



**AUSTIN-ROUND ROCK TOXICS STUDY (ARTS)
FINAL REPORT**

Prepared for:

**Capital Area Council of Governments
6800 Burleson Road
Building 310, Suite 165
PO Box 17848
Austin, Texas 78760**

Prepared by:

**Albert Hendler
Shona Briscoe
URS Corporation
9400 Amberglen Boulevard (78729)
P.O. Box 201088
Austin, Texas 78720-1088**

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1.0 Introduction

This report describes the objectives, scope, and results of a year-long air toxics monitoring study that was conducted in the Austin-Round Rock area of central Texas during 2005-2006. The Austin-Round Rock Toxics Study (ARTS), which was sponsored by the United States Environmental Protection Agency (EPA) through a grant to the Capital Area Council of Governments (CAPCOG), was one of several local-scale air toxics assessments funded in Fiscal Year 2004 through the EPA National Air Toxics Monitoring Program Community Assessments Grant Program. The purpose of this EPA program is to assist state and local communities with characterizing their local air toxics problems and with tracking air toxics reductions.

The Capital Area Council of Governments is a regional planning commission that serves a 10-county area in central Texas, which includes the Austin-Round Rock Metropolitan Statistical Area (MSA). Among other things, CAPCOG serves as an advocate, planner, and coordinator of regional air quality initiatives including the Austin-Round Rock Early Action Compact (EAC) (TCEQ, 2004), which established preventive measures to help the region avoid going into ozone nonattainment. In 2003, CAPCOG applied for and received funds from EPA to conduct community-scale air toxics assessments in the Austin-Round Rock area. The EPA grant provided for the acquisition of field sampling equipment to outfit five air toxics sampling sites and to operate the sampling equipment for one year. CAPCOG contracted with URS Corporation of Austin, TX, and Eastern Research Group (ERG) of Research Triangle Park, NC, to collect and analyze the air toxics samples, respectively.

1.1 Background

Austin is not known nationally as a city with an air toxics problem; however, it has a rapidly growing population (Greater Austin Chamber of Commerce, 2006) and is ranked high in terms of traffic congestion among U.S. medium size cities (Texas Transportation Institute, 2005). For several years during 2000-2006, Austin appeared at risk of violating the national ambient air quality standard for ozone; although, as of December 2006 it was in attainment of the ozone standard as well as all the other EPA air quality standards. The EAC is intended to reduce the area's ozone precursor emissions and in doing so, will reduce the levels of some air toxics.

The Austin-Round Rock MSA, which is comprised of Bastrop, Caldwell, Hays, Travis, and Williamson counties, had a 2005 estimated population of over 1.4 million (Greater Austin Chamber of Commerce, 2006). Its two largest counties, Travis and Williamson (which composed 85% of the total MSA population) ranked 85th and 376th, respectively, in total Hazardous Air Pollution (HAP) emissions out of the 1207 U.S. urban counties (Figure 1-1) according to the 1999 National Emission Inventory (NEI) (EPA, 2003). About half the estimated HAP emissions were from on road mobile sources while most of the remainder was from nonroad mobile and area sources (Figure 1-2). Only 1% of the 1999 estimated HAP emissions in Travis and Williamson counties were from major industrial sources.

