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

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This work was the primary focus of two PhD students at Carnegie Mellon University. Jennifer Logue developed the automated gas phase organic air toxics instrument and performed most of the data analysis. Andrew Lambe deployed the TAG instrument and led the analysis of diesel particulate matter concentrations.

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Executive Summary

In January 2002, Carnegie Mellon University in collaboration with the Allegheny County Health Department embarked on a project to investigate air toxic concentrations, risks and sources in Allegheny County. The project was motivated by the concerns of citizens living near Neville Island, a heavily industrialized area in the City of Pittsburgh.

Concentrations of 36 volatile organic air toxics were measured at six sites specifically chosen to represent different source/exposure regimes. Two of the sites were in residential areas adjacent to Neville Island; two of the sites were in downtown Pittsburgh, which has substantial mobile source emissions; and two of the sites were located to characterize regional air toxic concentrations. The two downtown sites and the two residential sites adjacent to Neville Island were specifically chosen to represent high exposure areas with substantial local emissions. At four of the six sites, 24-hour-average concentrations were measured on a one-in-six-day schedule for a two-year period to characterize long-term and seasonal exposures. At three of the sites, state-of-the-art instrumentation was deployed for shorter periods of time to make hourly measurements of air toxic concentrations for source apportionment analysis.

Study-average concentrations of 13 of the target organic air toxics were greater than the national 75th percentile at one or more of the baseline sites, including benzene, toluene, propionaldehyde, tetrachloroethene, ethyl benzene, methylene chloride, styrene, 1,4-dichlorobenzene, trichloroethene, m/p- and o-xylenes, methyl isobutyl ketone, and chloromethane. Concentrations of many of these air toxics were a factor of two or more greater at the urban sites than in South Fayette (the regional background site), indicating the substantial influence of emissions from local sources. Concentrations of only two air toxics were greater than the national 75th percentile in South Fayette: benzene and propionaldehyde. Therefore, these two toxics present a countywide problem.

High-time resolved measurements revealed that most air toxics are characterized by periods of low, relatively stable concentrations with intermittent, relatively short periods of higher concentrations. The frequency and magnitude of these events varied from site to site, as a function of wind direction and with the time of day. The high-time resolved data revealed strong correlations between concentrations of certain air toxics and wind direction, helping to link high

concentration events with emissions from specific source regions. For example, at all three intensive sites, high concentrations of benzene and other air toxics were observed when the sites were downwind from Neville Island and Clairton, two areas with large industrial facilities.

Cancer and non-cancer health risks were estimated using traditional and advanced risk models and published toxicity data. Figure ES-1 indicates that the additive cancer risk of the 36 target organic air toxics varied by less than a factor of 1.5 between the four baseline sites. The highest risks were estimated for the downtown site. The spatial variation in cancer risks was surprisingly modest given that three of the four baseline sites were in locations with substantial emissions from local sources. The spatial variation in risk was so modest because two of the most important air toxics, formaldehyde and carbon tetrachloride, are regionally distributed. Benzene also contributed significantly to the cancer risks at all sites. Concentrations of chlorinated air toxics such as trichloroethene and 1,4-dichlorobenzene were greatly elevated downtown. Only one of the target air toxics, acrolein, was estimated to pose a non-cancer health risk.

To more comprehensively assess air toxics risks in Allegheny County, the project also analyzed archived air quality data measured by earlier studies. This broader assessment considered 65 different air toxics. Figure ES-2 compares the additive cancer risks for four different classes of air toxics: the 36 target organic air toxics, metals, polycyclic organic matter (POM) and diesel particulate matter (DPM). Of these four classes of air toxics, DPM presented the greatest cancer risks at all sites. DPM risks are 3 to 11 times the additive cancer risk of the next highest class of air toxics, with the highest risks downtown. Only limited data are currently available on the DPM levels in the county. These data indicate that downtown is a DPM hotspot, with levels that are a factor of three to four higher than in other areas in the county. However, even outside of the downtown area, DPM levels are still high enough such that it still poses the greatest cancer risk.

A major goal of this project was to compare air toxic concentrations and risks in Allegheny County to other locations in the United States. Figure ES-1 compares the cancer risk estimates for Allegheny County to estimates for 14 other U.S. cites. The additive cancer risk of the 36 target organic air toxics varied by about a factor of 16 across this set of cities. Risks at all of the

Allegheny County are near the 50th percentile for the cities studied. The DPM levels in Pittsburgh also appear comparable to those in other US cities.

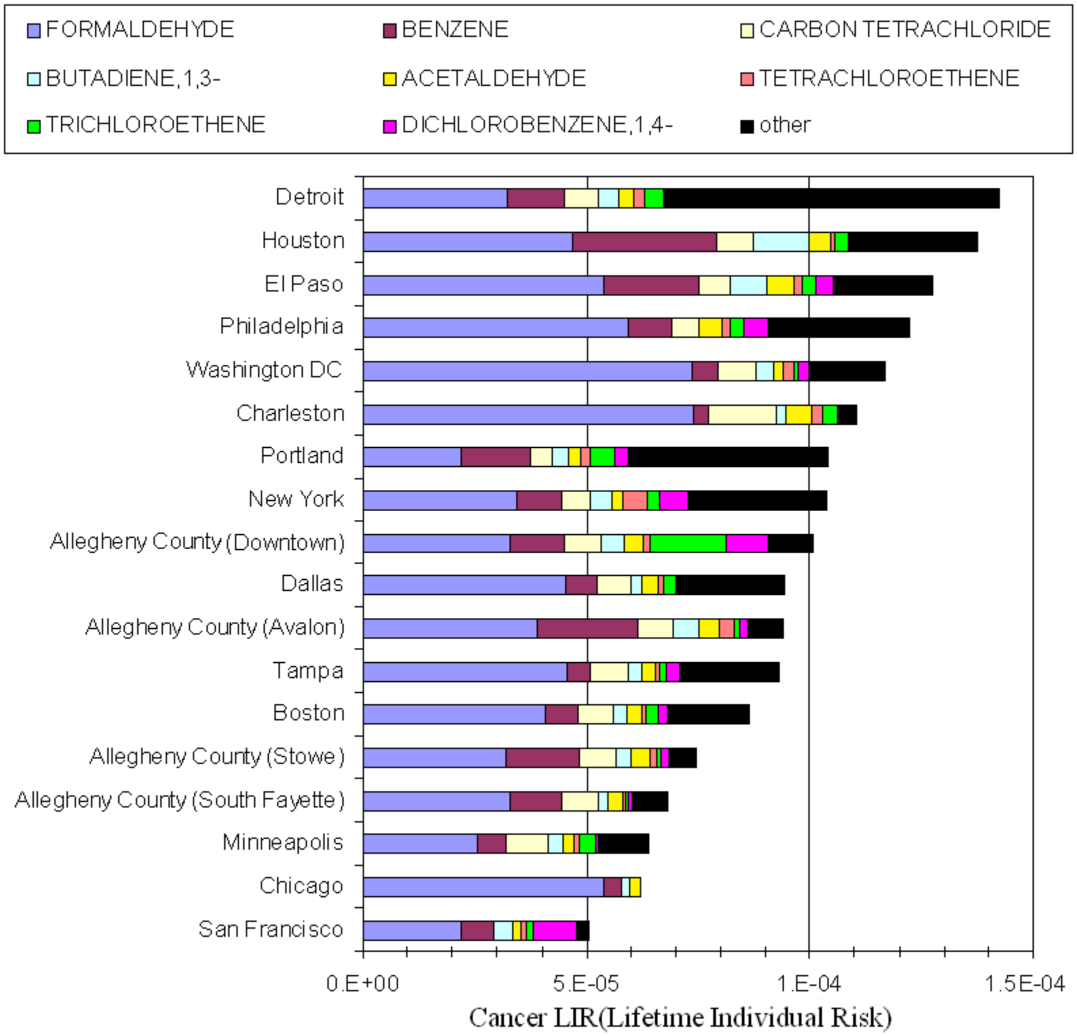


Figure ES-1 Additive cancer risks at the four baseline sites in Allegheny County and selected other United States Cities. The risk estimates are based on long-term average outdoor concentrations of 36 organic gas-phase air toxics considered in this study. The additive risk of 30 air toxics that pose a relatively low cancer risk in Allegheny County are lumped into the category “other.”

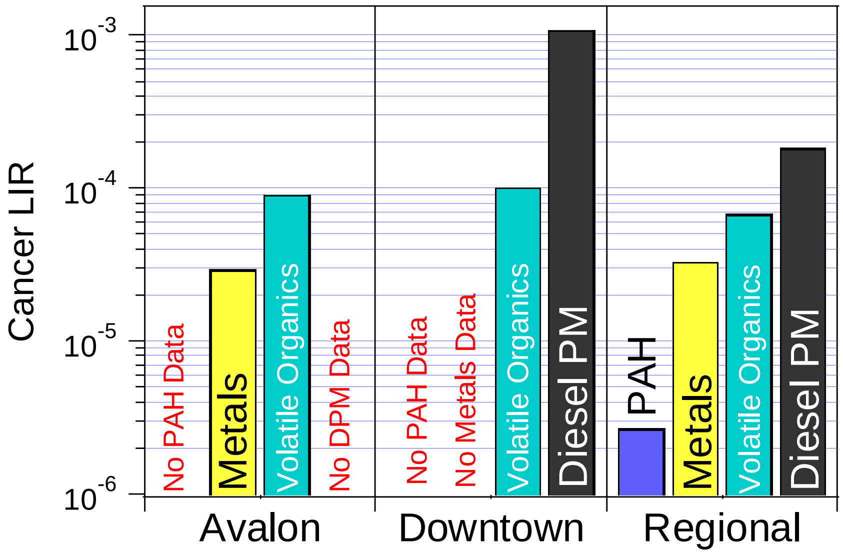


Figure ES-2 Additive cancer risk for different classes of air toxics. The estimates for the regional background are based on data from South Fayette and archived data from the Pittsburgh Supersite in Schenley Park (PAH, metals, and diesel PM).

Based on the measured air toxic concentrations and risk estimates, a set of priority air toxics for Allegheny County were identified. These priority toxics are listed in Table ES-1. Four air toxics were designated as the highest priority: DPM, benzene, formaldehyde and trichloroethene. All of these air toxics pose lifetime cancer risks greater than 10^{-5}. Air toxics with a lifetime cancer risk between 10^{-6} and 10^{-5} or estimated to pose non-cancer risks were classified as moderate priority. The category “Potential Concerns” includes air toxics with higher than average concentrations relative to national data but that are not estimated to pose health risks.

Table ES-1 Priority Air Toxics for Allegheny County

Highest Priority	Moderate Priority	Potential Concerns
Diesel particulate matter	Carbon tetrachloride	Propionaldehyde
Formaldehyde	1,3-butadiene	Styrene
Benzene	Acetaldehyde	Ethylbenzene
Trichloroethene	Tetrachloroethene	Toluene
	1,4-dichlorobenzene	Methylene chloride
	Chloroform	MIBK
	Hexachlorobutadiene	Xylenes
	Benzyl chloride	
	1,2-dichloroethane	
	Acrolein	
	Arsenic	
	Chromium	

Source- and receptor-based air quality models were used to apportion air toxics to sources. The goal was to identify the sources of the air toxics posing the greatest health risk. Figure ES-3a summarizes the source apportionment of the target gas-phase organic air toxics. For this group of compounds, the majority of the risks were from regional or secondary sources. At Avalon, coke works emissions were the most important local source. In downtown, non-mobile sources were the dominant local source of cancer risk, largely due the high levels of chlorinated compounds. Dry cleaning appears to be one important source of these compounds in the downtown area, but much of the risk associated with chlorinated air toxics could not be attributed to specific sources.

Figure ES-3b indicates that when DPM is included in the risk assessment, emissions from mobile sources are the dominant contributor to the cancer risks. Although the DPM toxicity data are uncertain, mobile risks still dominate the overall cancer risk even with a lower bound risk estimate for DPM.

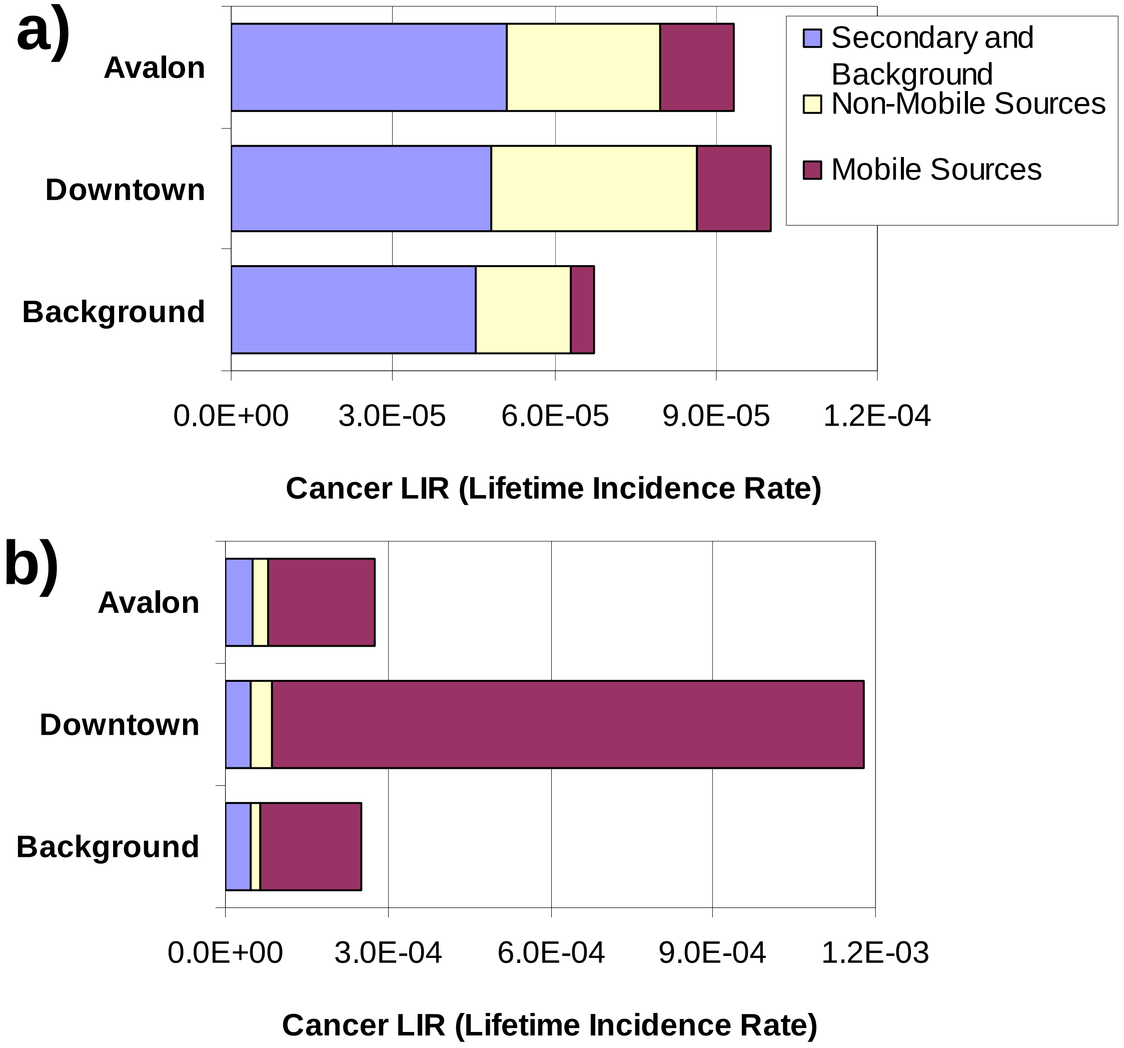


Figure ES-3. Apportionment of additive life time cancer risks by source class. Panel (a) estimated risks for target gas phase organic air toxics; panel (b) estimated risks for gas phase air toxics plus diesel particulate matter.

The results of this study were used to evaluate preliminary results from the 2002 National Air Toxics Assessment (NATA). Predicted concentrations of the air toxics that are the primary risk drivers were generally within a factor of two of the measured values, therefore NATA accurately risk ranks the pollutants. However, NATA appears to consistently underestimate the emissions associated with large point sources and overestimates the risks from mobile sources.

The report concludes with some recommendations to reduce air toxic risks in Allegheny County. DPM must be given the highest priority. Although the county has already implemented retrofit and idling programs to help reduce exposures to DPM, these programs are primarily aimed at reducing exposures of school children. It is unclear if they will effectively address the downtown DPM hotspot. To reduce DPM concentrations in the downtown area will likely require new initiatives, including activity based and retrofit programs. More data are needed to quantify the spatial extent of the downtown DPM hotspot. Benzene is another important air toxic with substantial local emissions. Currently, a large effort is underway to reduce emissions from the Clairton Coke Works, the largest point source of benzene in Allegheny County. This should reduce benzene risks throughout the county, but there are also substantial benzene emissions from sources on Neville Island. New programs are needed to more effectively control those emissions.

Table of Contents

Table of Figures

Table of Tables

Chapter 1. Introduction

This is the final technical progress report of the project “Air Toxics in Allegheny County: Sources, Airborne Concentrations, and Human Exposure,” supported by the Allegheny County Health Department under Agreement #36946. This project was motivated by concerns of citizens about exposures to air pollutants emitted by large industrial facilities and other sources. Although 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 toxic emissions (1). In addition, much of this industrial activity is clustered in certain areas, potentially creating concerns with environmental inequality (2).

This project specifically investigated the exposures, health risks, and sources of hazardous air pollutants or air toxics. 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 (3). The Environmental Protection Agency (EPA) currently classifies 187 pollutants as air toxics. The list includes a diverse set of compounds including organics, chlorinated compounds, and metals.

In the 1990s EPA initiated the National Air Toxics Assessment (NATA) to determine the air toxics that pose the greatest risk to human health. The 1996 NATA estimated nationwide exposures to 33 air toxics which were thought to pose the greatest health 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) (4). 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 are needed to evaluate predicted concentrations and to determine actual exposure.

This project investigated 65 different air toxics that were specifically chosen because they were identified as priority pollutants by NATA and/or there are known substantial emissions in Allegheny County. Atmospheric concentrations of as many as 52 air toxics were measured at different sites throughout the county. To provide a more comprehensive assessment, the project also utilized archived data for 13 additional air toxics. Concentrations at different sites were compared to assess the spatial variation in exposure. Traditional and advanced models were used to assess the air toxic health risk. Source- and receptor-based models were used to apportion air toxics concentrations and health risks to sources. Finally, air toxic concentrations and risks in Allegheny County were compared to other data from other United States cities.

1.1 Project Objectives

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.

1.2 Outline of the report

Chapter 2 describes the location of the monitoring sites, the instrumentation, and the experimental protocols. Air toxic concentrations measured during the baseline and intensive studies are compared to evaluate instrument performance.

Chapter 3 presents the baseline data to quantify the spatial variation in air toxics concentrations within Allegheny County and to compare those concentrations to national data. Chapter 3 also contains a detailed health risks analysis including non-cancer risks, cancer risks, and mixture interactions. Cancer and non-cancer health risks are estimated for different classes of air toxics and compared to data from other United States cities. Chapter 3 concludes by identifying priority air toxics for Allegheny County.

Chapter 4 describes the high time resolved data measured during the intensive campaigns. The data are analyzed for daily, weekly and seasonal patterns. Correlations in toxics as a function of wind direction are also presented.

Chapter 5 describes results from receptor-model analysis to apportion a subset of measured air toxics to sources. The factor analysis model, PMF2, was applied to high time resolved measurements from the intensive studies. Comparisons with source profiles and correlations with wind direction were used to associate factors with specific sources.

Chapter 6 presents receptor model analysis to estimate diesel particulate matter concentrations at two sites in Allegheny County.

Chapter 7 synthesizes the risk estimates by source using the results from Chapters 5 and 6. First the gas gas phase air toxics not apportioned using PMF in Chapter 5 are apportioned to sources. Then all the source apportionment results are combined to provide a comprehensive picture of the sources of air toxics in Allegheny County.

Chapter 8 compares the measured data to dispersion model predictions from National Air Toxics Assessment (NATA). The comparison considers air toxic concentrations, risk rankings, and sources.

Chapter 9 discusses the concentrations, sources, and risks of individual priority air toxics for Allegheny County. Chapter 9 ends with a brief discussion for recommendations to reduce air toxic exposures in Allegheny County.

Chapter 2. Experimental Methods: Monitoring Sites and Instrumentation

One of the main goals of this project was to measure the ambient concentrations of a large number of gas- and particulate-phase air toxics in residential areas around Neville Island, in downtown Pittsburgh, and at a background site. To achieve this goal, baseline and intensive measurements were conducted. During the baseline period, 24 hr average air toxic concentrations were measured on a one-in-six day basis for two full years (2006-2007). The baseline measurements provide information on long-term exposures, seasonal variations in exposure, and the spatial pattern of exposure in Allegheny County. During the intensive periods, about one month's worth of hourly air toxic concentrations were measured over one-to-two month periods. High time resolved measurements provided information for acute exposure assessments and were critical in the identification of air toxic sources.

2.1 Measurement Locations

Air toxics concentrations were measured at six different sites in and around Pittsburgh, PA (Figure 2.1). Four of these sites are operated by the Allegheny County Health Department (ACHD) as part of their compliance monitoring network: 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 final two sites were the Diamond Building in downtown Pittsburgh and on the campus of Carnegie Mellon University. Table 2.1 summarizes the types and timeframes for the measurements taken at each of the sites.

Baseline measurements were taken at four of the sites, Avalon, Stowe, South Fayette, and Flag Plaza. The Avalon and Stowe sites are located in 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. Mobile sources are expected to be a major air pollutant source in the downtown area (Flag Plaza site). South Fayette is a regional background site not located near any major sources.

Intensive measurements were made at three sites: Avalon, the Diamond Building, and on the Carnegie Mellon University Campus. 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 intensive study because of problems with access and infrastructure. The Carnegie Mellon University campus site is representative of urban background conditions.

Table 2.1 Summary of measurements taken during project.

Measurement Site	**Baseline Measurements**	**Intensive Measurements**
Neville Island Influenced		
Avalon	1 in 6 for 2006-2007	Oct. 2006 - Jan. 2007
Stowe	1 in 6 for 2006-2007	--------------------
Downtown		
Flag Plaza	1 in 6 for 2006-2007	--------------------
Diamond Bldg.	--------------------	Feb. 2008 - May 2008
Urban Background		
Carnegie Mellon University	--------------------	Jun. 2007 - Nov. 2007
Regional Background		
South Fayette	1 in 6 for 2006-2007	--------------------

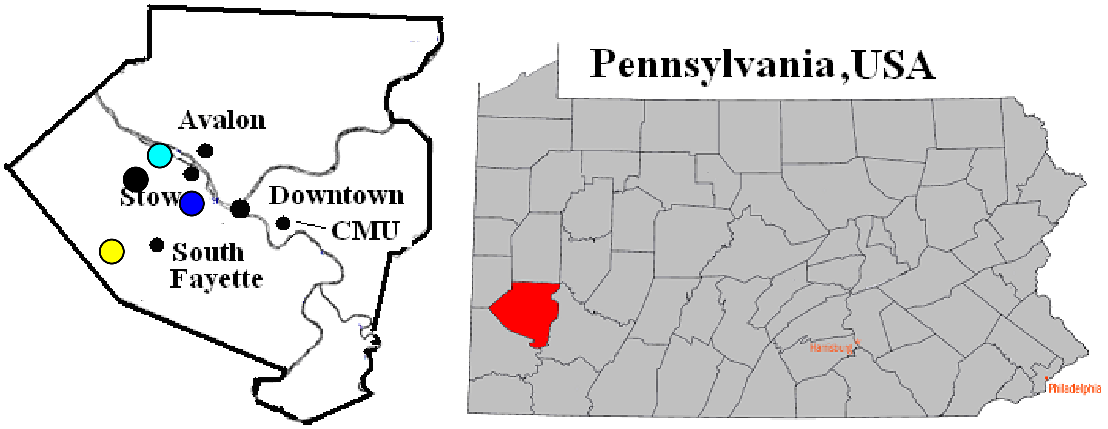


Figure 2.1 Location of air toxics monitoring sites.

2.2 Target Compounds

This study investigated ambient concentrations, health risks, and sources of the air toxics listed in Table 2.2. The baseline and intensive sampling characterized concentrations of volatile organic air toxics using the techniques described below. This included many air toxics with high annual point source emissions in Allegheny County and mobile source air toxics (MSAT) (5).

To more comprehensively assess air toxic risks in Allegheny County, the risk component of the project also considered archived air quality data for metals and polycyclic aromatic material (POM). Much of these data were collected at an urban background site adjacent to the Carnegie Mellon Campus during 2001 and 2002 as part of the Pittsburgh Air Quality Study (6). Archived data were also available from some of the Allegheny County Health Department compliance monitoring sites.

Although this project considered 65 different air toxics, these pollutants represent only a subset of the 187 air toxics currently regulated by EPA. There are also likely other toxic air pollutants that are not officially designated as an air toxic and therefore not currently regulated. Based on emissions data and previous risk assessments such as NATA, our target list includes the expected priority toxics, except acrylonitrile. Acrylonitrile concentrations were measured during a six month period in 2008 at the Flag Plaza site (31 24hr averaged concentration measurements).

Table 2.2 Air toxics considered in this study and the locations and timeframes of their measurement.

Chemical Name	Baseline Monitoring	Intensive Measurements	Archived Data	Point Source Emissions (TPY)
Acetaldehyde	A,S,SF,FP	D,CMU,SS	---------	0.58
Acrolien	A,S,SF,FP	---------	---------	0.65
Benzene	A,S,SF,FP	A,D,CMU,SS	---------	86.00
Benzyl chloride	A,S,SF,FP	A,D,CMU,SS	---------	0.45
Bromoform	A,S,SF,FP	A,D,CMU	---------	0.02
Bromomethane	A,S,SF,FP	A,D,CMU	---------	---------
Butadiene, 1,3-	A,S,SF,FP	A,D,CMU	---------	0.02
Carbon disulfide	A,S,SF,FP	A,D,CMU	---------	18.91
Carbon tetrachloride	A,S,SF,FP	A,D,CMU	---------	0.00
Chlorobenzene	A,S,SF,FP	A,D,CMU	---------	8.25
Chloroethane	A,S,SF,FP	D,CMU	---------	0.56
Chloroform	A,S,SF,FP	A,D,CMU,SS	---------	2.10
Chloromethane	A,S,SF,FP	---------	---------	20.81
Dibromoethane, 1,2-	A,S,SF,FP	A,CMU	---------	0.00
Dichlorobenzene, 1,4-	A,S,SF,FP	D,CMU	---------	0.58
Dichloroethane, 1,1-	A,S,SF,FP	A,D,CMU	---------	0.00
Dichloroethane,1,2-	A,S,SF,FP	A,D,CMU	---------	0.08
Dichloroethene, 1,1-	A,S,SF,FP	D,CMU	---------	0.00
Dichloropropane, 1,2-	A,S,SF,FP	A,D,CMU	---------	0.00
Ethyl benzene	A,S,SF,FP	A,D,CMU,SS	---------	14.30
Formaldehyde	A,S,SF,FP	---------	---------	7.25
Hexachlorobutadiene	A,S,SF,FP	A,D,CMU	---------	0.00
Hexane	A,S,SF,FP	A,D,CMU,SS	---------	22.04
Methyl isobutyl ketone	A,S,SF,FP	D	---------	18.20
Methylene chloride	A,S,SF,FP	A,D,CMU	---------	4.05
MTBE	A,S,SF,FP	D,SS	---------	8.59
Propionaldehyde	A,S,SF,FP	---------	---------	0.24
Styrene	A,S,SF,FP	A,D,CMU,SS	---------	56.00
Tetrachloroethane, 1,1,2,2-	A,S,SF,FP	D,CMU	---------	1.53
Tetrachloroethene	A,S,SF,FP	A,D,CMU	---------	2.17
Toluene	A,S,SF,FP	A,D,CMU,SS	---------	109.00
Trichlorobenzene, 1,2,4-	A,S,SF,FP	D	---------	0.00
Trichloroethane, 1,1,1-	A,S,SF,FP	A,D,CMU	---------	0.13
Trichloroethane,1,1,2-	A,S,SF,FP	A,D	---------	0.10
Trichloroethene	A,S,SF,FP	A,D,CMU	---------	1.02
Vinyl chloride	A,S,SF,FP	---------	---------	2.10
Xylene, m/p	A,S,SF,FP	A,D,CMU,SS	---------	1.46
Xylene, o-	A,S,SF,FP	A,D,CMU,SS	---------	0.06
Hydrogen Sulfide	---------	A	---------	168.00
Diesel Particulate Matter	---------	D	SS	---------
Naphthalene	---------	D	SS	14.58
Acenaphthene	---------	D	SS	1.71
Acenaphthylene	---------	D	SS	0.82
Fluorene	---------	D	SS	1.39
Phenanthrene	---------	D	SS	4.90
Anthracene	---------	D	SS	0.94
Fluoranthene	---------	D	SS	2.54
Chrysene	---------	D	SS	1.64
Benzo[A]Anthracene	---------	D	SS	1.54
Benzo[B]Fluoranthene	---------	D	SS	---------
Benzo[K]Fluoranthene	---------	D	SS	---------
Dibenzo[A,H]Anthracene	---------	D	SS	0.10
Benzo[G,H,I]Perylene	---------	D	SS	0.26
Benzo[A]Pyrene	---------	D	SS	0.71
Indeno[1,2,3-Cd]Pyrene	---------	D	SS	0.35
Pyrene	---------	D	SS	1.90
Antimony (PM10)	---------	---------	SS	0.61
Arsenic (PM10)	A	---------	SS	0.26
Beryllium (PM10)	A	---------	SS	0.02
Cadmium (PM10)	A	---------	SS	0.14
Chromium (PM10)	A	---------	SS	2.75
Cobalt (PM10)	---------	---------	SS	0.23
Lead (PM10)	A	---------	SS	8.99
Manganese (PM10)	A	---------	SS	5.19
Nickel (PM10)	A	---------	SS	2.89
Dibenz(A-H)Anthracene (PM10)	---------	---------	SS	0.10
Selenium (PM10)	---------	---------	SS	6.31

Site names:

A: Avalon	D: Downtown (Diamond Bldg.)
S: Stowe	CMU: Urban Background at CMU
SF: South Fayette	SS: Pittsburgh Supersite
FP: Flag Plaza	

Point Source Emissions Inventory 2004 Allegheny County Health Department

2.3 Baseline Measurements

Twenty-four average concentrations of gas-phase organic air toxics were measured at the four baseline sites listed in Table 2.1 on a one-in-sixday schedule from 2/4/06 until 01/19/08. At each site the Allegheny County Health Department deployed an Atec model 2200 air toxics sampler to collect SUMMA canisters and carbonyl samples (silica cartridges impregnated with dinltrophenylhydramine (DNPH)).

The SUMMA canisters were analyzed by the Maryland State Department of Environmental Protection laboratory using Method TO-15, "The Determination of Volatile Organic Compounds (VOCs) in Air Collected in SUMMA canisters and Analyzed by Gas Chromatography/Mass Spectrometer (GC/MS)." During this study, 58 individual volatile organic compounds were quantified in the SUMMA canisters.

The carbonyl cartridges were analyzed by the Air Management Laboratory operated by the City of Philadelphia Department of Public Health using EPA Compendium Method TO-11A, "Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC).". During this study, ambient concentrations of 6 individual carbonyls (aldehydes and ketones) were quantified from the cartridge samples.

2.3 Intensive Measurements

Carnegie Mellon University conducted intensive sampling campaigns at three sites. The dates of these campaigns are listed in Table 2.1; separate intensives were conducted at each site. The intensive campaigns featured high time resolved measurements to characterize the temporal patterns of the air toxic exposure.

2.3.1 Automated Gas Phase Measurements

During each intensive campaign, an automated GC-MS/FID (gas chromatograph/ mass spectrometer/ flame ionization detector) based instrument was used to measure hourly concentrations of gas phase organic air toxics and other volatile organic compounds (VOCs). The instrument consisted of an automated inlet developed at CMU 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. (7) with different sorbent traps, GC columns, and analysis protocols.

A schematic of the automated instrument to measure gaseous organic air toxics is shown in Figure 2.2. The automated inlet system collects and pre-concentrates ambient air toxics for subsequent analysis by GC-MS. To provide information on as wide a range of compounds as possible, two separate measurement channels were be used, equipped with different preconditioning systems, preconcentration traps, chromatography columns, and detectors. Channel 1 was designed for preconcentration and separation of C3-C6 non-methane hydrocarbons, including alkanes, alkenes and alkynes, using an Rt-Alumina PLOT column (Restek) and subsequent detection by flame ionization detector (FID). Channel 2 was designed for preconcentration and separation of the volatile organic compounds (VOCs) targeted by EPA method 8260B, using a Rtx-200 column (Restek) with subsequent detection by quadropole mass selectivity detector.

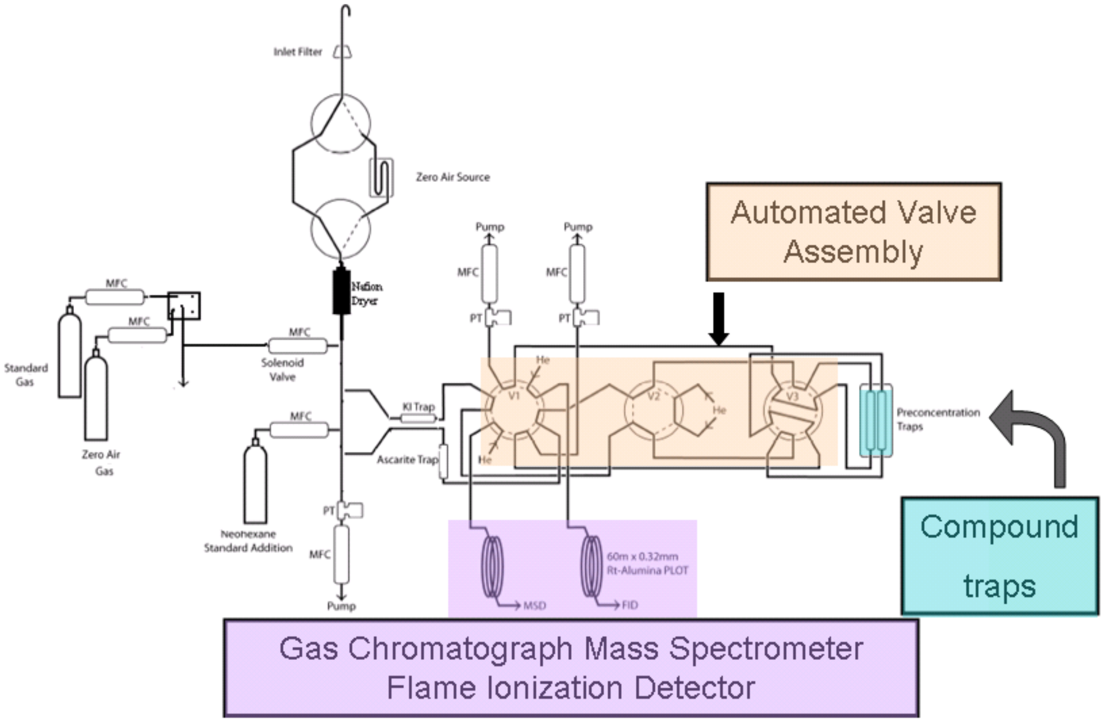


Figure 2.2 Schematic of automated gas-phase organic air toxic instrument developed and deployed by Carnegie Mellon University during intensive studies (Millet, 2005).

The instrument 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 columns. Samples were collected by drawing ambient air at 4 sl/min through a 2-µm Teflon particulate filter. Two 15 scc/min subsample flows are drawn from this main sample line, and through pretreatment traps for removal of O_3 and CO_2. For the Rt-Alumina/FID channel, a trap to remove CO_2 and O_3 (Ascarite II, Thomas Scientific) was located upstream of the valve box. For the Rtx-200 channel, an ozone trap (KI-impregnated glass wool) was located upstream of the valve box (Figure 2.2). For the Avalon and CMU campaigns a Nafion dryer was used to remove water; for the intensive campaign at the Diamond Building a new water removal system was deployed. This system drew the sample though an electrically cooled aluminum block that condensed the majority of the water out of the sample. All flows are controlled using Mass-Flow Controllers (MKS Instruments, Alicat Corp.).

During sampling, the valve array (V1, V2, and V3) is switched so that there is flow across the preconcentration traps where the VOCs are trapped prior to analysis. The preconcentration traps used are #10 traps containing 8 cm each of Tenax, Silica gel, and carbon molecular sieve (OI Anaytical). These traps absorb the full range of target compounds and do not require cooling below room temperature for trapping.

When sample collection is complete, the preconcentration traps and downstream tubing were purged with ultra-high purity (UHP) helium for 30 seconds to remove residual air. The valve array are then switched to inject mode, the preconcentration traps heated rapidly to 190ºC, and the trapped analytes thermally desorbed into the helium carrier gas and transported to the GC for separation and quantification. The traps are small enough to permit rapid thermal desorption (30ºC to 190ºC in 25 seconds), eliminating the need to cryofocus the samples before chromatographic analysis. After sample collection and the helium purge, the preconcentration traps are isolated via V3 (see Figure 2.2) until the start of the next chromatographic run.

To minimize artifacts and compound losses, all wetted surfaces contacted by the sampled airstream prior to the valve array are constructed of Teflon (PFA or FEP). All subsequent tubing and fittings, except the internal surfaces of the valves V1, V2, and V3, are Silcosteel (Valco Valves). The valve array, including all silcosteel tubing, was housed in a temperature controlled box held at 50ºC to minimize losses through condensation and adsorption.

Chromatographic separation and detection of the analytes is achieved using an Agilent 6890N GC/ 5975B MS/FID. The temperature program for the GC oven was: 40ºC for 10 minutes, 5ºC/minute to 100ºC, hold for 1 minute, 5ºC/minute to 120ºC, hold for 5 minutes, 30ºC/minute to 200ºC, hold for 11 minutes. The oven was then ramped down to 40ºC in preparation for the next analysis cycle. The carrier gas flow into the MSD is pressure controlled so that flow into the MSD is at approximately at 1 mL/min at 40ºC. The entire analysis cycle takes around 50 minutes. During analysis, the next sample is being collected, so the maximum data rate is determined by the analysis cycle (50 minutes). The analyte trapping time was 40 minutes.

The FID channel carrier gas flow was controlled mechanically by setting the pressure at the column head such that the flow is approximately 5 mL/min at an oven temperature of 40ºC. The carrier gas for both channels was UHP (99.999%) helium which was further purified using oxygen, moisture and hydrocarbons (traps from Supelco). Air and propane used for FID line were also further purified using moisture and hydrocarbons traps (Supelco). Zero air for blank runs and for calibration was generated by flowing ambient air over a bed of platinum heated to 370ºC.

The valve array (V1, V2 and V3) and the preconcentration trap heater were automatically controlled by GC using its auxiliary output circuitry. The computer controlling the GC was also interfaced with a CR10X datalogger (Campbell Scientific Inc). Relevant engineering data (time, temperatures, flow rates, pressures, etc.) for each sampling interval were recorded by the CR10X datalogger with an AM416 multiplexer (Campbell Scientific Inc.), then uploaded to the PC and stored with the associated chromatographic data.

The MSD was operated in single ion mode (SIM) for optimum sensitivity and selectivity of response. Ion-monitoring windows were timed to coincide with the elution of the compounds of interest. Details of the SIM method and compound quantification can be found in the appendix. Chemstation software was used to integrate the chromatograms. A series of MATLAB programs was written to quantify pollutant concentrations based on peak area, calibration curves, and mass spectrometer degradation.

2.3.1 Instrument Calibration

Before sampling, retention times for each target analyte were determined and a SIM (single ion mode) method was developed to maximize MS sensitivity. In order to quantify the response of the MS to different concentrations of VOCs in the air, a 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. These standards were dynamically diluted over concentrations ranging from 1 ppt to 146 ppb to span the expected range of ambient concentrations using an automated calibration system. 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.

During measurement intensives, single point calibration runs for both standards and zero air runs were performed on a regular basis. The single point calibrations were used to correct for degradation in the mass spectrometer. The zero runs were used to quantify and correct for any sample contamination. The system was automated to run on a 26 hr cycle, which involved 26 individual runs. The first run in this cycle sampled and analyzed zero air. The second run sampled and analyzed the TO-15 standard, dynamically diluted to atmospherically relevant concentration. The thirteenth run sampled and analyzed the dynamically diluted 1 ppmv mixture of light VOCs from Scott Specialty Gas. The ambient air was characterized by all of the other sample runs.

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 main line to achieve a wide range of concentration levels to test instrument performance.

2.3.1 Instrument Evaluation

During Oct. 2006 to Jan. 2007, baseline and intensive samples were taken simultaneously at the Avalon site. The intensive samples were taken with the automated GC-MS/FID system by Carnegie Mellon University and the baseline samplers were collected using SUMMA canisters for offline analysis using the EPA TO-15 protocol by the Allegheny County Health Department. There were six days (Oct. 2, Oct. 8, Oct. 20, Nov. 25, Dec. 1, and Dec. 7) when both canister and automated measurements where made. The two datasets were compared by averaging hourly concentrations measured made with the automated instrument into 24 hour blocks corresponding to the SUMMA canister collection times.

Good agreement was observed between the canister and automated measurements for 25 compounds. To illustrate this agreement, Figure 2.3 presents scatter plots for 12 of these compounds. Each plot lists the slope, intercept, and R^2 value for linear regressions. The R^2 values of these regressions were greater than 0.8, showing strong correlations between the two methods. The slopes and intercepts indicate that concentrations of these toxics agreement to within ±20%. Comparable agreement was also observed for fourteen other compounds: 1,1,1-trichloroethene, 1,1-dichloroethane, 1,2,4-trimethylbenzene, 1,2-dichloroethane, 1,3-dichlorobenzene, 4-ethyltoluene, bromomethane, carbon disulfide, carbon tetrachloride, Freon 114, heptane, trichloroethene, 1,3-butadiene, and vinyl chloride.

There was relatively poor agreement between the automated and canister measurements for 18 compounds. For eight of these compounds the canister concentrations were well below the national average data but the automated GC-MS/FID concentrations were comparable with national data. Therefore, we believe that concentrations of these eight compounds were accurately characterized by the automated GC-MS/FID system but not the canister samples. These eight compounds are 1,2-dichloropropane, 1,2-dichlorobenzene, 1,1,2-trichlroethane, bromoform, chlorobenzene, 1,1,2,2,-tetrachloroehtane, benzyl chloride, and MTBE.

Ten compounds were shown to have poor agreement between the canister measurements and the automated GC-MS/FID, including six air toxics and four volatile organic compounds. The six air toxics were 1,1-dichloroethene, 1,2,4-trichlorobenzene, 1,4 dichlorobenzene, hexachlorobutadiene, MIBK and vinyl acetate. The automated measurements of these air toxics were not consistent with national air toxic data; therefore these compounds were either poorly characterized or below the automated instrument's detection limit. The four VOCs were: acetone, MBK, MEK and trans-1,2-dichlroethane. It is not clear if the problem for these compounds was with the canister or automated instrument or both techniques.

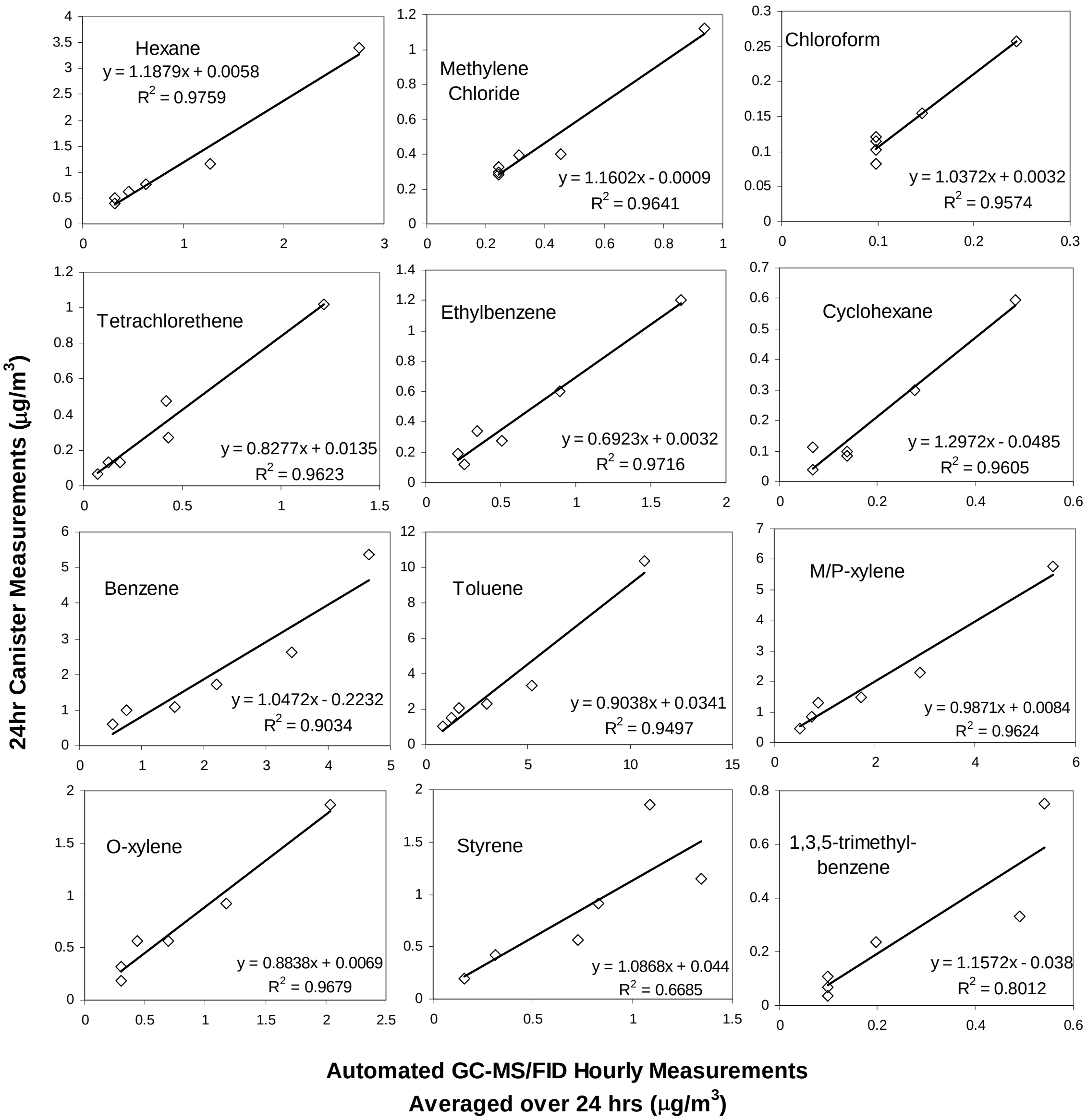


Figure 2.3. Comparison of air toxic concentrations measured with automated GC-MS/FID system and the SUMMA canisters at the Avalon Site.

2.4 Measurement of semivolatile and condensed phase air toxics

During the intensive campaign at the Diamond Building, additional instrumentation was deployed to better characterize motor vehicle emissions and measure diesel particulate matter. Sub-daily (two to ten hour) concentrations of semivolatile polycyclic aromatic hydrocarbons (PAHs) and other motor vehicle molecular markers were measured using a Thermal Desorption Aerosol GC-MS based system (TAG) (8). A seven wavelength aethalometer (Magee Scientific AE31) was used to measure five minute average concentrations of black carbon (BC) (9).

A schematic of the TAG inlet is shown in Figure 2.4; the instrument is described in detail by Williams et al. (10). 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 12 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. 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), 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.

