics exhibited little spatial variability in Allegheny County. These twelve are 1,2-dichloropropane, 1,2-dibromomethane, bromoform, hexachlorobutadiene, chlorobenzene, bromomethane, 1,2-dichloroethane, 1,2,4-trichlorobenzene, chloromethane, carbon tetrachloride, formaldehyde and propionaldehyde. Urban concentrations of twelve air toxics were 1.25 to 2 times greater than the regional background site. These include 1,1 dichloroethane, 1,1,2-trichloroethane, 1,1,-dichloroethene, 1,1,2,2-tetrachloroethane, MTBE, 1,1,1-trichloroethane, benzyl chloride, chloroform, methyl isobutyl ketone, acetaldehyde, toluene and benzene. Fifteen of the thirty-nine measured pollutants exhibited significant site-to-site variable (at least a factor of 2), indicating important local sources. These fifteen are vinyl chloride, chloroethane, acrolein, hexane, 1,3-butadiene, carbon disulfide, m/p-xylene, o-xylene, tetrachloroethene, ethyl benzene, methylene chloride, styrene, 1,4-dichlorobenzene, trichloroethene, and hydrogen sulfide. The greatest spatial variability was seen for chlorinated compounds, which were highest at the Flag Plaza site in downtown Pittsburgh.

Study-average concentrations of twenty air toxics were above the national 50th percentile at at least one of the sites. Of these, twelve appear to be strongly influenced by local emissions with urban concentrations a factor of two or more greater than the regional background. Concentrations of benzene, toluene, propionaldehyde, tetrachloroethene, ethyl benzene, methylene chloride, styrene, 1,4-dichlorobenzene, trichloroethene, and hydrogen sulfide were greater than the national 75th percentile at all of the sites. This indicates a problem with regional emissions in southwestern Pennsylvania.

Lifetime cancer risks and non-cancer hazard quotients were determined for each compound. Historically been concern that spatial variation in air toxics sources and emissions rates may dominate risks and the estimated cancer risks across these four very different sites varied by less than a factor of two. In addition, the same pollutants contributed the majority of the cancer risks at all sites: formaldehyde, benzene and carbon tetrachloride. Two of these three pollutants, formaldehyde and carbon tetrachloride, are regional distributed which limited the site to site variability in health risks. Trichloroethene and 1,4-dichlorobenzene also added substantial risks at the downtown site. Only acrolein is predicted to pose a non-cancer health risk.

A mixture-interactions model was used as a first-cut screening tool to prioritize pollutant pairs for further study based on their plausible synergistic/antagonistic impacts on the toxicity of mixtures of gas phase air toxics for both cancer and non-cancer risks.
The greatest potential for interactions was predicted for acrolein and formaldehyde for respiratory non-cancer effects and formaldehyde and acetaldehyde for respiratory cancers. The method presented here for analyzing potential mixture can provide an informed basis for prioritizing particular interactions effects based on observed co-occurrence data.

The time series at each site are characterized by relatively stable background concentrations with short periods of higher concentrations. These short-duration, high-concentration events are likely associated with plumes from local sources influencing the site. The frequency and magnitude of these events varied from site to site and as a function of wind direction.

Preliminary source apportionment analysis has been performed using Positive Matrix Factorization (PMF). The goal of the analysis is to identify the sources of the air toxics posing the greatest health risk. The analysis indicates the importance of emissions from metallurgical coke production to benzene concentrations at the residential sites adjacent to Neville Island. Concentrations of 1,4-dichlorobenzene and trichloroethene were 12 and 26 times higher downtown compared to the regional background. This indicates an important local source(s) of these compounds, but the nature of these sources is not known. Only minor sources of these chlorinated toxics are contained in the Allegheny County Point Source Emissions Inventory (ACHD 2006) and they are not emitted by mobile sources (USEPA 2007).

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