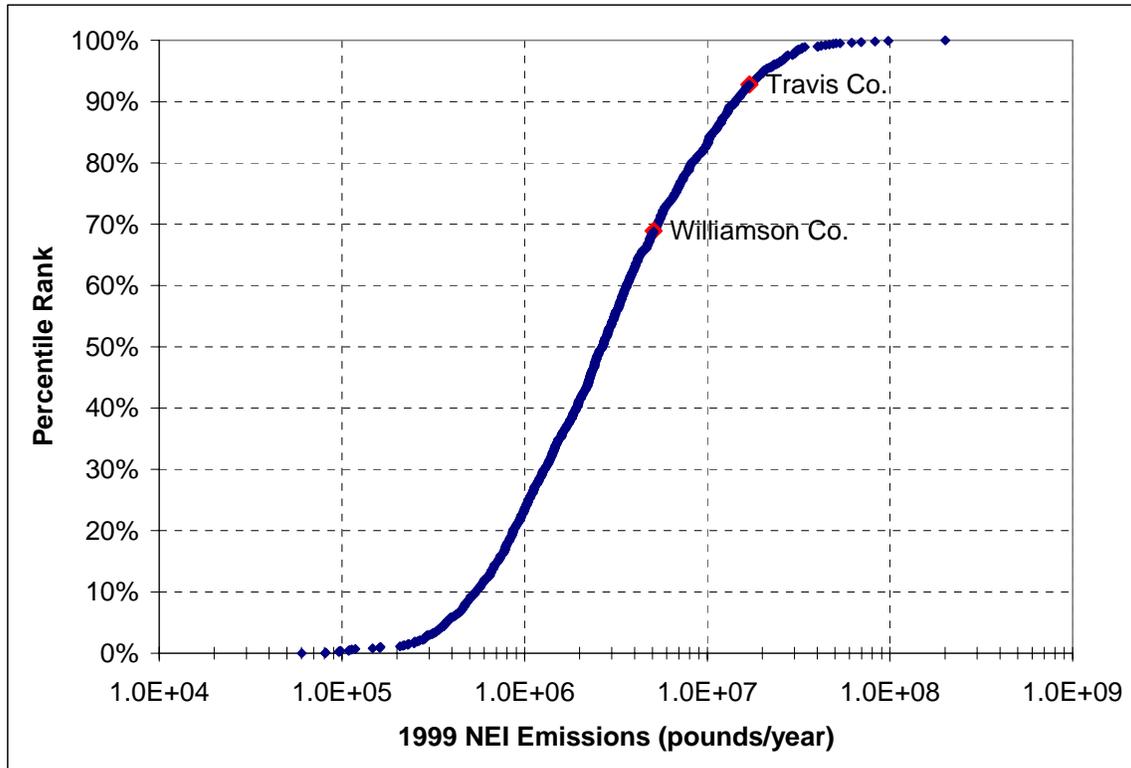


Figure 1-1. Travis and Williamson County Percentile Rankings for 1999 Total HAP Emissions (Data Source: <http://www.epa.gov/air/data/index.html>)

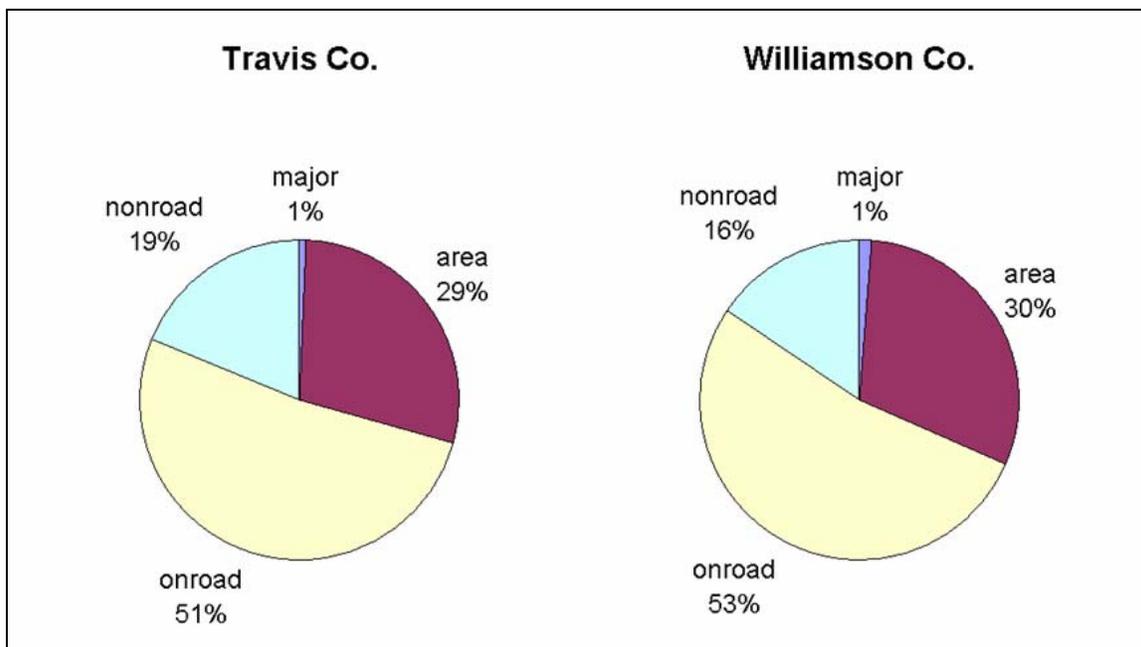


Figure 1-2. Travis and Williamson County Source Sector Breakdown of 1999 Total HAP Emissions (Data Source: <http://www.epa.gov/air/data/index.html>)