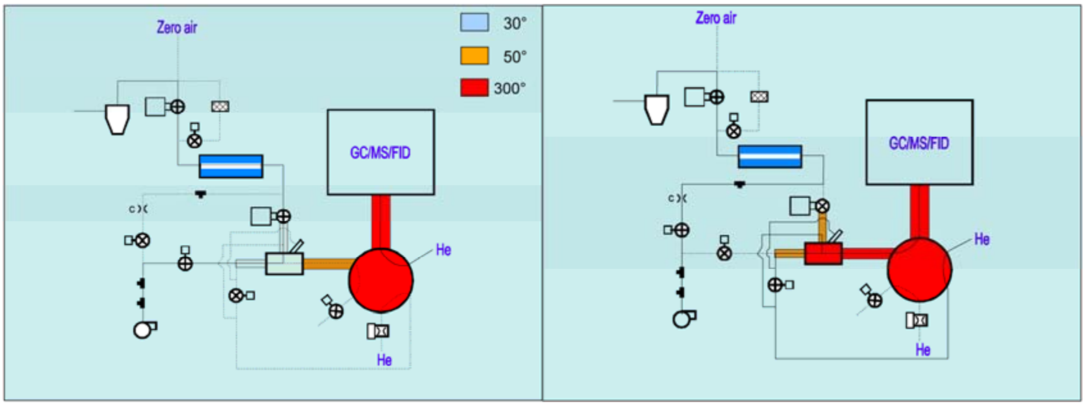


Figure 2.4 Schematic diagrams showing heated zones and flow paths during sampling/analysis mode (left) and thermal desorption mode (right). (From Dr. Nathan Kreisberg, Aerosol Dynamics Inc.)

2.5 Meteorology Measurements

Wind speed and direction data were collected during each intensive study. The county health department operates a MET station at the Avalon site. There was no MET station at the downtown and urban background (CMU) sites. At these sites measurements from the Hammerfield site located on Tasso Street in Hazelwood were used to provide regional wind direction as a function of time. Figure 2.5 shows the location of the Hammerfield site relative to Diamond Building and Carnegie Mellon University intensive sites.

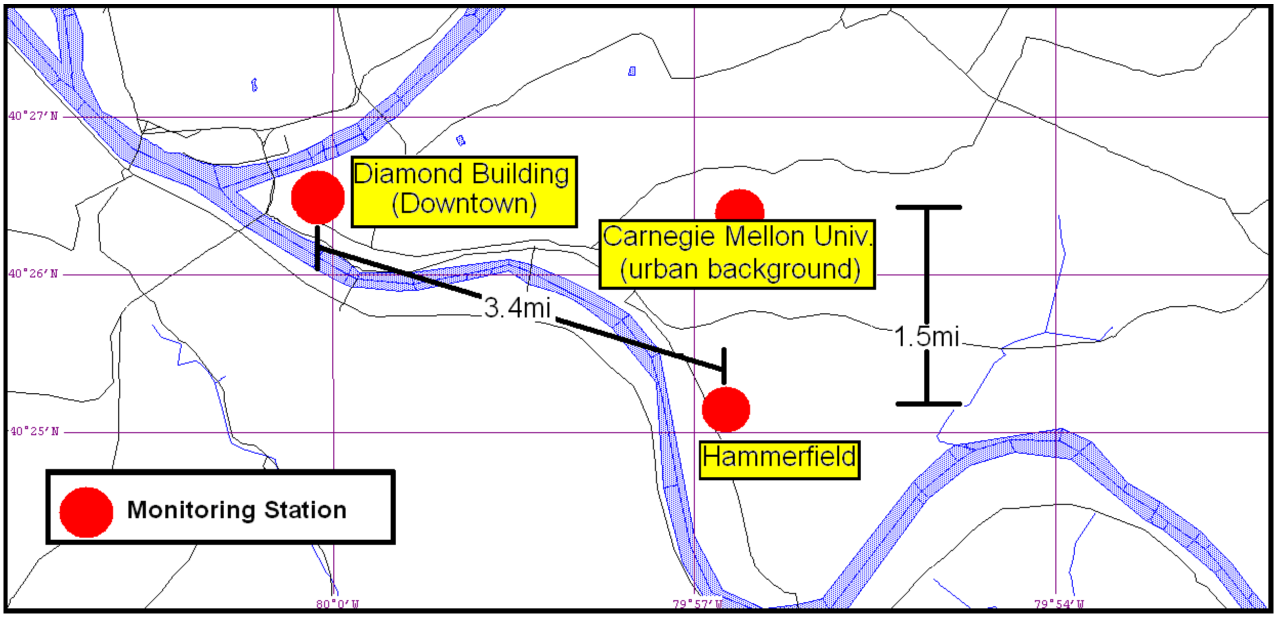


Figure 2.5 Location of Hammerfield site relative to Diamond Building and Carnegie Mellon University intensive sites.

Chapter 3. Spatial Variation in Air Toxic Concentrations and Health Risks

The goal of this chapter is to compare air toxic concentrations and health risks at the four baseline sites. The spatial variation in air toxic concentrations with the County is assessed and air toxic concentrations in Allegheny County are compared to national data. Both traditional and advanced risk models are used to estimate cancer and non-cancer health risks. Risk estimates for the different sites and for different classes of air toxics are compared. The risk estimates for Allegheny County are also compared to estimates derived from data collected in other US cities. Finally, the results of this chapter are used to identify priority air toxics for Allegheny County.

3.2 Methods

3.2.1 Statistical Analysis of Baseline Data

Hypothesis testing, correlation analysis and other statistical techniques were used to compare air toxics concentrations between sites and to calculate average concentrations for the health risk assessment. These techniques require knowing the underlying probability distribution of the concentration data. This distribution is not known, but the Kolmogorov-Smirnov test indicates that the data varied significantly from the normal distribution. A log normal distribution is often assumed to calculate upper confidence levels and means of environmental data. However if the data are skewed compared to traditional log normal models, this approach can significantly overestimate the upper confidence limit (11).

A bootstrap or re-sampling method provides an alternative approach to estimate confidence intervals for the means and for hypothesis testing of environmental data (11). The bootstrap method is a re-sampling technique with replacement. Data is sampled from the original measurements with replacement and averaged multiple times. The method creates a distribution of mean values. The confidence interval is determined by finding the 95% of the distribution of the means. It has been shown that environmental data can be significantly over dispersed relative to a log-normal distribution (12) and that methods of measuring the upper confidence limit of the mean based on the log-normal distribution, such as the Land procedure and Chebyshev’s inequality, can lead to large over estimates of the upper confidence limit of the mean (11, 12). For the rest of this chapter the terms mean or average concentration refers to the 95th percentile upper confidence level of the mean determined using the bootstrap method.

The spatial variability of air toxic concentrations was assessed by comparing study average concentrations measured at each site. Hypothesis testing was used to determine whether any differences in study average concentrations were statistically significant. This hypothesis testing was done using the bootstrap method (11). For hypothesis testing the bootstrap method is used to determine the means of two data sets and the difference is calculated. This is repeated multiple times, at least 10,000, to product a distribution of differences in the mean. If 0 was below the 5th percentile or above the 95th percentile it was assumed that the means of the two data sets were different.

The spatial variability of air toxics was also assessed using a correlation analysis. For this analysis, the 24-hour average air toxic concentrations were transformed into log space and the MATLAB “corr” function was used to determine the correlations between pairs of different toxics. The p-values for each pair of toxics were then used to test the null hypothesis of no correlation. If the p-value was greater than 0.05 the null hypothesis could be rejected and the data were assumed to not be correlated.

3.2.2 Risk Assessment Models

Health risk analyses were performed to estimate lifetime cancer risks, and acute and chronic non-cancer risks. These estimates were made with both traditional and advance risk models. The estimates were based on the measured outdoor concentration data from 2006. Outdoor concentrations provide an estimate of the maximum risks associated with emissions from outdoor sources.

Since measurements were taken on a one-in-six-day schedule, the sample mean is not necessarily the same as the long-term average concentration. Therefore, we used the bootstrap method to determine the mean and the 95th percentile confidence interval of the mean. To provide a conservative estimate, we use the upper confidence limit on the 95th percentile interval of the mean to estimate chronic risks.

The toxicity data used for the risk assessment were taken from the EPA, CAL EPA, the Agency for Toxic Substances and Disease Registry, and the DOE Risk Assessment Information System. These data are summarized in Table 3.1.

3.2.2.1 Traditional Health Risk Models

A linear no-threshold model was used to asses the lifetime cancer risk for 65 air toxics. This is the standard first-order method of assessing cancer risk (14). The lifetime cancer risk, LIR, for individual air toxics was determined by

$$LIR = URE * C \tag{3.1}$$

where C is the 95th upper confidence level of the study-average concentration and URE is the unit risk estimate for the target species. The URE values used for this study are listed in Table 3.1.

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 (15):

$$URE = \frac{OSF * IR}{BW} \tag{3.2}$$

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).

To quantify non-cancer health risks, the hazard quotient, HQ, was calculated for each of the measured compounds (14):

$$HQ = \frac{C}{RFC} \tag{3.3}$$

where C is the 95th percentile upper confidence limit of the study average concentration and *RFC* is reference concentration. The hazard index was also determined for each site by adding all of the *HQ* values across the set of species at the same location.

Table 3.1 Toxicity data for 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	

<u>Organ Systems</u>	
Hem:	Hematological
Hep:	Hepatic
Ren:	Renal
Rep:	Reproductive
Res:	Respiratory
N:	Neurological
L:	Lymphatic
D:	Digestive

<u>Toxicity Data</u>	
IRIS:	http://www.epa.gov/iris/
Cal EPA:	http://www.oehha.org/air/hot_spots/index.html
Calc:	Calculated from Equation 3.2
ATSDR:	URL: http://www.atsdr.cdc.gov/mrls.html
HEAST:	EPA Health Effect Assessment Summary Tables (13)

3.2.2.2 Advanced Risk Models

Traditional risk analysis does not account for interaction of pollutants. The EPA (16) has proposed a model for determining interactive risks based on the work of Mumtaz and Durkin (17). 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 (16):

$$\begin{aligned}
HI_{\text{int},p} &= \sum_{j=1}^{n} HQ_{pj} \left(\sum_{k \neq j}^{n} f_{pjk} (M_{jk})^{Bjk*gpjk} \right) \\
f_{pjk} &= \frac{HQ_{pk}}{HI_{add,p} - HQ_{pj}} \\
HI_{add,p} &= \sum_{j=1}^{n} HQ_{pj} \\
g_{pjk} &= \frac{\sqrt{HQ_{pj} * HQ_{pk}}}{(HQ_{pj} + HQ_{pk})/2}
\end{aligned} \tag{3.4}$$

Where:

HQ_{pj} = hazard quotient for pollutant *j* for system *p* (equation 3.3)

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 (18)

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, that the equation reduces to the additive model when interactions are minimized, and that 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 (18) to evaluate the potential for interaction among inorganic contaminates in US drinking water. In this project, the model is used to investigate the potential magnitude of interaction of air toxics. Since there are essentially no interactions data, this analysis provides only an estimate of the potential interactive health risks. The results also can be used as a screening tool 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 of this interactions model, 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 (16):

$$HQ_n = \sum E_n / DR_n = \sum LIR_n / RT \qquad (3.5)$$

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.

3.3 Air Toxic Concentrations in Allegheny County

Table 3.2 summarizes the air toxic concentrations measured during the baseline sampling. To illustrate the temporal variability of the data, the table lists the geometric mean, median, standard deviation, 95th, 75th, median, 25th, and 5th percentile of the 24-hr concentrations measured at each baseline site. Average concentrations at each baseline site are plotted in Figures 3.1a and 3.2a.

Daily air toxics concentrations at the four baseline sites ranged from below detection limit to 24.4 ppbv. Concentrations of some toxics such as carbon tetrachloride exhibited little temporal or spatial variability. Others exhibited significant temporal and/or spatial variability. Toluene, acetone, formaldehyde and benzene had the highest one-day concentration spikes at all sites except downtown where there were large spikes in methylene chloride. As discussed below, these temporal and spatial patterns provide insight into pollutant sources.

Table 3.2 Summary of baseline air toxic concentrations in pptv

	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.**
Acetaldehyde	1000	950	380	630	1260	2000	470	800	790	440	630	950	1270	270
Acrolein	55	40	3	25	64	170	58	35	31	7	20	46	72	20
Benzene	420	340	160	220	550	850	270	330	210	80	150	340	600	470
Benzyl Chloride	5	0	0	0	10	20	7	3	0	0	0	0	11	6
Bromoform	1	0	0	0	0	10	2	1	0	0	0	0	0	2
Bromomethane	10	10	0	10	10	20	6	8	10	0	8	10	11	5
Butadiene,1,3-	65	50	10	30	90	160	55	22	10	0	0	30	72	32
Carbon disulfide	69	20	10	20	40	260	180	35	20	10	20	60	71	27
Carbon tetrachloride	84	80	70	80	90	110	11	85	80	70	80	90	100	12
Chlorobenzene	1	0	0	0	0	10	4	3	0	0	0	10	10	5
Chloroethane	7	0	0	0	10	20	17	4	0	0	0	10	10	5
Chloroform	27	20	10	20	30	40	12	18	20	10	10	20	21	6
Chloromethane	640	630	540	580	690	760	72	570	560	490	530	610	690	66
Dibromoethane,1,2-	0	0	0	0	0	0	2	0	0	0	0	0	0	2
Dichlorobenzene,1,4-	130	110	60	80	150	240	60	11	10	0	10	10	20	6
Dichloroethane,1,1-	1	0	0	0	0	10	3	1	0	0	0	0	0	2
Dichloroethane,1,2-	9	10	0	10	10	20	6	8	10	0	10	10	10	4
Dichloroethene,1,1-	1	0	0	0	0	10	4	1	0	0	0	0	10	3
Dichloropropane,1,2-	1	0	0	0	0	10	2	2	0	0	0	0	10	4
Ethylbenzene	100	70	40	50	130	260	71	39	30	10	20	43	81	27
Formaldehyde	1700	1270	490	840	2470	3590	1130	1690	1310	580	990	2220	3500	1170
Hexachloro-1,3-Butadiene	4	0	0	0	10	10	5	5	0	0	0	10	10	6
Hexane	200	140	60	100	250	500	170	99	90	40	60	120	180	48
Methyl Isobutyl Ketone	32	20	0	0	40	80	45	26	20	0	0	43	61	27
Methylene Chloride	220	110	70	80	140	500	430	69	60	50	60	80	110	25
MTBE	11	10	0	0	20	30	20	6	0	0	0	10	11	8
Propionaldehyde	320	250	80	170	380	790	220	270	220	130	170	350	570	160
Styrene	34	20	10	10	40	100	36	19	15	0	10	20	41	21
Tetrachloroethane,1,1,2,2-	1	0	0	0	0	10	3	1	0	0	0	0	0	2
Tetrachloroethylene	38	30	10	20	50	100	27	14	10	0	10	20	31	10
Toluene	850	520	230	380	970	1920	1080	510	400	90	240	590	990	620
Trichlorobenzene,1,2,4-	3	0	0	0	10	10	6	4	0	0	0	10	11	6
Trichloroethane,1,1,1-	25	20	20	20	30	40	12	16	15	10	10	20	21	6
Trichloroethane,1,1,2-	1	0	0	0	0	10	2	0	0	0	0	0	0	0
Trichloroethene	110	20	0	10	85	620	190	5	0	0	0	10	10	6
Vinyl Chloride	1	0	0	0	0	10	3	0	0	0	0	0	0	2
Xylene, m/p-	300	230	100	140	430	710	220	100	75	30	58	110	250	95
Xylene, o-	110	80	40	50	150	270	80	40	30	10	20	50	100	33

Table 3.2 (continued) Summary of baseline air toxic concentrations in pptv

	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.**
Acetaldehyde	1030	850	410	670	1280	1960	550	1120	970	600	730	1300	2180	500
Acrolein	65	60	10	28	84	140	56	72	62	17	49	100	160	50
Benzene	520	360	130	230	530	1330	470	730	610	180	320	1010	1460	580
Benzyl Chloride	2	0	0	0	0	10	4	3	0	0	0	10	10	6
Bromoform	0	0	0	0	0	0	0	0	0	0	0	0	0	2
Bromomethane	9	10	0	5	10	20	6	9	10	0	10	10	20	6
Butadiene,1,3-	42	30	10	20	50	110	41	70	50	10	30	80	150	69
Carbon disulfide	29	20	10	15	30	69	21	33	20	10	20	40	88	26
Carbon tetrachloride	82	80	70	80	90	100	13	83	80	70	80	90	98	9
Chlorobenzene	2	0	0	0	0	10	4	2	0	0	0	0	10	5
Chloroethane	11	10	0	0	10	29	13	3	0	0	0	10	10	5
Chloroform	19	20	10	10	20	30	8	25	20	10	20	30	48	10
Chloromethane	590	560	500	530	650	700	79	580	570	480	540	620	680	64
Dibromoethane,1,2-	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Dichlorobenzene,1,4-	20	20	1	10	30	40	12	23	20	10	10	30	50	16
Dichloroethane,1,1-	0	0	0	0	0	0	0	0	0	0	0	0	0	1
Dichloroethane,1,2-	8	10	0	10	10	10	5	8	10	0	10	10	10	5
Dichloroethene,1,1-	0	0	0	0	0	0	2	0	0	0	0	0	0	2
Dichloropropane,1,2-	0	0	0	0	0	0	2	1	0	0	0	0	8	2
Ethylbenzene	130	60	30	40	110	440	210	120	95	43	80	130	250	72
Formaldehyde	1670	1250	430	930	2470	3300	1080	2110	1720	960	1200	2780	4140	1190
Hexachloro-1,3-Butadiene	3	0	0	0	10	10	5	3	0	0	0	10	10	5
Hexane	150	110	51	70	170	370	120	200	170	73	110	220	390	130
Methyl Isobutyl Ketone	34	30	0	10	50	79	29	53	40	0	0	78	180	61
Methylene Chloride	95	80	60	70	100	170	42	100	90	60	70	120	200	45
MTBE	8	0	0	0	10	30	10	11	10	0	0	20	28	11
Propionaldehyde	320	240	130	170	420	710	210	340	270	150	210	440	690	180
Styrene	78	50	20	30	80	220	100	110	100	20	60	160	240	69
Tetrachloroethane,1,1,2,2-	0	0	0	0	0	0	0	0	0	0	0	0	0	1
Tetrachloroethylene	30	20	10	10	35	89	28	55	30	10	20	40	120	110
Toluene	680	540	210	390	880	1700	450	980	770	390	560	1290	2120	580
Trichlorobenzene,1,2,4-	3	0	0	0	5	10	5	5	0	0	0	10	10	6
Trichloroethane,1,1,1-	15	20	10	10	20	20	5	17	20	10	10	20	20	5
Trichloroethane,1,1,2-	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Trichloroethene	6	0	0	0	10	20	9	7	10	0	0	10	18	7
Vinyl Chloride	0	0	0	0	0	0	0	0	0	0	0	0	0	1
Xylene, m/p-	270	170	61	100	330	780	260	360	290	120	200	400	870	250
Xylene, o-	120	80	21	45	130	310	110	150	120	53	90	180	340	90

3.3.1 Spatial Variation in Gas Phase Air Toxic Concentrations

One of the main goals of this project was to quantify the spatial variability of air toxic concentrations throughout Allegheny County. Of particular interest was to compare concentrations at the heavily urbanized sites (Avalon, Stowe, and Flag Plaza) to those in the regional background (South Fayette). Such a comparison provides insight into the influence of local sources on human exposure.

We quantified the spatial variability by calculating ratios of the study average concentrations at each urban site to those in South Fayette. These concentration ratios are plotted in Figures 3.1b and 3.2b. Air toxics with concentration ratios greater than one indicate significant influence of local emissions.

Figures 3.1b and 3.2b indicate that average concentrations of 12 of the air toxics varied by less than 25% across the four baseline sites (concentration ratios less than 1.25), indicating little spatial variation in average concentrations. These 12 are 1,2-dichloropropane, 1,2-dibromomethane, bromoform, hexachlorobutadiene, chlorobenzene, bromomethane, 1,2-dichloroethane, 1,2,4-trichlorobenzene, chloromethane, carbon tetrachloride, formaldehyde and propionaldehyde. Of these 12, hypothesis testing indicates that the differences in average concentrations between sites of only one toxic, formaldehyde, were statistically significant. The average formaldehyde concentrations in Avalon appear to be 20% higher than those at the other sites. Correlation analysis was also performed to assess the regionality of these air toxics. A regional toxic is one in whose concentration at one site is more strongly correlated with the same toxic at other sites than with other pollutants at the same site. This correlation analysis showed that there may be modest local emissions of some these 12 toxics at Stowe and Avalon, but that these local emissions do not have a large effect on concentrations.

Concentrations of 27 air toxics were more than 25% higher at one or more of the urban sites compared to South Fayette, indicating some influence of local sources. Twelve of these toxics had moderate concentrations ratios between 1.25 and 2. This included 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. Average concentrations of 15 of the 39 air toxics measured during the baseline study were a factor of two higher or more higher at one of the urban sites compared to South Fayette, indicating strong effects of local sources. These 15 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.

Chlorinated compounds at the Flag Plaza site had the largest concentration ratios; for example, study average trichloroethylene and 1,4-dichlorobenzene concentrations were 26 and 12 times higher downtown compared to South Fayette, respectively. Concentrations of many air toxics were enhanced at the Avalon and Stowe sites compared to South Fayette. For example, concentration ratios of toxics such as styrene, tetrachloroethylene, methyl isobutyl ketone, benzene and ethylbenzene ranged from 4.8 to 1.6 times higher in Avalon than in South Fayette. The Allegheny County Point Source Emissions Inventory (1) indicates that the industrial facilities located on Neville Island are major sources of many of these toxics.

National data provide one benchmark for identifying potentially problematic air toxics in Allegheny County. Figure 3.3 plots study average air toxic concentrations measured at each baseline site to multi-year average concentrations measured in about 150 urban and suburban sites throughout the United States. The national data are presented using a box and whisker plot; the boxes extend from the 25th percentile to the 75th percentile of the national data with the center line representing the median concentration. The whiskers extend to the 5th and 95th percentiles of the national data. These distributions were derived by Sonoma Technology, Inc. using data 2003 through 2005 downloaded from the EPA Air Quality System, AQS.

In South Fayette, concentrations of most air toxics were less than the 25th percentile of the national data and only four of the 38 measured air toxics were greater than the median of the national value at all sites: toluene, chloromethane, benzene and propionaldehyde. However, concentrations of 20 air toxics are above 50th percentile at one or more of the urban sites. Therefore, emissions from local, urban sources shift exposures from below to above the national median value. The extreme example is trichloroethylene with study average concentrations comparable to the national 95th percentile at the Flag Plaza site versus the 5th percentile at other sites.

Figure 3.3 indicates that study-average concentrations of 13 air toxics were greater than the national 75th percentile at one or more of the baseline sites: benzene, toluene, propionaldehyde, tetrachloroethene, ethyl benzene, methylene chloride, styrene, 1,4-dichlorobenzene, trichloroethene, m/p- and o-xylenes, methyl isobutyl ketone, and chloromethane. Concentrations of only two air toxics were greater than the national 75th percentile in South Fayette: benzene and propionaldehyde. Therefore, these two toxics present a countywide problem.

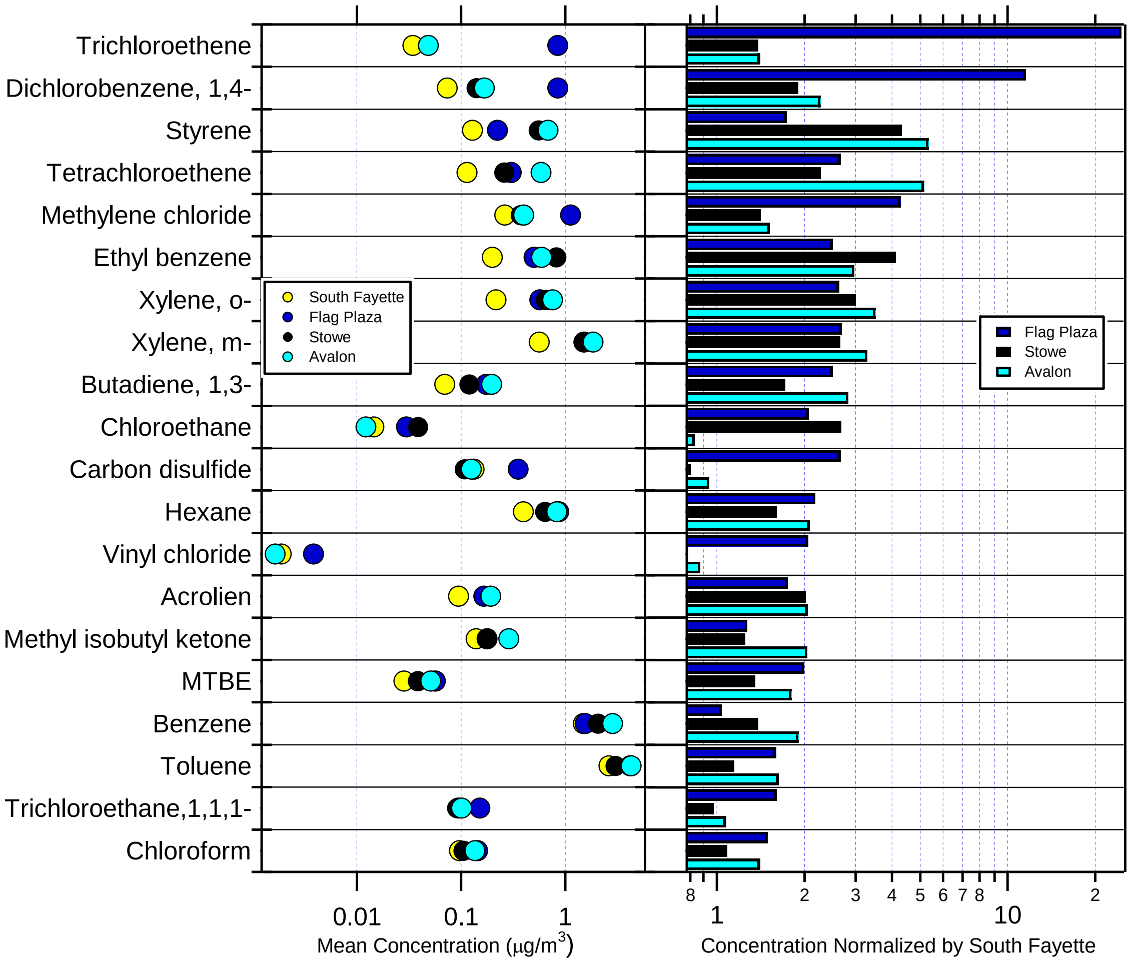


Figure 3.1. (a) Study-average air toxic concentrations measured at the four baseline sites. (b) Ratio of study average concentrations measured at the three urban baseline sites to those measured in South Fayette. Ratios greater than one indicate that concentrations at the urban site are greater than those in South Fayette.

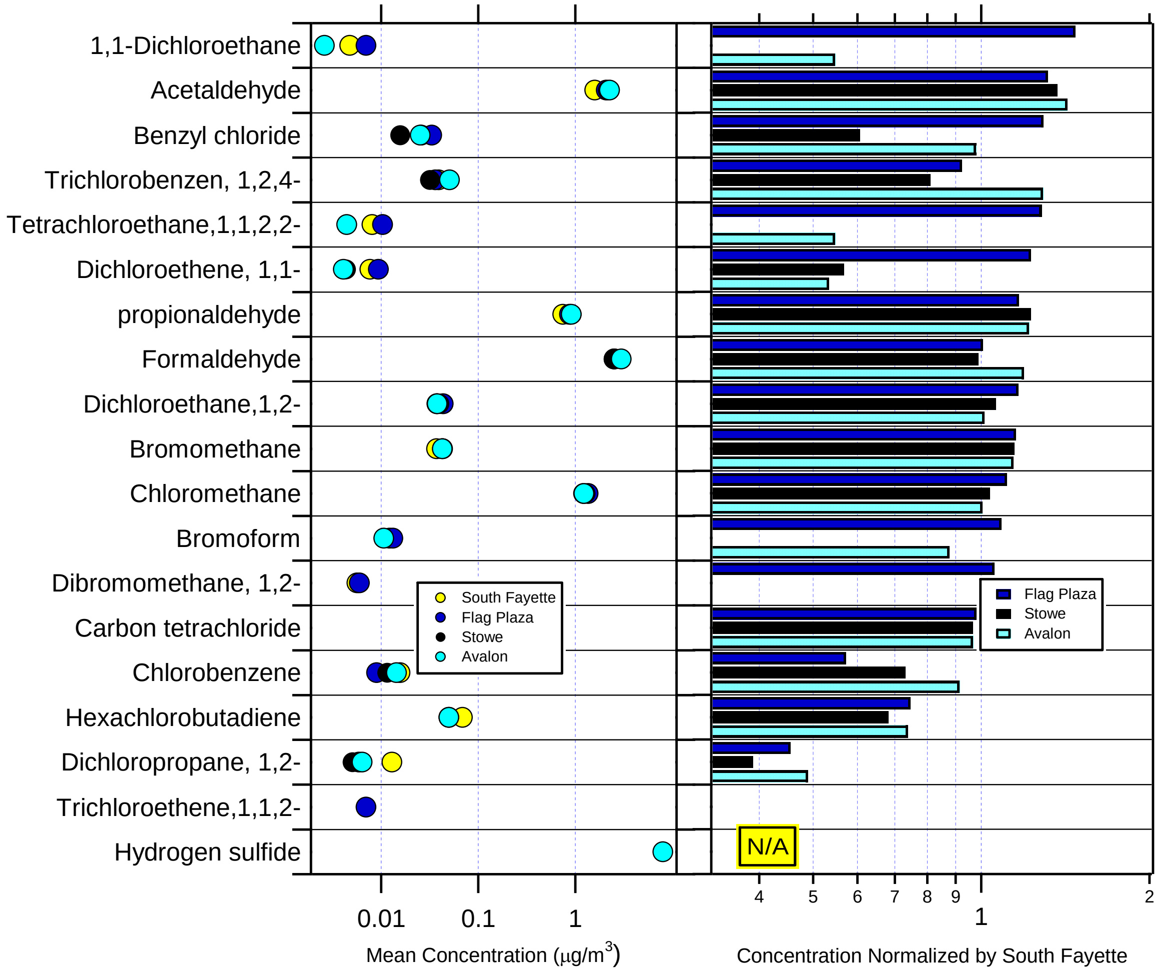


Figure 3.2. Same as in Figure 3.1but for more regional air toxics. (a) Study-average air toxic concentrations measured at the four baseline sites. (b) Ratio of study average concentrations measured at the three urban baseline sites to those measured in South Fayette. Ratios greater than one indicate that concentrations at the urban site are greater than those in South Fayette.

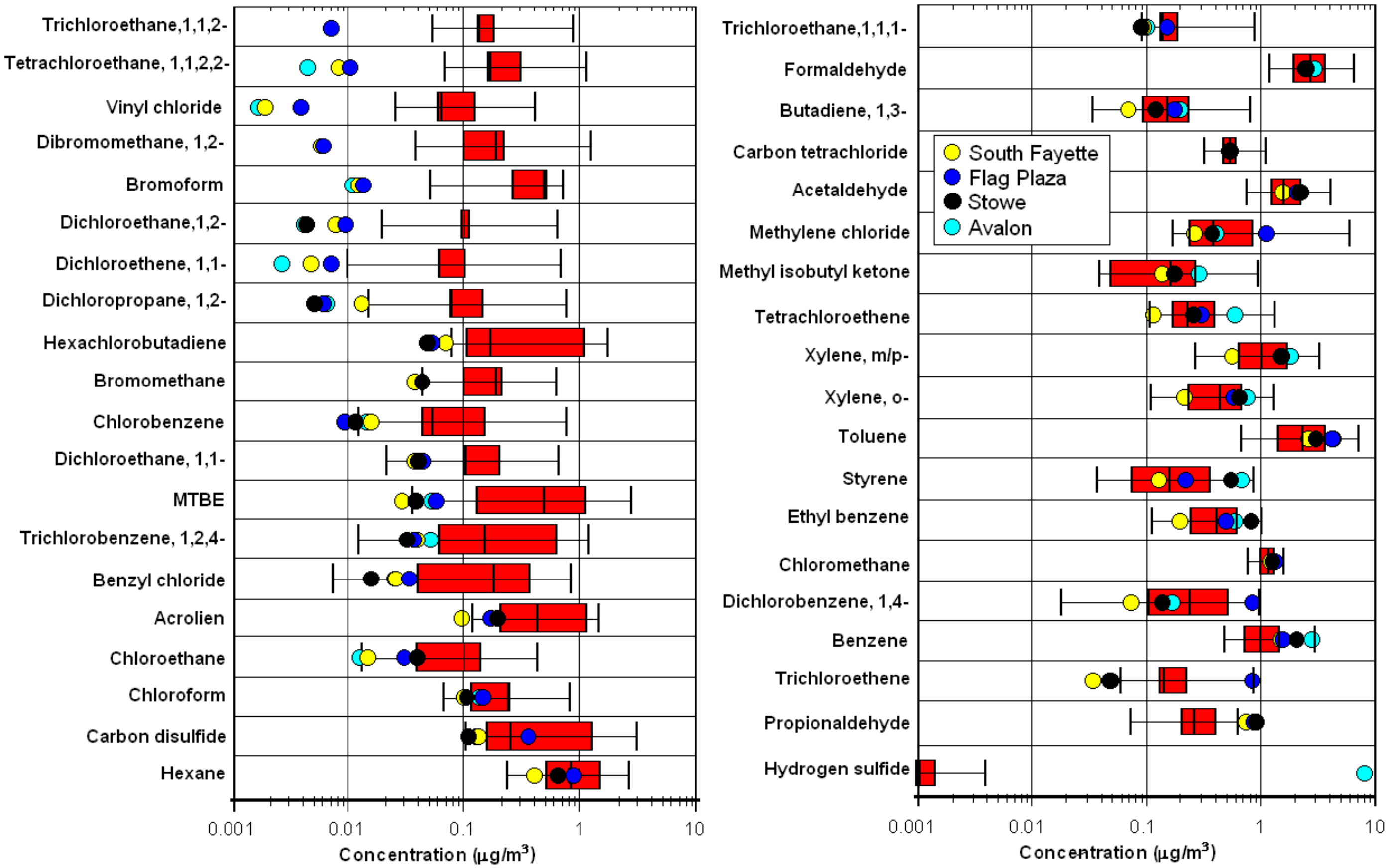


Figure 3.3. Comparison of study-average concentrations measured at the four baseline sites to national air toxic data. The national data are multi-year average concentrations measured at about 150 urban and suburban sites throughout the United States; these data are presented using a box and whisker plot. The boxes extend from the 25th percentile to the 75th percentile of the national data with the center line representing the median concentration. The whiskers extend to the 5th and 95th percentiles of the national data.

3.3.2 Diesel Particulate Matter (DPM)

Diesel particulate matter (DPM) is a complex mixture of elemental carbon (EC), organic carbon (OC), sulfate, nitrate, and trace metals and ions. EC and OC comprise most of the emissions on a mass basis. Because of the inherent complexity of DPM, as well as potential contributions of these PM species by other sources, it is impossible to directly measure DPM concentrations. Instead DPM concentrations must be inferred using a source apportionment model. The measurements of BC and condensed phase molecular markers at the Diamond Building were used to estimate DPM concentrations in downtown area. Similar analysis was performed using archived data to estimate DPM concentrations in Schenley Park. These analyses are described in detail in Chapter 6; here we summarize the results which are used in the risk assessment. Average DPM concentrations at the Diamond Building were estimated to be 3.6 $\mu g/m^3$ versus 0.6 $\mu g/m^3$ in Schenley Park. Therefore, there are significant spatial variations in DPM concentrations in Allegheny County.

To further assess the spatial variation of DPM in the Pittsburgh Area, Figure 3.4 compares average BC concentrations measured at six sites in and around the Allegheny County. BC contributes roughly half of the DPM and, therefore, provides a reasonable proxy for DPM exposures. Archived BC data were available for Schenley Park, Hazelwood, Lawrenceville, Florence and Greensburg. At the Diamond Building, BC levels were about four times higher than at any of the other Pittsburgh area sites. Therefore, the downtown area is a DPM hotspot, which is not surprising given the high density of diesel vehicles in the area (buses, trucks, and construction equipment). BC levels at the other four urban sites are very similar, about 0.6 $\mu g\ m^{-3}$. The relative contribution of local sources can be estimated by comparing BC concentrations in Pittsburgh to data from Florence, a rural site in Washington County that is generally upwind of the city. Except at the Diamond Building, BC concentrations at the other Pittsburgh sites were only about 50% higher than in Florence. Therefore, about two-thirds of the BC outside of the downtown area comes from regional transport, which implies that a substantial fraction of the DPM outside of the downtown area comes from regional transport. However, local emissions dominate DPM exposures at the Diamond Building.

Figure 3.4 also presents BC data from fifteen other urban and rural locations in the United States. These data were collected during the summertime in 2001 through 2004 by the EPA

Speciation Trends Network. Data from multiple sites in Chicago and New York City are shown to illustrate the spatial variation of BC in urban areas. Except for the Diamond Building, BC concentrations at the three other city of Pittsburgh sites (Hazelwood, Lawrenceville, and Schenley Park) are at or below concentrations in other US cities. The BC concentrations at the Diamond Building are the highest of any of the sites, comparable to measurements made in Elizabeth NJ near exit 13 of the New Jersey Turnpike. However, it is not known how representative the BC measurements made at the Diamond Building are of the larger downtown area. The Diamond Building is located at the intersection of Fifth and Liberty Avenues; both of these streets are major bus thoroughfares.

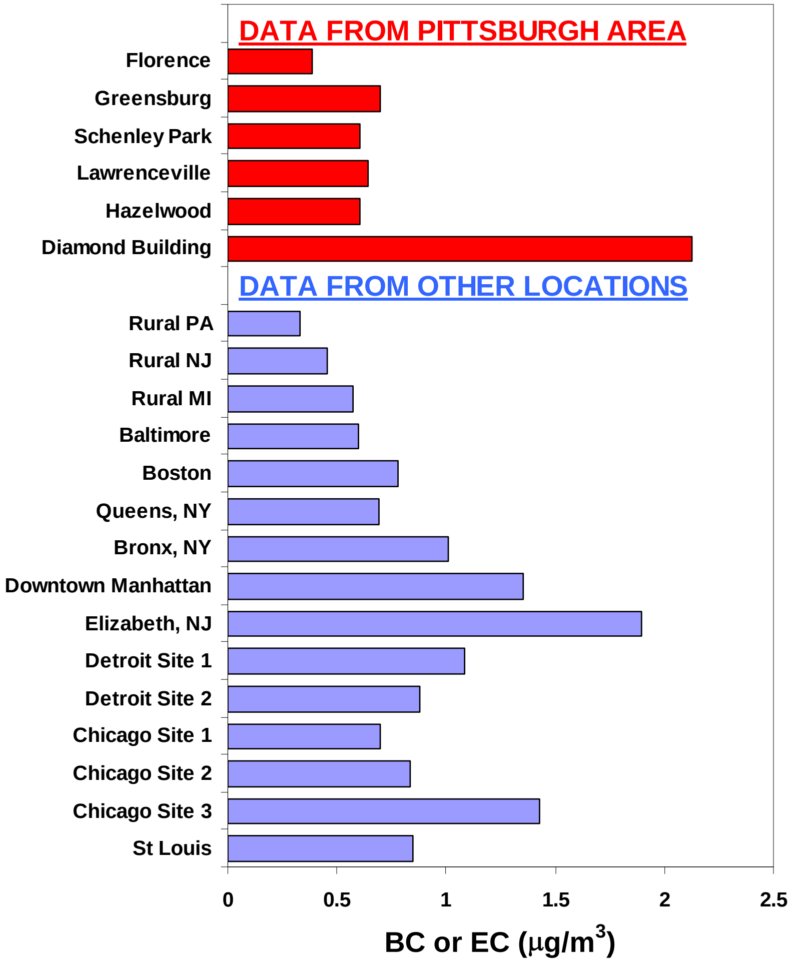


Figure 3.4. Average BC or EC concentrations at monitoring sites in and around Allegheny County and in other locations in the United States. Downtown measurements were made during the 2008 intensive at the Diamond Building; the data from the other Pittsburgh area sites were measured in 2001 and 2002 during the Pittsburgh Air Quality Study; the data from the other locations are averages of measurements collected as part of the EPA Speciation Trends Network (STN) during June, July and August of 2001 through 2004.

3.4 Risk Analysis

Although air toxic concentrations provide a measure of exposure, health risks depend on both the concentration and the toxicity of a pollutant. Since the toxicity of air pollutants can vary 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.

3.4.1 Cancer Risks of Gas Phase Organic Air Toxics

The LIR calculated for the organic air toxics measured during the baseline study are shown in Figure 3.5. At present there are no risk levels that represent acceptable or unacceptable regulatory thresholds for air toxics. However, EPA has made case-specific determinations such as the 1989 Benzene National Emission Standard for Hazardous Air Pollutants (NESHAP) that set up a two-part risk-based decision framework (http://www.epa.gov/ttn/atw/nata/natsafaq.html). First, it set an upper limit of acceptability of 1 in 10,000 lifetime cancer risk for highly exposed individuals. Second, it set a target of protecting the greatest number of persons possible to an individual lifetime risk level no higher than approximately 1 in 1,000,000.

Of the organic air toxics considered in this study, 11 present cancer risks above the 10^{-6} threshold with three above 10^{-5} at one or more of the sites. The three toxics above the 10^{-5} threshold are (in order of decreasing risk) formaldehyde, benzene, and trichloroethylene. The remaining eight that are above the 10^{-6} threshold are 1,4-dichlorobenzene, carbon tetrachloride, 1,3-butadiene, acetaldehyde, tetrachloroethene, chloroform, hexachlorobutadiene, benzyl chloride, and 1,2-dichloroethane. None of the organic air toxics are estimated to pose a risk greater than 10^{-4}.

Figure 3.5 indicates that the variation in LIR is much more pollutant dependent than site dependent. In other words, the cancer risks were largely driven by the same set of compounds at all of the sites because the pollutant-to-pollutant differences in toxicity are much greater than the site-to-site differences in concentrations. The exceptions to this trend are trichloroethylene and 1,4-dichlorobenzene, which pose substantially greater risk at the Flag Plaza site than at the other sites.

To compare the overall cancer risk posed by organic air toxics at the four baseline sites, Figure 3.6 plots the additive LIR. Although concentrations of six air toxics were at least a factor of two higher at the Stowe and Avalon sites, Figure 3.6 indicates that the additive cancer risks at these sites were only 25% greater than the estimated risk in South Fayette, mostly due to higher benzene concentrations. Organic air toxics pose the greatest cancer risk at the Flag Plaza site where concentrations of eight toxics were greater than a factor of two higher and concentrations of two toxics were more than a factor of ten higher than conditions in South Fayette. However, the additive cancer risk at Flag Plaza was only 50% higher than in the South Fayette. 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 at the other sites.

Why is the spatial variation in the additive cancer risk so small? Figure 3.6 indicates that two regionally distributed air toxics (formaldehyde and carbon tetrachloride) contribute about half of the total risk. Therefore, incremental additional risk caused by air toxics with elevated concentrations at one or more of the urban sites was relatively small.

Figure 3.7 shows the additive *LIR* for different organ 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.

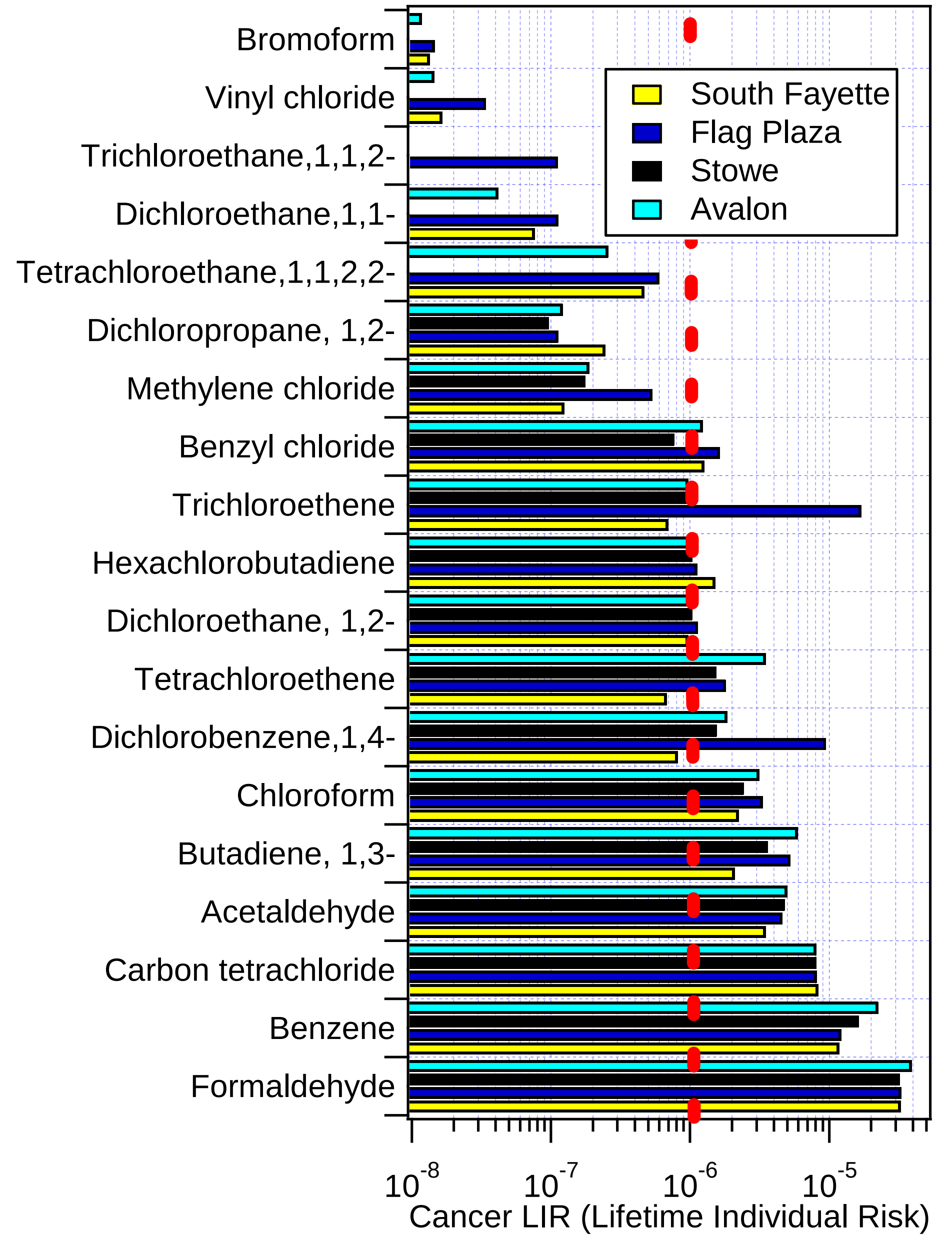


Figure 3.5. Cancer lifetime incidence rate, LIR, calculated using the study upper limit of the 95% confidence interval of the study-average concentration. The vertical red dashed line indicates a risk of 10^{-6} of (1 in a million).

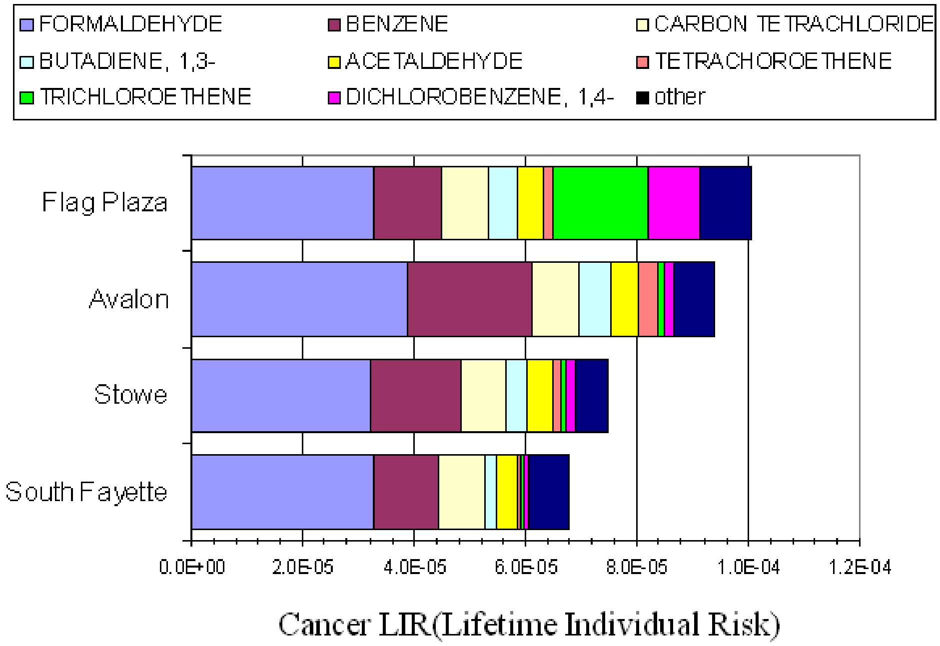


Figure 3.6 Additive cancer lifetime incidence rate, LIR, posed by the 38 gas-phase organic air toxics measured at the four baseline sites.

NATA and previous air toxic studies in other areas of the country have identified acrylonitrile as a potential risk. Acrylonitrile was only measured for 6 months of 2008 at the Flag Plaza site. The 95th percentile upper confidence limit on the mean of these data was 0.064 µg/m^3. This is between the 10th and 20th national percentile for acrylonitrile. The cancer *LIR* would be 4.4 x 10^{-6} and the *HQ* would be 0.032.

3.4.2 Non-Cancer Risks of Gas Phase Organic Air Toxics

Chronic non-cancer *HQ*s are shown in Figure 3.8. The hazard quotient is thought to be proportional to risk, but is not a direct measure of the probability of disease like the *LIR* (19). 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 how much ambient concentrations must be reduced to achieve a “safe” level.

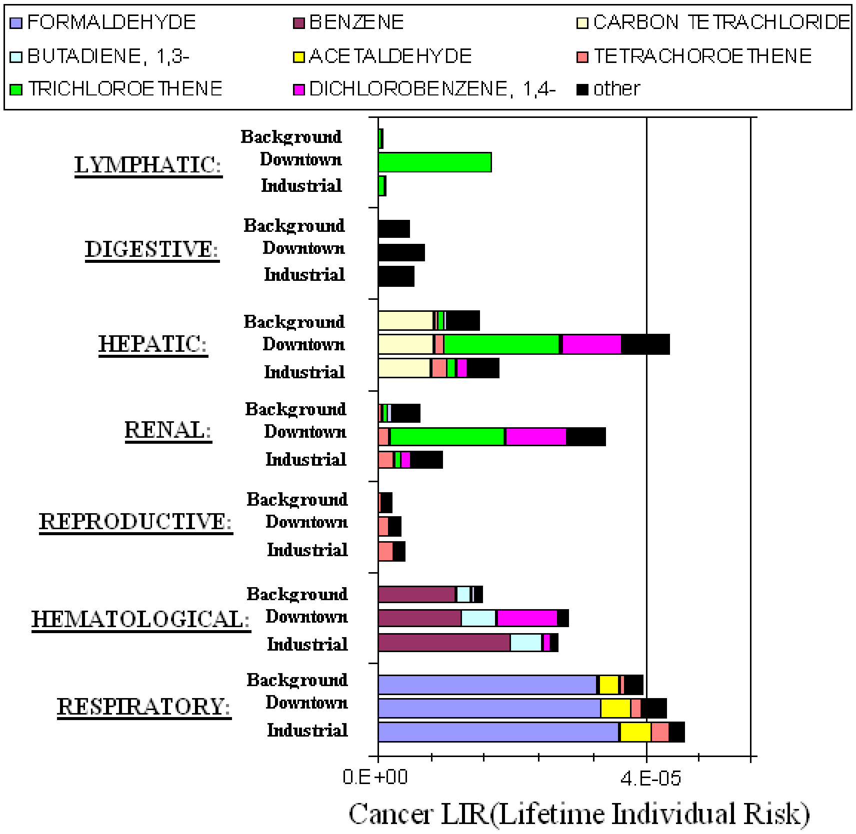


Figure 3.7 Additive cancer lifetime incidence rate, LIR, for different target posed by the 38 gas-phase organic air toxics measured at the four baseline sites.

Of the 38 gas phase organic air toxics measured in the baseline portion of this study, only acrolein posed a chronic non-cancer risk. The *HQ* for acrolein exceeds one at all of the sites.

Air toxics can also present acute non-cancer health risks. We used maximum value from the hourly measurements from the intensive campaigns to assess potential acute health risks. There were no acute health risks found at any of the sites.

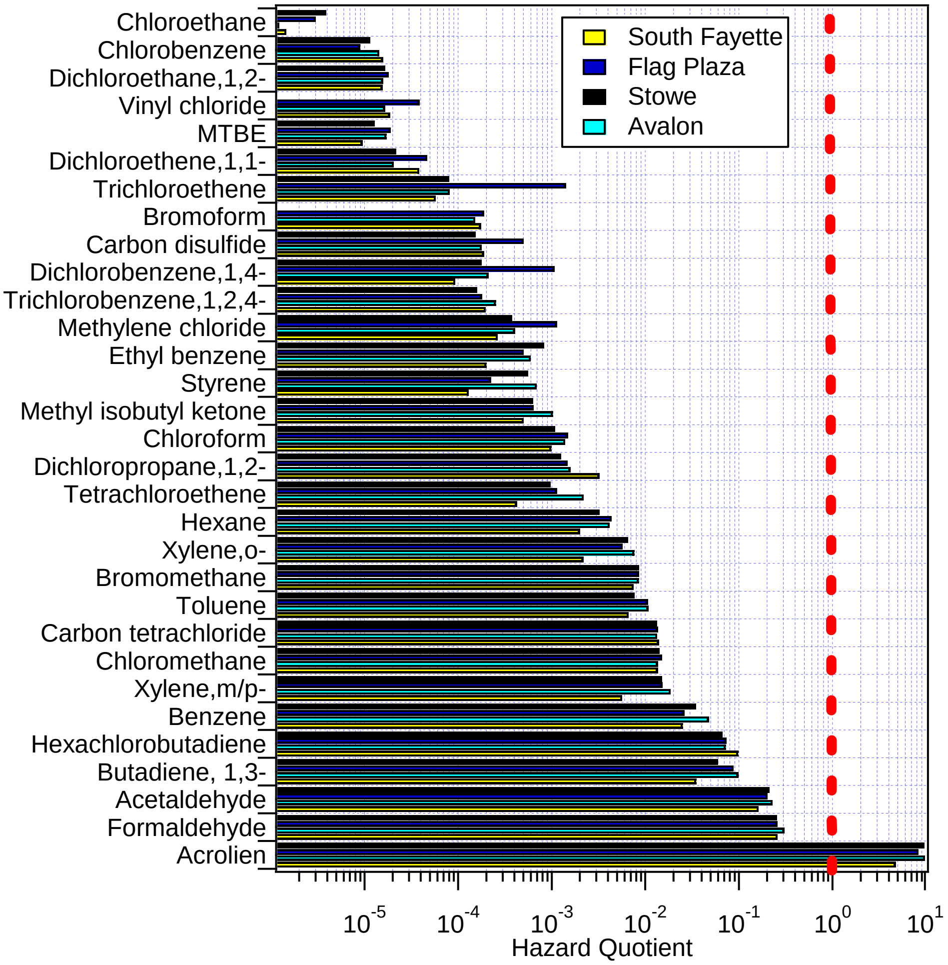


Figure 3.8 Hazard quotients (*HQ*) for non-cancer chronic health effects. The dashed vertical red line indicates a *HQ* of one. Air toxics with a *HQ* less than one are thought not to pose a non-cancer risk.

3.4.3 Diesel Particulate Matter Health Risks

Cancer and chronic non-carcinogenic risks of diesel particulate matter were estimated for the Diamond Building and Schenley Park. Although diesel particulate mater is thought to be a human carcinogen, EPA did not report quantitative cancer risk estimates for diesel particulate matter as part of the National Air Toxic Assessment (NATA) because of uncertainty in the diesel particulate matter toxicity data (i.e., unit risk estimate or URE). To assess carcinogenic risk, we applied a risk potency factor of 3 x 10^{-4} per µg m^{-3} DPM recommended by California's Office of Environmental Health Hazard Assessment (OEHHA). OEHHA estimates an overall range of lung cancer risk factors of (1.3 – 15) x 10^{-4} per µg m^{-3} for DPM, indicating that associated risk is subject to uncertainty of about an order of magnitude.

Our best estimate of the DPM carcinogenic risk is approximately 1.1 x 10^{-3} downtown and 1.8 x 10^{-4} at the PAQS Supersite. To the extent that BC or EC is a reasonable surrogate for DPM, these results suggest carcinogenic risk in the range of (1-2) x 10^{-4} elsewhere in the county since the average EC concentrations at the Florence, Greensburg, Hazelwood, and Lawrenceville PAQS sites are all within a factor of two of the PAQS Supersite (Figure 3.4).

Chronic non-cancer risk was assessed by calculating a DPM hazard quotient (*HQ*). The reference concentration for DPM is 5 $\mu g/m^3$ (20) translating to a DPM *HQ*=0.72 in downtown Pittsburgh and *HQ*=0.12 at the PAQS Supersite.

3.4.5 Comparing Health Risks of Different Classes of Air Toxics

Figure 3.9 compares cancer risks for four different classes of air toxics: gas-phase organics, metals, POMs, and diesel particulate matter. Separate estimates are shown for Avalon, downtown, and the regional background. To provide a more comprehensive assessment, the risk estimates of the regional background are based on data collected by this study in South Fayette and archived data for metals, polycyclic aromatic hydrocarbons (PAHs), and diesel particulate matter collected as part of the Pittsburgh Supersite at a site located in Schenley Park (6). The Schenley Park site was not strongly influenced by local sources and therefore data from it are representative of urban background conditions. The estimates for downtown are based on data from the Flag Plaza for volatile organics and Diamond Building for DPM.

Figure 3.9 indicates that diesel particulate matter presents the greatest risks. Although these risk estimates are uncertain, even our minimum cancer risk estimate for DPM is greater than additive cancer risks for these other classes of air toxics in downtown. At the regional background site the minimum DPM risk estimate is comparable to the volatile organic air toxics. The minimum cancer risk estimate was calculated using the minimum estimate of DPM concentrations and the lower limit of the OEHHA DPM URE 1.3 x 10^{-4} per $\mu g\ m^{-3}$. Therefore, the magnitude of the risks potentially associated with DPM makes it a top priority for minimizing risks in Allegheny County.

In the regional background, Figure 3.9 indicates that the additive gas-phase organic air toxics *LIR* is about two times higher than the additive metals *LIR* and about 25 times higher then the additive PAH *LIR*. At Avalon, the risk posed by metals is about a factor of three lower than that posed by volatile organic air toxics.

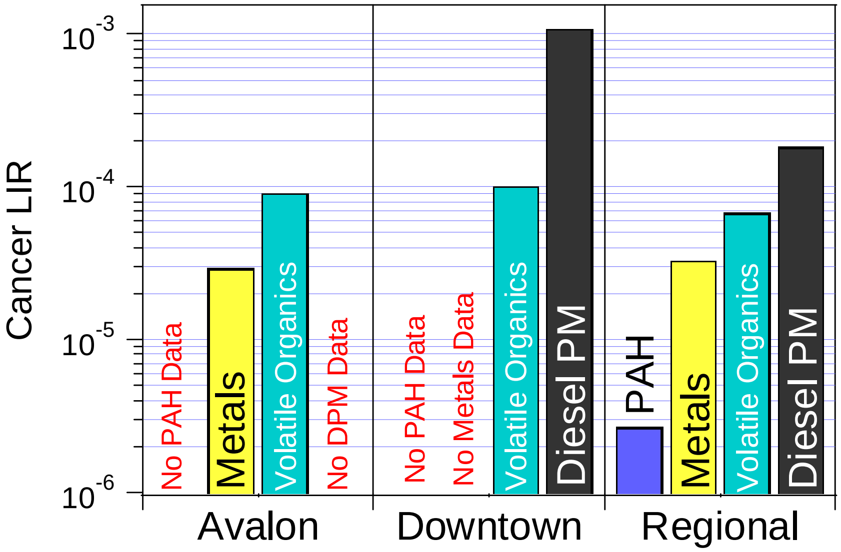


Figure 3.9 Comparison of additive cancer risk for different classes of air toxics. The estimates for the regional background are based on data from the South Fayette site collected as part of this study (volatile organics) and archived data from the Pittsburgh Supersite in Schenley Park (PAH, metals, and diesel PM).

Figure 3.10 compares non-cancer hazard quotients of air toxics for metals, DPM, and hydrogen sulfide. Metals do not appear to pose a significant non-cancer risk. All of the metals measured at the regional background site were more than a factor of ten less then their respective *RfC* values with the exception of manganese which was more than a factor of five less then it's *RfC* value. Figure 3.11 shows that there is little spatial variation in metal hazard quotients around Allegheny County. At all sites the additive metals hazard index is lower than 0.8.

Although no longer classified as an air toxic, hydrogen sulfide is a by product of coke plants that affects respiratory and neurological health (21). Figure 3.10 indicates that hydrogen sulfide does present a potential non-cancer risk at Avalon. It is uncertain how hydrogen sulfide contributes to health risks elsewhere in the county since it is not routinely measured at locations not immediately adjacent to large coke works.

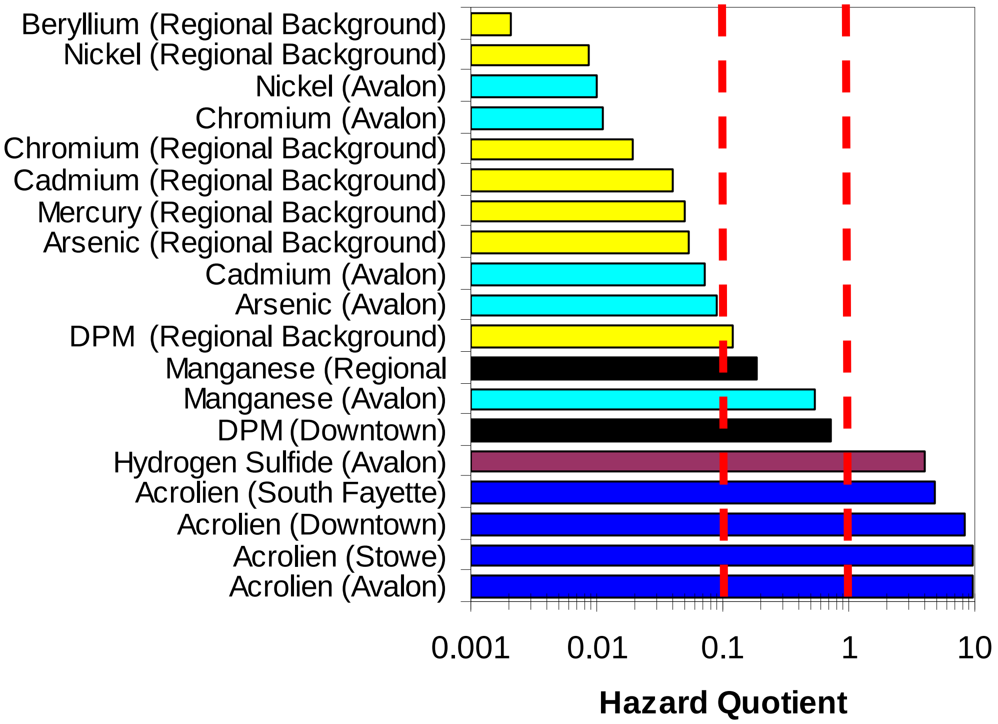


Figure 3.10 Comparison of hazard quotients for different classes of air toxics measured at regional background sites. The dashed line represents a hazard quotient of 1 indicating potential for non-cancer risks and a hazard quotient of .1, an indicator that concentrations being a factor of ten less then their *RfC* value.

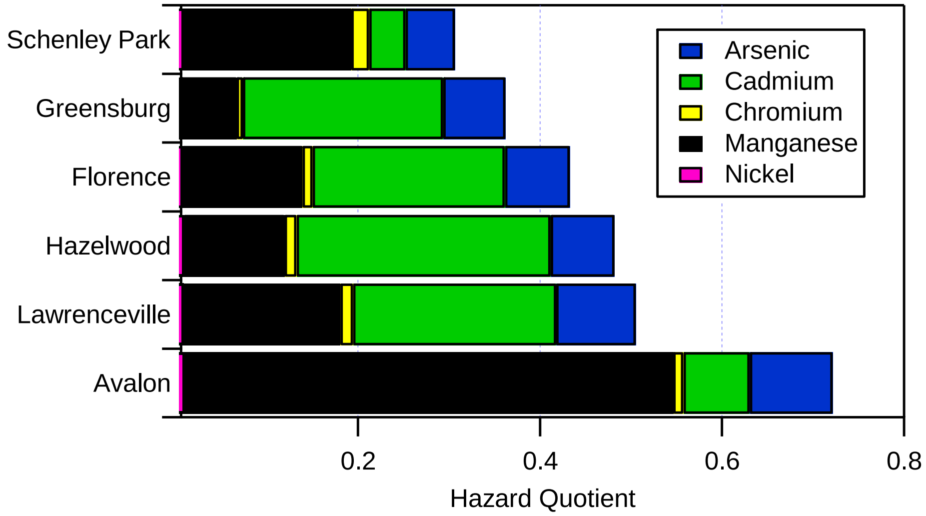


Figure 3.11 Non-cancer hazard quotients of metals calculated using archived data (6). The Schenley Park site is the urban background site.

3.4.6 Comparison of Risks in different U.S. Cities

Figure 3.12 compares the additive cancer risk posed by the 38 gas-phase organic air toxics at the four baseline sites in Allegheny County to estimates for 14 other United States cities. The risk estimates for the other cities are based on annual average concentrations for the same set of air toxics using data from 2006 that are archived in the EPA AQS (22).

Figure 3.12 indicates that the estimated risks vary by less than a factor of three across the set of cities, with the lowest risk being estimated for San Francisco and the highest risk in Detroit. Allegheny County falls within the middle two quartiles of this distribution. Therefore, the risks in Allegheny are comparable to those in other US cities.

Figure 3.12 also illustrates the similarity in the risk profiles between the cities. The toxics that are driving the health risks in Allegheny County are largely the same as those posing the risks elsewhere in the United States.

Figure 3.13 compares the additive *LIR* for metals measured in Allegheny County and six different cities. The metal risks for Allegheny County were estimated using archived data from the six sites in and around Allegheny County. Most of the archived data were collected as part of the Pittsburgh Supersite during 2001 and 2002. The analysis also used more recent metals data taken at Avalon.

The comparison reveals that the cancer risk posed by metals in Allegheny County are comparable to those in other US cities. The metals risks in Allegheny County are somewhat greater than those in Seattle, Boston, Portland, and Washington DC, but significantly less than the risks of metals in Tampa and Houston.

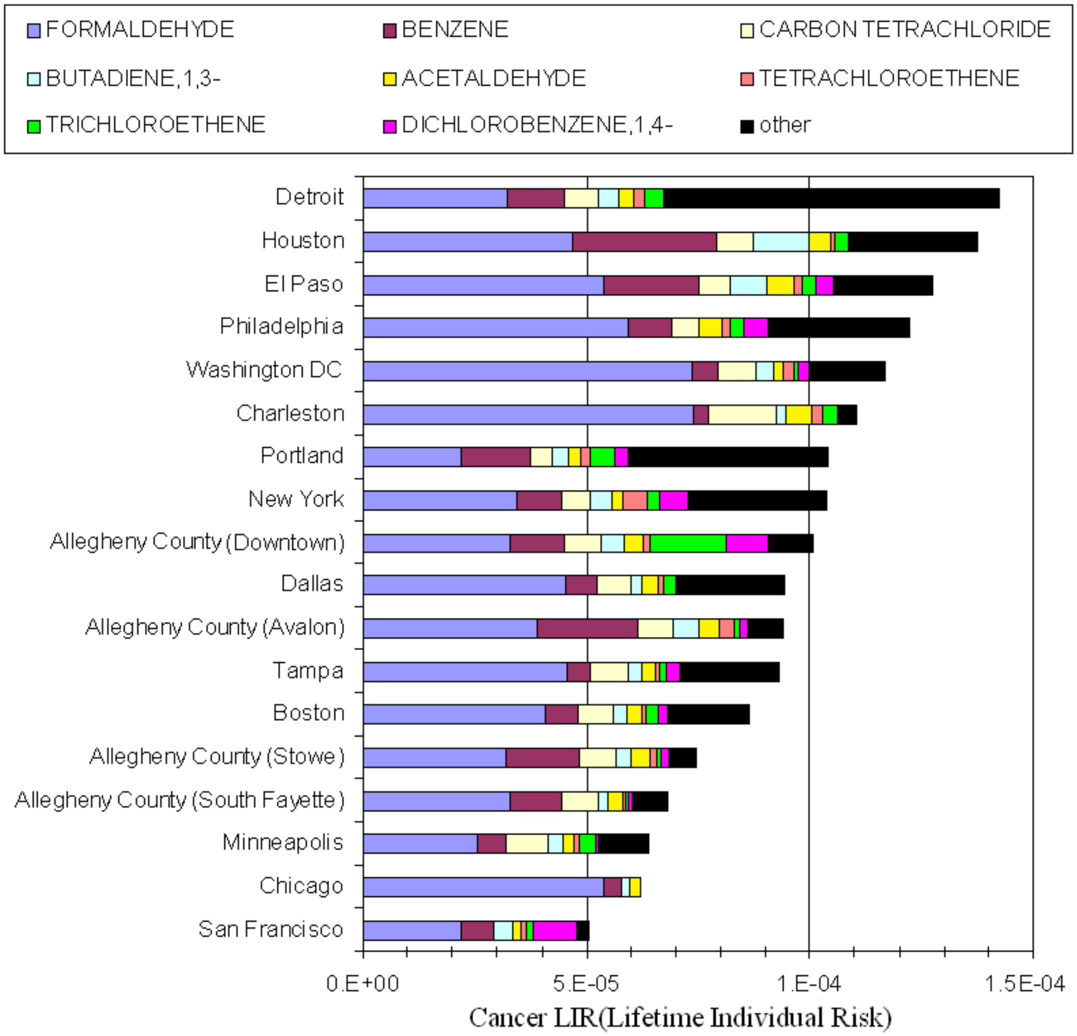


Figure 3.12 Comparison of additive cancer risks at the four baseline sites in Allegheny County to other cities in the United States. The comparisons are based on the 38 organic gas-phase air toxics considered in this study.

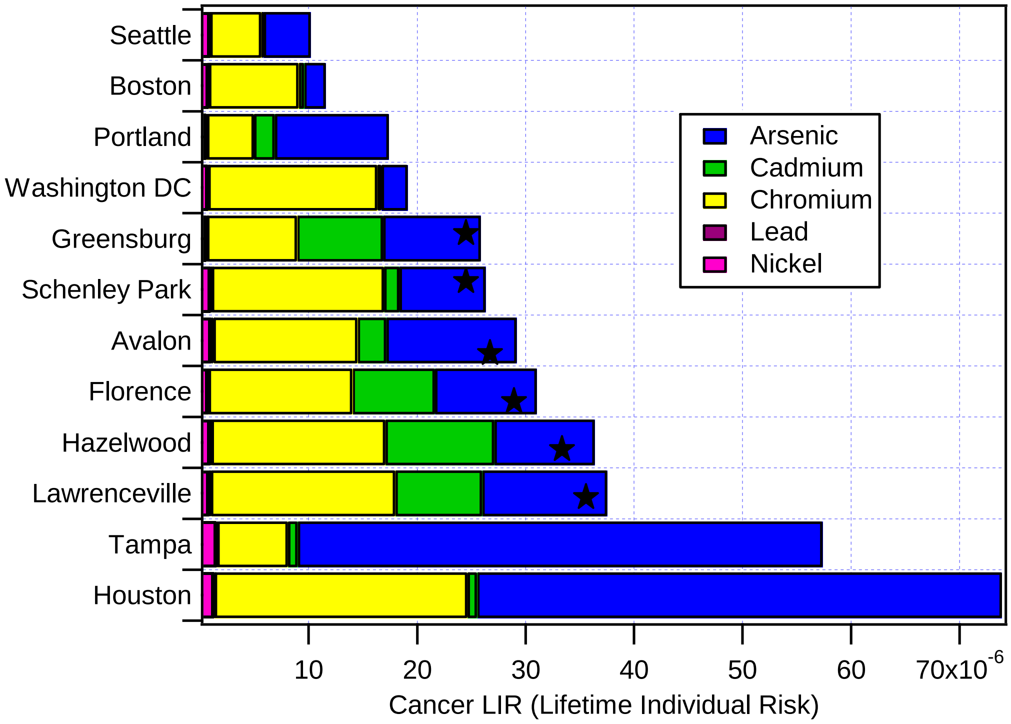


Figure 3.13. Comparison of additive lifetime incidence rate (LIR) due to metal exposures for selected cities and six sites in the Pittsburgh area (indicated by * symbol).

3.4.7 Interactive Risk Model Analysis

The interactive risk model was used to help bound potential uncertainty on risk estimates for the 38 gas phase air toxics measured in the baseline study. Also included in the analysis were hydrogen sulfide and select metals measured at the regional background site as part of the PAQS study. Figure 3.14 shows the best and worst case scenarios 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 (C), 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 10^{-6}, but respiratory, renal and hepatic systems may face a risk greater than 10^{-4}.

Figure 3.15 plots the risk enhancement ratio, $HI_{int,p}/\mathrm{HI}_{add,p}$ 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 $LIR_{int,p}>1 \times 10^{-4}$. 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 3.15. The interactions driving non-cancer risk enhancement were independent of source regime. The estimated risk enhancement for these systems ranged from two to eight 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 of the United States acrolein concentrations are higher than in Allegheny County (Figure 3.3).

Hydrogen sulfide targets the respiratory system and manganese targets the respiratory and neurological systems (20). Including these two pollutants in the non-cancer interactive risk analysis suggested additional potentially important interactions (Figure 3.14a). For example, acrolein/hydrogen sulfide may be important. This analysis only includes a subset of air toxics; other pollutants may substantially alter results making identifying important pollutants a priority.

For cancer risks, pollutant interactions have the potential to increase the cancer risk of respiratory, hematological and hepatic systems to greater than 1×10^{-4}. The pollutants that drive these interactions are shown in Figure 3.15. Only the respiratory system has the potential for cancer risk above the threshold at all of the sites. Formaldehyde/acetaldehyde interaction is the most significant potential contributor to respiratory risks in Allegheny County. For the hematological system, the benzene/1,3-butadiene interaction may be important.

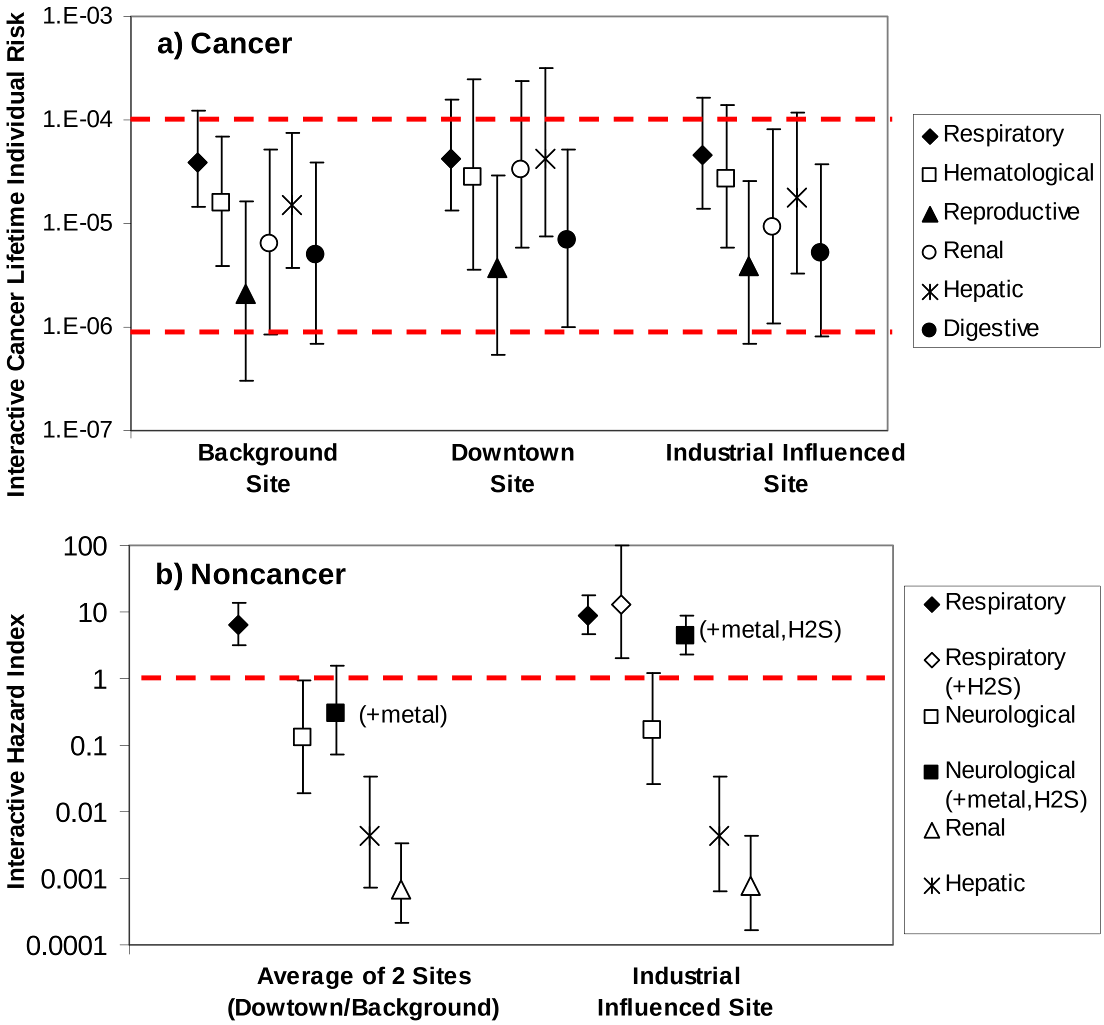


Figure 3.14 Best and worst case scenarios for synergistic/antagonistic non-cancer health effects. Symbols represent the additive hazard index; the error bars extend to the best and worse possible values for the hazard index.

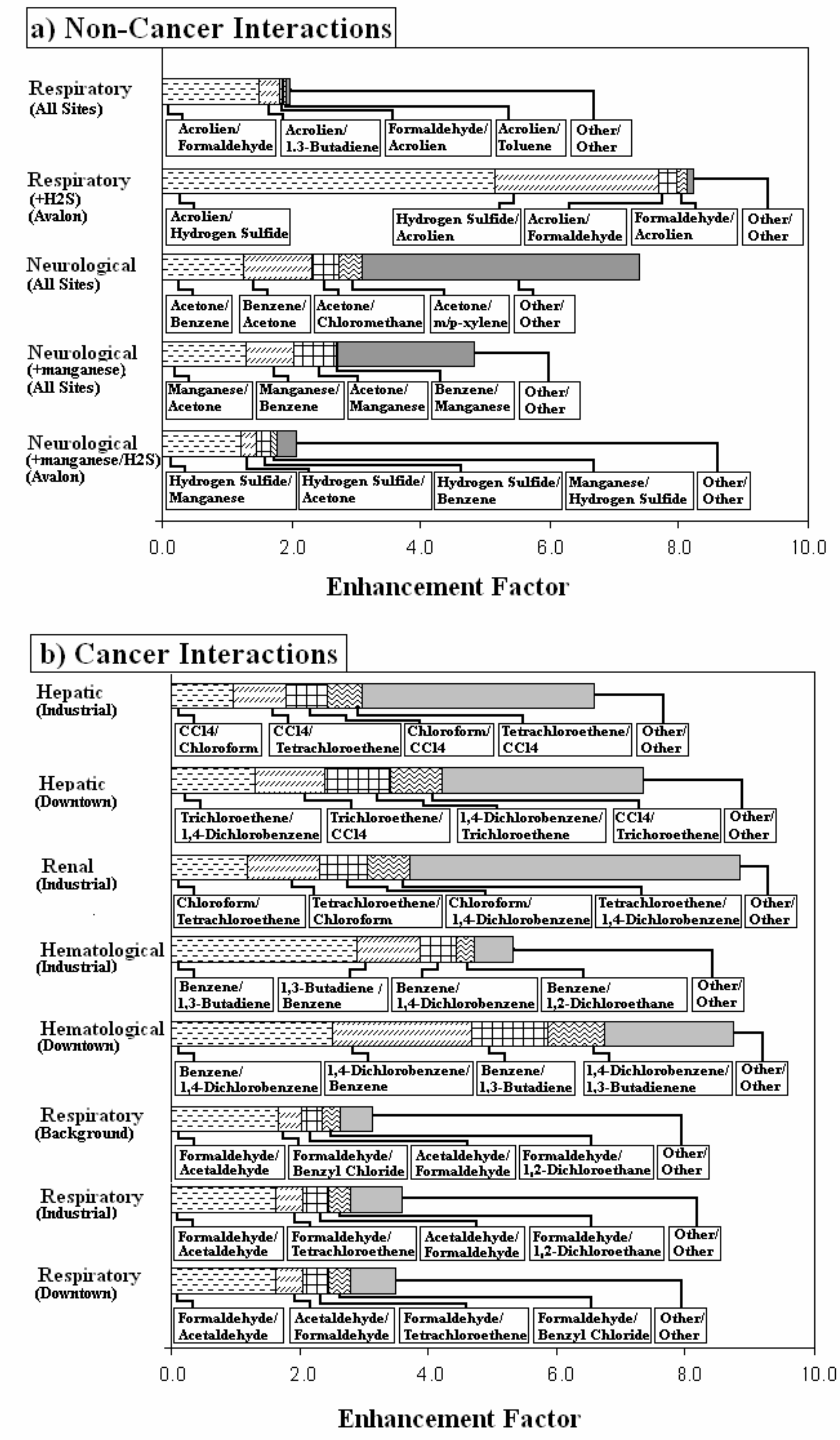


Figure 3.15 Enhancement factors for each target system that has a potential for risk above threshold. ($HI_{int,p}$ greater than 1, $LIR_{int,p}$ greater than 10^{-4}). The maximum possible enhancement is 10, the assumed value of M_{jk} in the interactive risk model. Format for listing interaction pairs is A/B where A is the pollutant being affected by pollutant B.

3.5 Indentifying Priority Air Toxics

The results of this chapter can be used to identify priority air toxics. We have done this based on both the estimated healthy risks and concentrations data. We did not solely classify air toxics based on risk because these estimates are uncertain. In addition, toxicity data are not available for some toxics.

Table 3.3 lists the priority air toxics. Four air toxics which pose lifetime cancer risks greater than 10^{-5} are designated as the highest priority: diesel particulate matter, benzene, formaldehyde and trichloroethene. Air toxics with a lifetime cancer risk between 10^{-6} and 10^{-5} or pose non-cancer risks are classified as moderate priority. Finally, the class "Potential Concerns" includes air toxics with high concentrations relative to national data but that are not estimated to pose health risks.

Table 3.3 Priority Air Toxics for Allegheny County

Highest Priority	Moderate Priority	Potential Concerns
diesel particulate matter	carbon tetrachloride	propionaldehyde
formaldehyde	1,3-butadiene	styrene
benzene	acetaldehyde	ethylbenzene
trichloroethene	tetrachloroethene	toluene
	1,4-dichlorobenzene	methylene chloride
	Chloroform	MIBK
	hexachlorobutadiene	xylenes
	benzyl chloride	
	1,2-dichloroethane	
	acrolein	
	arsenic	
	chromium	

Chapter 4. Temporal Variations in Air Toxics Concentrations

Intensive campaigns were conducted at three sites using high time resolution instruments to better understand the sources of air toxics in Allegheny County. High time resolved measurements allowed for direct observation of plumes and correlations of pollutant concentrations with wind direction and diurnal temporal patterns. In this chapter high time resolved concentration measurements focusing on the "priority" air toxics for Allegheny County are presented. In the next chapter these data are used to apportion air toxics to sources.

4.1 Times Series of Priority Air Toxics

Figures 4.1-4.3 present time series of hourly measurements, which illustrate the temporal variability of air toxic concentrations. Figure 4.1 plots data from October 2006 measured at the Avalon site; Figure 4.2 plots data from March/April 2008 measured at the Diamond Building downtown; and Figure 4.3 plots data from June 2007 measured at an urban background site at Carnegie Mellon University.

Air toxic concentrations at each site are characterized by periods of low, relatively stable concentrations with intermittent, relatively short periods of higher concentrations. These short-duration, high-concentration events are most 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. For example, the shaded sections of the time series shown in Figure 4.1 highlight two plume events at the Avalon site. The first event occurred when the Avalon site was downwind from Neville Island; the second event occurred with the wind direction was from downtown Pittsburgh. During the first event, benzene, toluene and styrene concentrations were all elevated. All three of these toxics are emitted by industrial facilities on Neville Island. The second plume event has a different chemical profile; it is characterized by high concentrations of toluene and tetrachloroethene with only small increases in the other pollutants.

Figure 4.2 indicates that large spikes in pollutant concentrations were also observed at the Diamond Building. However, these events were shorter in duration than at the Avalon site and the chemical profile of the plumes did not vary as much from event to event. Toluene and black carbon concentrations were frequently elevated during plume events at the Diamond Building; both of these species are associated with motor vehicle emissions. Tetrachloroethene concentrations at Diamond Building were also highly variable; tetrachlorethene is used by dry cleaners.

At the Carnegie Mellon University campus site, spikes in air toxic concentrations occurred relatively infrequently (Figure 4.3). When they did occur they were relatively short, lasting an hour or two. For the most part, concentrations were low and stable at the urban background site.

Although the time series shown in Figures 4.1 to 4.3 highlight the temporal variability in air toxic concentrations, they provide little insight into underlying causes of this variability. What fraction of the variability is driven by changes in wind direction? Are air toxics concentrations always higher during certain times of the day or during certain days of the week? The high time resolved data provide a unique opportunity to address these questions, which in turn provides substantial insight into sources. These questions are the focus of the next two sections.

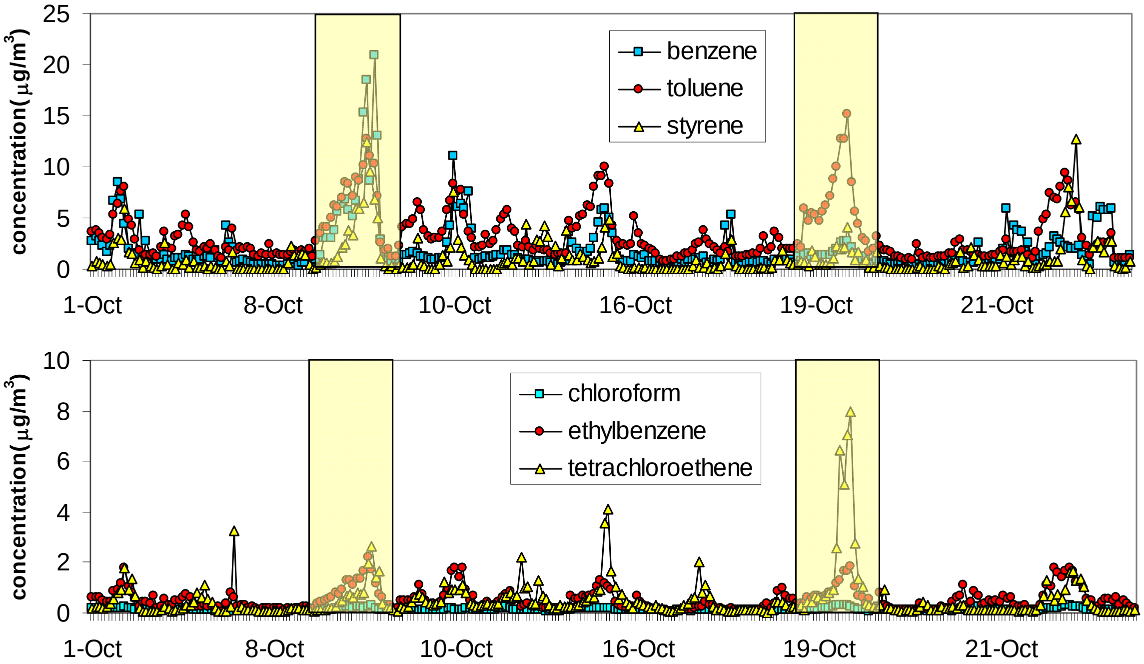


Figure 4.1 Time series of hourly concentrations measured during October 2006 at the Avalon site. The shaded regions indicate two of the many plumes that influenced this site.

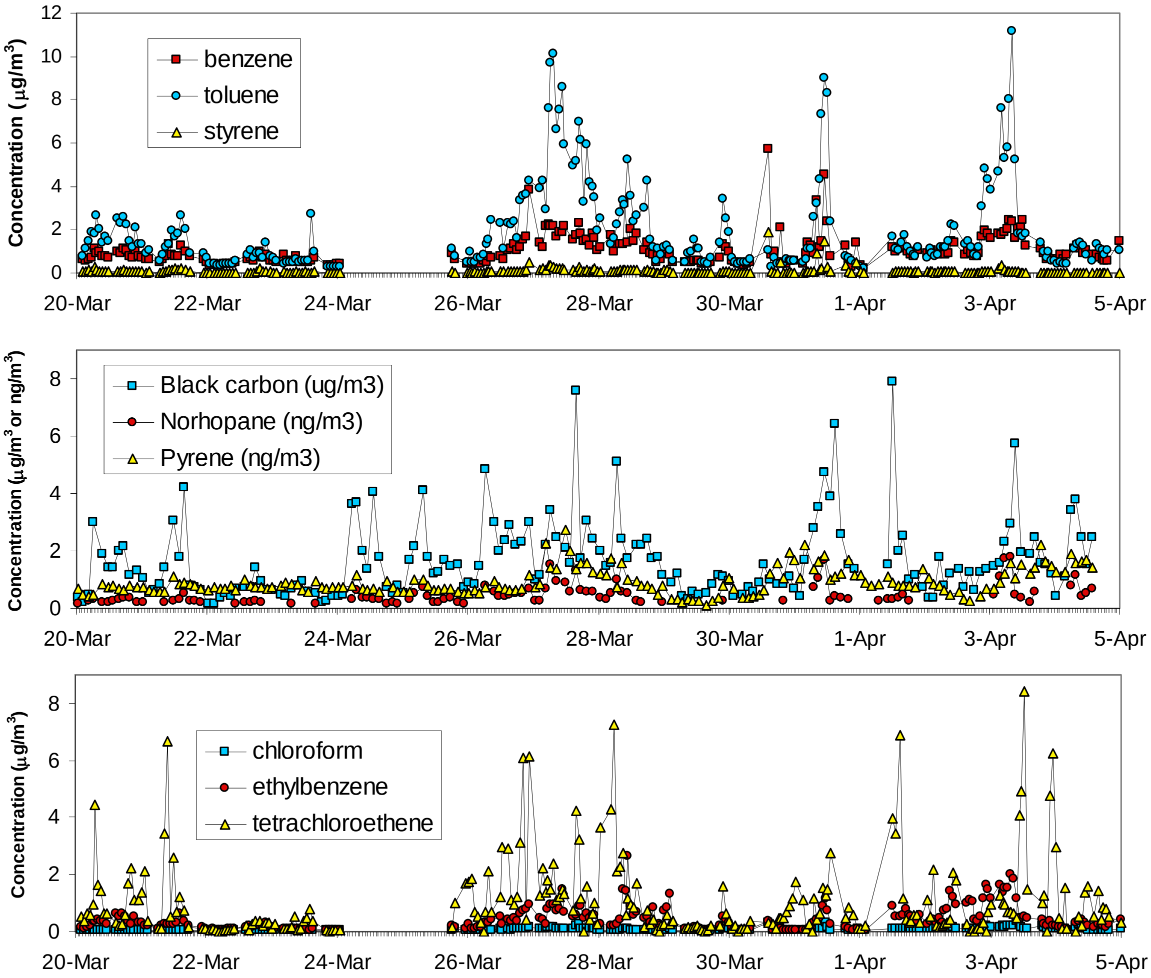


Figure 4.2 Time series of hourly air toxic concentrations measured during March-April 2008 at the downtown Diamond Building site.

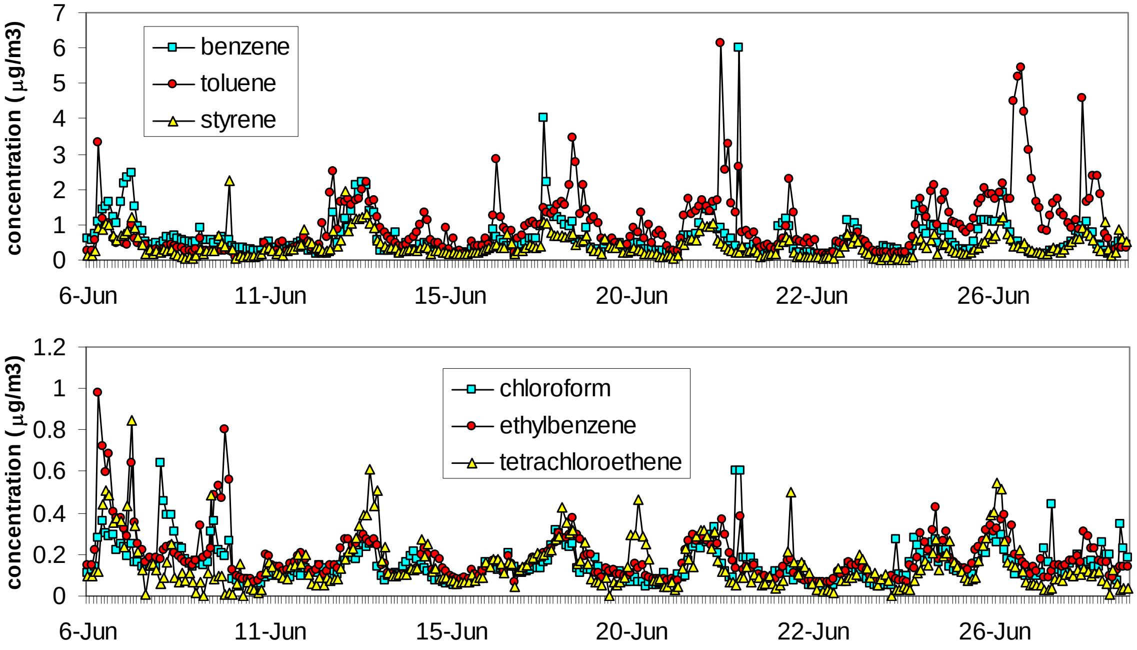


Figure 4.3 Time series of hourly air toxic concentrations measured during June 2007 at Carnegie Mellon University.

4.2 The Effect of Wind Direction on Air Toxics Concentrations

Correlations of air toxic concentrations with wind direction can provide substantial insight into the location of source regions. At Avalon a MET station was co-located with the high time resolved instrument that measured wind speed and direction every minute. There was no MET station at the downtown and urban background sites. To help interpret the air toxic data from these sites, we used wind speed and direction measurements from the Hammerfield site located on Tasso Street in Hazelwood.

Figure 4.4 shows wind roses for the Avalon and Hammerfield sites during the intensive periods. The Avalon data are from September 2006-Febuary 2007. The Hammefield data are from June 2007-February 2008. During the Avalon intensive, the wind came most frequently from the west or Neville Island region. During the other intensives, the wind came most frequently from the southwest and southeast.