1.2 Objectives

ARTS is an exploratory study of air toxics levels in the Austin-Round Rock area, designed to identify any chemicals in the air that might pose a significant health risk, either regionally or at a particular location. The study is also intended to establish a baseline for measuring future air toxics trends brought about by VOC control measures in the EAC, cleaner burning vehicles, or other factors including those that might counteract air pollution controls such as increased vehicular traffic and congestion.

1.3 Study Overview

Measurements were made at five fixed sites over a 12-month period to estimate the annual average concentrations of 83 hazardous air pollutants, including 19 core air toxics that are measured at National Air Toxics Trends Sites (NATTS) throughout the U.S. The monitoring sites were oriented north to south from Round Rock to south Austin, near areas of relatively high population density (Figure 1-3). All the measurements were performed using standard EPA sampling and analytical methods.

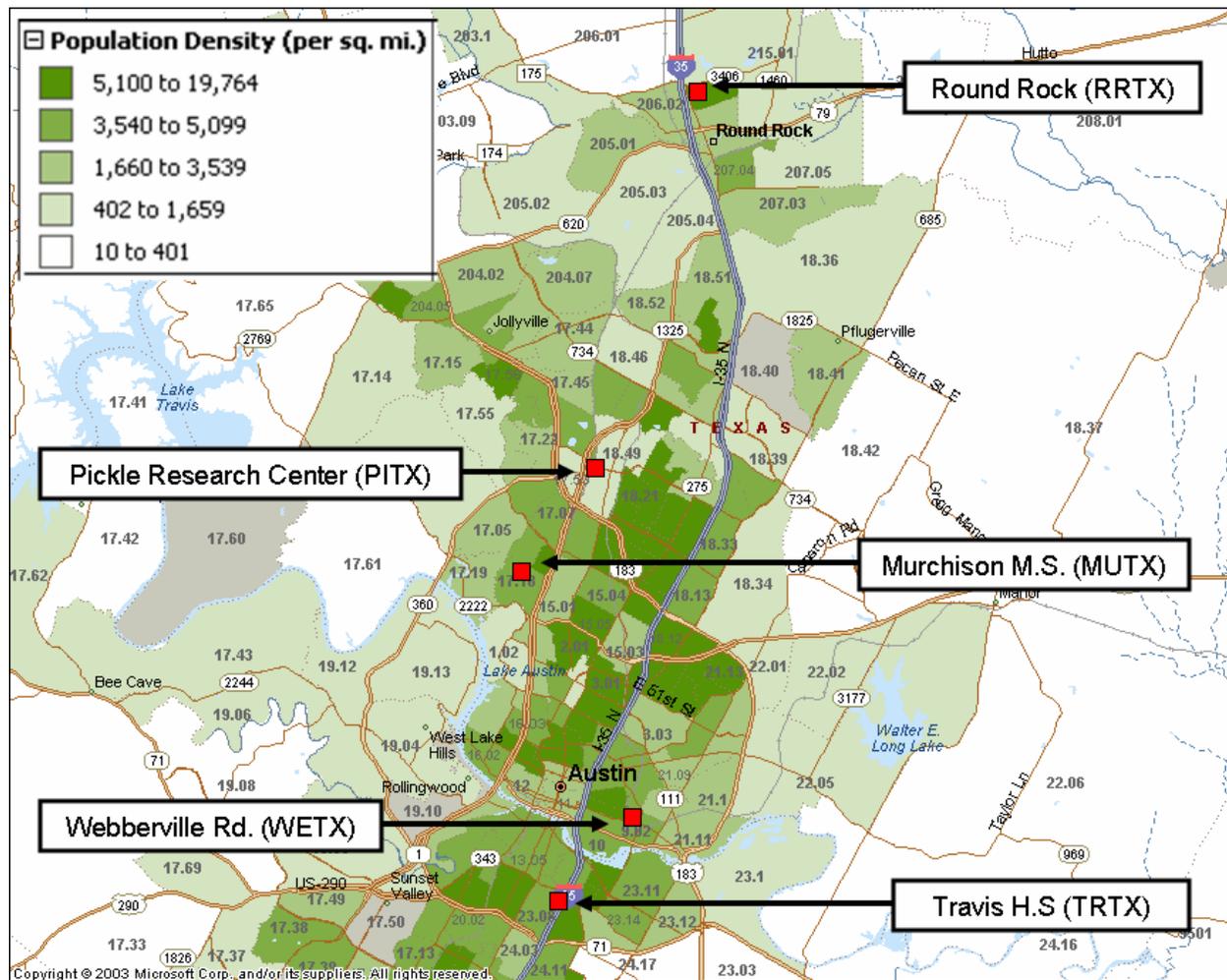


Figure 1-3. ARTS Monitoring Sites



1.4 Summary of Key Findings

With one exception, the levels of the 19 core air toxics averaged over all ARTS monitoring sites were comparable to or less than the average levels in most other U.S. cities where similar measurements have been made. Acrolein is the one core compound that was found at significantly higher concentrations in ARTS compared with most other U.S. cities. Acrolein was found to have the greatest potential for producing non-cancer health effects of all ARTS target compounds and it is also the most significant non-cancer air toxics risk driver on a national scale, according to the EPA 1999 National Air Toxics Assessment (EPA, 2006). Acrolein is emitted by motor vehicles, electricity generating units, wildfires, and other combustion processes including smoking cigarettes; however, no known sources account for the differences between the ARTS data and measurements collected elsewhere. Acrolein is also produced in the atmosphere from chemical reactions and some suspect it can be produced inside the sampling vessels used for its measurement, perhaps rendering the measurements unreliable (Heaton, 2006). CAPCOG, TCEQ, and EPA are planning additional measurements and data quality assessments in summer 2007 to address the reliability of the ARTS acrolein results.