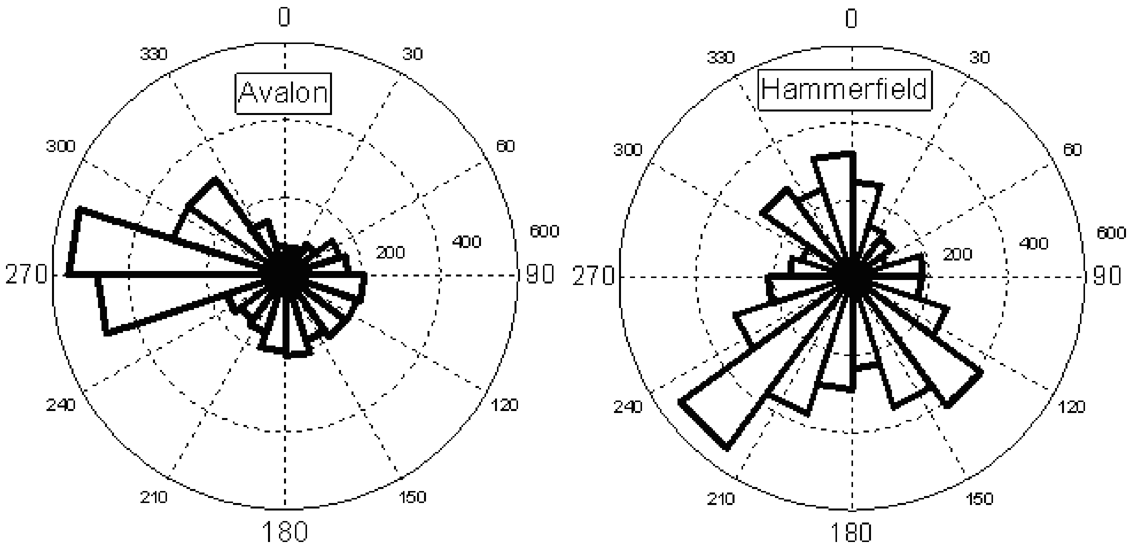
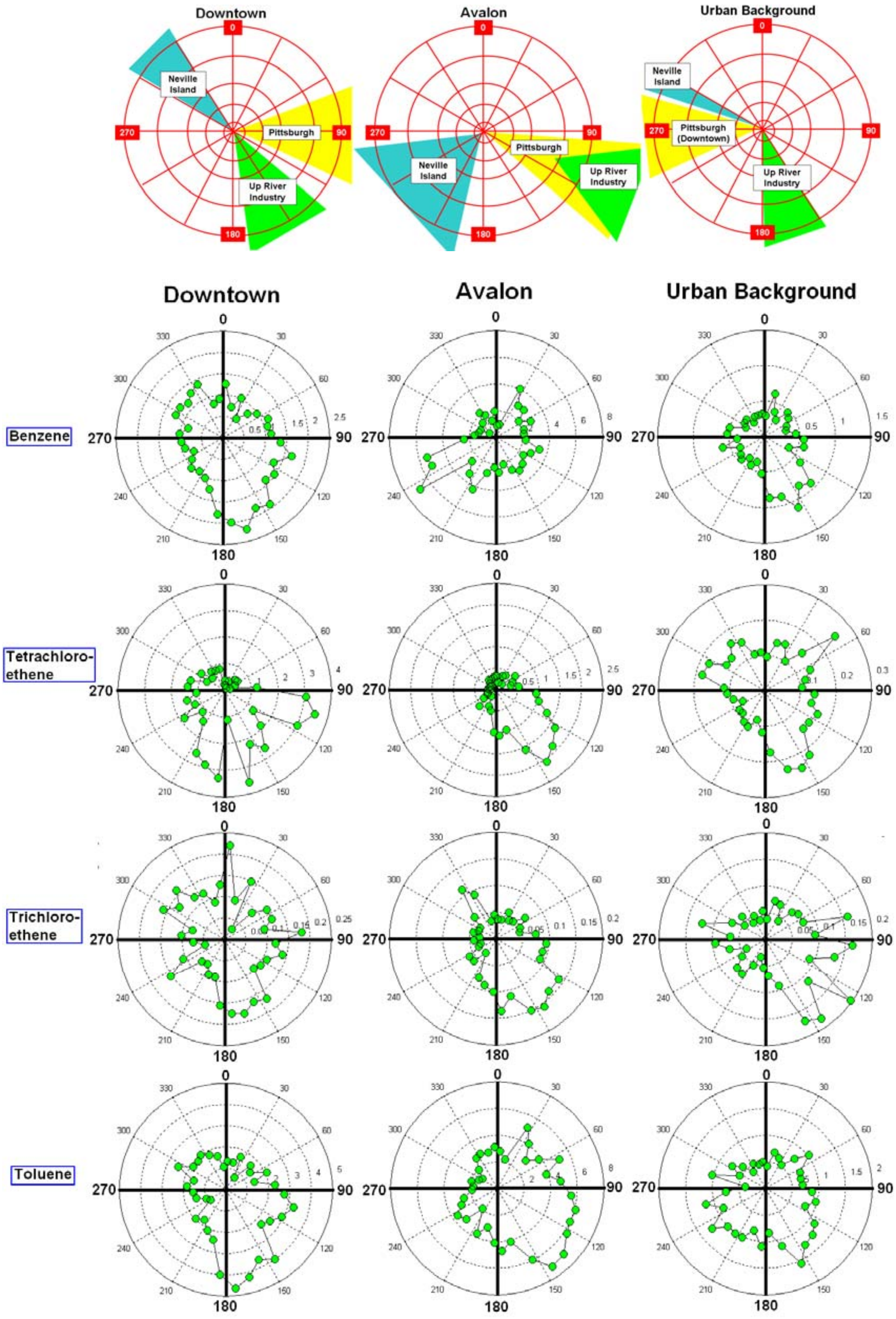


Figure 4.4 Wind roses for the two meteorological stations, Avalon and Hammerfield.

Pollutant dispersion depends on a variety of meteorological factors in addition to wind direction -- simply being downwind of a source is not sufficient to be strongly impacted by the plume. Therefore, air toxic concentrations were binned by wind direction and then averaged. Figure 4.5 plots the average concentrations of 7 priority air toxics and carbon disulfide as a function of wind direction.



(Figure 4.5 cont. on next page)

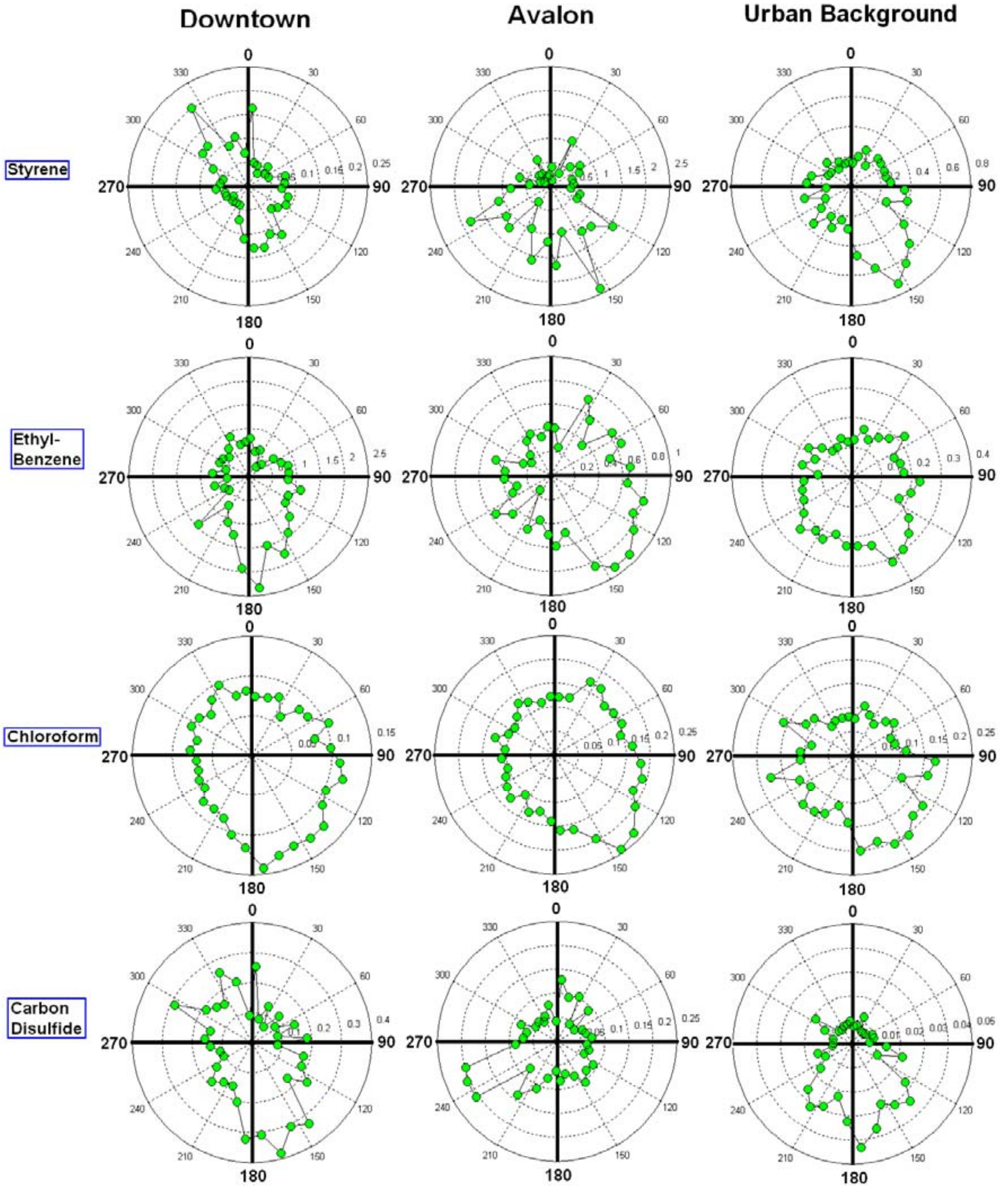


Figure 4.5 Average air toxic concentrations (μg/m^3) as a function of wind direction for high time resolved measurements downtown, at the urban background site, and at the Avalon site. Averages calculated by binning data based on wind direction, as discussed in the text.

Figure 4.5 indicates that the concentrations of many air toxics exhibited strong wind directional dependencies at all three sites. To help interpret these correlations, Figure 4.6

presents maps of Allegheny County showing the location of the monitoring sites used by this project and major point sources. Allegheny County is the home to significant industry; there are 187 large point sources (>25 tons per year) that are required to report emissions to the Allegheny County Health Department (1). As discussed below, emissions from two heavily industrialized areas, the Neville Island area and the Clairton area, contributed significantly to gas-phase air toxic concentrations at all three intensive sites.

Figure 4.7 shows a map of the Neville Island Area. It is highly industrialized with multiple chemical manufacturing facilities and the Shenango Coke Works facility. The Allegheny County Sanitary Authority (ACSA), a large source of chlorinated compounds, and the Valspar Corporation, a large source of methyl isobutyl ketone (MIBK), are both located about one mile up the Ohio River from Neville Island. There are large residential communities adjacent to the Neville Island area, including the Stowe and Avalon neighborhoods.

Figure 4.8 shows a map of the sources in the heavy industrial area along the Monongahela River. Of particular note is the Clairton area with three facilities that are among the largest emitters of air toxics in the county: USS Clairton Coke Works, Hercules Inc., and the Eastman Chemical Resins Inc. For example, the combined emissions of these three sources are 207 TYP of toluene (71% of total large point source toluene emissions in Allegheny County) and 87 TPY of Benzene (84% of total large point source benzene emissions).

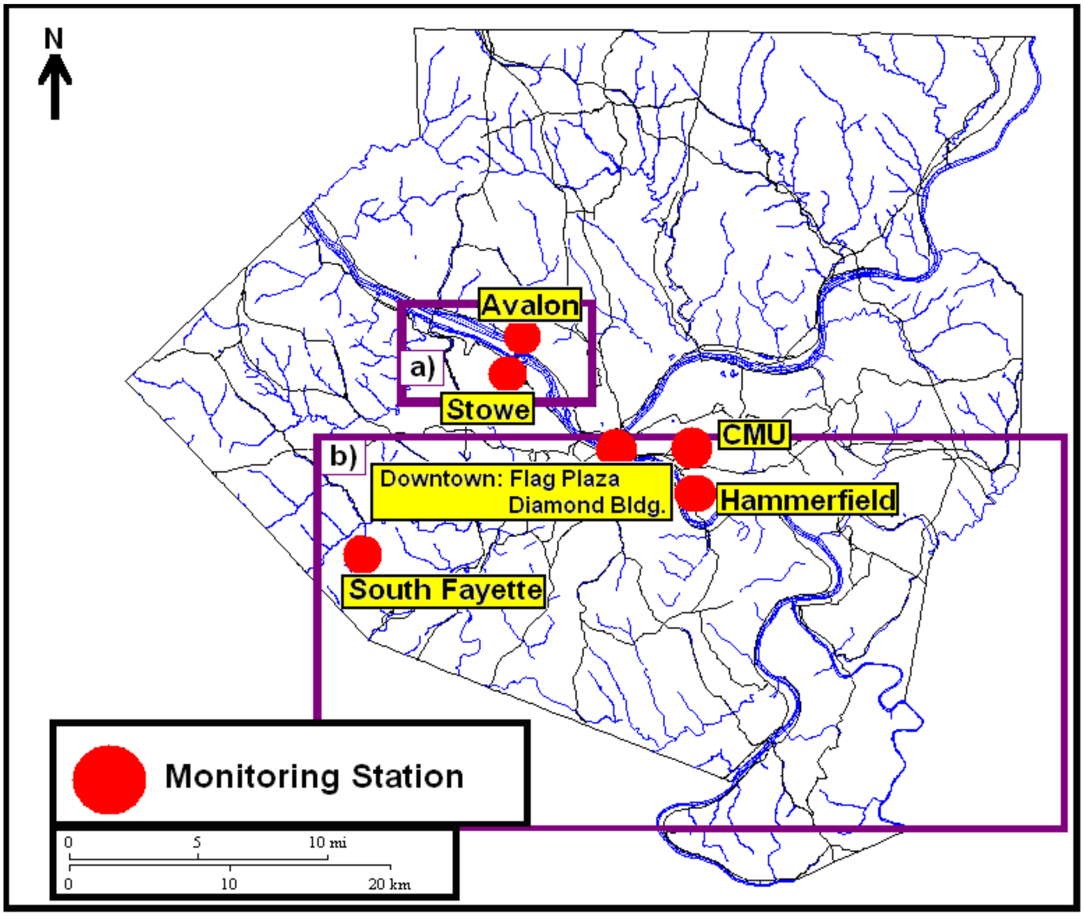


Figure 4.6 Map of Allegheny County with the two industrial areas affecting air toxics concentrations outlined. a) Neville Island area and b) up river industrial area

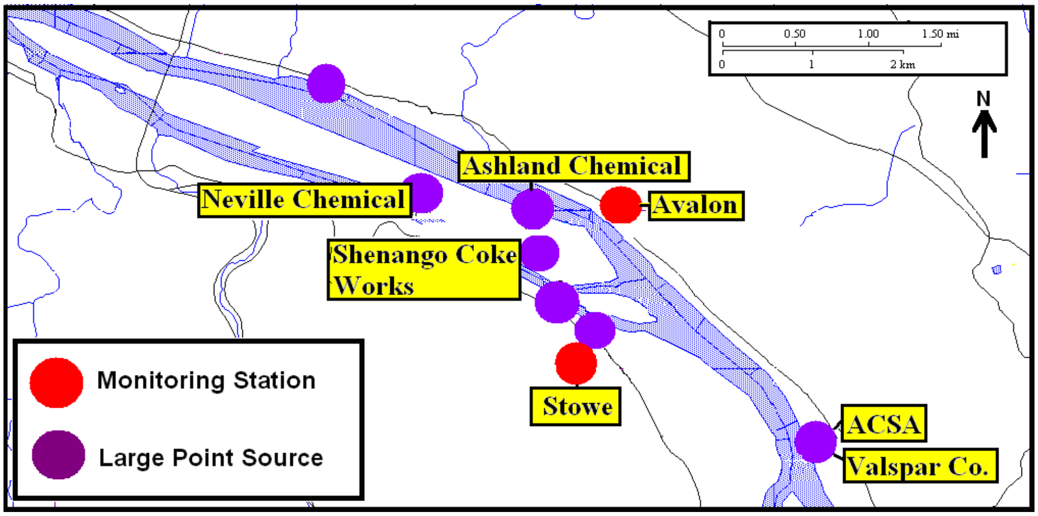


Figure 4.7 Map of the Neville Island area shown in section (a) from Figure 4.6

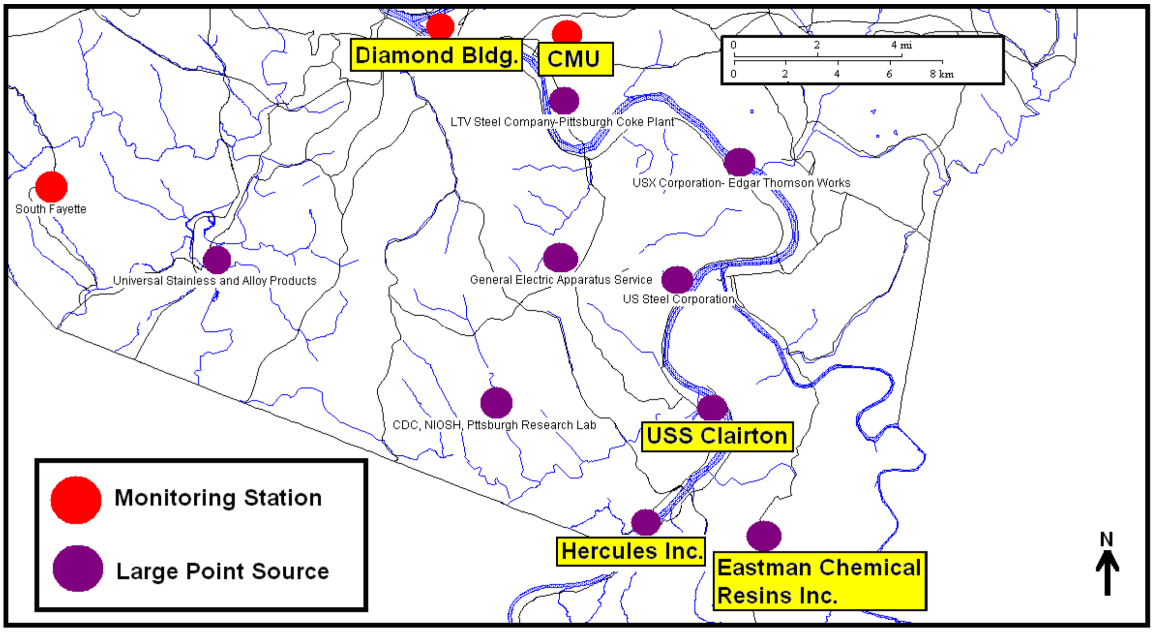


Figure 4.8 Map of the upriver industrial area shown as section (b) in Figure 4.6.

Figure 4.5 indicates that Neville Island is a major source of air toxics in Avalon. For example, the concentrations of benzene and carbon disulfide were, on average, much higher when the site was downwind of Neville Island. All of these toxics are emitted by industrial facilities on the island. However, the industrial facilities on Neville Island are not the only important local sources of air toxics in Avalon. For example, the concentrations of chloroform, tetrachloroethene, toluene and trichloroethene were all elevated when Avalon was downwind of downtown Pittsburgh (i.e., when the wind was blowing down the Ohio River).

The wind directional dependence of selected air toxics measured at the Diamond Building in downtown Pittsburgh are also shown in Figure 4.5. Concentrations of benzene, toluene, and carbon disulfide at the Diamond Building are higher when the wind is blowing from either the Neville or Clairton source regions. Other compounds are only elevated when the wind is blowing in one of these two directions. For example, ethylbenzene concentrations are elevated when the wind is blowing down the Monongahela River. Styrene and to a lesser extent trichloroethene concentrations are often elevated when the wind is blowing from Neville Island but not from the Clairton industrial area. There are several large sources of styrene on Neville Island.

The wind directional dependence of air toxics measured at Carnegie Mellon University is shown in Figure 2.5. For example, concentrations of many toxics are higher when the wind is blowing from the Clairton area. Neville Island does not appear to have an effect on concentrations at CMU.

Concentrations of some air toxics did not exhibit strong wind directional dependencies. For example pollutants with few sources and thought to be regionally distributed, such as carbon tetrachloride, bromoform, and 1,2-dichloroethane, did not show any wind directional dependence and pollutants with a large number of small emitting sources such as chloroform.

4.3 Temporal Patterns in Air Toxics Concentrations

Temporal patterns of air toxic concentrations provide information on sources and acute exposures. Day of the week and hour of the day patterns were investigated using the high time resolved data. Seasonal patterns were investigated with the baseline data. High time resolved data were used to determine diurnal, weekly, and wind directional patterns for air toxics concentrations. The data were binned by hour of the day or day of the week and the bootstrap method (11) was used to determine confidence intervals on the mean.

4.3.1 Day of the Week Patterns in Air Toxics Concentrations

Figure 4.9 plots average weekend and weekday concentrations of selected air toxics. There were statistically significant differences between weekday and weekend concentrations, but not between individual week days (e.g., Monday versus Tuesday) or between weekend days (Saturday versus Sunday). The weekend/weekday patterns indicate the importance of local sources whose emissions are higher during the work week.

Many air toxics at the Diamond Building have a strong weekday/weekday pattern, with lower concentrations observed on weekends. For example, concentrations of mobile source air toxics such as toluene, benzene, and ethylbenzene concentrations are about 50% higher on weekdays then weekends. Weekday concentrations of condensed phase markers of motor vehicle emissions (BC, hopanes, steranes) were about a factor of two higher than weekend concentrations. Other, non-mobile source air toxics, such as tetrachloroethene, also follow a distinctive weekend/weekday pattern. These patterns mirror the economic activity downtown. The relatively large variation in concentrations of BC and other mobile tracers relative to benzene may imply that the gas phase species have more sources.

Many air toxics also have statistically significant weekday/weekend variation at the Carnegie Mellon University campus (the site of the background intensive). Therefore, local sources with emissions during the normal work week are important at this site. However, Figure 4.9 indicates that there were no clear weekend/weekday patterns in the Avalon air toxics concentrations. This underscores the large contribution that emissions from industrial facilities that operate seven days a week make to the Avalon site.

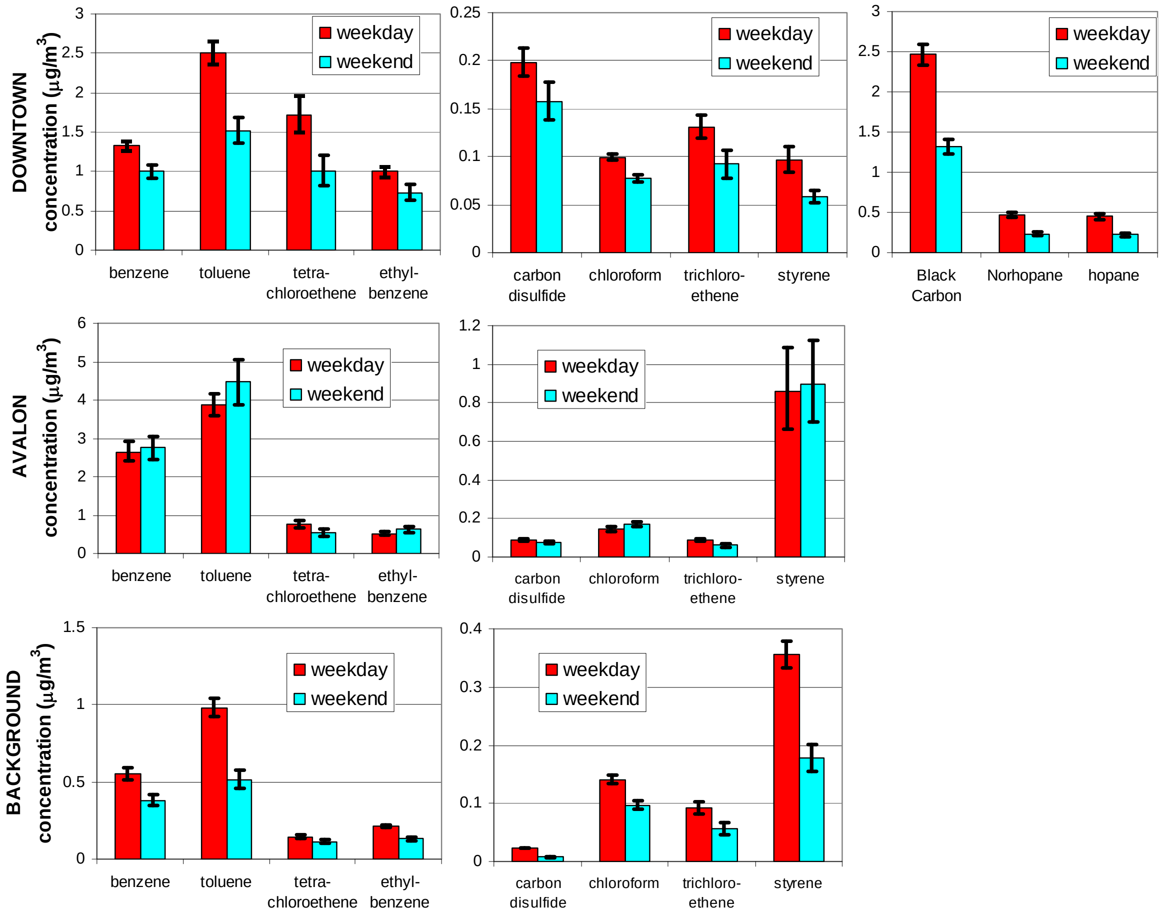


Figure 4.9 Average weekday and weekend concentrations of air toxics measured during the intensive campaigns. The error bars indicate the 5th and 95th percentile confidence interval of the mean using the bootstrap method.

4.3.2 Diurnal Patterns of Air Toxics Concentrations

Average diurnal patterns for eight air toxics are shown in Figure 4.10. Except for a few compounds, air toxic concentrations were lower during the day than at night. This reflects the strong influence that mixing or boundary layer height has on pollutant concentrations. During the night the boundary layer is low, which traps local emissions and creates higher pollutant concentrations. During the day, the boundary layer rises, reducing pollutant concentrations. Minimum concentrations often occurred around noon when the boundary layer is highest.

The magnitude of the diurnal pattern reflects the strength of local sources. At one extreme is carbon tetrachloride which exhibits no diurnal pattern (Figure 4.10). Carbon tetrachloride is a chlorofluorocarbon with a long atmospheric lifetime. Its emissions were substantially reduced by the Montreal Protocol. The net result of these two factors is that carbon tetrachloride is more or less homogeneously distributed throughout the atmosphere. Therefore, diurnal variations in the mixing layer height do not affect local concentrations. At the other extreme is styrene concentration at the Avalon site (Figure 4.10). The chemical facilities on Neville Island are large sources of styrene, and changes in boundary layer height causes the styrene concentrations to vary by more than a factor of three over the course of the day.

Daily cycles in emissions can also contribute to diurnal patterns in air toxic concentrations. At the downtown site, concentrations of air toxics associated with mobile source emissions begin increasing around four in the morning, reaching a peak around seven in the morning. The ethylbenzene concentrations plotted in Figure 4.10 provide the clearest example of this pattern. It is caused by the combined effects of varying emissions and varying boundary layer height. Motor vehicle use begins increasing in the very early in the morning, but the peak air toxic concentrations do not correspond to the peak in traffic volume because of the strong influence of boundary layer height on pollutant concentrations. A much weaker peak can also be observed in the afternoon for benzene, toluene, and ethylbenzene. This peak is presumably caused by the evening rush hour. It is much smaller than the morning peak because of the large difference in boundary layer height. Another factor may be evening rush hour may be spread out over a longer period of time than the morning rush, essentially dispersing the emissions in time.

Concentrations of several chlorinated air toxics also exhibit distinctive diurnal patterns. For example, tetrachloroethene concentrations at the Diamond Building have a unique diurnal pattern. There is a spike in the early morning mirroring the spike in mobile source air toxics concentrations and a second peak between around 10 AM and 2 PM. Tetrachloroethene is used as a solvent by dry cleaners; mobile sources are not a source of chlorinated air toxics.

At the Avalon site, the mixing layer height has a strong effect on concentrations of chloroform, ethylbenzene and toluene but not on benzene. Local emissions of benzene appear to increase concentrations during midday.

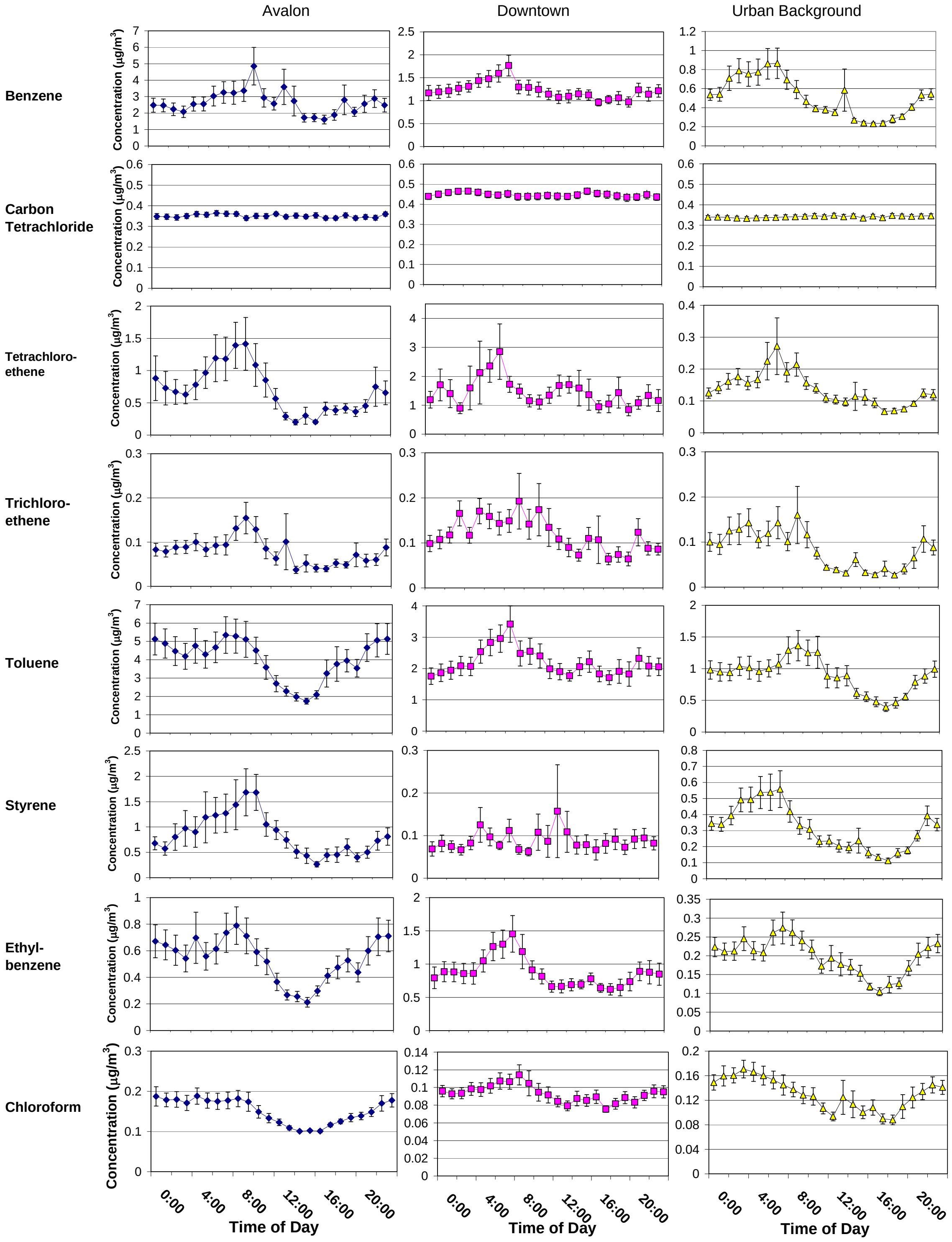


Figure 4.10 Average diurnal profiles of air toxic concentrations at the three intensive sites. Symbols indicate the mean concentration at each hour and error bars represent 95th percentile confidence interval on the mean. Note that concentration scale changes between sites.

The magnitude of the diurnal variations at the Carnegie Mellon University site was significantly smaller compared to those in Avalon or downtown. For example, only minor diurnal patterns can be seen for mobile compounds. This underscores that emissions from very local sources are a large contributor to air toxic concentrations at the Carnegie Mellon University site.

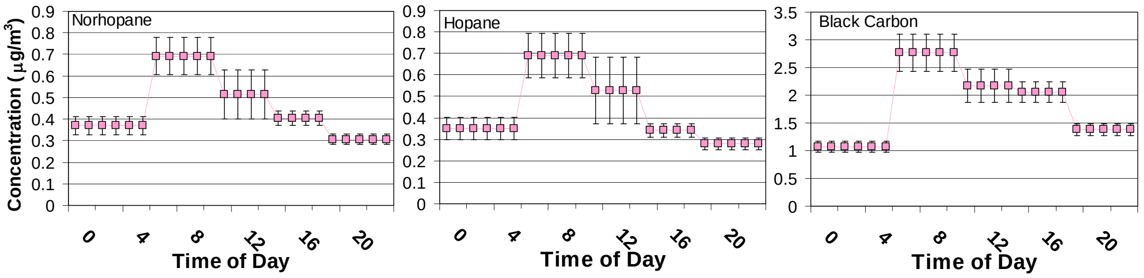


Figure 4.11 Average diurnal profiles of condensed phase compounds associated with motor vehicle emissions measured at the Diamond Building. Symbols represent the mean concentration and error bars represent the standard error of the mean. Note that concentration scale changes between sites.

4.3.3 Seasonal Patterns of Air Toxics Concentrations

We analyzed the baseline data for seasonal patterns in air toxic concentrations. Figure 4.12 plots seasonal average concentrations for a few air toxics with interesting seasonal patterns. Concentrations of most toxics did not exhibit a statistically significant seasonal pattern.

Seasonal patterns (or the lack thereof) provide insight into the sources of air toxics that are both directly emitted by sources and photochemically produced in the atmosphere. Formaldehyde and acetaldehyde are examples of two toxics with primary and secondary sources. Figure 4.12 indicates that formaldehyde concentrations were substantially higher during the summer than during other seasons at all four baseline sites. There is a significant increase in photochemical production in the summer. Therefore, atmospheric oxidation of volatile organic compounds is an important source of formaldehyde in Allegheny County. In contrast, acetaldehyde does not exhibit any seasonal pattern; therefore primary emissions (presumably motor vehicles) are the dominant source of acetaldehyde in Allegheny County.

Figure 4.12 indicates that propionaldehyde concentrations also exhibited a distinctive seasonal pattern. Propionaldehyde concentrations were about a factor of two higher at the four baseline sites in the fall than during other seasons. Biomass burning is one source of propionaldehyde. Previous research has shown the highest levels of biomass smoke in Allegheny County occur in the fall (23).

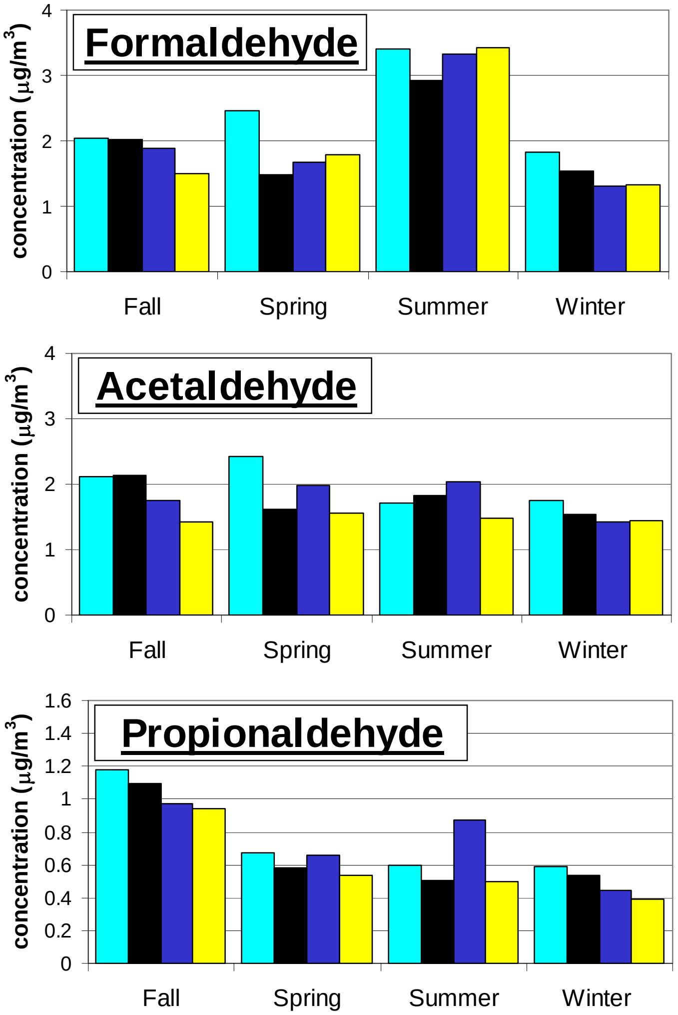


Figure 4.12 Seasonal patterns of selected air toxics measured during the baseline study.

4.4 Chlorinated Compounds

Several chlorinated air toxics posed large cancer risks downtown, but not at the other baseline sites. Many of these chlorinated compounds are commonly used as solvents, but this project has not been able to define the emission sources of many of these toxics. This section presents data on temporal and wind direction patterns for selected chlorinated toxics in the downtown area.

Trichloroethene: Trichloroethene is estimated to pose a lifetime cancer risk of 2 x 10^{-5} at the Flag site, which is about a factor of twenty higher than cancer risk it poses at any other site. Figure 4.13 shows a time series of trichloroethene measured at the Flag Plaza site over a ten year period. Trichloroethene concentrations at this site are highly variability, with most of the exposure being driven by short periods of days or months with relatively elevated concentrations.

High concentrations of trichloroethene were not observed during the intensive study at the Diamond Building which is about 1/2 km from Flag Plaza. However, Figure 4.13 indicates trichloroethene concentrations were also low at Flag Plaza during this study (first six months of 2008). Therefore, the spatial extent of the trichloroethene hotspot in the downtown area is not well understood. It could be extremely localized around the Flag Plaza area or it could affect the larger downtown area.

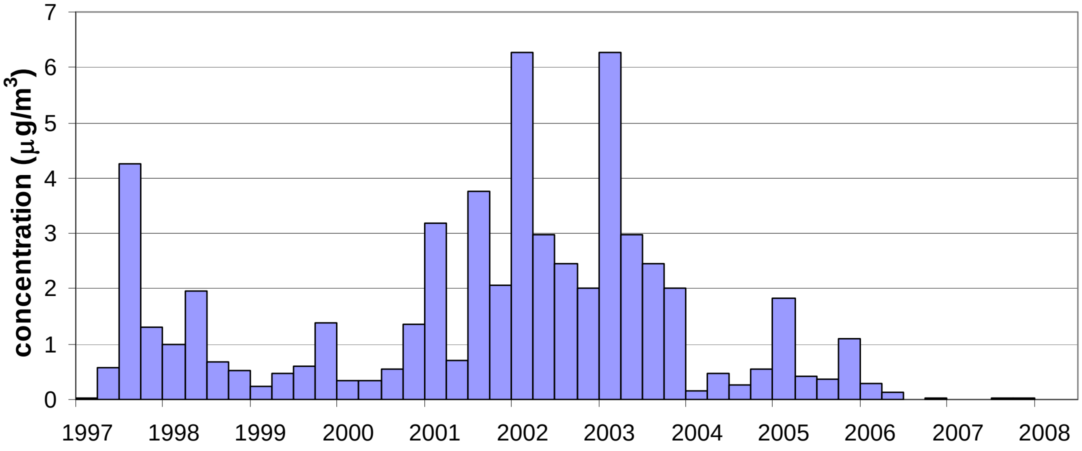


Figure 4.13 Quarterly average concentrations of trichloroethene measured at the Flag Plaza site from 1997 to the second quarter of 2008.

1,4-Dichlorobenzene: 1,4-dichlorobenzene is another chlorinated toxic that posed substantially higher risks downtown than at the other baseline sites. Of the 36 target organic air toxics, 1,4-dichlorobenzene poses 9% of the cancer risks downtown versus 1-2% of the risks at the background and industrial influence sites (Avalon and Stowe). Elevated concentrations of 1,4-dichlorobenzene were also observed during the intensive study at the Diamond Building indicating that the problem is not localized to the Flag Plaza site.

The intensive data at the Diamond Building indicate that 1,4-dichlorobenzene concentrations downtown have distinctive temporal and wind directional patterns. Figure 4.14 indicates that

1,4-dichlorobenzene concentrations increase at night with a rapid decrease in concentrations when the boundary layer breaks up in the morning. In addition, it also exhibits a distinctive weekday/ weekend pattern. Both of these features are characteristic of pollutant with a local source.

Figure 4.15 plots the average 1,4 dichlorobenzene concentrations measured at the Diamond Building as a function of wind direction. Concentrations are much higher when the wind is from the south and southeast. Figure 4.15 also indicates the location of the only two point sources that report 1,4-dichlorobenzene emissions in Allegheny County.

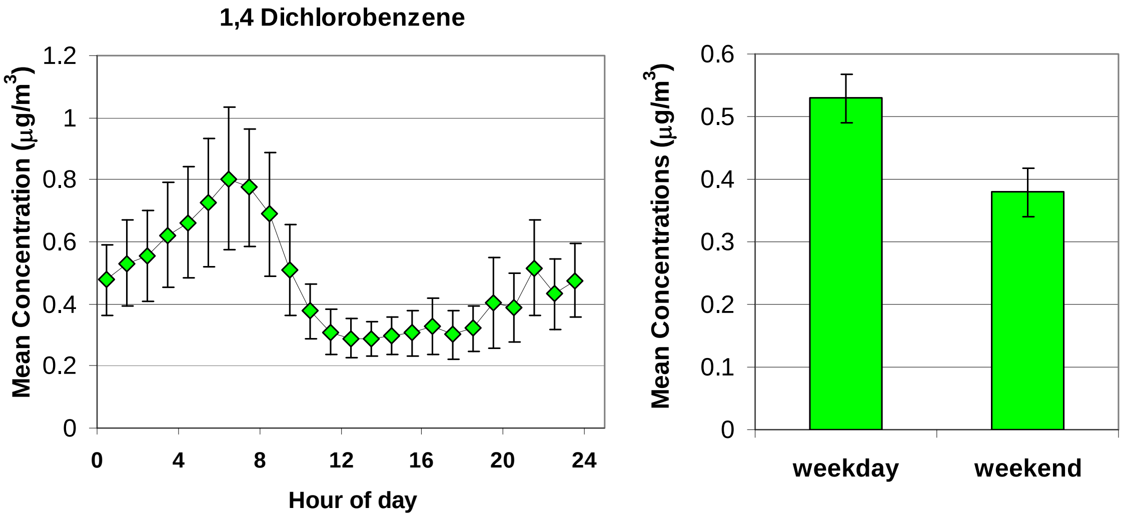


Figure 4.14 1,4 dichlorobenzene exposure by day of the week and the average concentration by hour of the day.

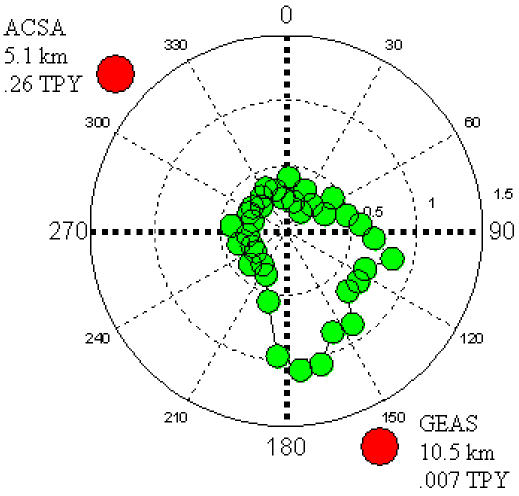


Figure 4.15 1,4-dichlorobenzene concentrations as a function of wind direction. Also shown are the location and distance to the two point sources that report 1,4-dichlorobenzene emissions in Allegheny County.

Methylene chloride: Although methylene chloride risks in Allegheny County are low, methylene chloride concentrations downtown are comparable to the national 75th percentile. Figure 4.16 indicates that these high concentrations are associated with a source located to the south or east of the Diamond Building. Methylene chloride also has a distinctive weekend/ weekday pattern.

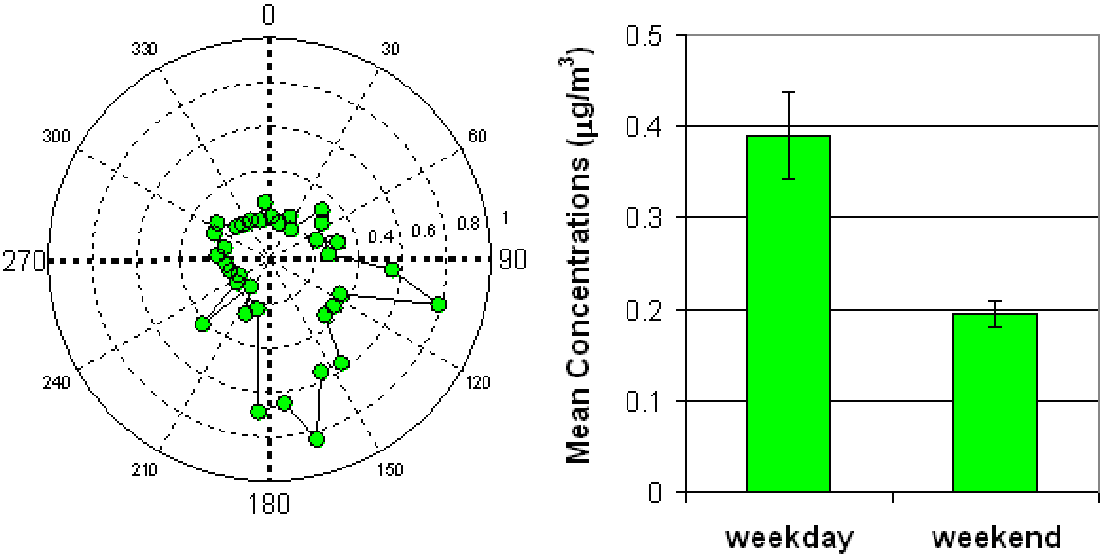


Figure 4.16 On the left is the average concentration of methylene chloride as a function of wind direction. On the right is the average concentration during the week and weekend. The error bars indicate the 95th percentile confidence intervals of the mean.

Chapter 5. Receptor Modeling of Air Toxic Concentrations and Risks

One of the main goals of this project was to identify the sources of priority air toxics in Allegheny County. The high time resolved measurements from the intensive studies are ideally suited for source apportionment because they resolve plume events helping to pinpoint source locations. In this chapter a receptor model was used to apportion 27 air toxics and 13 volatile organic compounds (VOCs) to sources.

5.1 Cancer Risk from Baseline and Intensive Studies

Before presenting the source apportionment results we compare the cancer risks estimated from the baseline and intensive datasets. This comparison is important because the source apportionment modeling was performed on the high time resolved data collected during the intensive studies. These data were collected over a much shorter period and therefore may not accurately represent chronic risks.

Figure 5.1 compares the risk profiles from the intensive and baseline studies for the subset of the compounds included in the source apportionment model. There is excellent agreement between the two risk profiles for the Avalon site. Therefore the intensive sampling was long enough to accurately characterize chronic risks at this site.

Figure 5.1 indicates that there is only reasonable agreement between the risk profiles derived from the other two sets of data. This is not surprising since the intensive and baseline studies conducted to characterize background and downtown air toxic concentrations were not made at the same sites. The background intensive site was located at Carnegie Mellon University, 13.4 miles away from the baseline background site, South Fayette. The downtown intensive site was located in the Diamond Building, 1.2 km away from the Flag Plaza site used for the baseline study.

The main differences between the risk profiles at the two downtown sites are associated with chlorinated air toxics. The cancer risks associated with trichloroethene are much lower and the cancer risk associated with tetrachloroethene is much higher at the Diamond Building compared to Flag Plaza. The major differences between the risk profiles at the two background sites are associated with benzene and chloroform. Given the good agreement between the baseline and intensive risk profiles for Avalon, we suspect that the downtown and background differences are mainly due to the different measurement locations.

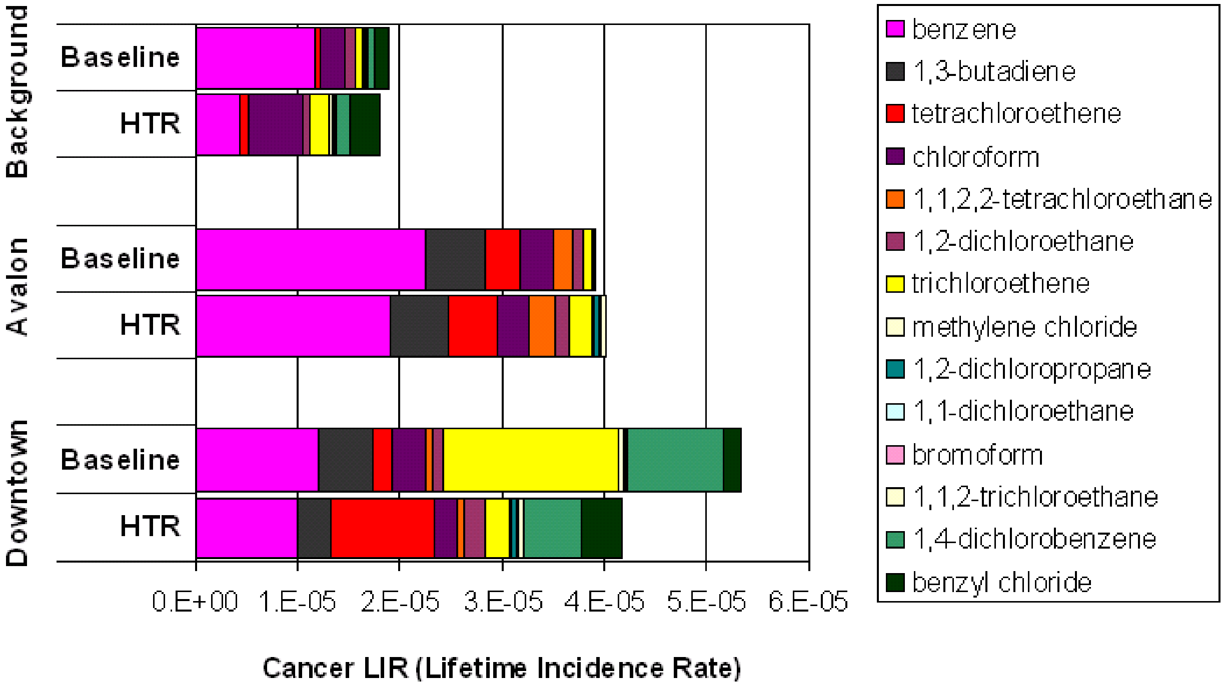


Figure 5.1 Comparison of calculated cancer risks from intensive and baseline studies.

5.2 Receptor Modeling

5.2.1 Positive Matrix Factorization (PMF)

We used the two-way factor analytic model PMF2 to analyze the hourly data measured during at each of the intensive campaigns (24). PMF2 is a factor analysis program with a non-negativity constraint that is commonly used to analyze air quality data (25-32). PMF solves the equation:

$$X = GF + E \tag{5.1}$$

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

$$Q = \sum \sum (e_{ij} / s_{if})^2 \qquad (5.2)$$

Two important user inputs for PMF analysis are the number of factors and the degree of matrix rotation. These parameters were systematically varied and a number of diagnostic tools were used to select the optimum solution.

Interpretability was the key basis for judging the optimum values for the number of factors and degree of matrix rotation. Interpretability was assessed by examining factor contributions as a function of wind direction and comparing factor profiles with actual source profiles. For example, factor contributions that are strongly correlated with wind direction can point directly to the source of the emissions. Weekend/weekday patterns can help identify whether the factor is associated with an industrial or mobile source. Factor profiles were compared to source profiles from the ACHD point source emission inventory (1), the EPA Mobile Source Air Toxics website (5) and the literature(33-38). We also considered several measures of statistical quality of the fit including included plotting the maximum individual column mean of the residual matrix, IM, as a function of the maximum individual column standard deviation, IS; examining the largest element in the rotmax matrix; miminizing the Q value, and G-space mapping (39). However multiple solutions satisfied these statistical tests.

5.2.2 Pollutants Apportioned Using PMF

Table 5.1 lists the compounds included in the PMF analysis. Separate analyses were performed for each intensive site, and slightly different sets of pollutants were included in the PMF models for each site.

PMF identifies factors based on varying pollutant concentrations. Therefore, only air toxics with significant spatial and/or temporal concentration variations were included in the model. Although this represents only a subset of the air toxics measured by this study, toxics with time varying concentrations are the ones strongly influenced by emissions from local sources. The sources of other air toxics not included in the PMF model are discussed in Chapter 8.

Table 5.1 Pollutants included in PMF analysis

		Avalon	Downtown	Background
benzene	Air Toxic	X	X	X
benzyl chloride	Air Toxic	-----	-----	X
bromoform	Air Toxic	X	X	X
butadiene, 1,3-	Air Toxic	-----	X	-----
carbon disulfide	Air Toxic	X	X	X
chlorobenzene	Air Toxic	X	X	X
chloroform	Air Toxic	X	X	X
dibromoethane, 1,2-	Air Toxic	X	-----	-----
dichlorobenzene, 1,4-	Air Toxic	-----	X	X
dichloroethane, 1,1-	Air Toxic	X	X	X
dichloroethane, 1,2-	Air Toxic	-----	X	X
dichloroethene, 1,1-	Air Toxic	-----	-----	X
dichloropropane, 1,2-	Air Toxic	X	-----	-----
ethylbenzene	Air Toxic	X	X	X
hexane	Air Toxic	X	X	X
methylene chloride	Air Toxic	X	X	X
MIBK	Air Toxic	-----	X	X
MTBE	Air Toxic	-----	X	-----
styrene	Air Toxic	X	X	X
tetrachloroethane, 1,1,2,2-	Air Toxic	X	-----	-----
tetrachloroethene	Air Toxic	X	X	X
toluene	Air Toxic	X	X	X
trichloroethane, 1,1,1-	Air Toxic	X	X	X
trichloroethane, 1,1,2-	Air Toxic	X	X	-----
trichloroethene	Air Toxic	X	X	X
xylene, m/p-	Air Toxic	X	X	X
xylene, o-	Air Toxic	X	X	X
acetone	VOC	X	X	X
bromodichloromethane	VOC	-----	X	X
cyclohexane	VOC	X	X	X
dibromochloromethane	VOC	X	X	X
dichlorobenzene, 1,2-	VOC	X	X	-----
dichloroethene, cis-1,2-	VOC	X	-----	-----
dichloropropene, cis-1,3-	VOC	X	-----	-----
ethyltoluene, 4-	VOC	X	X	X
heptane	VOC	X	-----	X
MBK	VOC	-----	X	-----
MEK	VOC	X	X	X
trimethylbenzene, 1,2,4-	VOC	X	X	X
trimethylbenzene, 1,3,5-	VOC	X	X	X

5.2 Avalon PMF solution

A five-factor solution with a -10 rotation provided the most interpretable solution for the Avalon intensive data set. Figure 5.2 plots the average contribution of each factor to each species. Figure 5.3 shows the apportionment of the additive cancer risk for the air toxics included in the PMF model to the five factors; two of the factors contribute more than 75% of the cancer risks.

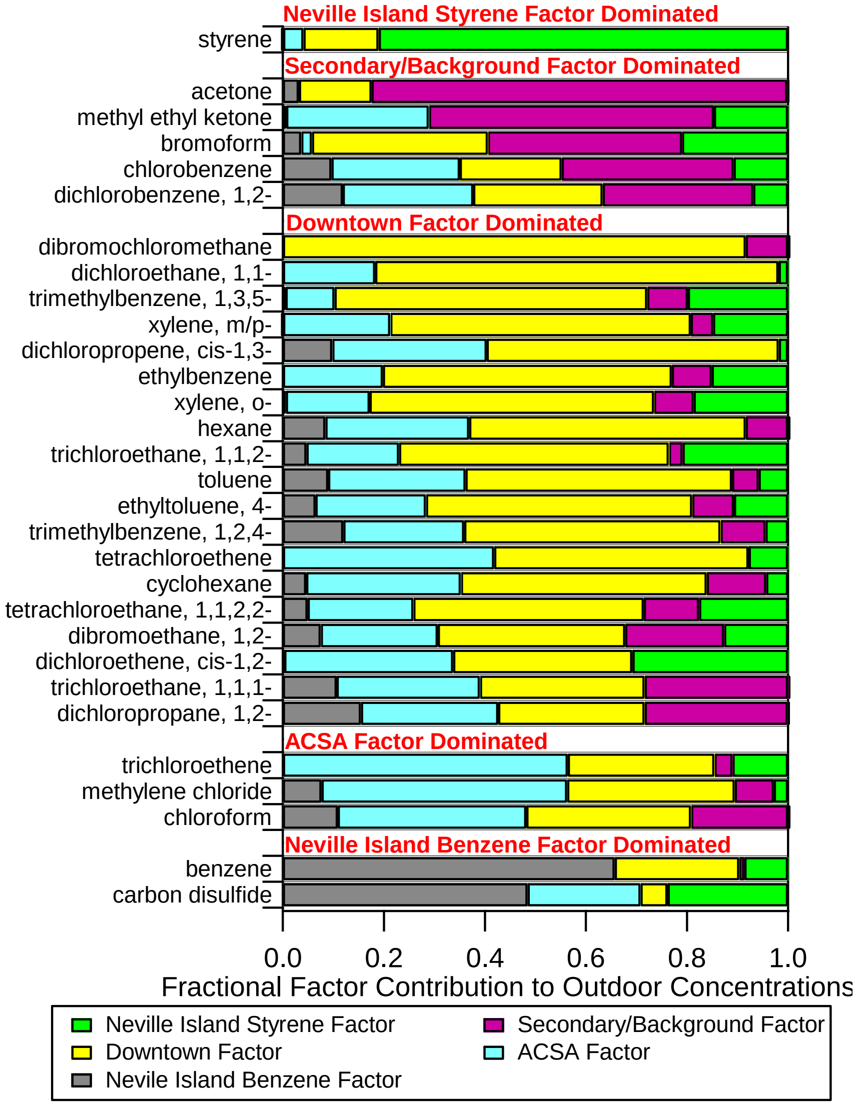


Figure 5.2 Factor contributions to air toxic concentrations at the Avalon site.

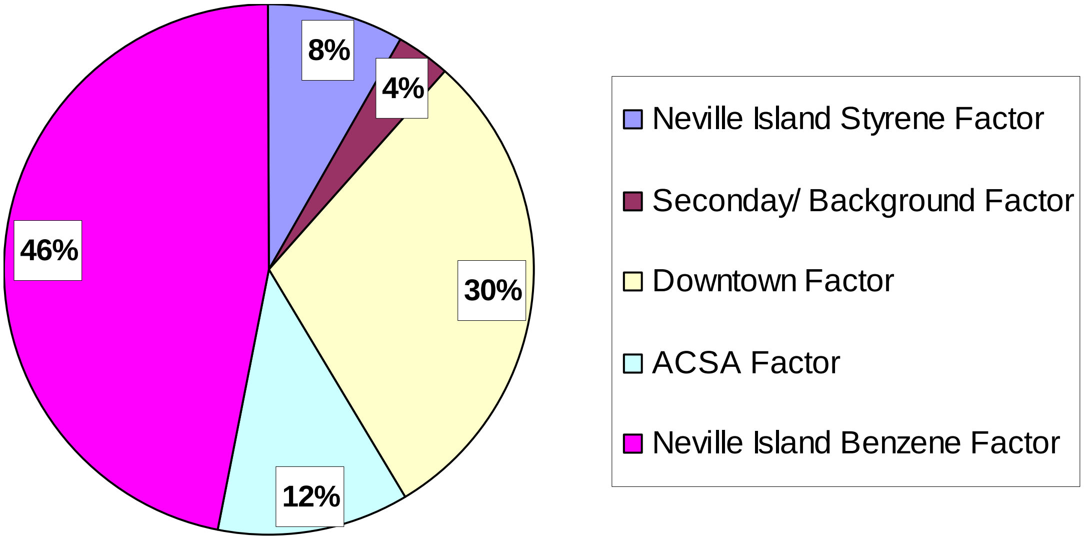


Figure 5.3 Apportionment of cancer risk for the Avalon site.

Neville Island Benzene Factor: One factor contributed 66% of the benzene and nearly half of the risks at Avalon site. Two pieces of evidence strongly link this factor with emissions from Shenango Coke Works on Neville Island. First, Figure 5.4 shows that the contribution of this factor is extremely wind directionally dependent with its contributions being significantly elevated when wind is coming from the Shenango Coke Works on Neville Island, a large source of benzene (1). Second, Figure 5.6 indicates excellent agreement between the benzene factor profile and the Shenango source profile. Finally, Figure 5.5 indicates that there is no weekend/weekday pattern in the contribution of this factor, consistent with an industrial source that operates all of the time. Therefore, this factor appears associated with emissions from industrial sources on Neville Island, specifically the Shenango Coke Works.

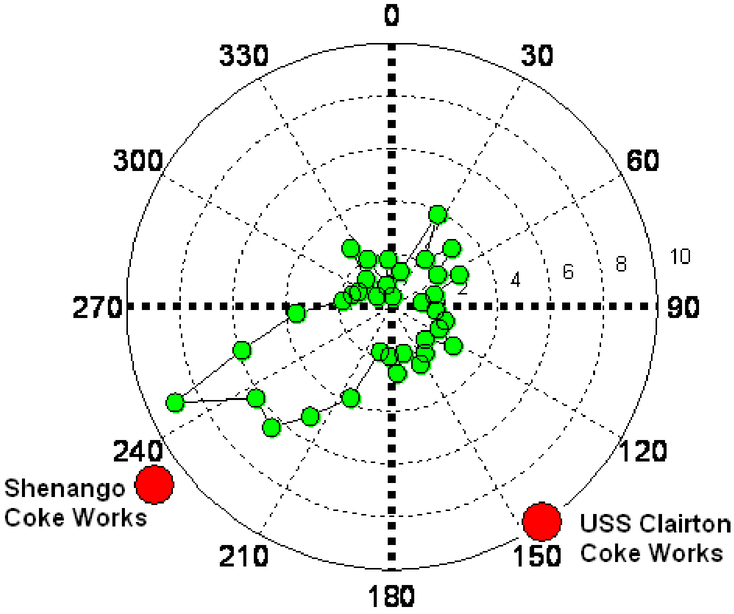


Figure 5.4 Mean contribution for Benzene factor as a function of wind direction.

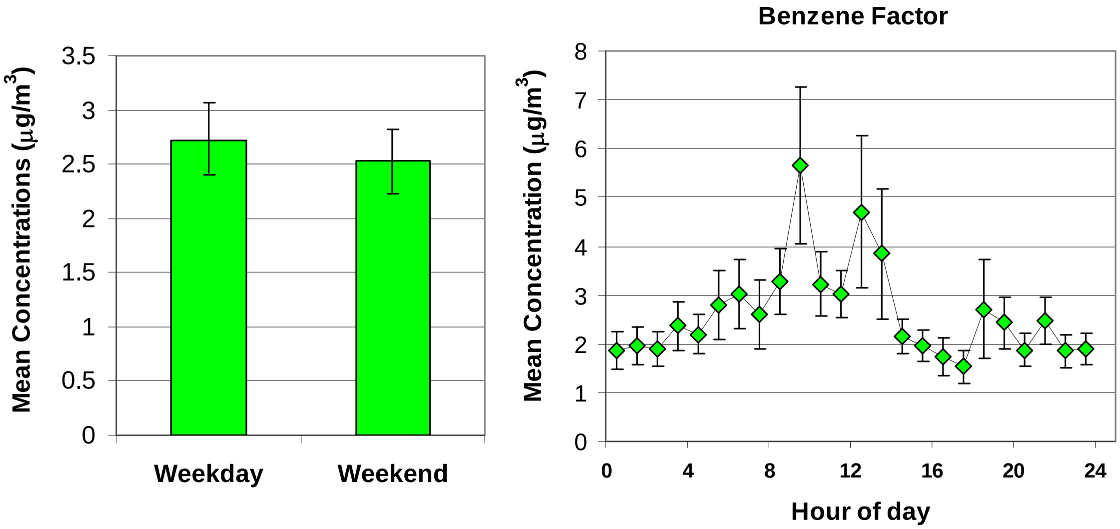


Figure 5.5 Diurnal patterns of factor contribution and factor contribution as a function of day of the week for the Benzene factor.

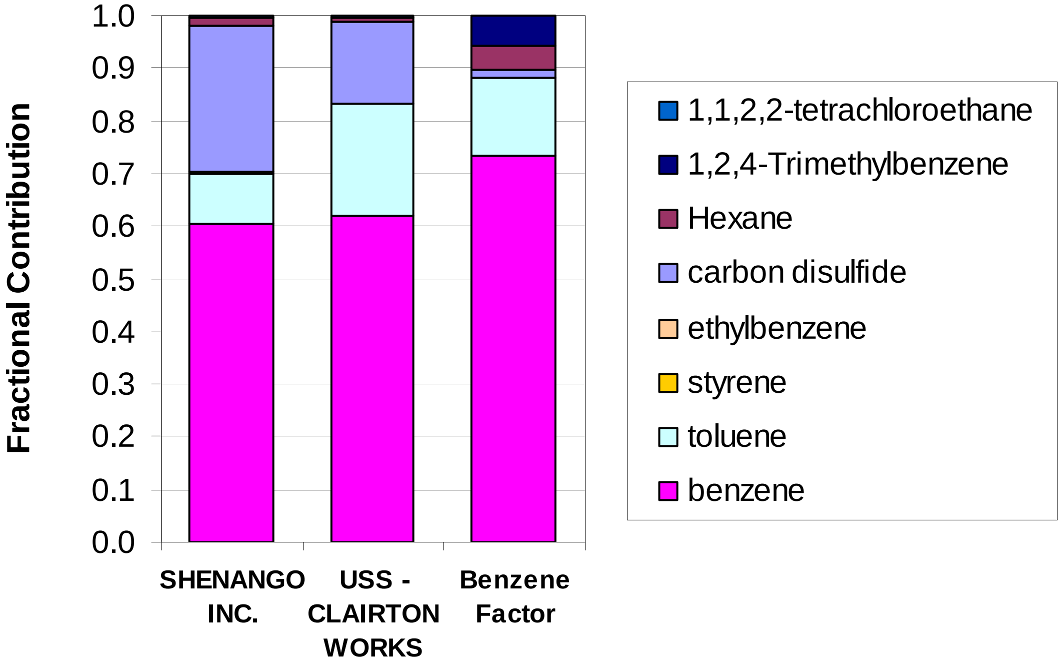


Figure 5.6 Comparison of the Neville Island Benzene Factor to emission profiles for two coke works in Allegheny County. Shenango is located on Neville Island near Avalon and Clairton is the largest coke works in Allegheny County.

Downtown Factor: The downtown factor is the second largest contributor to risks in Avalon. This factor was named the downtown factor because its contribution was elevated when the wind was coming from the east, the direction of downtown Pittsburgh (Figure 5.7). The downtown factor contributes 53%, 60%, and 25% of toluene, xylenes and benzene in Avalon, respectively. All of these compounds are emitted by mobile sources.

Figure 5.8 compares the species distribution in the downtown factor to gasoline and diesel vehicle source profiles. The downtown factor profile agrees well with the gasoline vehicle source profile. Therefore, we associated this factor with gasoline vehicle emissions. However, emissions of non-mobile source air toxics were also apportioned to this factor. For example, the chlorinated compounds in this factor are from non-mobile sources in the downtown area. These chlorinated toxics are likely from sources in downtown Pittsburgh that are co-varying with the mobile source emissions. Sixty percent of the risks apportioned to the downtown factor come from mobile source air toxics and 40% come from chlorinated compounds.

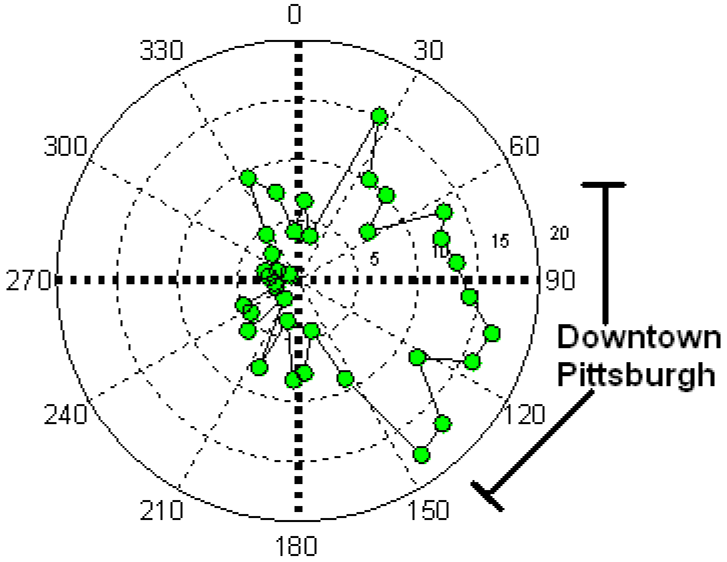


Figure 5.7 Mean factor contribution of the downtown factor in Avalon as a function of wind direction.

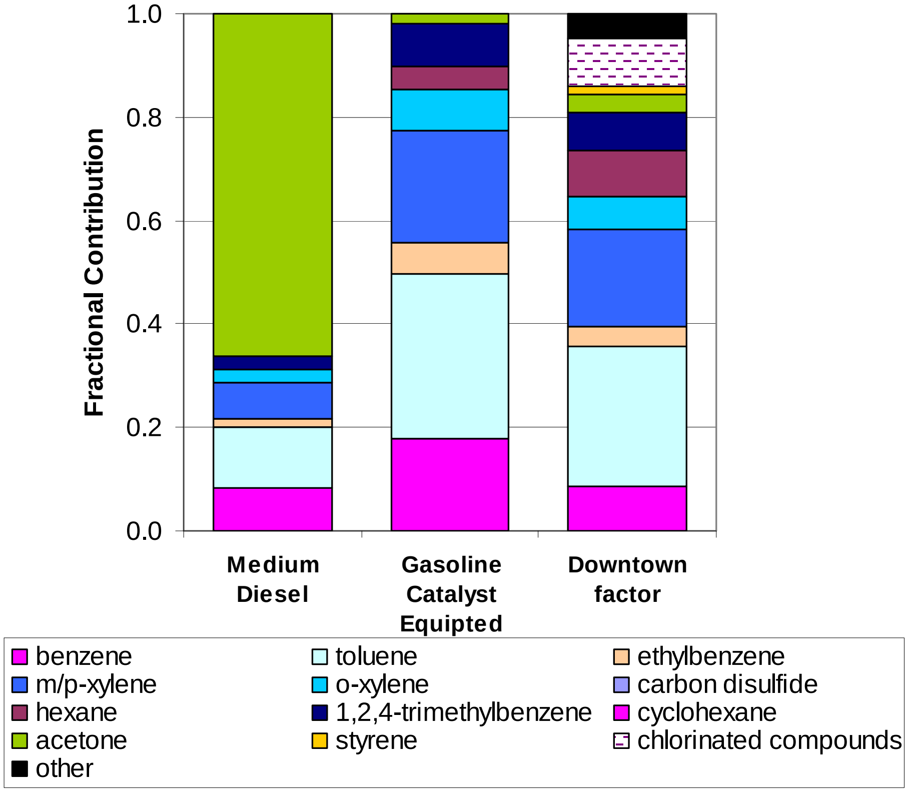


Figure 5.8 Comparison of the downtown factor to mobile source profiles (33, 34).

<u>ACSA Factor:</u> PMF apportioned 56% of the trichloroethene and 46% of the tetrachloroethene measured in Avalon to one factor. Two pieces of evidence strongly link this factor to emissions from the Allegheny County Sanitary Authority (ACSA). First, Figure 5.9 indicates that the factor profile closely matches the emissions profile from ACSA. Second, the factor contribution has a strong wind directional dependence with highest concentrations being associated with wind coming from the direction of ACSA, Figure 5.10. This factor contributes 12% of the additive cancer risk at the Avalon site.

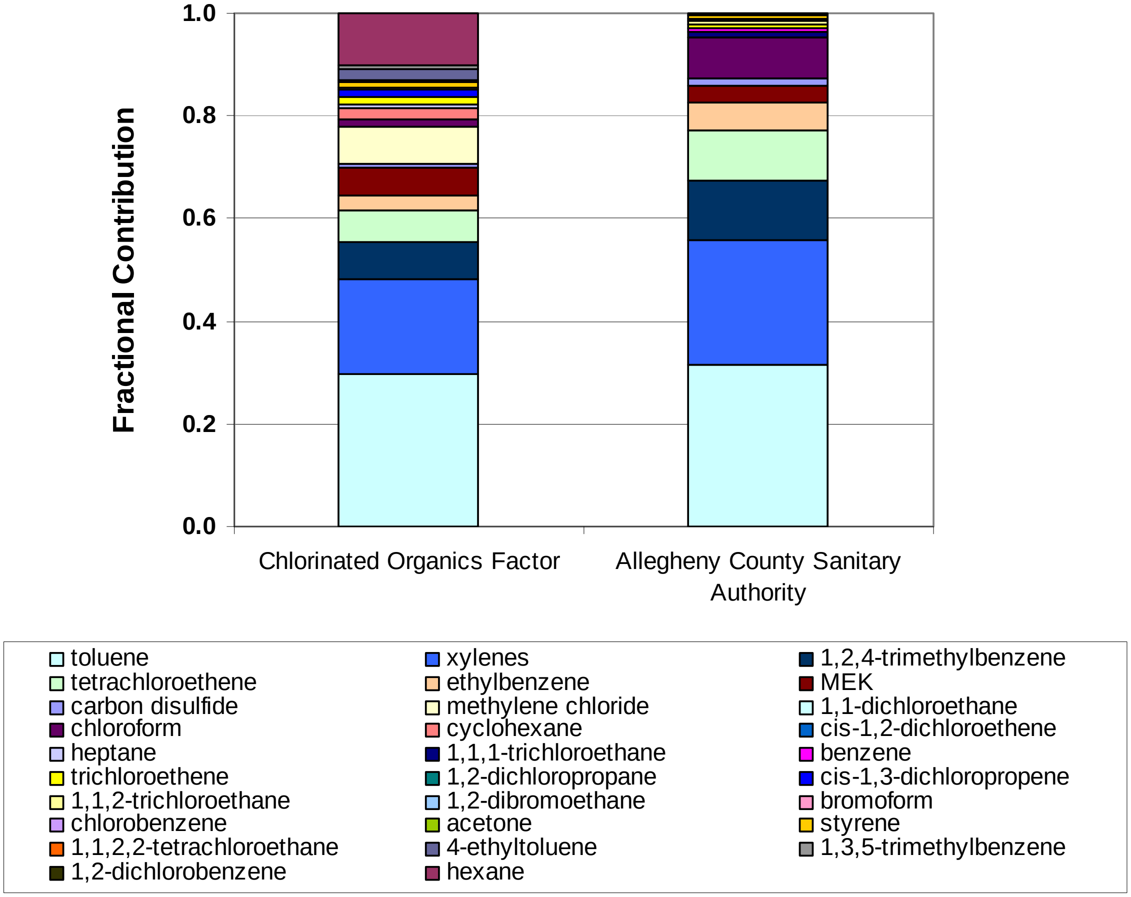


Figure 5.9 Comparison of Allegheny County Sanitary Authority emissions profile and the profile of the ASCA PMF factor

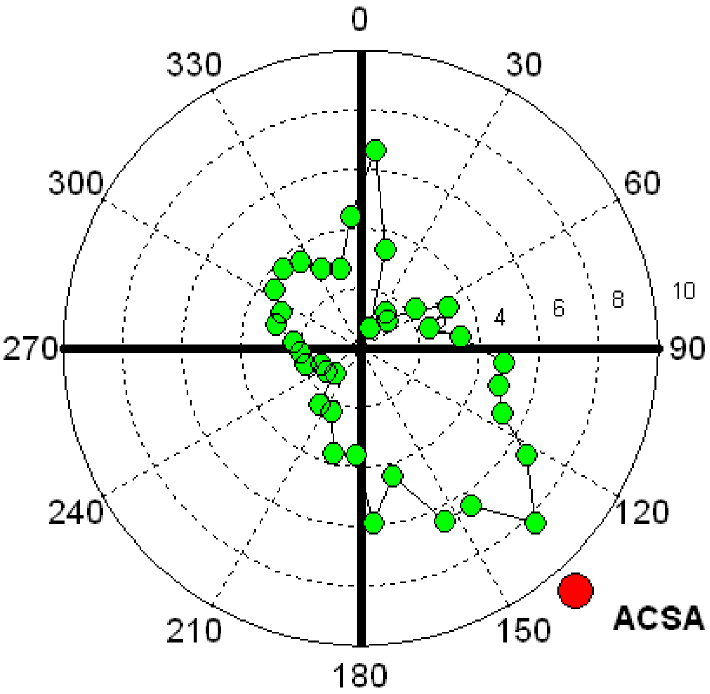


Figure 5.10 Mean concentration of the ACSA as a function of wind direction.

Neville Island Styrene Factor: One factor contributed almost 80% of the styrene and 8% of the cancer risk in Avalon. Figure 5.11 indicates that this factor contribution is higher when Avalon is downwind of Neville Island or downtown Pittsburgh. The contribution of this factor does not vary with day of the week (Figure 5.12) suggesting an industrial source. Its contribution varies diurnally increasing overnight followed by a rapid decrease associated with the break-up of the boundary layer in the morning.

Two large chemical companies are located on Neville Island, The Neville Chemical Company and Ashland Specialty Chemical Co. Both facilities are major sources of styrene (1). Figure 5.13 compares the factor profile of the Styrene factor to a composite source profile that is an emissions weighted average profile of these two facilities (1). There is excellent agreement with this factor and this composite source profile.

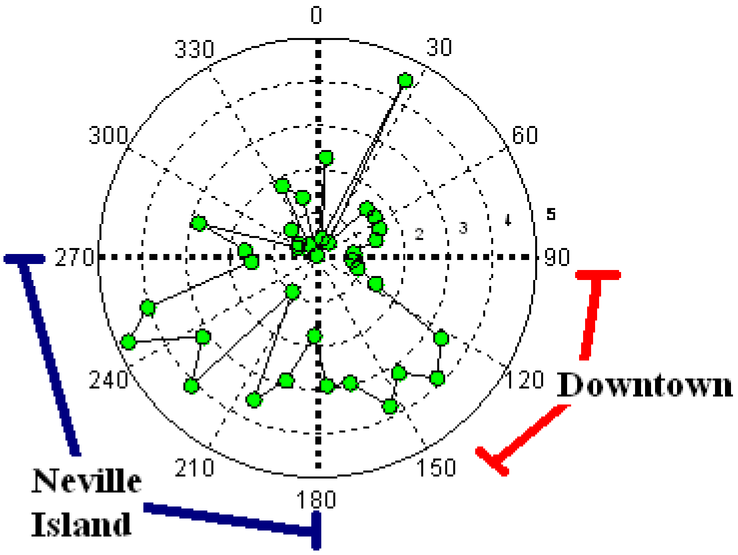


Figure 5.11 Mean contribution of styrene factor as a function of wind direction.

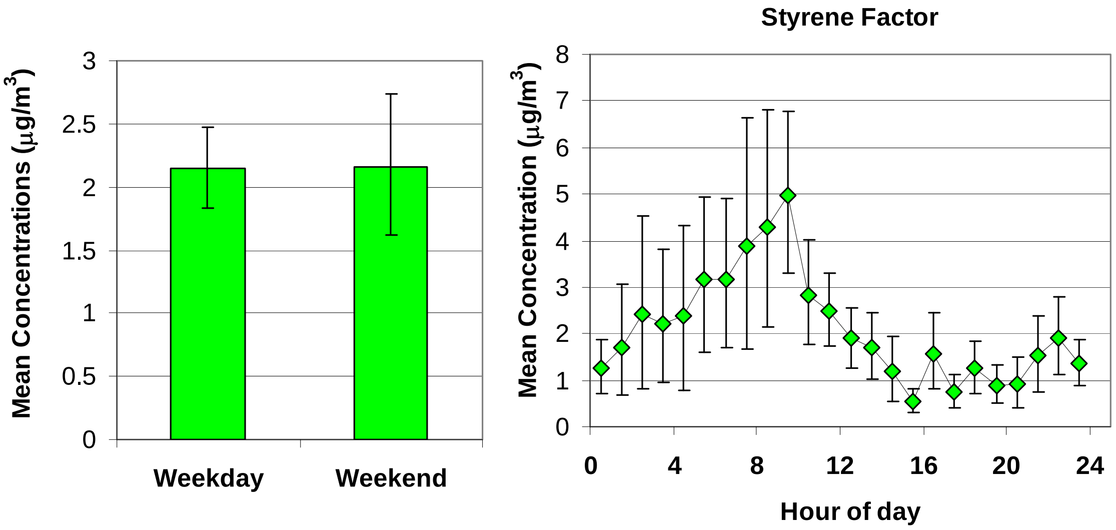


Figure 5.12 Diurnal patterns of factor contribution and factor contribution as a function of day of the week for the Styrene factor.

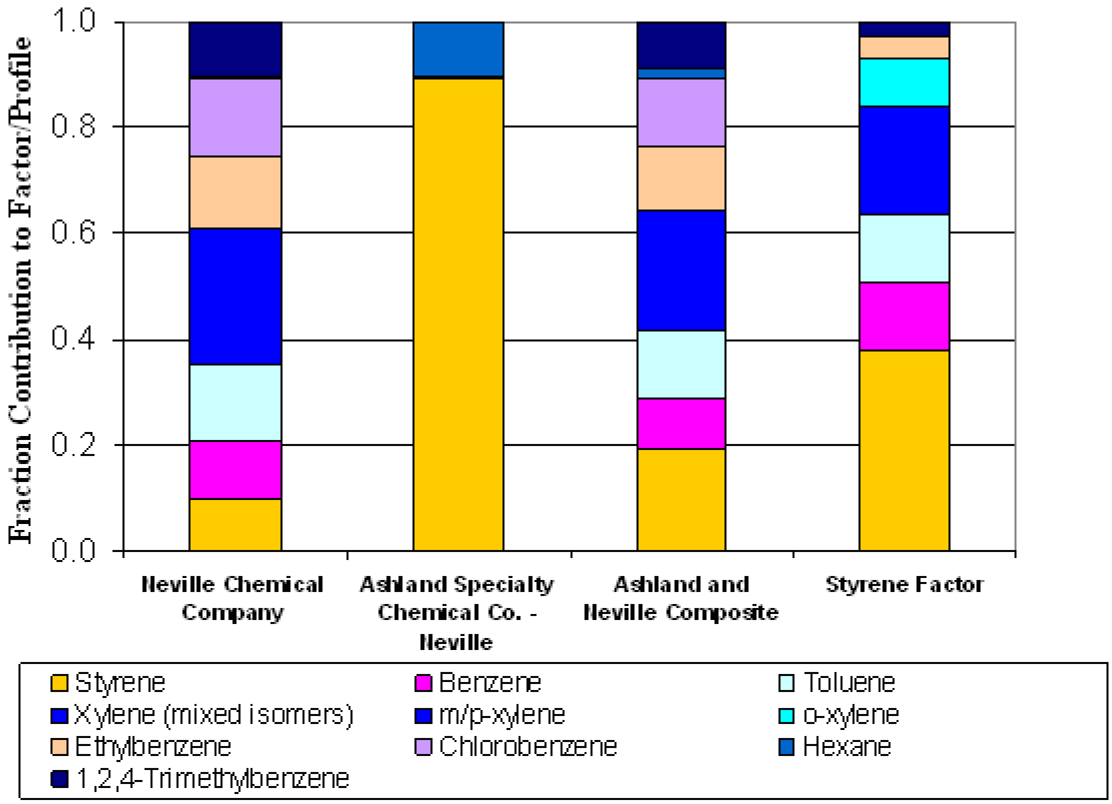


Figure 5.13 Comparison of large styrene emitting point source profiles and the profile of the Styrene Factor.

<u>Secondary/Background Factor:</u> PMF attributed the majority of the methyl ethyl ketone and acetone, two secondary components, to one factor. This factor shows no wind directional dependence or diurnal pattern (Figures 5.14 and 5.15) consistent with secondary sources. This factor is a minor contributor to risk.

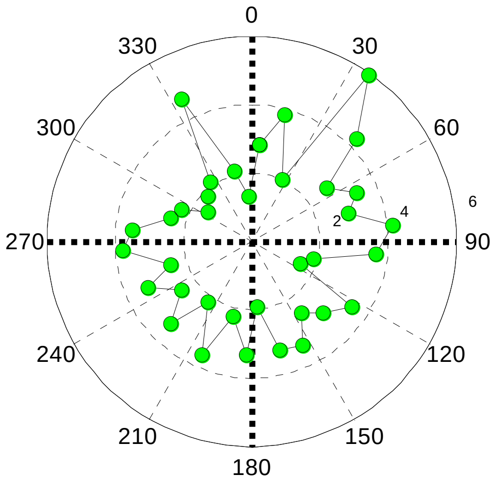


Figure 5.14 Mean concentration of secondary/background factor as a function of wind direction.

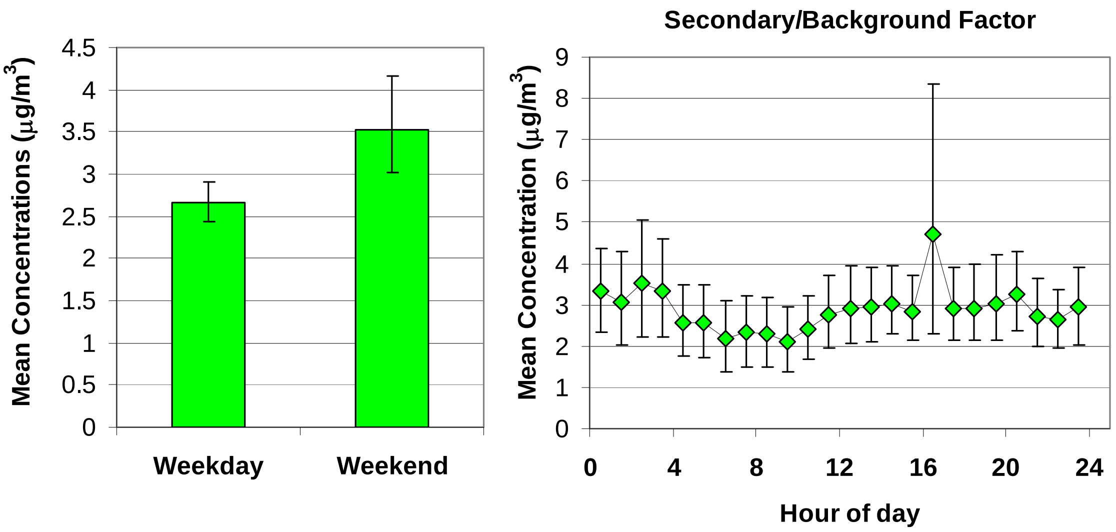


Figure 5.15 Diurnal patterns of factor contribution and factor contribution as a function of day of the week for the Secondary/Background Factor.

5.2.1 Discussion of Avalon PMF Results

The risk apportionment by PMF is summarized in Figure 5.16. First, the compounds included in the PMF model only contributed 34% of additive cancer risk of the 36 target organic air toxics. As previously discussed, only air toxics with significant temporal and/or spatial variability were included in the PMF model. These toxics are the ones that are strongly influenced by emissions from local sources. Chapter 8 synthesizes all of the risk estimates, quantifying the contribution of regional sources and other compounds not included in the PMF model.

Of the compounds included in the Avalon PMF model, Figure 5.16 indicates that PMF apportioned 55% of the additive cancer risk to emissions from sources on Neville Island. The majority of this risk is associated with emissions from the Shenango Coke Works (Neville Island benzene factor). Therefore, industrial facilities on Neville Island are not the only local sources of air toxics in Avalon. Emissions from downtown Pittsburgh and ACSA contributed 30% and 12% of the additive cancer risk, respectively.

The PMF results also highlight potential discrepancies in the reported emissions from industrial sites on Neville Island. According to the ACHD point source emissions inventory (1), both Shenango and Neville Chemical Company emit similar quantities of benzene per year, 2.96 TPY and 3.64 TPY, respectively. However, PMF apportioned seven times more benzene to the coke factor than the chemical company factor.

Figure 5.16 also shows that the PMF solution also provides insight into the relative importance of emissions from mobile, non-mobile, and regional sources in Avalon. Three of the factors are clearly associated with emissions from non-mobile or industrial sources: the two Neville Island factors and the ACSA factor. However, the downtown factor is a mixture of emissions from mobile and non-mobile sources. A reasonable assumption is to assign the risk contributed by Mobile Source Air Toxics (MSATs) (benzene toluene, etc. (5, 33, 34)) apportioned to the downtown factor to mobile source emissions and to attribute any remaining risk to non-mobile sources. This approach splits the risk apportioned to the downtown factor: 60% to mobile and 40% to non-mobile sources. Therefore, 79% of the cancer risk apportioned by PMF in Avalon is due to mobile sources and only 17% of the risks to non-mobile sources. Finally, Figure 5.16 indicates that the risks from non-mobile sources can be further broken done into specific sources with coke works emissions dominating non-mobile source contribution.

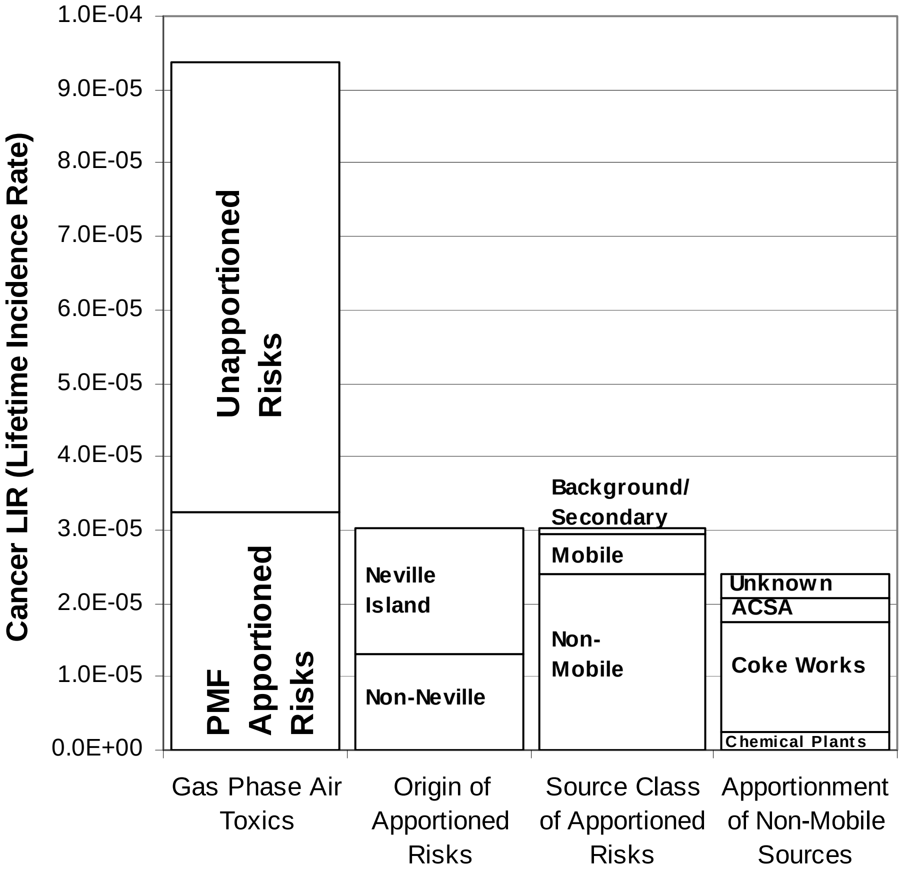


Figure 5.16 Apportionment of risk associated with 36 target gas phase organic air toxics.

5.3 Downtown PMF solution

Figure 5.17 shows the species apportionment for the most interpretable PMF solution for the downtown intensive data set. This was five-factor solution with a -8 rotation ; G-space mapping (1) showed that no two of the factors were highly correlated, indicating a good split.

Figure 5.18 shows the risk apportionment for the set of compounds included in the PMF model for the Diamond Building. Two of the factors contribute about 75% of the additive cancer risk for this set of air toxics, the southern toluene/benzene factor and the Pittsburgh factor.

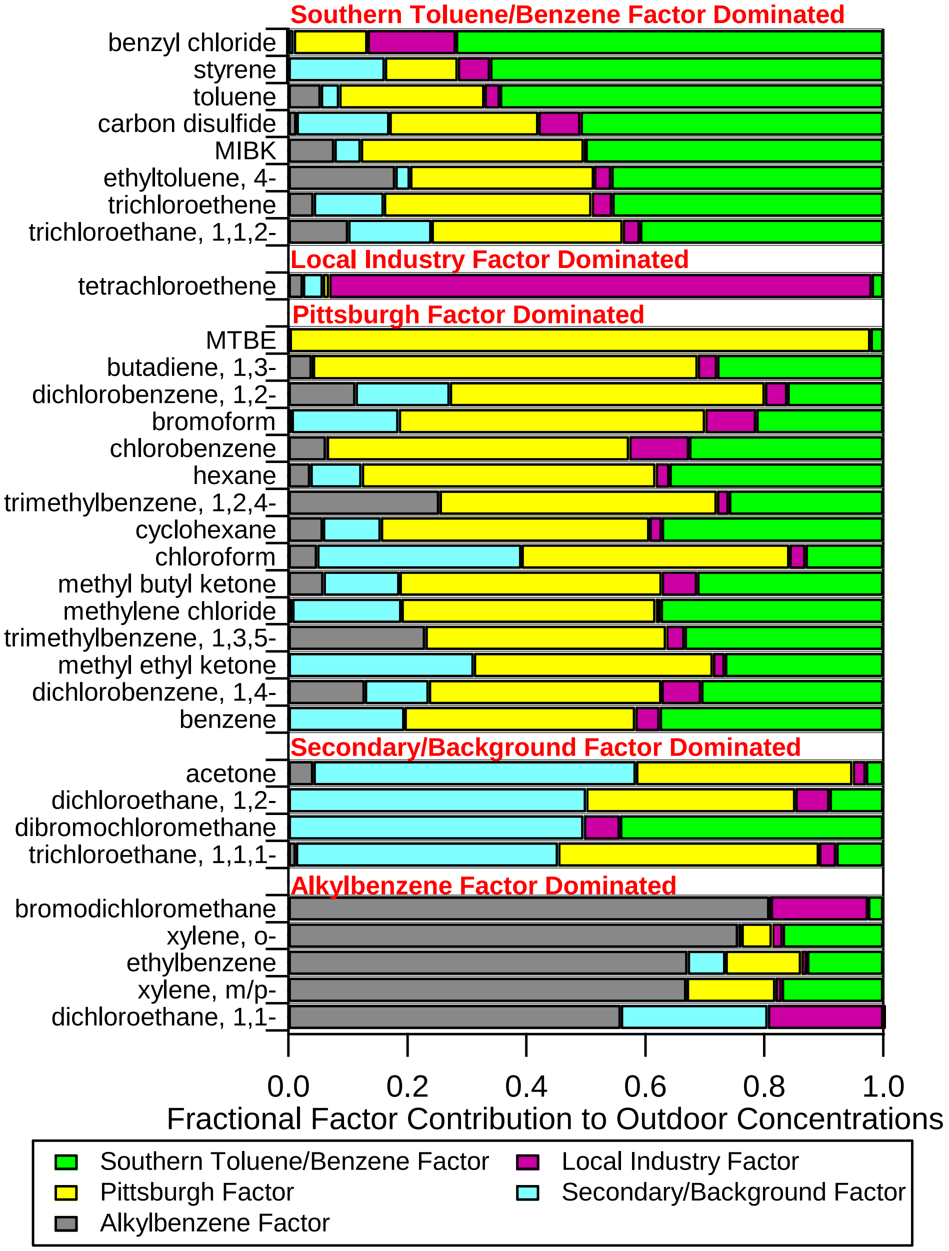


Figure 5.17 Factor contributions to individual compound concentrations at the downtown site.

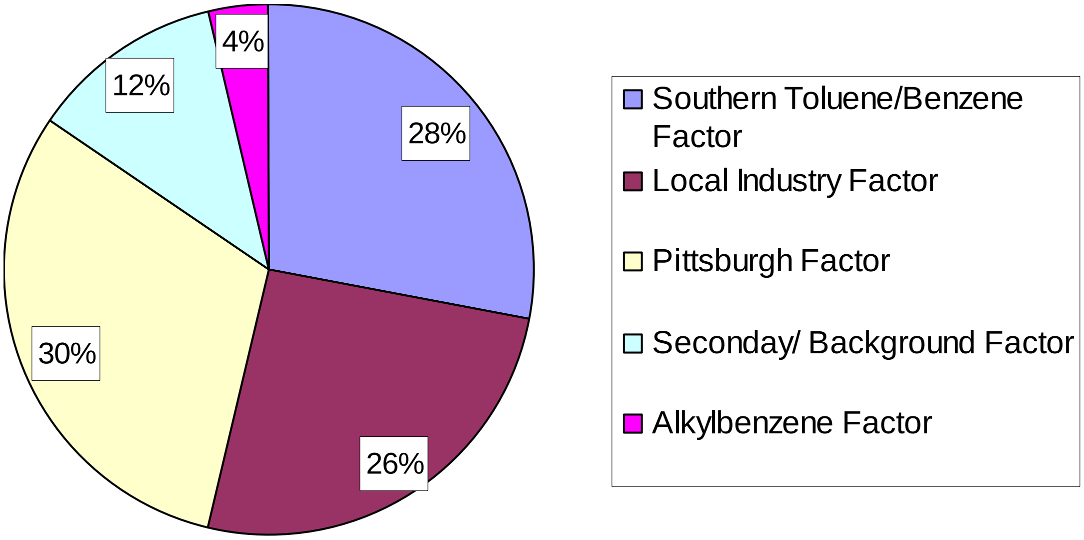


Figure 5.18 Risk apportionment at the Diamond Building site.

Pittsburgh Factor: Figure 5.17 indicates that PMF apportioned a complex mixture of 15 air toxics to one factor include many mobile and non-mobile air toxics. Figure 5.19 indicates that this factor was about 50% higher on weekdays than on the weekend. The wind directional dependence of the factor contribution was similar to black carbon, a marker for diesel vehicle emissions (Figure 5.20).

Figure 5.21 compares the Pittsburgh factor profile to diesel and gasoline vehicle source profiles (33, 34). The factor compares well to the diesel profile. The only major difference is that hexane levels are higher in the factor profile compared to the source profile. Therefore this factor appears to be primarily associated with mobile source emissions, or more specifically diesel emissions. Black carbon concentrations were 3.5 times higher downtown than at other sites in Pittsburgh (Figure 3.4).

Emissions from non-mobile sources are also apportioned to the Pittsburgh factor. For example, this factor contributes substantial amounts to several chlorinated air toxics such as 1,4 dichlorobenzene. For the Pittsburgh Factor, 55% of the risks appear to be from mobile sources and 45% of the risks were from non-mobile sources.

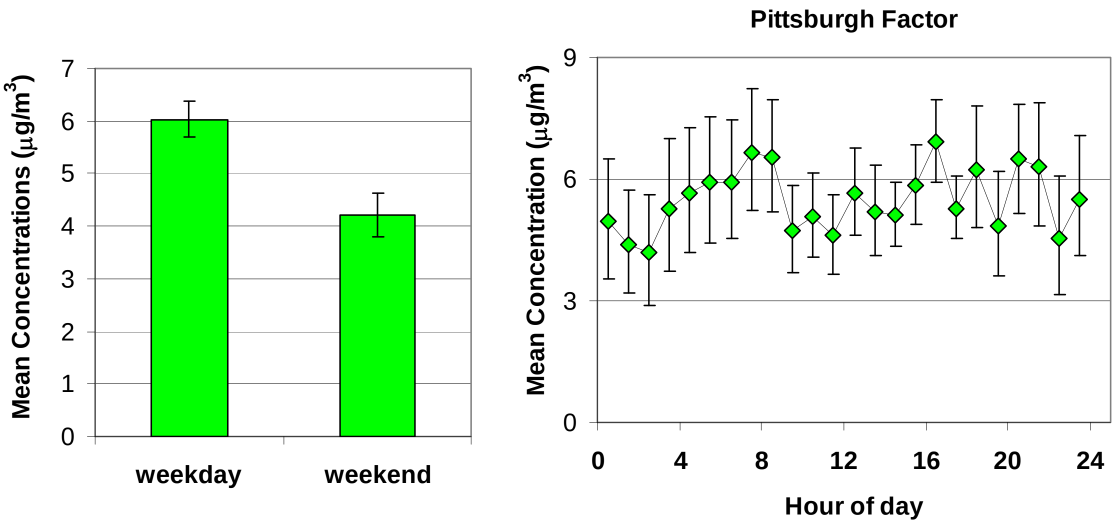


Figure 5.19 Average contribution of Pittsburgh Factor as a function of the day of the week or time of the day.

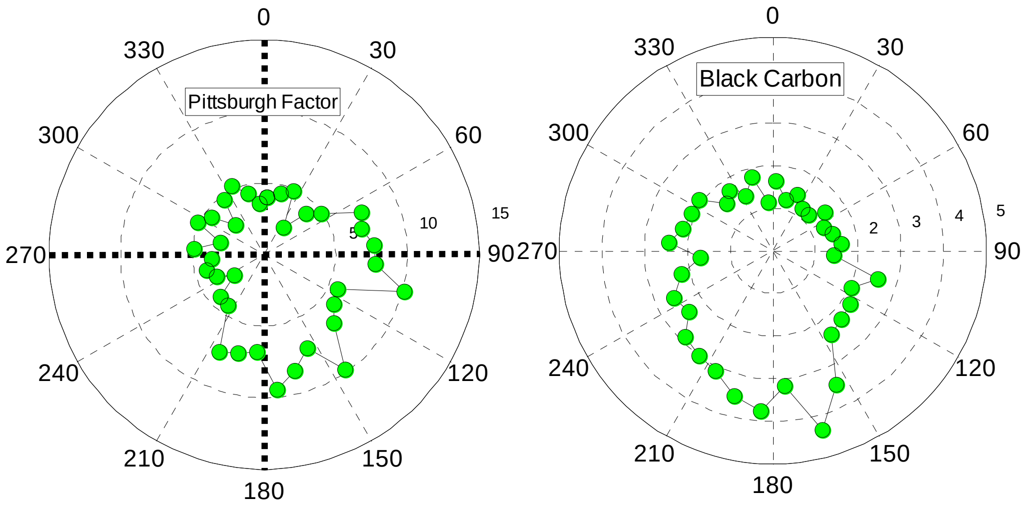


Figure 5.20 On the left is the mean concentration of the Pittsburgh factor as a function of wind direction. On the right is the mean concentration of black carbon (μg m^{-3}), BC, as a function of wind direction.

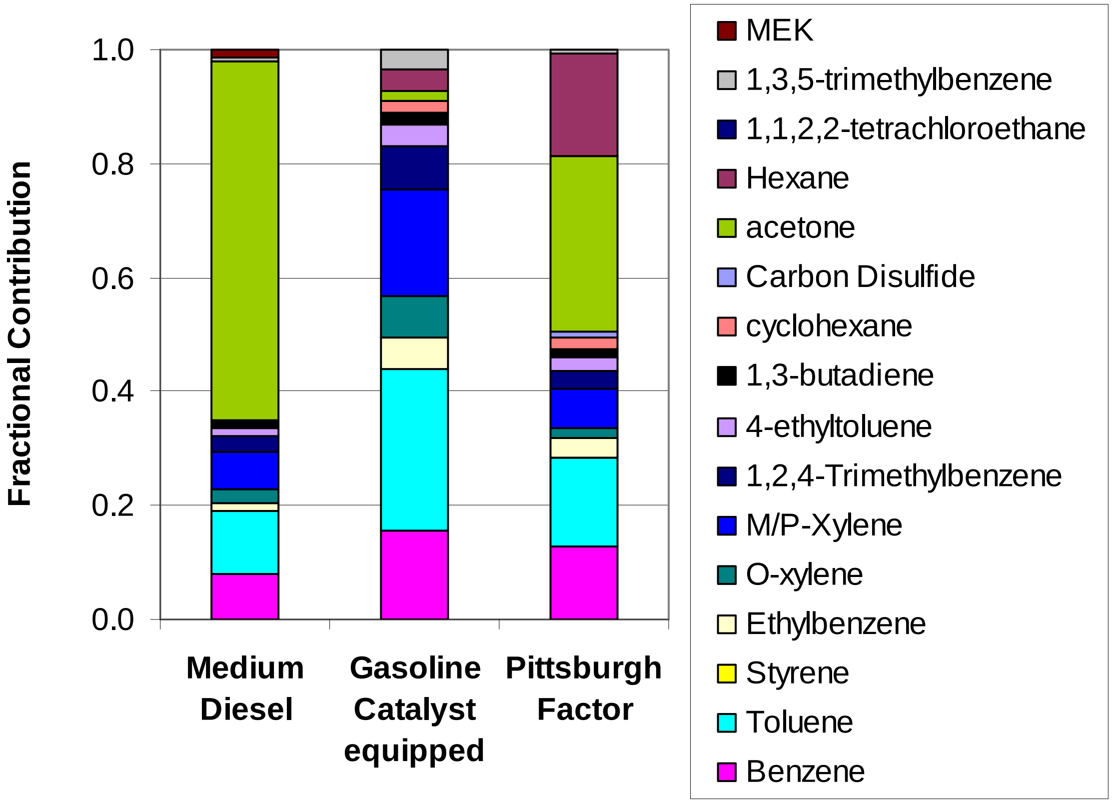


Figure 5.21 Comparison of the species distribution in the Downtown Factor to source profiles for gasoline and diesel vehicles (33, 34). Comparison based on compounds reported in gasoline and diesel profiles, 89% of the factor mass.

<u>Southern Toluene/Benzene Factor:</u> PMF apportioned 64%, 38%, and 36% of the toluene, benzene, and hexane respectively to a single factor. Figure 5.21 that the factor was very wind directionally depended with high contributions when the wind was from the southeast direction, the Clairton source region.

Figure 5.22 shows the weekend/weekday pattern with factor contributions two-thirds higher during the week than during the weekend. Figure 5.23 compares the factor profile to source profiles from the three largest point sources in the Clairton source area, to a profile for gasoline vehicle emissions, and to an emissions weighted composite of the three Clairton source profiles. The factor contains many of the species emitted by gasoline vehicles but the ratios of benzene and toluene relative to other mobile source markers are high relative to the published source profiles indicating an excess in toluene and benzene. The factor contributes 51% of the carbon disulfide, a marker for emissions from coke works and other industrial sources. The factor appears to be a composite of emissions from gasoline vehicles and industrial sources in the

Clairton area. It is unclear what fraction of the pollutants are coming from mobile sources and what fraction are coming from industrial sources; however the factor will be attributed to industrial sources due to its highly wind directional nature.

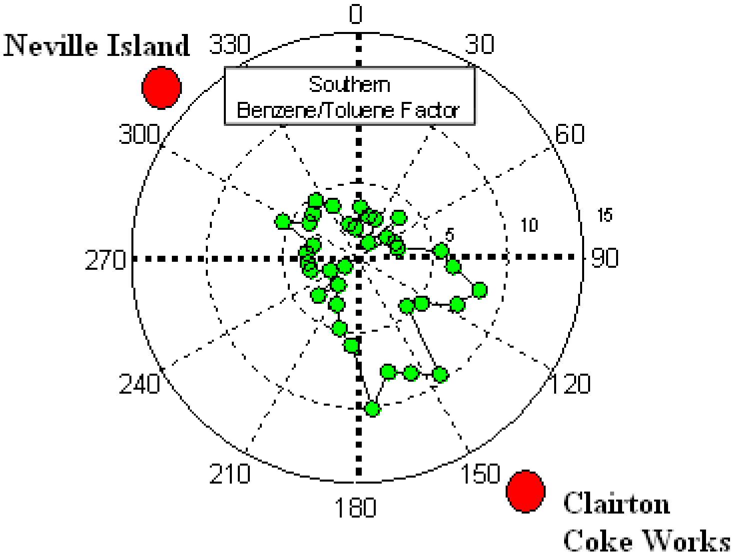


Figure 5.22 The mean contribution of the Southern Toluene/Benzene Factor as a function of wind direction.

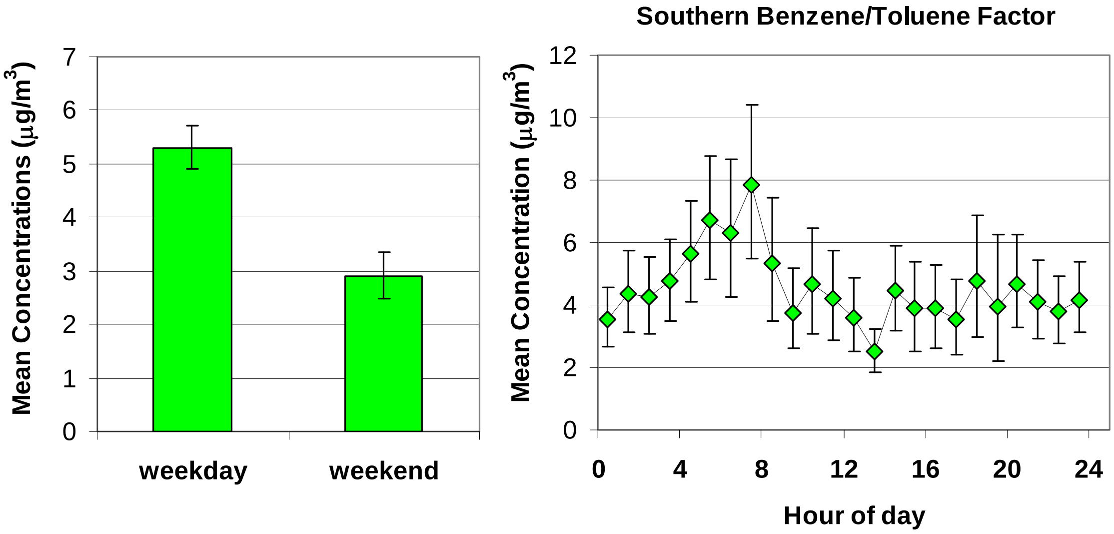


Figure 5.23 Diurnal patterns of factor contribution and factor contribution as a function of day of the week for the Southern Benzene/Toluene Factor.

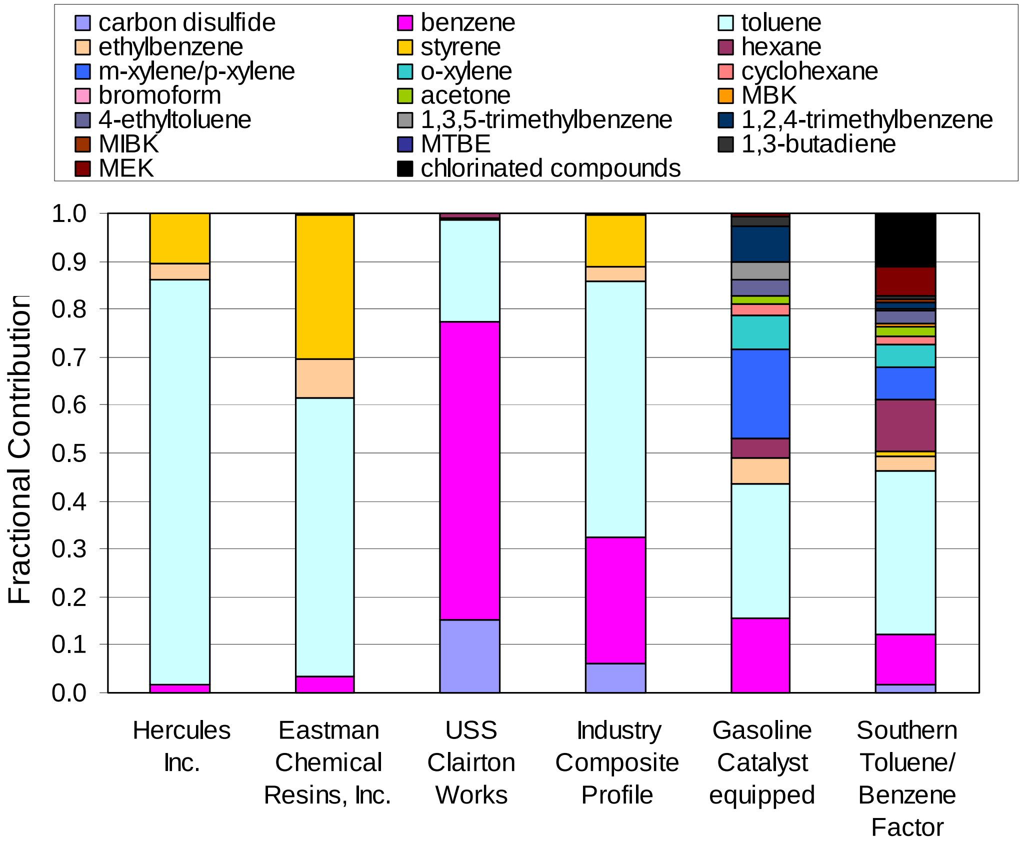


Figure 5.24 Comparison of the species distribution in Southern Toluene/Benzene Factor to source profiles for large industrial in Clairton area and gasoline vehicle emissions.

Local Industry Factor: PMF identified one factor that was dominated by tetrachloroethene. Figure 5.25 indicates that the contribution of this factor was elevated on weekdays and that it exhibits a strong diurnal profile, with higher contributions in the early morning that are not associated with morning traffic patterns. High concentrations were not observed at the baseline downtown site, Flag Plaza, indicating that this factor is likely associated with an extremely local source. Tetrachloroethene is emitted by dry-cleaning facilities (21) and a dry cleaner is located within of 200 m of the Diamond Building site. This factor contributed 26% of the risks.

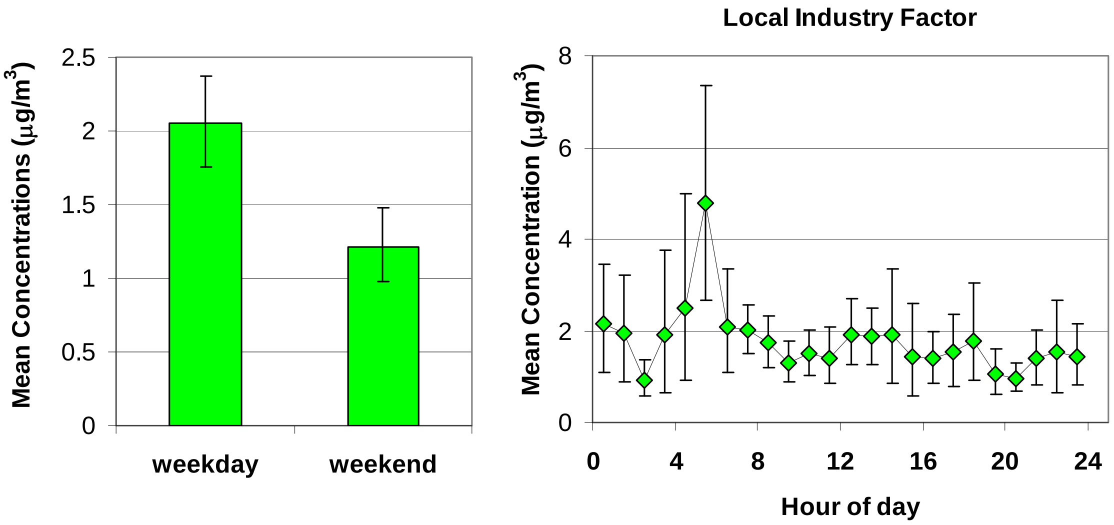


Figure 5.25 Diurnal patterns of factor contribution and factor contribution as a function of day of the week for the local industry factor.

<u>Secondary/Background Factor:</u> PMF apportions the majority of the acetone and 1,2-dichloroethane at the downtown site to one factor. Acetone is a product of VOC oxidation and 1,2 dichloroethane was shown to be a regional/background pollutant in Chapter 3. The contribution of this factor showed no distinct temporal (Figure 5.25) or wind direction dependence. Therefore this factor was attributed to secondary production or background emissions.

The secondary/background factor contributed 12% of the additive cancer risk, mostly due to benzene (20% of the benzene at the downtown site was apportioned to this factor). The ratios of toluene and benzene to carbon disulfide in this factor are similar to coke oven emissions; therefore this factor may also include the background coke levels in downtown.

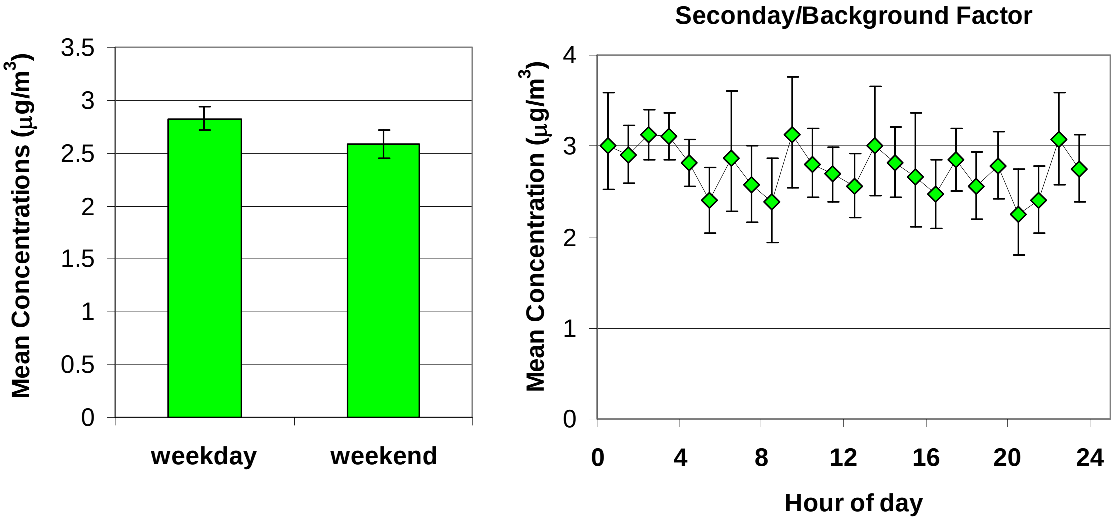


Figure 5.26 Diurnal patterns of factor contribution and factor contribution as a function of day of the week for the Secondary/Background Factor.

Alkybenzene Factor PMF apportioned a set of alkybenzenes, such as ethylbenzene and xylenes, to a single factor. This factor exhibited a distinctive temporal profile with higher concentrations in the morning followed by a rapid decrease associated with the breakup of the boundary layer (Figure 5.27). Figure 5.28 indicates that the contribution of the alkybenzene factor was highly wind-direction dependent, with high contributions when the wind was from the south. These two pieces of evidence indicate a local non-mobile source. This factor contributes 4% of the risk.

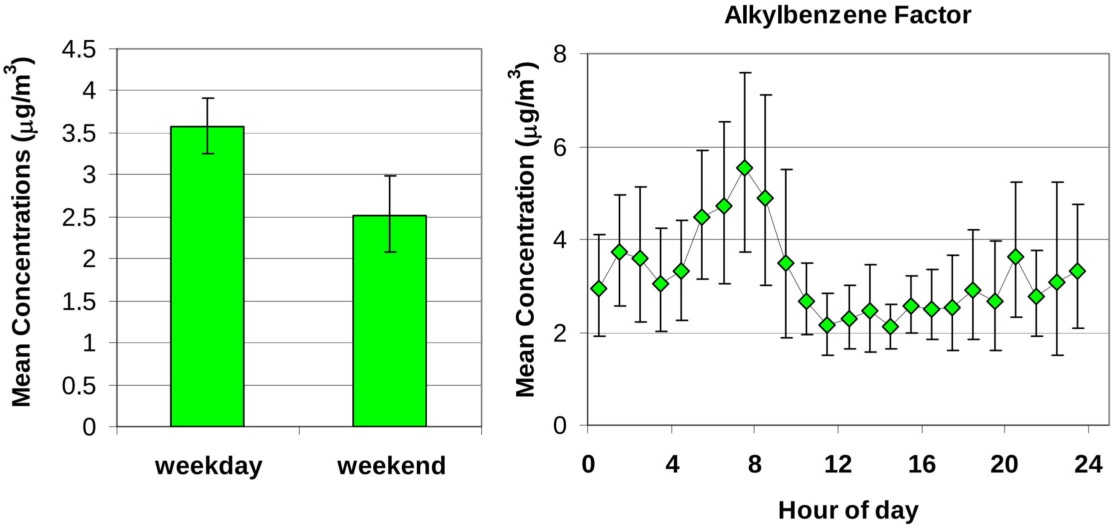


Figure 5.27 Temporal patterns of the Alkybenzene Factor.

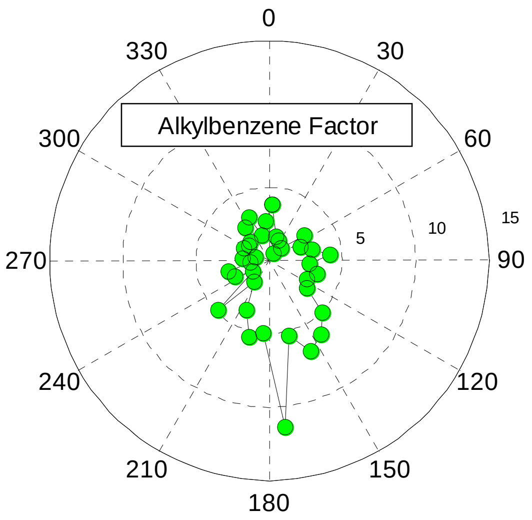


Figure 5.28 The contribution of the alkyl benzene factor as a function of wind direction at the Diamond Building.

5.3.1 Discussion of Downtown PMF Results

Figure 5.29 shows the breakdown of PMF apportioned risks from the downtown intensive by source classes (mobile, non-mobile, and secondary/background) and by location of source (Pittsburgh, non-Pittsburgh, uncertain). Note that this figure only shows the apportionment of the risk of the set of organics included in the PMF model. First, emissions from both mobile and non-mobile sources contribute significantly to the risk at the downtown site. Both diesel vehicles (Pittsburgh factor) and emissions from industrial sources in the Clairton area (Southern

Factor) are important. However, quantifying the contribution mobile versus non-mobile is complicated by most of the factors clearly mixing emissions from multiple sources. To separate mobile from non-mobile contributions in the Pittsburgh factor, all of the mobile source air toxics (MSATs) in this factor were attributed to mobile sources and non-MSATs were attributed to non-mobile sources.

Figure 5.29 indicates that non-mobile sources contribute the majority of the risk of the compounds included in the PMF model for the Diamond Building. Figure 5.29 also provides a breakdown of the risks from different non-mobile sources. In this breakdown, the benzene in the background/secondary factor and the benzene in the Southern Benzene/Toluene factor were apportioned to coke works since both factors were thought to include coke emissions. The dominant fraction of the non-mobile risks is from dry cleaning facilities. A large fraction of the non-mobile risks, 30%, have sources that are unidentified.

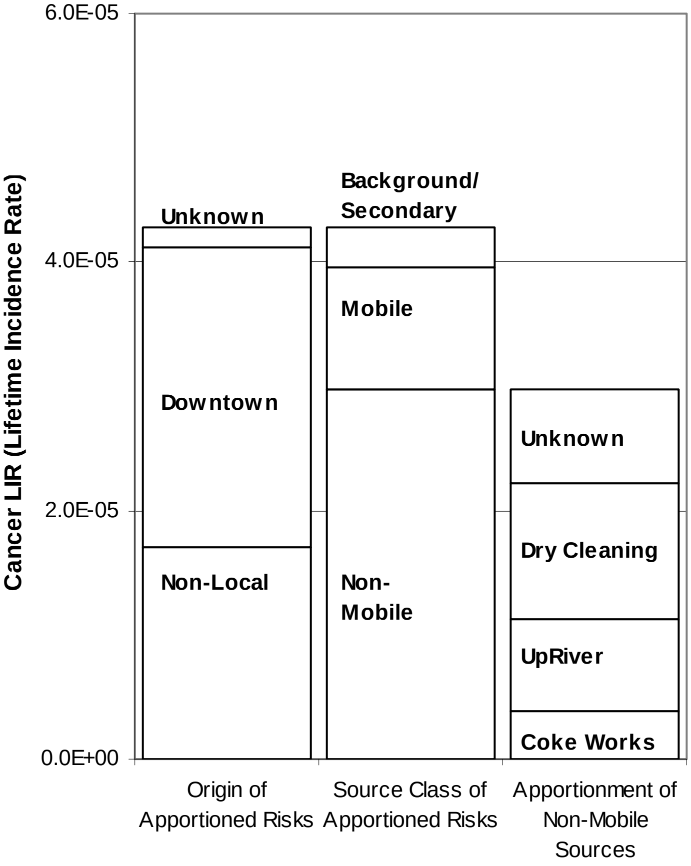


Figure 5.29 PMF apportionment of cancer risks at the Diamond Building.

5.4 Carnegie Mellon University PMF Results

Figure 5.31 shows the species distribution for the most interpretable Carnegie Mellon University PMF solution. This was a six factor solution with a -10 rotation. Figure 5.31 shows the risk apportionment. Again, two of the factors contribute about two-thirds of the cancer risk at the Carnegie Mellon University site.

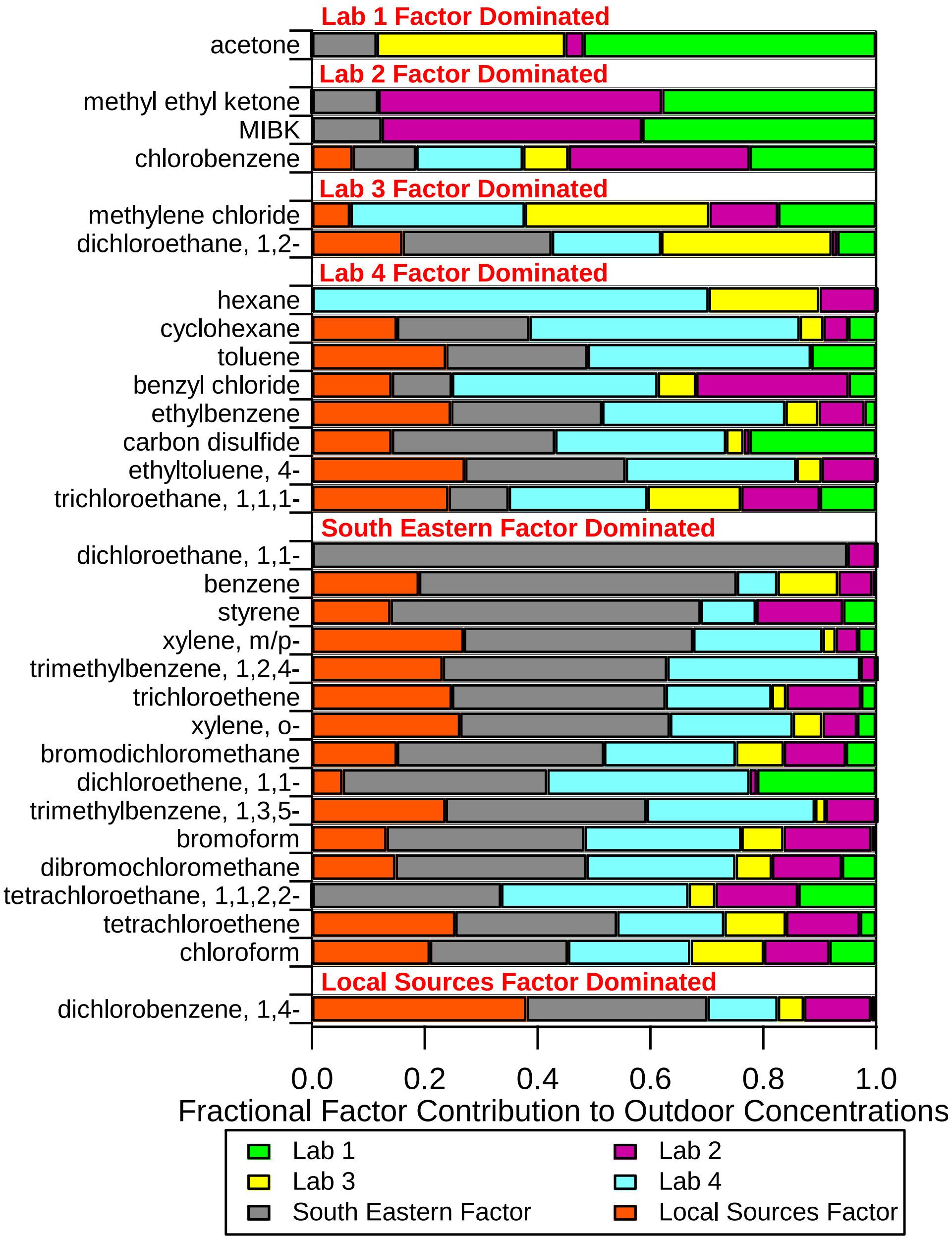


Figure 5.31 Factor contributions to individual compounds concentrations at the urban background (CMU) site.

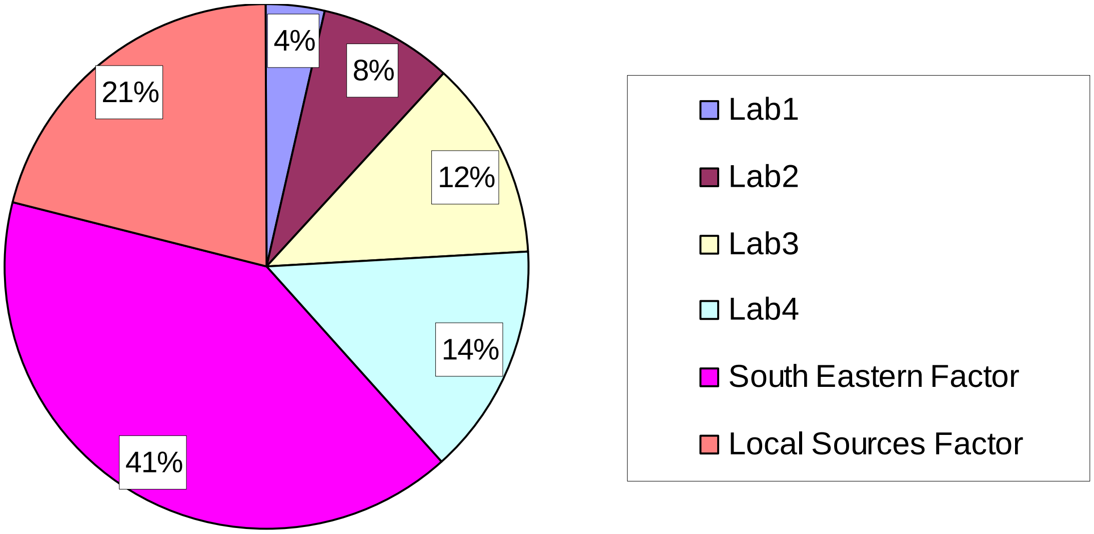


Figure 5.32 Risk apportionment at the Carnegie Mellon University site.

Southeastern Factor: Figure 5.31 indicates that PMF apportioned the majority of the 1,1-dichloroethane, benzene, styrene, and xylenes to one factor. This factor contributed 45% of the risk at the Carnegie Mellon site.

Figure 5.33 shows that the contribution of this factor is strongly correlated with wind direction. Its contribution was much higher when the wind was from the southeast when the site was downwind of Clairton area. Figure 5.34 indicates that comparisons with source profiles support the conclusion that emissions from the Clairton area are strongly influencing air toxic concentrations at Carnegie Mellon University.

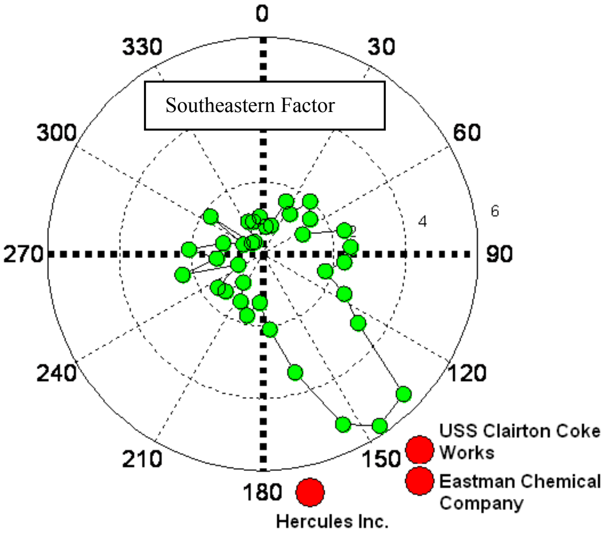


Figure 5.33 Average contribution of the southeastern factor as a function of wind direction. The direction of the three major air toxics emitters in the Clairton Area relative to the Carnegie Mellon University site are indicated on the graph.

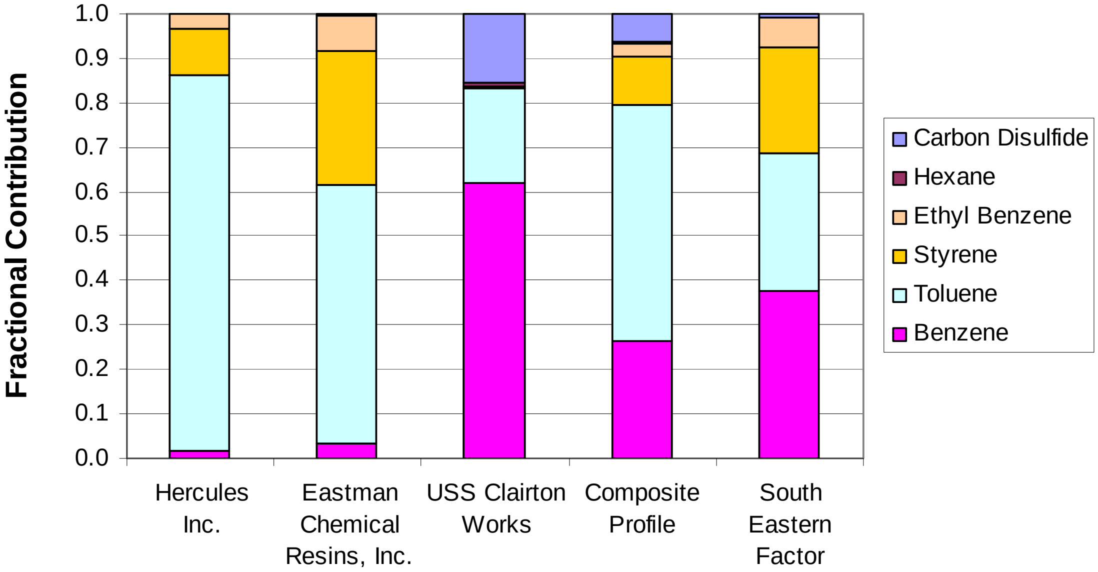


Figure 5.34 Comparison of the Southeastern Factor and the dominant point sources from the up river industrial areas for the pollutants reported emitted by the point sources.

Local Sources Factor: PMF apportioned the majority of the 1,4-dichlorobenzene at the Carnegie Mellon site to one factor. The factor contribution was episodic, but was not wind-direction dependent. Figure 5.35 indicates that the ratios of mobile air toxics and VOCs to one another in this factor are similar to published gasoline vehicle source profiles (5, 33, 34, 38).

Therefore, mobile emissions contribute to this factor. The remaining compounds in the factor are chlorinated compounds that are not associated with mobile source emissions.

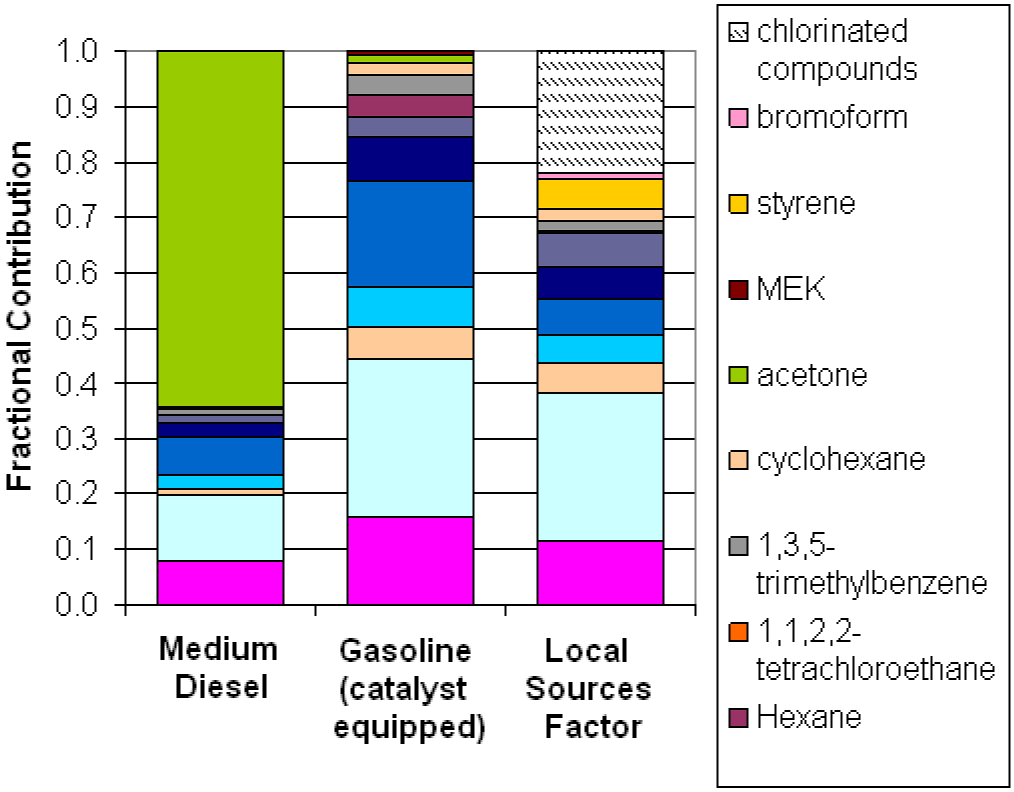


Figure 5.35 Comparison of the local sources factor to motor vehicle source profiles.

Lab Factors: The PMF model apportioned air toxics to four factors that we associated with local emissions. The sampling at Carnegie Mellon University was conducted outside of a laboratory building within a 100 m of several exhaust ducts. These four lab factors are dominated by methyl ethyl ketone, acetone, and hexane, common organic solvents used in laboratory work. The temporal patterns of these factors are consistent with laboratory work – higher on weekdays than on weekends and higher during the day. These factors contribute 35% of the cancer risks.

5.4.1 Discussion of the Carnegie Mellon University PMF Results

Figure 5.36 shows the apportionment of the cancer risk estimated for the Carnegie Mellon University site to different source classes and source regions. The analysis illustrates that urban areas not located near industrial facilities can be strongly influenced by emissions from these facilities. The risks are dominated by local, non-mobile sources (emissions from the CMU labs) but industry from the Clairton source area also substantially effect risks, contributing a total of the 45% of the risks.

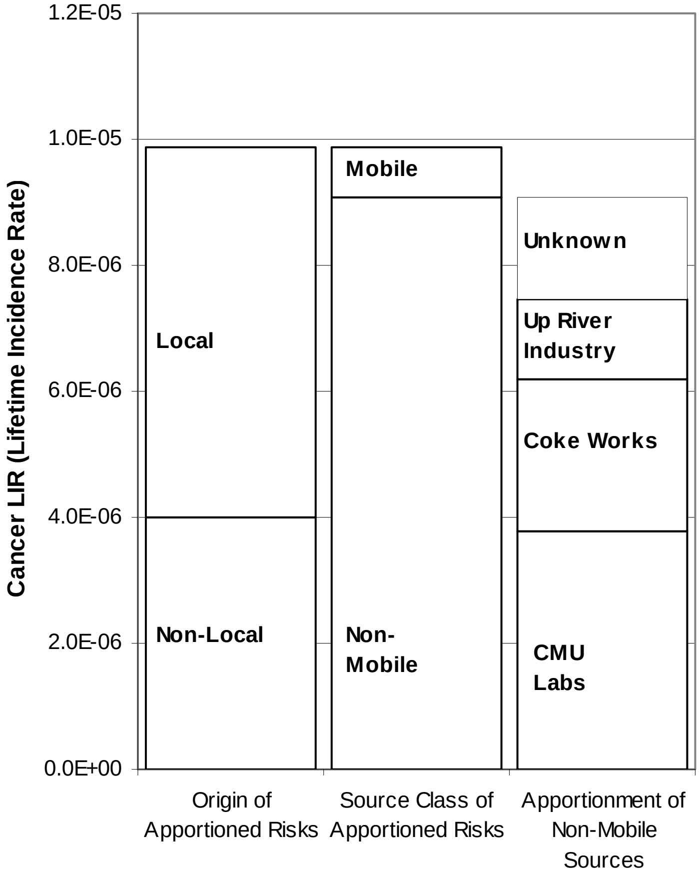


Figure 5.36 Sources of risks from for PMF apportionment of the CMU intensive risks.

5.5 Conclusions

In this chapter PMF was used to apportion cancer risk associated with a set of organic air toxics to sources. The analysis focused on the risks of pollutants with large spatial variability, and unsurprisingly secondary/background source contributions to risks were minimal.

For the subset of the compounds included in the model, non-mobile sources contributed more than three quarters of the apportioned risks at all of three intensive sites. In Avalon slightly more than half of the risks, 55%, are associated with emissions from Neville Island. The majority of the risks in downtown, 62%, were apportioned to local sources.

Comparing the factors associated with mobile sources at the three sites reveals that diesel emissions appear dominant downtown, while gasoline vehicle emissions were more important at the other two intensive sites.

Chapter 6. Source Apportionment of Diesel Particulate Matter Using Highly Time-Resolved Measurements of Organic Molecular Markers and Black Carbon

6.1. Introduction

Diesel particulate matter (DPM) is a complex mixture of elemental or black carbon (BC), organic carbon (OC), sulfate, nitrate, and trace metals and ions. BC and OC comprise most DPM on a mass basis. Because of its inherent complexity, it is impossible to directly measure DPM concentrations. Instead DPM levels must be inferred using a source apportionment model.

In this chapter, the chemical mass balance (CMB) and positive matrix factorization (PMF) models were used to investigate sources of BC and to estimate diesel particulate matter concentrations in downtown Pittsburgh. The analysis was performed using ambient concentrations of BC, and a suite of hopanes and VOCs measured at the Diamond Building. Archived data were also analyzed using CMB to estimate diesel particulate matter concentrations at Schenley Park.

6.2 PMF Analysis

PMF analysis was performed to investigate the sources of BC at the Diamond Building site. BC is often used as a tracer for diesel vehicle emissions. The compounds included in the PMF model are shown in Figure 6.1a – many of these compounds have been used previously in receptor modeling studies as markers for motor vehicle emissions. Hopanes are pentacyclic triterpanes that are found in unburned lubricating oil. Hopanes are emitted by both gasoline and diesel vehicles. BC is enriched in diesel particulate matter. The VOCs included in the model (toluene, benzene, ethylbenzene, xylenes, and heptane) are enriched in gasoline vehicle exhaust. In addition to these motor vehicle markers, a number of alkanes and polycyclic aromatic hydrocarbons are included in the PMF model.

The PMF analysis was performed using data for 275 samples collected from February - April 2008. We considered 3-, 4-, and 5-factor PMF solutions. The three factor solution proved to be optimal PMF solution in terms of both fitting statistics and interpretability. Rotational ambiguity of the solution was examined by rotating the factors using the FPEAK parameter. The most interpretable solution was obtained from a small negative rotation (FPEAK = -0.2).

Figure 6.1a shows the PMF results for the three factor solution. One factor explains 67% of the BC, 25% of the hopanes/steranes and about 50% of the C13 - C18 n-alkanes. Figure 6.1b indicates that this factor exhibits strong diurnal and weekday-weekend patterns, which are consistent with a mobile source. The fractional apportionment of BC to this factor is consistent with previous work apportioning 67% - 94% of BC in Pittsburgh to diesel emissions Subramanian et al. (40). Therefore, this factor appears to be associated with diesel vehicle emissions. The Diamond Building was in close proximity to several major bus routes.

A second PMF factor explained about 20% of the BC, 45% of the norhopane, 54% of hopane, and almost all of the VOCs included into a model. This factor is also distinguished by strong diurnal and day-of-week patterns consistent with mobile source activity. From the factor composition, this factor appears associated with gasoline vehicle emissions.

About 13% of the BC is associated with a factor containing high loadings for many of the PAHs, n-alkanes, 6,10,14-trimethyl-2-pentadecanone (TM2PD) and 20% of the benzene. This factor cannot be associated with a specific source. Its substantial contribution to hopanes/steranes indicates a fossil fuel-based source. However, the n-alkanes and PAHs included in the PMF model are emitted by many different sources. One possibility is that this factor explains BC and associated organic markers transported into Pittsburgh as part of the regional air mass. This hypothesis is supported by both the lack of diurnal/day-of-week patterns and the factor composition. Another possibility is that this factor corresponds to emissions from some industrial facility. A large industrial source would also display weak average diurnal and day-of-week patterns.

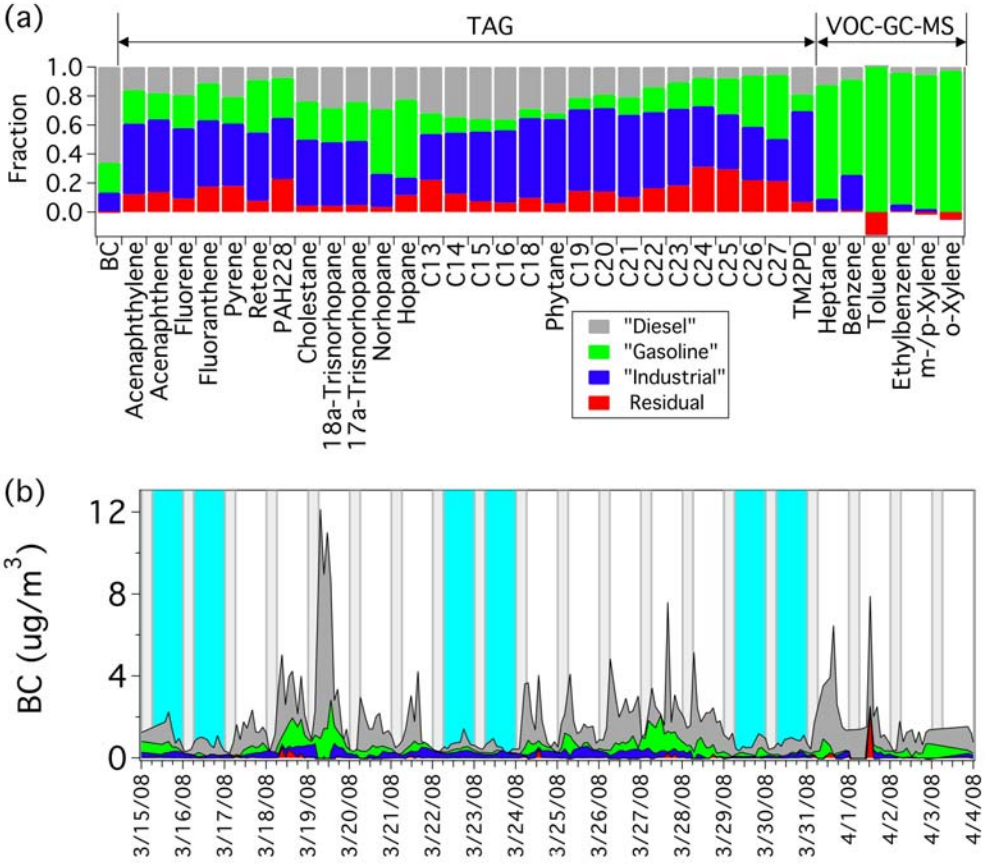


Figure 6.1: (a) PMF apportionment for compounds included as fitting species in a three-factor model (FPEAK = -0.2). (b) Time series for BC apportioned to each source factor over a three-week period. Vertical grey bars are overnight periods (12-6AM), and vertical cyan bars are weekends.

To help interpret the PMF factors we compared the factor profiles to published source profiles using ratio-ratio plots. Ratio-ratio plots are scatter plots of concentrations of two marker compounds with the concentration of a third reference species. These plots are useful to visualize the PMF solution space. The methodology is described in detail elsewhere (41, 42).

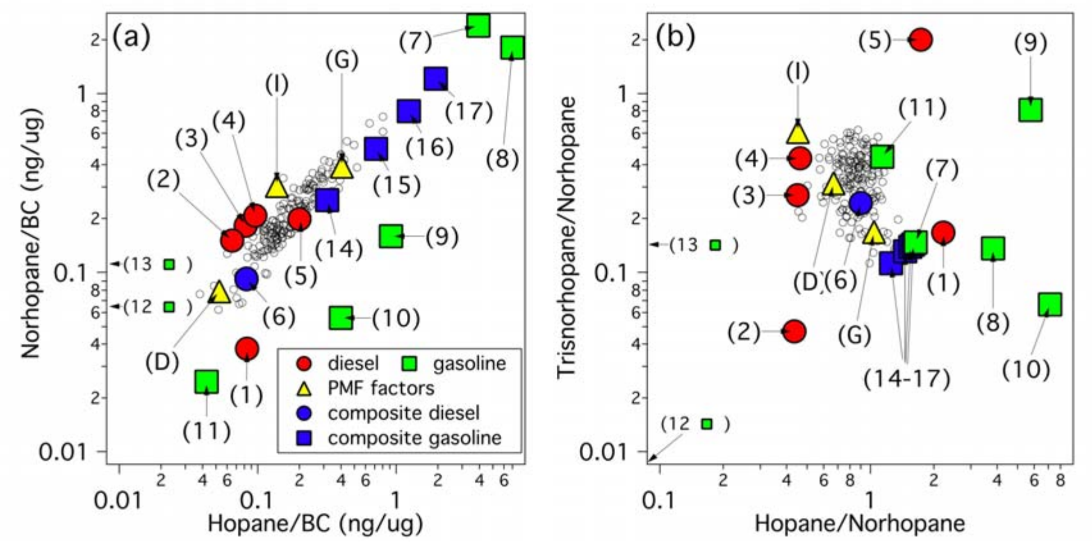


Figure 6.2: (a) Ratio-ratio plot for norhopane and hopane with BC used as the reference species. (b) Ratio-ratio plot for trisnorhopane and hopane, with norhopane used as the reference species. Ambient data are shown in black circles and source profiles are shown in colored markers. Numbers indicate source profiles: (1) Fujita MDD (2) Fujita HW (3) Fujita HDD (4) Fujita HCS (5) Schauer MDD (6) Fujita MDD-HDD (50%-50%) composite (7) Fujita SI-HC (8) Fujita SI-HW (9) Fujita SI-BW (10) Fujita SI-BC (11) Schauer catalyst auto (12) Fujita SI-LW (13) Fujita SI-LC (14) Fujita SI-LW-HC (99%-1%) composite (14) Fujita SI-LW-HC (97.5%-2.5%) (15) Fujita SI-LW-HC (95%-5%) (16) Fujita SI-LW-HC (90%-10%) (D) PMF "Diesel" (G) PMF "Gasoline" (I) PMF "Industrial". Fujita source profiles are from (43, 44); Schauer source profiles are from (33, 34).

Figure 6.2 shows a ratio-ratio plot for norhopane and hopane normalized by BC. Ambient data, emissions profiles for motor vehicles, and the PMF factors are shown. The source profiles were taken from the literature (33, 34, 43, 44). The ambient data organize along a diagonal mixing line in the ratio-ratio plot. Several diesel source profiles cluster around the bottom left edge of the data, including the PMF "diesel" factor. Hopane-to-BC ratios of the gasoline source profiles vary widely, spanning the range of the ambient data. Low-emitting gasoline vehicles are enriched in BC relative to hopanes while high-emitting vehicles have low BC emissions. The data can be explained by a combination of diesel emissions and a fleet of low and high-emitting gasoline-powered vehicle emissions. The PMF "gasoline" factor is located near the upper right edge of the data, near a cluster of gasoline vehicle source profiles.

The PMF "industrial" factor is located between the "diesel" and "gasoline" factors on the mixing line. This supports the hypothesis that this factor may relate to a regional source containing a mixture of gasoline and diesel vehicle emissions. It is unlikely to be an industrial source because published source profiles for fuel oil combustion or coal combustion have extremely high hopane-to-BC ratios and would appear in the top right corner of a ratio-ratio plot off the scale of Figure 6.2.

6.3 CMB Analysis

CMB analysis was performed to estimate ambient concentrations of diesel particulate matter. Ambient concentrations of BC and several hopanes (norhopane, hopane, cholestane, trisnorhopane and homohopane isomers) were fit by CMB using one diesel and one gasoline vehicle source profile. Different combinations of gasoline and diesel source profiles were fit to quantify the uncertainty in the solution due to source profile variability. The CMB analysis was performed on data from 177 samples. All CMB solutions had acceptable statistical performance, with average $r^2 > 0.82$ and $\chi^2 < 1$.

The CMB anlaysis considered three different diesel source profiles: a composite medium-duty diesel profile (profile #1 in Figure 6.2), a composite heavy-duty diesel profile (profile #3 in Figure 6.2), and an emissions-weighted average of these two profiles (profile #6 in Figure 6.2). Only one diesel profile is fit at a time by the CMB model. To apportion gasoline vehicle emissions, we examined vehicle fleets with different amounts of low- and high-emitting vehicles. This was done by creating composite profiles using the low- and high-emitting profiles plotted in Figure 6.3 (profiles #12 and #6 or #8). Separate CMB models considered vehicle fleets of 1%, 2.5%, 5%, and 10% high emitters (profiles #14-17 in Figure 6.3).

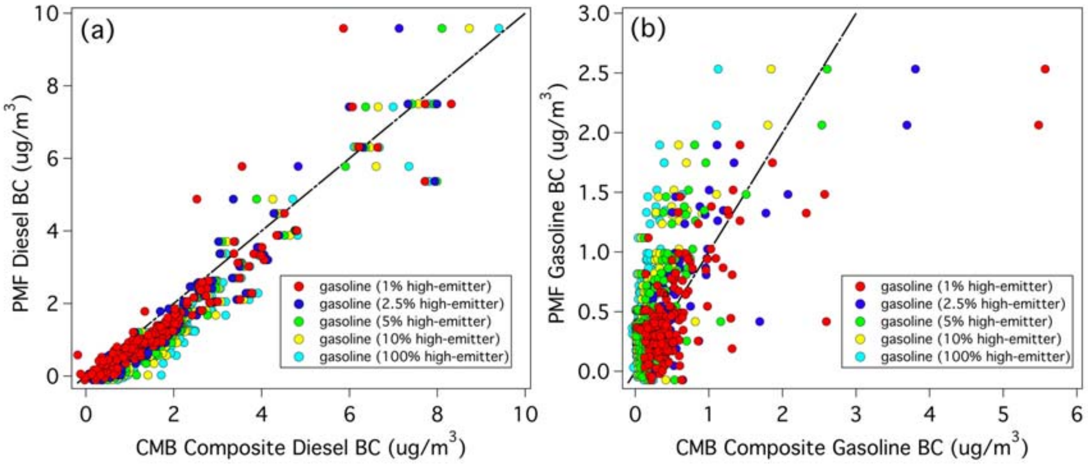


Figure 6.3: Comparison of PMF and CMB apportionment of black carbon (BC) to (a) diesel and (b) gasoline vehicles. Results are shown CMB solutions with different composite gasoline profiles, as discussed in the text.

Figure 6.3 shows scatter plots for BC apportioned by PMF to the mobile source factors versus BC apportioned by CMB to the gasoline and diesel source profiles. Results from several CMB scenarios are shown; each scenario used the same composite diesel profile (#6) paired with a different composite gasoline profile (#14-17 and #7). All of the different models apportion roughly the same fraction BC to diesel vehicles ($m = 0.98 - 1.02$, $r^2 = 0.88 - 0.94$), indicating that the solutions are well constrained. The BC apportioned to gasoline vehicles by the different models usually agrees to within a factor of two, with many data points clustered around the 1:1 line for the 1 to 5% high-emitter scenarios.

The good agreement between the PMF and CMB solutions provides confidence in the source apportionment results, especially for diesel vehicles. Each CMB model also provides an estimate of the study-average DPM concentrations in downtown Pittsburgh. These estimates ranged from 3.0 to 4.3 $\mu g\ m^{-3}$. Figure 6.4 presents the CMB results as a histogram to illustrate the variability in the DPM estimates.

CMB analysis was also performed using archived hopanes and BC data measured in Schenley Park as part of the Pittsburgh Air Quality Study (6). This site is considered an “urban background” site not strongly influenced by local sources. The DPM estimates for the Schenley Park site are presented in Figure 6.4. These are based on the same combinations of source profiles used for the analysis of the downtown data. In Schenley Park, annual average DPM concentrations range from 0.8 to 1.1 $\mu g\ m^{-3}$, which are more than a factor of three lower than those at the Diamond Building. This underscores that the downtown area is strongly influenced by diesel vehicle emissions.

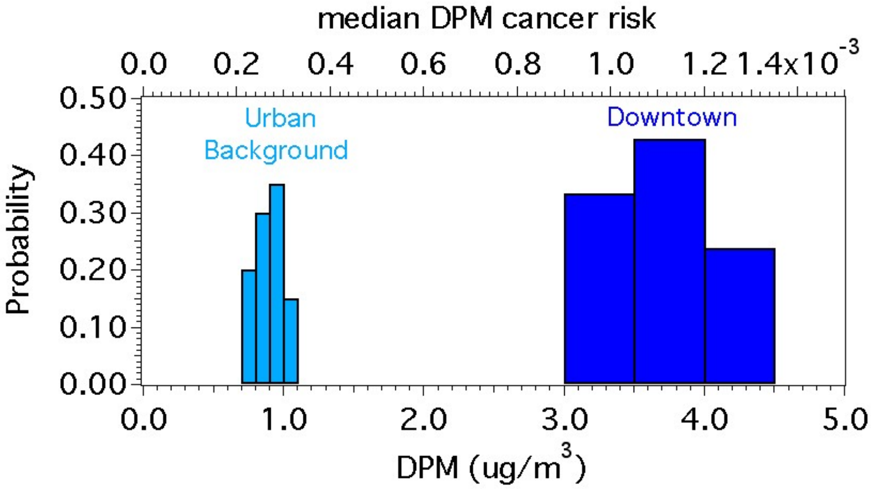


Figure 6.4: Histogram of DPM concentrations estimated using CMB at the downtown and urban background (PAQS Supersite) sites. Study average DPM estimates at the downtown site ranged from 3.0 – 4.3 µg m^{-3} depending on the CMB scenario, compared to 0.8 – 1.1 µg m^{-3} at the urban background site for the same set of CMB scenarios. Also shown are "median" estimates of the DPM cancer risks which are based on the best-estimate DPM potency factor.

Figure 6.4 also shows a range of estimates of DPM cancer risk calculated using a potency factor of 3 x 10^{-4} per µg m^{-3}, the value recommended by the California Office of Environmental Health Hazard Assessment (OEHHA). OEHHA estimates an overall range of lung cancer risk factors of (1.3 – 15) x 10^{-4} per µg m^{-3} for DPM, indicating an order of magnitude in DPM toxicity. A best estimate for DPM carcinogenic risk was calculated using the most probable value for the DPM concentrations and the OEHHA recommended potency value. This estimate is 1 x 10^{-3} downtown and 3 x 10^{-4} in Schenley Park.

Given the uncertainty in both the source apportionment estimates and the DPM potency factor, we also calculated lower and upper bound risk estimates. These were determined by multiplying the maximum and minimum DPM estimates with the maximum and minimum potency factors. The lower bound on the DPM cancer risk estimate is 4 x 10^{-4} for downtown and 1 x 10^{-4} for Schenley Park. The upper-bound cancer risk estimate for DPM is 6 x 10^{-3} for downtown and 2 x 10^{-3} in Schenley Park

Chapter 7. Risk Synthesis: Apportioning Risks to Sources in Allegheny County

In previous chapters, Positive Matrix Factorization (PMF) was used to apportion a subset of gas phase organic air toxics to sources and the Chemical Mass Balance (CMB) model was used to estimate the ambient concentrations of diesel particulate matter. This chapter first discusses the sources of air toxics not included in these models and then all of the results are combined to apportion cancer risks to source classes. Metals are also an important subset of air toxics, but not enough information is available on the sources in Allegheny County to include them in the analysis.

7.1 Apportioning Risks from Air Toxics not included in PMF

Several air toxics that contribute substantial risk were not included in the PMF or CMB models because they did not vary temporally or were not measured during the intensive campaigns. This section discusses the apportionment of formaldehyde, carbon tetrachloride, acetaldehyde, 1,3-butadiene, hexachlorobutadiene, vinyl chloride, benzyl chloride and acrolein.

7.1.1 Formaldehyde

Of the gas-phase organic air toxics considered by this study, formaldehyde contributes the largest cancer risk throughout Allegheny County, 33%-48% of the additive cancer risk with the highest relative contribution at the regional background site.

Formaldehyde is emitted by point and mobile sources as well as formed in the atmosphere from the oxidation of hydrocarbons (21). Previous research has found that secondary formation of formaldehyde is often more important than primary emissions (45) and data from the four baseline sites lead to the same conclusion for Allegheny County. First, formaldehyde concentrations were about a factor of two higher during the summer than during any other season (Figure 4.12) – a clear indication of secondary production. Second, two statistical tests indicate that formaldehyde is primarily a regional pollutant in Allegheny County that is not strongly influenced by local emissions. First the bootstrap method was used to compare the study-average concentrations measured at the four baseline studies. For the Stowe, South Fayette and

Flag Plaza sites, the null hypothesis that the study-average concentrations were the same could not be rejected at the 95th percentile level. This means that study-average concentrations at Stowe, South Fayette, and Flag Plaza are not statistically different from each other. However, for Avalon the null hypothesis could be rejected, meaning that the mean concentration at Avalon could be different than the mean concentration at the other sites. Formaldehyde concentrations in Avalon were 17% higher (0.45 $\mu g/m^3$) than in South Fayette, with 95% confidence intervals for this difference of 0.17 to 0.71 $\mu g/m^3$. Therefore, local emissions appear to contribute modestly to formaldehyde exposures in Avalon.

The second statistical test was to compare the linear correlation between formaldehyde measured at different sites to correlations of formaldehyde with other pollutants measured at the same site. Formaldehyde concentrations in Avalon and Flag Plaza are more strongly correlated with formaldehyde concentrations in South Fayette than with other pollutants from the same site, further supporting the conclusion that formaldehyde is a regional pollutant. In Stowe, formaldehyde concentrations were most correlated with other carbonyls (acetaldehyde, acetone, and acrolein) measured at the Stowe site than with formaldehyde in South Fayette. This potentially indicates a local source of carbonyls in Stowe, but may simply be due to concentrations of this set of secondary pollutants co-varying in time.

Based on this analysis, 100% of the formaldehyde will be apportioned to regional/secondary sources at the regional background site (South Fayette), and downtown (Flag Plaza). At Avalon 83% of formaldehyde was apportioned to regional/secondary sources and 17% apportioned to local, industrial emissions.

7.1.2 Carbon tetrachloride

Carbon tetrachloride contributes 9%-12% of the total cancer risk in Allegheny County. Its concentration and absolute risk did not vary between the four sites. High time resolved measurements showed little to no temporal variation at any of the sites. Therefore, carbon tetrachloride is a regional pollutant.

Carbon tetrachloride is a CFC that was used extensively in the early part of the 20th century as a refrigerant that was largely banned by the Montreal Protocol. It is currently used in small quantities as an industrial solvent (21), and there are negligible emissions of carbon tetrachloride in Allegheny County (1). Carbon tetrachloride has a relatively long atmospheric lifetime on the order of 30-50 years (21), which means that outdoor exposures in Allegheny County today to carbon tetrachloride are due to historical emissions across the globe. Therefore, carbon tetrachloride was classified as regional/secondary pollutant at all sites and 100% of carbon tetrachloride risks were assigned to secondary/background sources.

7.1.3 Acetaldehyde

Acetaldehyde contributes 4%-6% of the cancer risk attributed to the target organic air toxics throughout Allegheny County. Acetaldehyde is emitted by chemical processing, mobile sources such as automobiles, tobacco smoke, and is a natural product of combustion and reactions of other hydrocarbons in the atmosphere (21).

Only a small set of high time resolved data were available from this study to investigate the sources of acetaldehyde. A previous study attributed 40% of the acetaldehyde from mobile sources and 60% from atmospheric production at an urban background site in Pittsburgh (Schenley Park) (7). We assumed the same split for the South Fayette data, apportioning 0.65 $\mu g/m^3$ of acetaldehyde to mobile-source emissions and 0.94 $\mu g/m^3$ to secondary production. Furthermore, we assumed that the regional/secondary contribution would be the same at all sites, 0.94 $\mu g/m^3$, and that any excess acetaldehyde was due to mobile source emissions. This may somewhat overestimate the mobile source contribution in Avalon, the site with the highest acetaldehyde concentrations. In Avalon some of the emissions from industrial sources may also be important, but this uncertainty is small, affecting less than 10% of the acetaldehyde risks. The risks apportionments were: Avalon 58% mobile, 42% background/ secondary; downtown 54% mobile, 46% background/secondary; background 40%mobile, 60% background/secondary.

7.1.4 1,3-butadiene

1,3-butadiene contributes 3%-6% of the gas-phase organic air toxics cancer risk in Allegheny County. Although 1,3-butadiene is one of the top ten risk contributors, concentrations of 1,3-butadiene in Allegheny County are at the national average at the three urban baseline sites and below the 25th percentile at the regional background site (Figures 3.1 and 3.2). 1,3 butadiene is emitted from mobile vehicles, cooking, and point sources that produce/use polymers (21, 33, 35).

High time resolved measurements of 1,3-butadiene were taken at Avalon and downtown. 1,3-butadiene was included in the downtown PMF model but not the Avalon model because the Avalon 1,3 butadiene dataset was incomplete. The downtown PMF results apportioned 65% of the 1,3 butadiene to the downtown factor, which is thought to be mobile diesel, and 24% from the southeastern factor, which is thought to be a mixture gasoline vehicle and industrial emissions from the Clairton area. Since there are no reported industrial emissions of 1,3 butadiene from the Clairton area, all of the 1,3 butadiene in southeastern factor was attributed to mobile sources.

Concentrations of 1,3-butadiene at Avalon are slightly higher than in downtown. The Neville Chemical Company near Avalon reports 110 kg of 1,3-butadiene emissions per year (1). At the Avalon site it was assumed that the increase in concentration was from non-mobile sources. At Avalon 88% of the 1,3-butadiene is from mobile sources and 12% of the 1,3-butadiene is from non-mobile sources, specifically industry. It was assumed that 100% of the 1,3 butadiene is from mobile sources at the background site, South Fayette.

7.1.5 Hexachlorobutadiene, 1,2-Dichloropropane, and Vinyl Chloride

Hexachlorobutadiene, 1,2-dichloropropane, and vinyl chloride concentrations were similar at all four baseline sites. Therefore all of these species were apportioned to regional emissions at each site.

7.1.6 Acrolein

Acrolein is the only air toxic estimated to pose a non-cancer risk in Allegheny County. Although the hazard quotient of acrolein is above one at all of the sites, acrolein concentrations in Allegheny County are low compared to the rest of the nation (Figure 3.3). Baseline measurements showed that acrolein concentrations were a factor of two higher at the urban sites as compared to South Fayette with highest concentrations at Avalon and Stowe.

Acrolein is emitted by manufacturing processes and in combustion exhaust (21). At South Fayette acrolein did not correlate very strongly with any other pollutants. At Avalon and Stowe acrolein correlates most highly with carbon disulfide and styrene, two tracers of emissions from industrial facilities on Neville Island. According to the inventory there are no significant sources of acrolein on Neville Island, but that does not appear to be the case. Given the current data set it is difficult to apportion acrolein to sources.

7.2 Apportionment of Risks to Sources

Results from the PMF apportionment of air toxics, the DPM concentration calculations, and the apportionment of air toxics in this chapter were combined to apportion risks to source classes. Figures 7.1 to 7.3 shows the apportionment of risks at all sites for sources class, origins of risks and apportionment of non-mobile risks. For the 36 target organic air toxics, regional/secondary pollutants, mainly formaldehyde and carbon tetrachloride, are the dominant contributor to the cancer risk at each site. Non-mobile sources are the second largest contributor followed mobile-source emissions.

Figure 7.4 combines the risk estimates for gas-phase organic air toxics with estimates for diesel PM (DPM). DPM estimates were only available for the downtown and urban background sites. Given the modest spatial variation in BC concentrations outside of the downtown area (Figure 3.4), it was assumed that the Avalon diesel PM risk was equal to the background diesel PM risk. When diesel PM is included in the analysis, Figure 7.4 indicates mobile source risks are much greater than all of the other source classes.

In Chapter 3 it was shown that the metals risks were one third to one half the magnitude of additive cancer risks attributed to the organic air toxics. Not enough is known about the metals apportionment in Allegheny County to include them in this apportionment. DPM would still dominate risks even if metals were included and therefore mobile sources would still dominate risk contributions. Adding metals may alter the relative importance of non-mobile to regional/background sources.

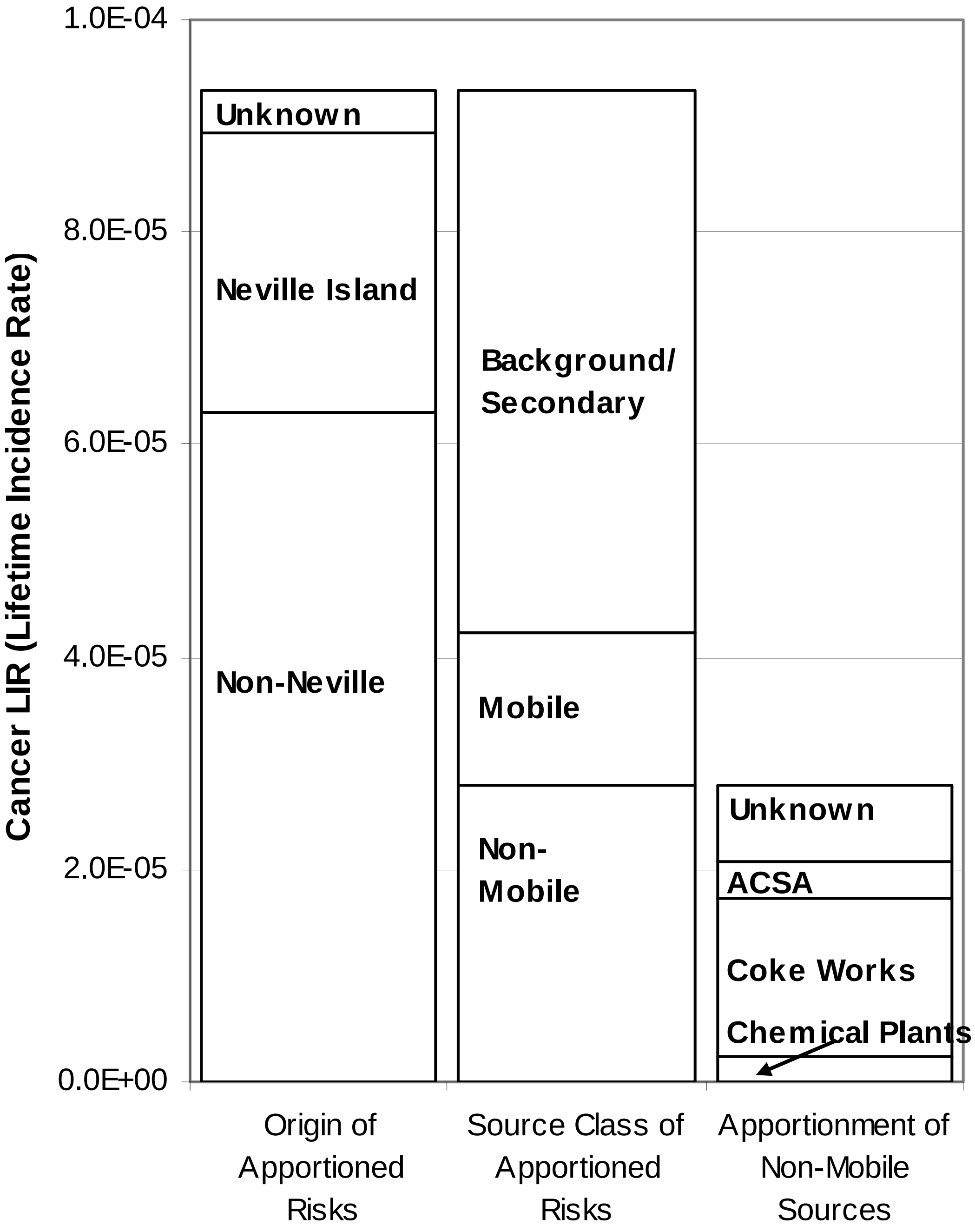


Figure 7.1 Source apportionment of the additive cancer risk for the 36 target gas-phase organic air toxics at the Avalon site.

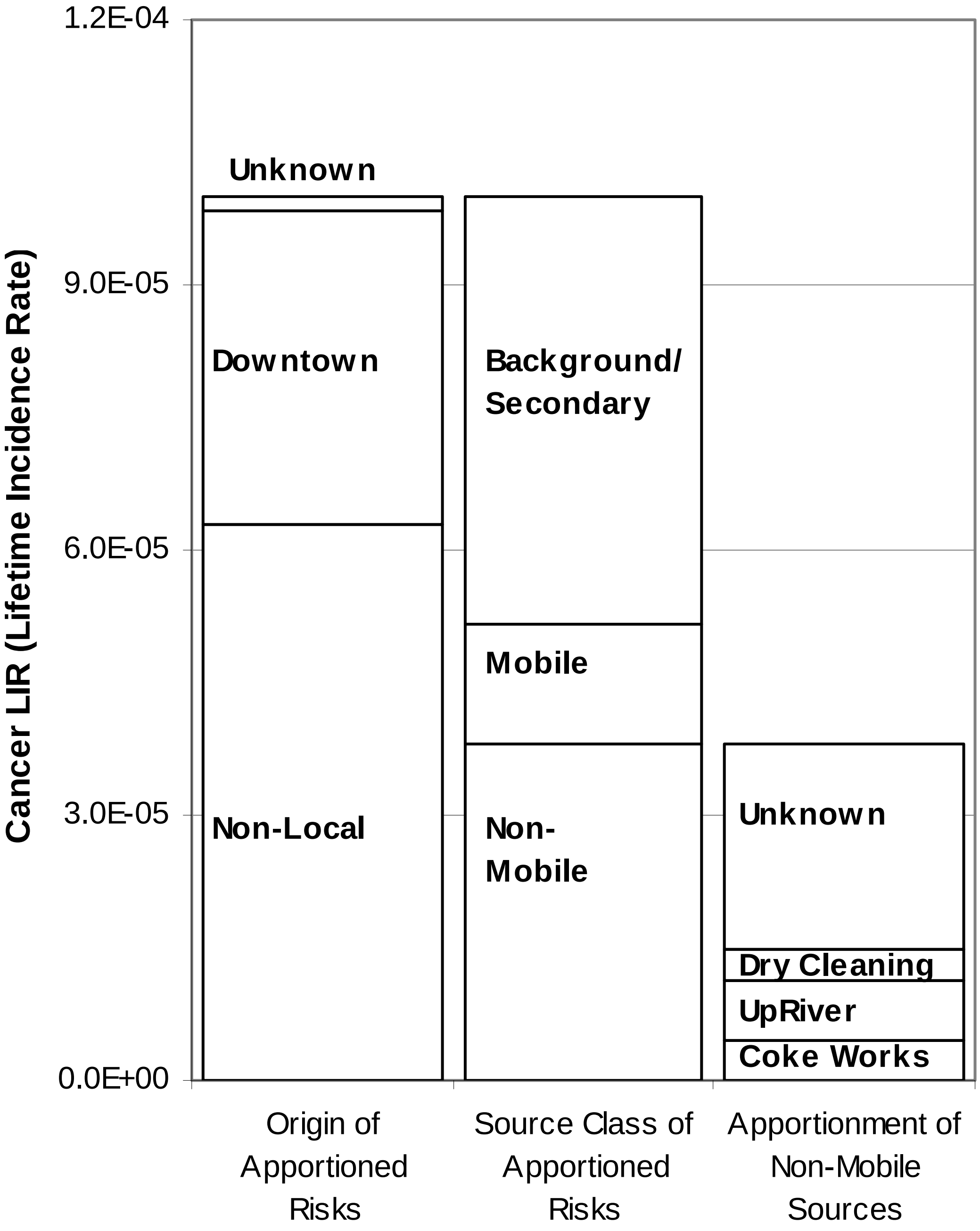


Figure 7.2 Source apportionment of the additive cancer risk for 36 target gas-phase organic air toxics in downtown Pittsburgh.

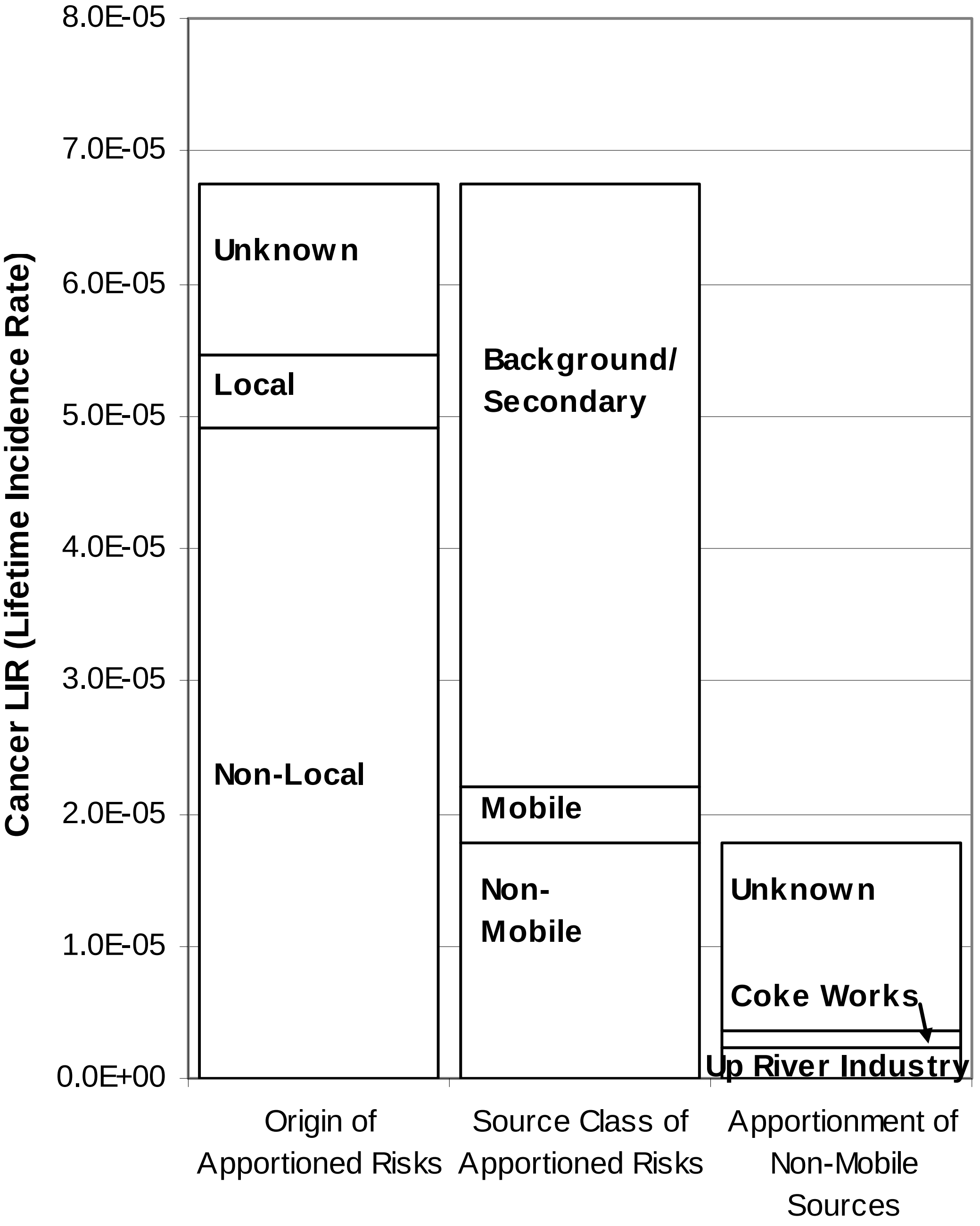


Figure 7.3 Source apportionment of the additive cancer risk for 36 target gas-phase organic air toxics in South Fayette.

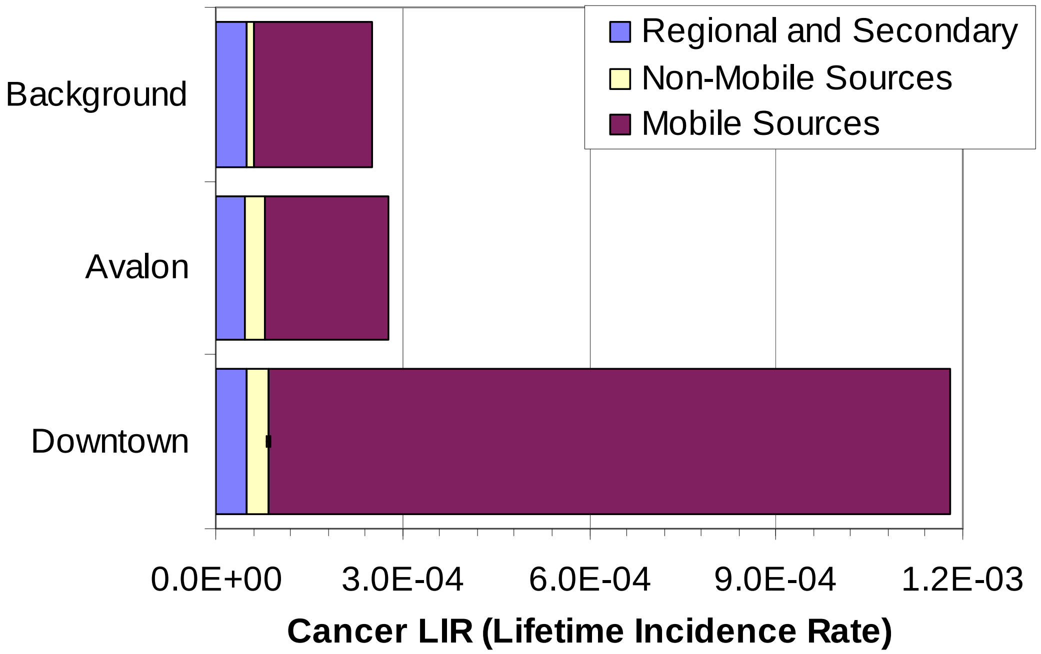


Figure 7.4 Additive cancer for gas-phase organic air toxics and DPM for each of the sites divided into regional/secondary contribution, mobile source contribution, and industrial contribution.

7.3 Conclusions

If only gas-phase organic air toxics are considered, background/regional sources dominate the risk profile. Non-mobile gas phase risks were dominated by risks associated with coke works emissions, primarily from benzene, at the Avalon site. At the downtown site non-mobile risks were dominated by point source emissions of chlorinated compounds, specifically trichloroethene. The sources of these chlorinated compounds are unknown.

Including diesel particulate matter in the risks apportionment dramatically changes the results. DPM risks are greater than gas phase risks at each of the sites making mobile sources by far the most dominate source class. The highest contributions to risks were seen downtown.

Chapter 8. Evaluating NATA: Comparison of predicted and measured air toxic concentrations, sources, and risks

The Government Performance and Results Act set a goal of reducing air toxic emissions by 75% from the 1993 levels (46). In order to make informed policy decisions, air toxic concentrations, sources, and risks throughout the nation need to be determined. To help achieve this goal, the EPA conducted the National Air Toxics Assessment (NATA). The initial assessment estimated exposures and risks of 33 of the 189 air toxics at the census track level throughout the county using an integrated emissions, dispersion, exposure and risk modeling framework. In 1999 NATA was expanded to include 177 pollutants. EPA is currently working on the 2002 NATA.

NATA consists of four main components: compiling a national emissions inventory of outdoor sources, modeling annual average outdoor concentrations of air toxics at the census tract level, determining human exposure to outdoor air toxics, and finally estimating health risks associated with inhalation of air toxics. Critical inputs are the National Toxics Inventory (NTI), meteorology and topographical data, NATA simulates pollutant dispersion and chemical reaction during transport using a version of AERMOD that has been implemented as part of the Assessment System for Population Exposure Nationwide (ASPEN) (47).

NATA estimates the concentration, sources, and health risks of air toxics at the census tract level throughout Allegheny County. The NATA results can be used to prioritize pollutants and emissions sources and indentify potential air toxic hotspots. Therefore, the NATA source/inventory-based estimates of risks complement the receptor/ambient concentration based estimates that are the focus of this study. However, relatively few studies have compared predictions of the NATA modeling framework to measured concentrations (48, 49), and no evaluations have been conducted in Allegheny County. The published comparisons have shown that measured and predicted concentrations of gas-phase primary emissions are generally within a factor of 10. Larger discrepancies exist for regional and secondary pollutants. Previous studies have not evaluated the predicted source contributions or risks rankings.

In this chapter, predictions of the 2002 National Air Toxics Assessment (NATA) are evaluated using the experimental data. Measured concentrations are compared to census tract level predictions at the four baseline sites. The pollutant risk ranking from Chapter 3 is compared to the risks calculated from the NATA-modeled outdoor concentrations. Finally, the source apportionment results from Chapter 5 and 7 are compared to the NATA source apportionment. The chapter concludes with a brief discussion of how these comparisons refine our understanding of the sources and risks of air toxics in Allegheny County.

8.1 Target Air Toxics

This analysis investigated NATA performance for 47 air toxics listed in Table 8.1. This includes 37 gas phase organic air toxics, 10 metals, and all of the priority air toxics identified in Chapter 3.

Table 8.1 also indicates air toxics which are considered in each component of the evaluation. Predicted concentrations of each toxic are compared to measure data. All of the toxics with health risk data, *RFC* or *URE*s, were included in the risk ranking analysis. The source apportionment comparison focused on air toxics that pose substantial health risks.

Table 8.1 Pollutants included in the NATA evaluation.

	Risk Ranking	Annual Conc.	Source App.
Acetaldehyde	X	X	X
Acrolein	X	X	X
Benzene	X	X	X
Benzyl chloride	X	X	
Bromoform	X	X	
Bromomethane	X	X	
Butadiene, 1,3-	X	X	X
Carbon disulfide	X	X	
Carbon tetrachloride	X	X	
Chlorobenzene	X	X	
Chloroethane	X	X	
Chloroform	X	X	
Chloromethane	X	X	
Dibromoethane, 1,2 -	X	X	
Dichlorobenzene, 1,4-	X	X	
Dichloroethane, 1,1-	X		
Dichloroethane, 1,2-	X	X	
Dichloroethene, 1,1-	X	X	
Dichloropropane, 1,2-	X	X	
Ethylbenzene	X	X	
Formaldehyde	X	X	X
Hexachlorobutadiene	X	X	
Hexane	X	X	
Methyl isobutyl ketone	X	X	
Methylene chloride	X	X	
MTBE	X	X	
Propionaldehyde	X	X	
Styrene	X	X	
Tetrachloroethene	X	X	
Tetrachoroethane, 1,1,2,2-	X	X	
Toluene	X	X	
Trichlorobezene, 1,2,4-	X	X	
Trichloroethane, 1,1,1-	X	X	
Trichloroethene	X	X	
Trichloroethene, 1,1,2-	X	X	
Vinyl chloride	X	X	
Xylenes	X	X	
Antimony	X	X	
Arsenic	X	X	
Beryllium	X	X	
Cadmium	X	X	
Chromium	X	X	
Cobalt	X	X	
Lead	X	X	
Manganese	X	X	
Nickel	X	X	
Selenium	X	X	

8.2 Comparison of Predicted and Measured Outdoor Concentrations

NATA reports predicted annual average air toxic concentrations at the census tract level. In this section the study average air toxic concentrations measured at the four baseline sites are compared to preliminary predictions from the 2002 NATA. Although measurements and model results are for different years, there were no large changes in emissions in Allegheny County between 2002 and 2006 so year-to-year variations in air toxic concentrations are expected to be modest.

Figures 8.1 to 8.3 present scatter plots of predicted annual average outdoor concentration versus the measured geometric mean concentration for 29 air toxics. The error bars extend to the 95th percentile confidence interval of the mean. There is reasonable agreement between the measured and predicted concentrations. The best agreement is observed for carbon tetrachloride, chloromethane, bromomethane, and chloroform. Measured and predicted concentrations of these four pollutants rest almost on the 1:1 line on the scatter plots. Measured and predicted concentrations of acetaldehyde, benzene, formaldehyde, xylenes, toluene, tetrachloroethene, acrolein, ethylbenzene and hexane are generally within a factor of two at all sites. Measured and predicted 1,3-butadiene, tetrachloroethene, 1,4-dichlorobenzene, trichloroethene, 1,2 dibromoethane, and 1,2 dichloromethane concentrations are within a factor of two at three sites but at one site concentrations differ by more than a factor of two. Measured concentrations of MTBE, 111-trichloroethene, and MIBK were lower than the modeled concentrations by at least a factor of two at all sites.

Figures 8.1-8.3 reveal poor model performance for some air toxics. Measured concentrations of carbon disulfide, styrene, propionaldehyde, vinyl chloride, 1,2-dichloroethane, and chlorobenzene were consistently higher than modeled concentrations by at least a factor of two at all sites. Styrene was underpredicted by a factor of six at both Avalon and Stowe, the two sites next to Neville Island. Propionaldehyde was underpredicted by at least a factor of two at all sites and by a factor of four at the urban background site (South Fayette). 1,2-dichoroethane was underpredicted by a factor of 10-12 at all sites. Vinyl Chloride was underpredicted by a factor of 20 at Flag Plaza. Chlorobenzene concentrations are 16-30 times higher than the modeled values. Carbon disulfide concentrations were 15 times higher than predicted concentrations at Avalon and Stowe and 58 times higher downtown (Flag Plaza).

The predicted concentrations of the remaining eight air toxics were essentially zero ($<1.0 \times 10^{-4}$ μg/m^3). These eight toxics are: chloroethane, 1,1-dichloroethene, 1,1-dichloroethane, bromoform, benzyl chloride, 1,2,4-trichlorobenzene, and hexachlorobutadiene. All of these pollutants had concentrations less than 0.015 μg/m^3 at all sites, however concentrations were high enough for cancer risks to be greater than one in a million at all sites for hexachlorobutadiene and at three sites for benzyl chloride.

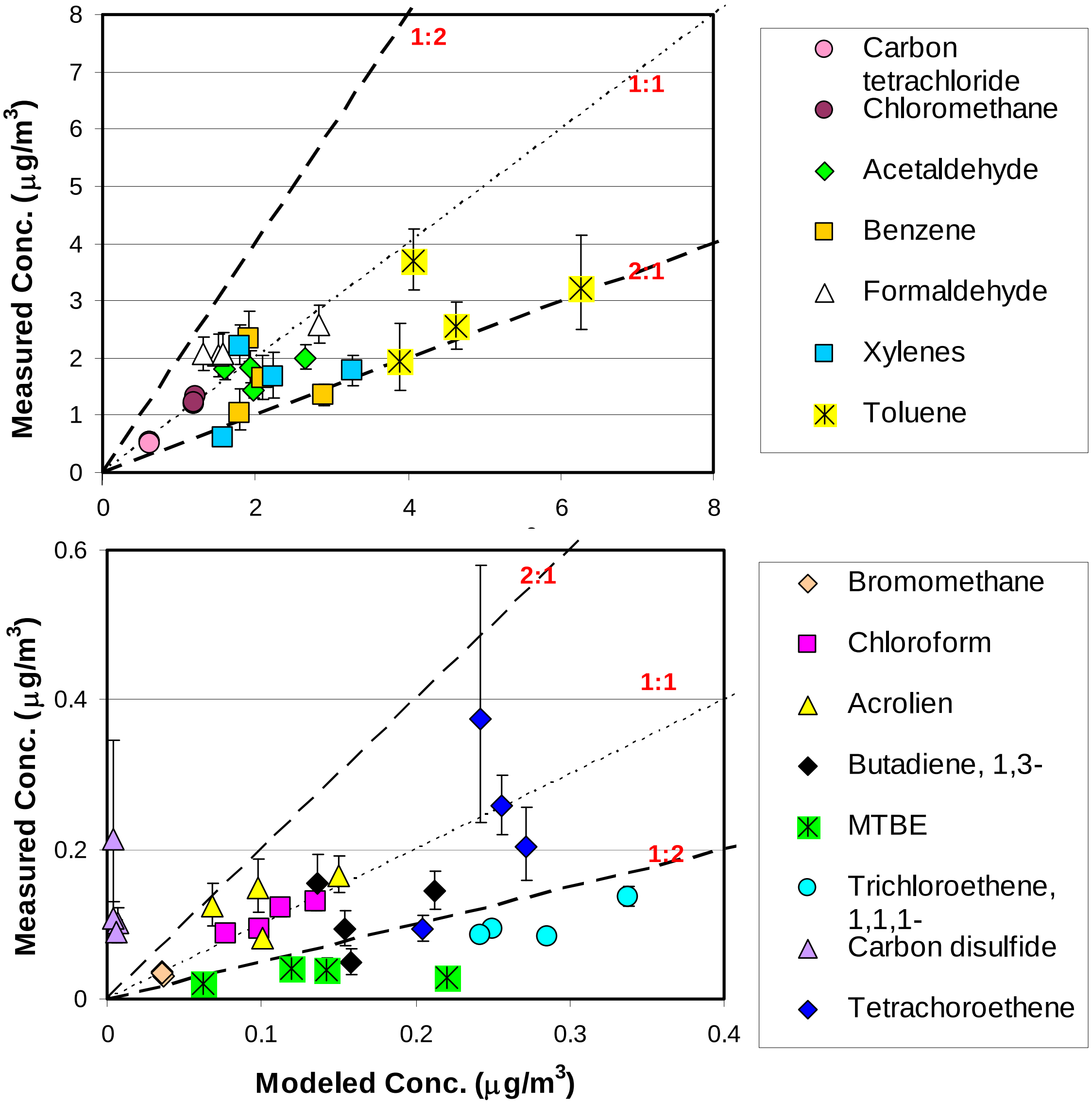


Figure 8.1 Comparison of measured and predicted annual average concentrations of gas-phase organic air toxics.

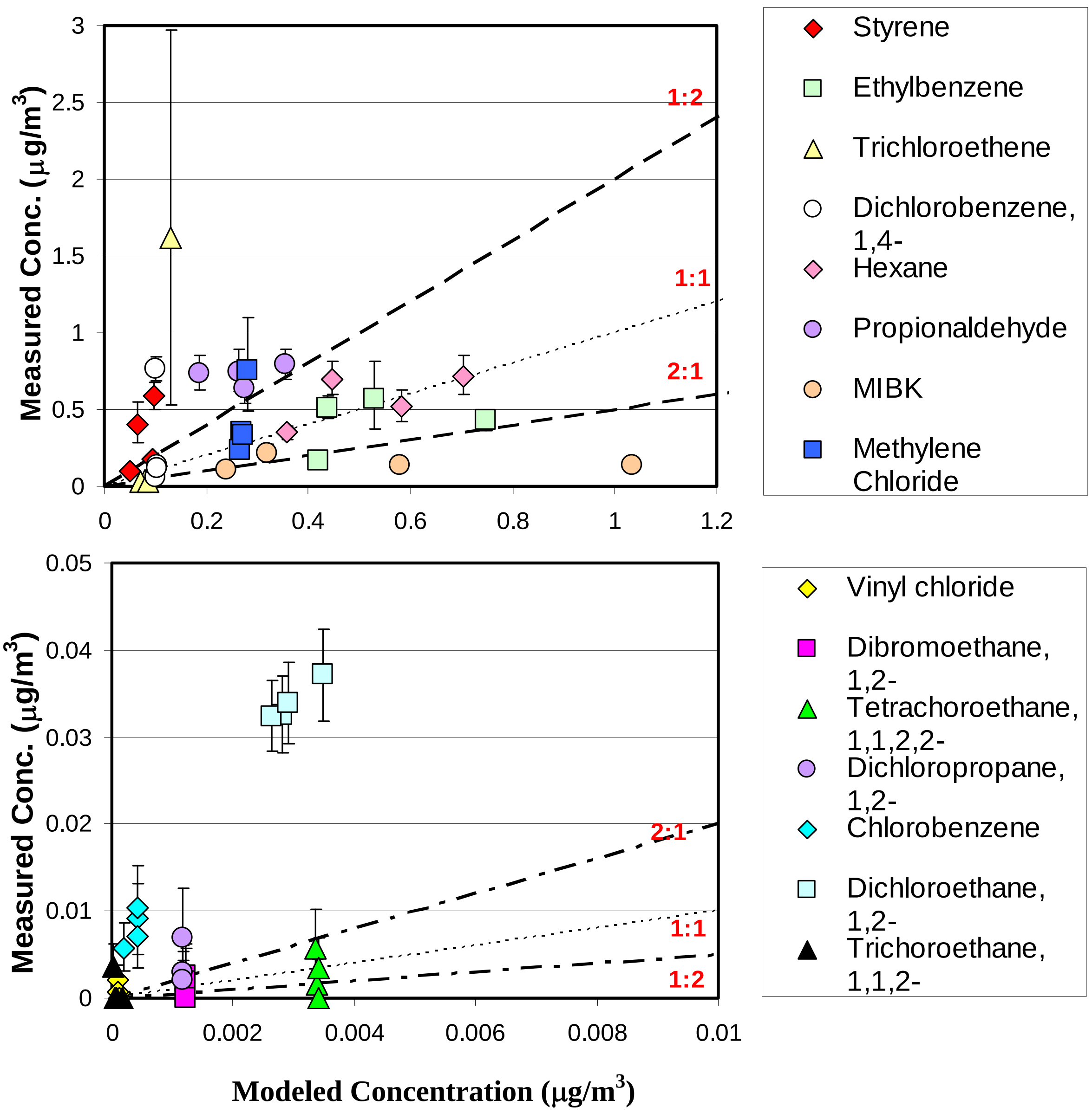


Figure 8.2 Comparison of measured and predicted annual average concentrations of selected gasphase organic air toxics.

Figure 8.3 presents scatter plots of measured versus predicted concentrations for metals at two sites -- Avalon and Schenley Park. Measured concentrations of most of the metals, with the exception of beryllium and arsenic, were underestimated at all of the sites. For example, arsenic concentrations are underestimated at Avalon by about a factor of two.

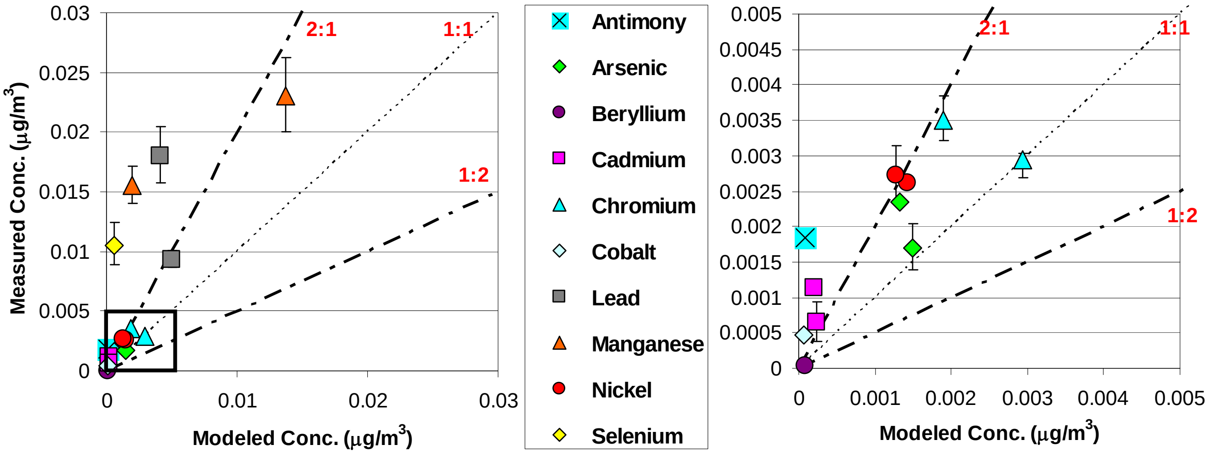


Figure 8.3 Measured versus modeled concentrations for metals measured at Avalon and Schenley Park sites.

Overall the level of agreement between the NATA predicted and measured air toxic concentrations in Allegheny County is comparable to other areas in the country (48, 49) The results suggest that emissions inventories of the modeled dispersion of chlorinated compounds need to be significantly improved as well as for carbon disulfide, styrene, and propionaldehyde. Of the 22 air toxics identified as priority air toxics in Section 3.5, measured and predicted concentrations for 12 were found to be within a factor of two. However, NATA substantially overpredicts MIBK concentrations and NATA severely underpredicts concentrations of 3 chlorinated air toxics (trichloroethene, 1,4-dichlorobenzene, and methylene chloride) at the Flag Plaza site, indicating problems with inventories in this specific area of the county. 1,3 butadiene is also underpredicted at the South Fayette site. Finally, five air toxics (hexachlorobutadiene, benzyl chloride, 1,2-dichloroethane, propionaldehyde, and styrene) were systematically underpredicted at all of the sites, indicting more widespread inventory problems. These are important non-mobile sources of these compounds including industry, biomass burning, and solvent use.

8.3 Risk Ranking of Pollutants

One of the intended uses of NATA is to identify priority or high risk air toxics (50). In Chapter 3 the cancer and non-cancer risks were estimated using measured concentrations. In this section, the same risk model is applied to the NATA predicted outdoor concentrations and the two sets of risk estimates are compared. Although outdoor concentrations are only one contributor to the total risk, risk estimates of outdoor concentration data allows for priority ranking of pollutants emitted by outdoor sources.

Figures 8.4 and 8.5 plot the additive LIR calculated from the measured and NATA predicted air toxic concentrations. Figure 8.4 shows results for gas-phase organic air toxics at the four baseline sites; Figure 8.5 shows results from metals at two sites (Avalon and Schenley Park). Both approaches provide consistent estimates of the overall risk and the relative contribution of each component.

Table 8.2 compares the risk ranking of NATA to the estimates based on measured concentrations. With a few exceptions, NATA provides basically the same risk ranking as the measured data. For example, at all of the sites, both approaches identify formaldehyde as the highest risk organic air toxic. The Flag Plaza site has the worst comparison, but even downtown, where there are unexpected sources of chlorinated compounds, only trichloroethene and 1,4-dichloropropane are ranked too low. Unsurprisingly, NATA does the best in areas where the major sources of air toxics are in the inventory. At the background site and at the sites dominated by large point sources the risks are better understood than at the downtown site where unidentified sources of chlorinated compounds are contributing substantially to risks.

Although the measurements and NATA both identify a similar set of priority toxics, NATA underestimates total cancer risks at all sites considered in this study. NATA underestimates the gas-phase cancer risk at the sites by 16%-58% with the largest difference at Avalon. At Stowe and South Fayette this is primarily due to an underprediction of formaldehyde. At Avalon it is due to an underprediction of both benzene and formaldehyde. At Flag Plaza both formaldehyde and benzene are overpredicted, but the two main chlorinated compounds, trichloroethene and 1,4-dichlorobenzene, are underpredicted. NATA also underestimates the risks of metals. NATA underestimates metal risks by 73% at Schenley Park and by 57% at Avalon. At Avalon NATA underestimates arsenic. At Schenley Park NATA underestimates chromium. At both of the sites NATA underestimates cadmium. These comparisons suggest that there may be more regional emissions of chromium and cadmium than NATA predicts and larger point source emissions of arsenic near Neville Island.

Even though NATA somewhat underpredicts risks, Figures 8.4 and 8.5 indicate that for most of the priority toxics NATA and the measured risks agree to within a factor of two. The only high priority toxic in Allegheny County that NATA does poorly with is trichloroethene. NATA underpredicts the risks posed by trichloroethylene at the Flag Plaza site by more than a factor of 10. NATA also underpredicts cadmium and lead by more than a factor of five and seven respectively, but these toxics pose lower risks. This indicates problems with either the emissions inventories or dispersion of these compounds in the model; however, these problems do not radically alter the conclusions one would derive from NATA.

Since the cancer unit risk estimates (*URE*) vary widely from toxic to toxic, NATA can accurately prioritize risks without precisely predicting outdoor concentrations for all air toxics. In order to accurately predict risks, NATA must accurately predict concentrations of the risk drivers. NATA predictions for priority air toxics are generally within a factor of two; therefore it gets the overall risks and risks rankings basically right. With the exception of the chlorinated compounds at Flag Plaza, the air toxics that NATA does a poor job of predicting are not risks drivers and therefore do not significantly alter conclusions regarding risk reduction priorities. Therefore, when evaluated on a risk basis, NATA performance is better than when it is considered on a concentration basis.

For non-cancer risks both approaches found that acrolein was the only air toxic that had a hazard quotient larger than one. Therefore, both approaches identified acrolein as the only air toxic potentially posing any non-cancer risks.

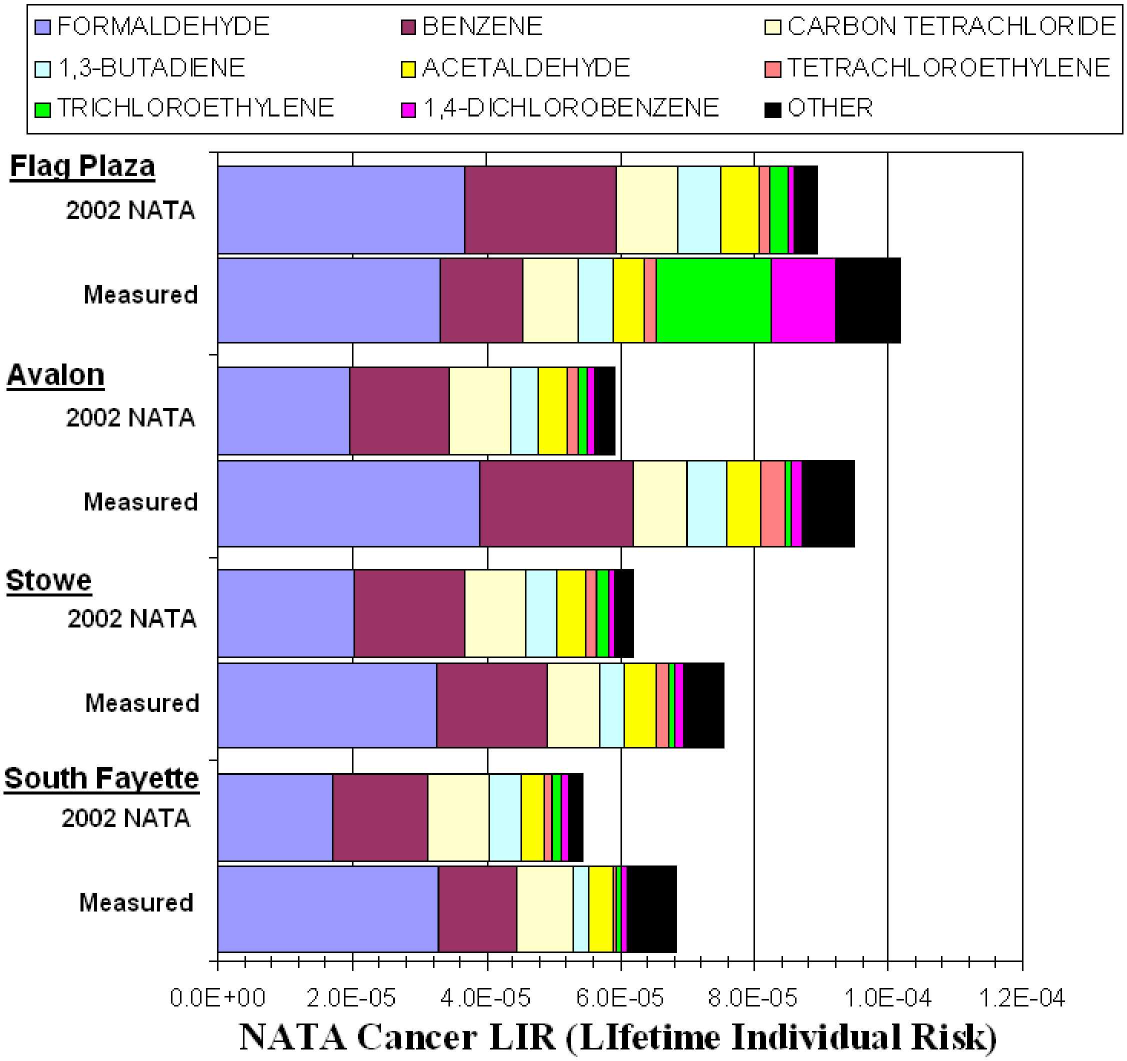


Figure 8.4 Comparison of additive cancer risk for preliminary 2002 NATA to estimates based on measured concentrations. The category "other" includes: chloroform, 1,2-dichloroethane, hexachlorobutadiene, benzyl chloride, methylene chloride, 1,2-dicloropropane, 1,1,2,2-tetrachloroethane, 1,1-dichloroethane, 1,1,2-trichloroethane, vinyl chloride, and bromoform.

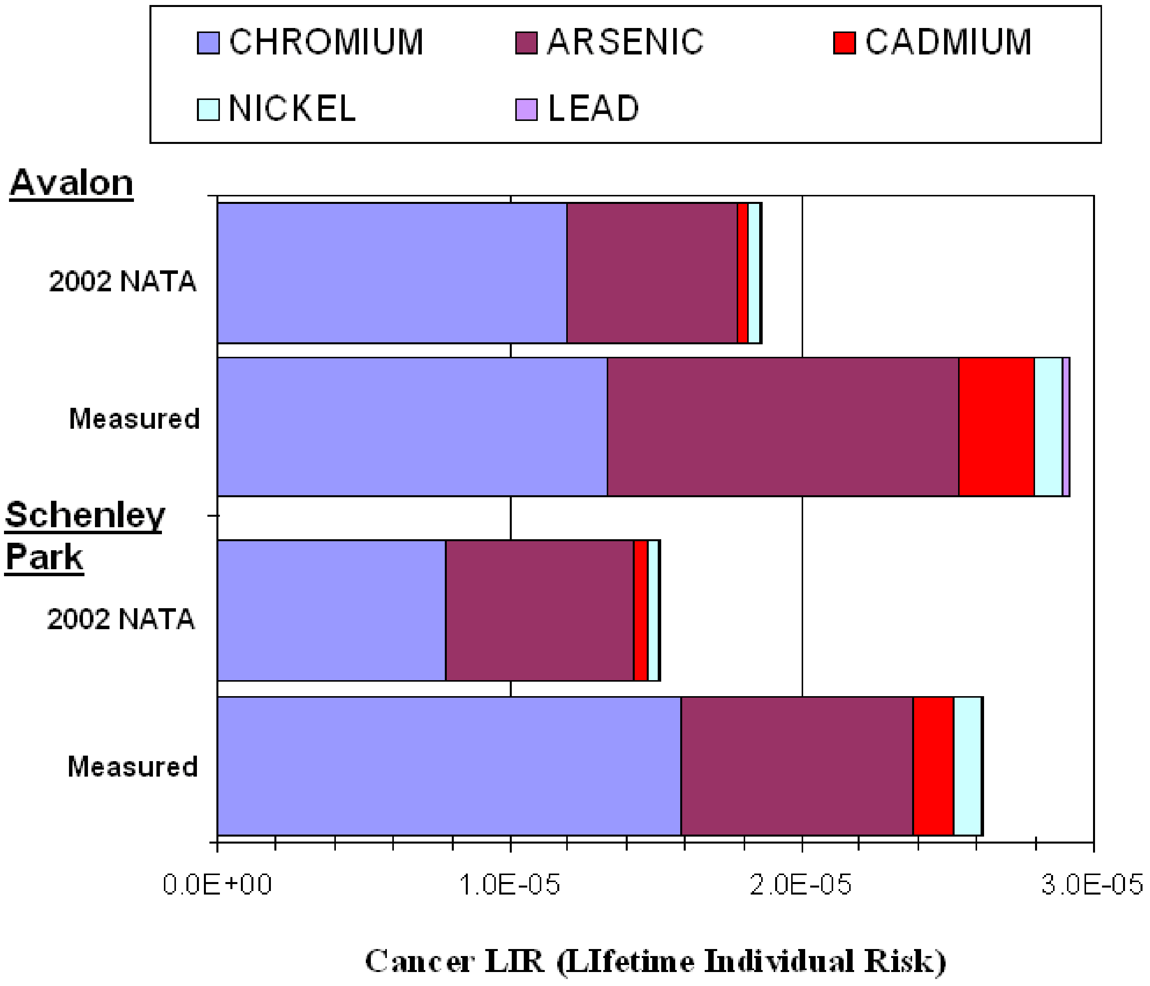


Figure 8.5 Comparison of additive cancer risk for preliminary 2002 NATA to estimates based on measured concentrations for metals.

Table 8.2 Risk ranking of air toxics from highest cancer risks to lowest for the 10 risk drivers from NATA and the health risks analysis presented in Chapter 3.

	South Fayette		Avalon	
risk ranking	Measured	Modeled	Measured	Modeled
1	Formaldehyde	Formaldehyde	Formaldehyde	Formaldehyde
2	Benzene	Benzene	Benzene	Benzene
3	Carbon tetrachloride	Carbon tetrachloride	Chromium	Chromium
4	Chromium	Chromium	Carbon tetrachloride	Carbon tetrachloride
5	Arsenic	Arsenic	1,3-butadiene	Arsenic
6	Acetaldehyde	1,3-butadiene	Arsenic	Acetaldehyde
7	Chloroform	Acetaldehyde	Acetaldehyde	1,3-butadiene
8	1,3-butadiene	Chloroform	Tetrachloroethene	Chloroform
9	Hexachlorbutadiene	Trichloroethene	Chloroform	Trichloroethene
10	benzy Chloride	Tetrachloroethene	1,4-dichlorobenzene	Tetrachloroethene

	Flag Plaza		Stowe	
risk ranking	Measured	Modeled	Measured	Modeled
1	Formaldehyde	Formaldehyde	Formaldehyde	Formaldehyde
2	Trichloroethene	Benzene	Benzene	Benzene
3	Benzene	Carbon tetrachloride	Carbon tetrachloride	Carbon tetrachloride
4	1,4-dichlorobenzene	1,3-butadiene	Acetaldehyde	1,3-butadiene
5	Carbon tetrachloride	Acetaldehyde	1,3-butadiene	Acetaldehyde
6	1,3-butadiene	Chloroform	Chloroform	Chloroform
7	Acetaldehyde	Trichloroethene	1,4-dichlorobenzene	Trichloroethene
8	Chloroform	Tetrachloroethene	Tetrachloroethene	Tetrachloroethene
9	Tetrachloroethene	1,4-dichlorobenzene	Hexachlorobutadiene	1,4-dichlorobenzene
10	Benzyl Chloride	1,1,2,2-Tetrachloroethane	Trichloroethene	1,1,2,2-Tetrachloroethene

8.4 Comparison of Source Apportionment Estimates

The development of effective regulatory strategies requires knowing the sources of priority air toxics. In Chapter 5, receptor modeling was used to apportion the measured concentrations to sources. NATA determines sources by modeling the dispersion of emissions. The receptor modeling results were compared to the NATA based source apportionment for nine priority air toxics (formaldehyde, benzene, 1,3-butadiene, acetaldehyde, trichloroethene, 1,4-dichlorobenzene, carbon tetrachloride, and tetrachloroethene) and acrolein, the only potential non-cancer risk. This section discusses two of the air toxics whose receptor-modeled apportionment and NATA based source apportionment are most divergent, formaldehyde and benzene, and what this implies about NATA.

NATA apportions air toxics to five source categories: major point sources, area sources, on-road mobile sources, non-road mobile sources, and background. The receptor model analysis can be grouped into three source categories: mobile sources, non-mobile sources and secondary/background sources. To compare the two estimates, the NATA on-road mobile and non-road mobile source categories were combined to compare with the receptor modeling mobile category, and the NATA major point sources and area point sources categories were combined to compare with the receptor modeling non-mobile category. NATA modeling includes chemistry and apportions secondary products to the category associated with primary emissions. However, regionally distributed secondary products are classified as regional for the receptor modeling. This may create some discrepancies between the NATA and receptor model determined background contributions.

Figure 8.6 compares the two source apportionment estimates for benzene, one of the highest priority air toxics. The receptor model analysis apportions a large fraction of the benzene at all sites to major point sources (metallurgical coke production). However, NATA attributes the majority of the benzene at all sites to mobile source emissions. This means that NATA predicts the highest benzene concentrations downtown, not in Avalon (contrary to the measurements). Relative to the receptor model analysis, NATA underestimated the non-mobile contribution to benzene concentrations at Avalon, downtown, and the regional background by a factor of 8.7, 1.5, and 10.9 respectively. Conversely, NATA overestimates the mobile contributions at each of these sites by a factor of 1.3, 1.9, and 8.7 respectively. Therefore, the relative success of NATA to predict absolute benzene concentrations appears to be due in part to compensating errors.

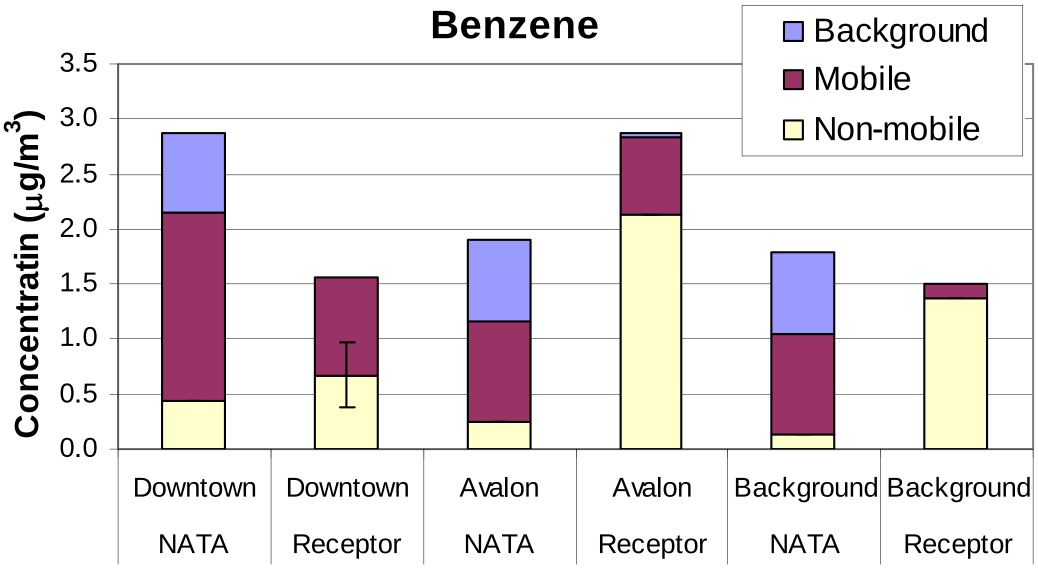


Figure 8.6 Comparison of NATA and receptor model source apportion for benzene.

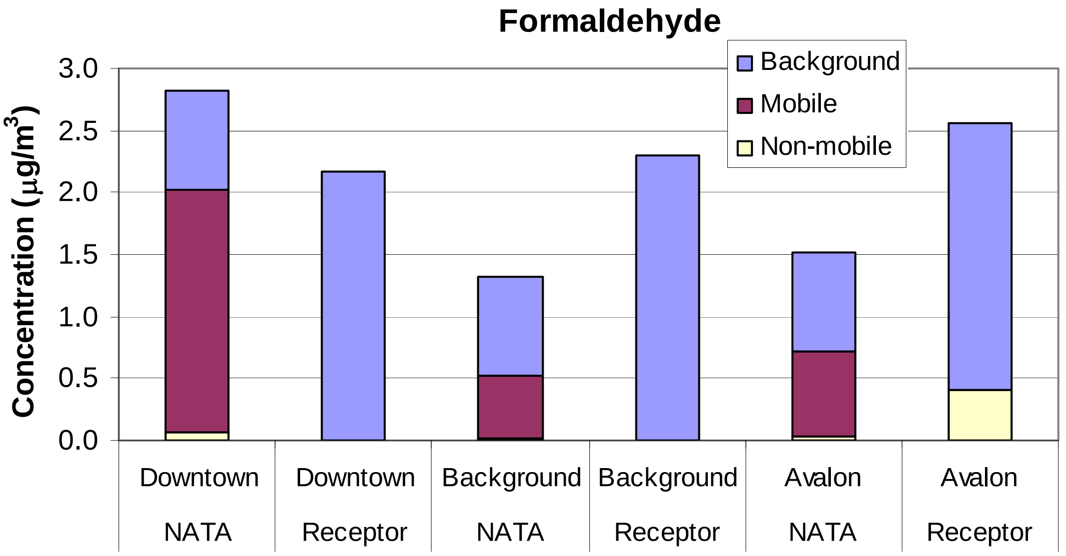


Figure 8.7 Comparison of NATA and receptor model apportionment of formaldehyde.

Formaldehyde is another priority mobile source air toxic that NATA appears to overestimate at mobile dominated sites and underestimate elsewhere. Figure 8.7 indicates large differences between the two source apportionment estimates for formaldehyde, another priority air toxic. As discussed in Chapter 3, formaldehyde concentrations are regionally distributed in Allegheny County. For this reason, we attributed the majority of measured formaldehyde to secondary/background sources. In contrast, NATA apportions most of the formaldehyde to local mobile source emissions. NATA also predicts large spatial gradients in formaldehyde concentrations with levels downtown being about a factor of two higher than the other sites. The result is that NATA overpredicts formaldehyde concentrations at Flag Plaza and underpredicts them at the other sites. Therefore, NATA is overestimating local formaldehyde emissions while underestimating regional secondary production.

In Allegheny County NATA appears to consistently overestimate the mobile source contribution of two major gas-phase risk contributors and underestimate the non-mobile or industrial contributions. Although most of the MSATs that were compared showed some overestimations of the mobile contribution, the magnitude did vary and acrolein, a MSAT with higher yields in diesel than gasoline vehicles(33, 34), was underestimated by the model. The discrepancies may be due to emissions factors, vehicle activity, fleet composition, or another cause. Another interesting MSAT is propionaldehyde. Propionaldehyde is a regionally distributed air toxic with peak concentrations in the fall. Propionaldehyde is also emitted by biomass combustion, and biomass smoke levels peak in the fall in the Allegheny County(23). NATA underestimates concentrations by a factor of 2.5-4 at all sites and apportions almost all of the propionaldehyde to mobile sources. Although no receptor modeling apportionment of propionaldehyde is available, the seasonal variation shows the likely influence of biomass burning that may not be captured in the NATA model.

NATA appeared to consistently underestimate non-mobile contributions while often overpredicting mobile contributions. For the air toxics that are not mobile sources, tetrachloroethene, trichloroethene, 1,4-dichlorobenzene, this can be seen in an underprediction of the outdoor concentrations, especially pollutants associated with large point sources. For the mobile air toxics, like benzene, it results in an overestimation of concentrations in the areas thought to be mobile dominated and underpredictions in areas thought to be non-mobile dominated. This conclusion is supported by the concentration comparisons shown in Figures 8.1-8.3. For example, NATA consistently underpredicts concentrations of chlorinated compounds and many metals; all of these species are associated with emissions from non-mobile sources.

8.5 Conclusions

When viewed from the perspective of risk, NATA performs well in Allegheny County. Except for chlorinated compounds at Flag Plaza, NATA more or less correctly ranks air toxic by risk. This is due to a combination of the large variation in pollutant toxicity and that NATA does a better job predicting concentrations of the air toxics that drive the risk estimates. However, there appear to be some problems in the NATA source apportionment.

Presumably if the NATA source apportionment and the receptor modeling agreed well, then there is a good sense of the sources for these pollutants. Where NATA and receptor modeling differ shows possible biases in the model. In Allegheny County, NATA underestimates the emissions and risks associated with large point sources and overestimates the emissions and risks from mobile sources. This may be due to several factors including underreporting of industrial emissions, errors in the emissions factors, or problems with dispersion modeling. More work needs to be done to identify the sources of these discrepancies.

Chapter 9. Synthesis, Conclusions and Recommendations

This chapter synthesizes results from throughout the report for priority air toxics, for important sources, and for the different measurement sites. The chapter concludes with recommendations for reducing air toxic exposures in Allegheny County and a discussion of important data gaps.

9.1 Synthesis by Pollutant

This study investigated the concentrations, health risks, and sources of 65 air toxics at seven sites in Allegheny County. Based on the measured concentrations and estimated risks, a subset of the investigated air toxics were classified as priority toxics (Table 3.3). Four air toxics were found to pose cancer risks greater than 1 in 100,000 at one or more of the baseline sites: diesel particulate matter, formaldehyde, benzene and trichloroethene. These four pollutants were classified as the highest priority toxics for Allegheny County. The estimated cancer risk for trichloroethene was greater than 1 in 100,000 only at the Flag Plaza site; the cancer risks for the other three highest priority toxics were greater than 1 in 100,000 at all four baseline sites.

9.1.1 Diesel Particulate matter (DPM)

Of the 65 air toxics considered in this study, DPM poses the greatest cancer risk at all of the sites. The best estimates for the DPM cancer risks were 1×10^{-3} downtown and 3×10^{-4} in Schenley Park. Figure 9.1 compares the estimated cancer risks to other common risks. Although a risk of 1×10^{-3} is well above typical regulatory thresholds for environmental pollutants, 10^{-4} or 10^{-6}, it is still well below the cancer incidence rate of 1 in 3 for women and 1 in 2 for men in the United States (51).

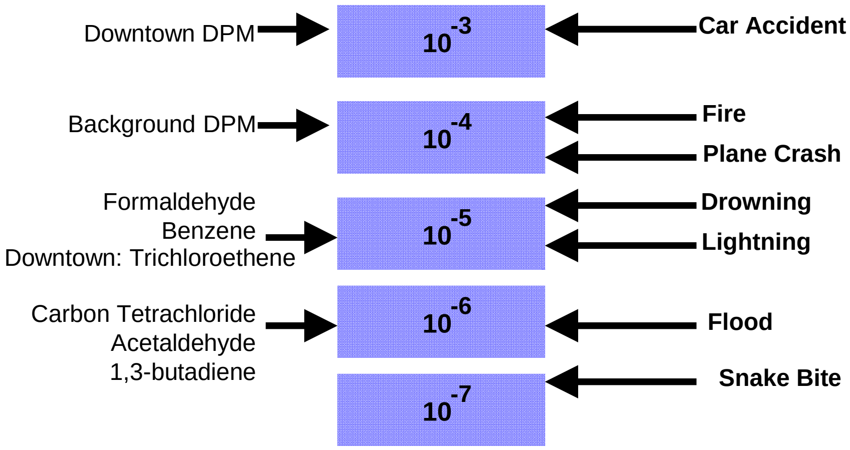


Figure 9.1 A comparison of air toxic cancer risks with other common risks.

Although the toxicity data for DPM are more uncertain than data for some other air toxics, even at its lower bound the cancer risk estimated for DPM was still greater than the best estimates for the other 65 air toxics considered here. Therefore, reducing DPM exposures should be given the highest priority.

Only limited data are currently available on the DPM levels in the county. These data indicate that downtown is a DPM hotspot, with levels that are a factor of three to four higher than in other areas in the county. However, even outside of the downtown area, DPM levels are still high enough such that it still poses the greatest cancer risk.

9.1.2 Formaldehyde

Formaldehyde poses the second highest health risk of the 65 air toxics considered by this project. However the cancer risks associated with formaldehyde are about a factor of ten lower than the best estimate for DPM.

Formaldehyde is both directly emitted by sources such as motor vehicles and formed in the atmosphere from oxidation of volatile organic compounds. The strong seasonal variability and relatively uniform spatial distribution in formaldehyde concentrations observed across the four baseline sites indicates that the vast majority in Allegheny County comes from regional and/or secondary sources. Therefore, there is little opportunity for the county to reduce formaldehyde exposures. Federal regulations to limit regional hydrocarbon emissions for ozone control should help reduce formaldehyde levels in the county.

9.1.3 Benzene

Benzene was the third most important air toxic studied, posing a lifetime cancer risk of 1 to 2 x 10^{-5}. The highest risks were in Stowe and Avalon, the two residential sites adjacent to Neville Island. Benzene concentrations and health risks in Allegheny County are high compared to the national data with concentrations near the 75th percentile in downtown and in South Fayette (regional background site) and at the 95th percentile at Stowe and Avalon. Therefore, there is a countywide problem with benzene.

Benzene is emitted by both mobile and industrial sources. Emissions from industrial facilities, in particular coke works, are a very important source of benzene in Allegheny County. For example, the high time resolved measurements revealed that benzene was frequently elevated at all three intensive sites when the wind was blowing from either the Clairton or Shenango Coke Works. In Avalon emissions from the Shenango Coke Works contribute 66% of the benzene exposure. Downtown is influenced by emissions from both the Shenango and Clairton Coke Works, which contribute almost 60% of benzene exposure with the balance from mobile source emissions. At the Carnegie Mellon University site, emissions from the Clairton Coke works contributed almost 60% of the benzene exposure. The surprisingly high levels of benzene in South Fayette may largely be due to emissions from outside of Allegheny County.

9.1.4 Chlorinated Compounds

Several chlorinated air toxics posed large cancer risks downtown, but not at the other baseline sites. At the Flag Plaza site, these chlorinated toxics contributed about 25% of the cancer risks attributed to the target organic air toxics. Many of these chlorinated compounds are commonly used as solvents, but this study was not able to identify specific sources for many of these toxics. They are not emitted by mobile sources. Most of the chlorinated air toxics did not co-vary, indicating that they are not emitted by the same source. As discussed in Chapter 4, concentrations of several of these chlorinated toxics were strongly wind-direction dependent, which provides insight into the location of sources.

Trichloroethene: Trichloroethene was estimated to pose a lifetime cancer risk of 2 x 10^{-5} at the Flag site, which is about a factor of twenty higher than the cancer risk it poses at any other site. The source of trichloroethene is not known. Elevated trichloroethene concentrations were not observed during the downtown intensive at the Diamond Building or the Flag Plaza sites. No major sources of trichloroethene emissions are reported in the Allegheny County emission inventory and NATA underestimates trichloroethene concentrations at the Flag Plaza site by about a factor of ten. Trichloroethene is used in degreasing operations as well as several industries including printing, plumbing and textiles (21).

Tetrachloroethene: Tetrachloroethene poses significant cancer risks at all of the urban sites. The highest tetrachloroethene concentrations were measured at Diamond Building. Mean concentration of tetrachloroethene at the Diamond Building was two-and-one-half times higher than at the Avalon site and five times higher than at the Flag Plaza site which is less than 1.2 km away from the Diamond Building. Given the close proximity of the two downtown sites, this indicates a very local source close to the Diamond Building. The elevated concentrations of tetrachloroethene are likely due to emissions from a local dry-cleaner, which illustrates how very small point sources can have a significant on local air toxic exposures. In Avalon the Allegheny County Sanitary Authority (ACSA) was an important source of tetrachloroethene.

1,4-Dichlorobenzene: 1,4-dichlorobenzene is another chlorinated toxic that posed substantially higher cancer risks downtown than at the other baseline sites. Of the 36 target organic air toxics, 1,4-dichlorobenzene poses 9% of the cancer risks downtown versus 1-2% of the risks at the background and industrial influence sites (Avalon and Stowe). Elevated concentrations of 1,4-dichlorobenzene were also observed during the intensive study at the Diamond Building indicating that the problem is not localized to the Flag Plaza site. We do not know the source of the 1,4-dichlorobenzene in the downtown area, but concentrations are much higher when the wind is from the south and southeast.

Chlorinated air toxics with regional sources: Concentrations of hexachlorobutadiene, benzyl chloride, and 1,2-dichloroethane varied little among the four baseline sites, indicating that they are not strongly influenced by local emissions. The risk posed by each of these toxics was relatively small, 1 to 3% of the additive cancer risk of the 36 target organic air toxics.

9.1.5 Carbon Tetrachloride

Carbon tetrachloride poses a lifetime cancer risk of 7 x 10^{-6}, which corresponds to 9%-12% of the additive cancer risk of the organic air toxics considered by this study. Carbon tetrachloride is a CFC that was used extensively in the early part of the 20th century as a refrigerant but is currently primarily used in small quantities as an industrial solvent (21). There are negligible carbon tetrachloride emissions in Allegheny County. Carbon tetrachloride has a relatively long atmospheric lifetime on the order of 30-50 years; therefore the risks posed by carbon tetrachloride in Allegheny County are due to historical global emissions. There is nothing the County can due to reduce these risks, but these risks will slowly fall over time because of the substantial reductions in global CFC emissions required by the Montreal Protocol.

9.1.6 1,3-Butadiene

1,3-butadiene contributes 3%-6% of the gas-phase organic air toxics cancer risk in Allegheny County. Concentrations of 1,3-butadiene in Allegheny County are at the national average in the downtown and the industrial influenced sites and below the 25th percentile at the regional background site. Motor vehicles are the dominant source of 1,3 butadiene in Allegheny County.

9.1.7 Acetaldehyde

Acetaldehyde contributes 4%-6% of the gas-phase organic air toxics cancer risk throughout Allegheny County. Acetaldehyde exposures in Allegheny County were estimated to be essentially half due to local mobile source emissions and half due to regional/secondary emissions.

9.1.8 Acrolein

Acrolein was the only air toxic estimated to present a significant non-cancer risk in Allegheny County. The hazard quotient of acrolein is above one at all of four baseline sites even though concentrations are low compared to the rest of the nation. Baseline measurements showed that acrolein concentrations were a factor of two higher at the urban sites as compared to South Fayette with highest concentrations at Avalon and Stowe. Diesel vehicles are the major source of acrolein downtown, while in Avalon and Stowe acrolein correlates most highly with carbon disulfide and styrene, two tracers of emissions from point sources on Neville Island.

However, no significant sources of acrolein are listed on the Allegheny County emissions inventory for Neville Island.

9.1.9 Metals

This project did not measure metals concentration, but archived data were used to estimate cancer and non-cancer risks. The cancer risks associated with chromium, arsenic and cadmium were greater than 10^{-6} at three sites in Allegheny County. Chromium poses the largest risks at all sites, greater than 10^{-5}. There is little spatial diversity between the sites and the site with the highest concentration was found to be Lawrenceville. Data were not available to identify the sources of these metals, but concentrations were not noticeably higher in Avalon.

9.2 Synthesis by Source

This work quantified the contribution of regional/secondary, mobile and non-mobile sources to the estimated risk at each site. Mobile sources, specifically diesel emissions, were the largest contributor to cancer risks at every site. However, the relative importance of different classes of diesel vehicles (on road, off road, city buses, school buses, long haul trucks, delivery trucks, construction equipment, etc.) cannot be determined from our data. If one excludes diesel particulate matter from the analysis, then cancer risks associated with regional/secondary pollutants were dominant.

Emissions from local industrial sources do contribute significantly to pollutant exposures and risk. Since Allegheny County has more regulatory authority over these sources, their contribution is important to understand. The high time resolved measurements indicate that emissions from industrial facilities in the Clairton and Neville Island area are major sources air toxics. From a risk perspective, the emissions from coke plants are particularly important because of their contribution to benzene levels. At the downtown site, sources of chlorinated air toxics contribute significantly to the risk. Unfortunately the source(s) of these chlorinated toxics is not well understood.

9.3 Spatial Variability

A major objective of this project was to quantify the spatial variability of air toxic exposures in Allegheny County. This was done by measuring air toxic concentrations at seven different sites. Four of these sites (Avalon, Stowe, Flag Plaza, and the Diamond Building) were specifically chosen because of concerns over high air toxic exposures due to emissions from local sources. At Avalon and Stowe, the local sources of concern are the very large industrial facilities on Neville Island. At the downtown sites, the local source of concern is the large amount of traffic. Much lower air toxic exposures were expected in South Fayette, a regional background site not strongly influenced by local sources.

For the 38 target organic air toxics, the additive cancer risk varied by less than a factor of two across the set of sites, with the highest risks seen downtown. There was only modest spatial variability in cancer risks because two of the most important toxics, formaldehyde and carbon tetrachloride, are regionally distributed. Benzene also contributed significantly to the cancer risks at all sites; the highest benzene risks were in Avalon and Stowe due to local emissions. Chlorinated compounds were elevated downtown including unexpectedly high concentrations of trichloroethene and 1,4-dichlorobenzene.

A major goal of this project was to compare air toxic concentrations and risks in Allegheny County to other locations in the United States. The additive cancer risk of the 36 target organic air toxics varied by about a factor of 16 across a set of fourteen U.S. cities. For this set of toxics, risks in Allegheny County were found to be at about the 50th percentile within this set of cities. Therefore, the health risks of air toxics in Allegheny County, even at sites close to local sources, are comparable to other urbanized areas in the United States.

9.4 Recommendations

Diesel Particulate Matter: The county, like all urban areas, has a problem with DPM. The County should make reducing diesel particulate matter concentrations the highest priority. The county has already implemented retrofit and idling programs to help reduce exposures to DPM. These are important programs, but they are primarily aimed at reducing exposures of school children. It is unclear if they will effectively address the downtown DPM hotspot. Although the specific diesel sources that are causing this hotspot are not known, likely candidates include Port

Authority Buses and delivery vehicles. To reduce DPM concentrations in the downtown area will likely require new initiatives, activity based and retrofit programs, aimed at these sources.

The DPM estimates made by this study were based on data collected at the Diamond Building, which is on a major bus thoroughfare. The spatial extent of the downtown DPM hotspot is not known. It is also not known if there are other hotspots in the county. Given the high risks posed by DPM, measurements to quantify the spatial extent of the downtown hotspot and to identify other hotspots in the county should be conducted to ensure that control programs are appropriately targeted.

Benzene: Benzene poses a countywide problem. The Clairton Coke Works is the largest point source of benzene in Allegheny County (1). A massive effort is currently underway to retrofit and upgrade the Clairton Coke Works to reduce air pollutant emissions. This should reduce benzene risks but likely will not eliminate elevated benzene problems in Allegheny County. The county should plan to measure benzene concentrations after retrofit is complete to quantify the reduction in benzene exposure. More controls are needed on the Shenango Coke Works to reduce the high benzene exposures in Neville Island area.

Chlorinated organics: Chlorinated organics substantially affect risks at the downtown sites. Emissions appear to be coming from multiple, small point sources. For example, at the Diamond Building, one local small business, a dry cleaner, appeared to substantially contribute to the risks and potentially any small point source can cause a local hotspot. To better understand the sources of trichloroethene in Allegheny County will require longer duration high time resolved measurements conducted, ideally, at the Flag Plaza site.

Other toxics: Using archived data this study found that metals posed significant risks; for example, chromium is the 5th highest contributor to cancer risks in the county and the 3rd highest contributor with local sources. However, the available data provide relatively little information on the sources of these metals. More data are needed to better characterize exposures and risks of toxic metals.

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