The greatest risks of contracting cancer from inhalation exposure to measured HAPs in the Austin-Round Rock area come from carbon tetrachloride and benzene. Carbon tetrachloride exists primarily as a background air pollutant resulting from prior widespread uses including in fire extinguishers, as a propellant for aerosol spray cans, as a cleaning fluid, and in the production of Freon refrigerants. Carbon tetrachloride production and use for consumer products has been phased out over concern for its toxicity and harm to the earth's ozone layer but it remains a background constituent of outdoor air because of its long half-life of 30-100 years (Argonne National Laboratory, 2005). The average levels of carbon tetrachloride measured in ARTS varied by less than 10% from the lowest to highest site and were within $\pm 10\%$ of the 2005 national median at all ARTS sites.

Benzene is a constituent of motor vehicle emissions and is also found in emissions from burning coal and oil, evaporative emissions from gasoline refueling, and in industrial solvents. About half the benzene measured in ARTS appears to come from motor vehicles. The average benzene levels were within $\pm 13\%$ of the 2005 national median at four ARTS sites but were almost twice the national median at Webberville Road where the highest levels of other motor vehicle emissions constituents were also measured. After carbon tetrachloride and benzene, the next greatest risks of contracting cancer from inhalation exposure to HAPs come from 1,3-butadiene and acetaldehyde, which along with benzene are classified by EPA as priority mobile source air toxics.

The ARTS measurement results agreed remarkably well with results of the 1999 National Air Toxics Assessment (NATA), based on its identification of key air pollutants, estimations of air toxics levels, and estimations of total risks due to inhalation exposure to toxic air pollutants. The NATA modeled estimate of total cancer risk for Travis County, 41 in a million, is equal to the total cancer risk estimated from ARTS measurement data. The NATA estimate for Williamson County, 28 in a million, differs by less than 20 percent from the 34 in a million estimated from the ARTS monitoring data collected in Round Rock. To place these risk estimates in perspective, note that one out of every three Americans (330,000 in one million) will contract cancer during a lifetime, when all causes are taken into account (EPA, 2006).



2.0 Project Description

The Austin-Round Rock air toxics monitoring network consisted of five stations that were oriented north to south from Round Rock to south Austin, near areas of relatively high population density. All the monitoring stations were classified as population exposure sites and had nearby emissions dominated by mobile sources. The street addresses and coordinates of each monitoring site are given in Table 2-1. Brief descriptions of each site follow.

**Table 2-1
ARTS Monitoring Locations**

Site Name	Site ID	AQS Monitor ID	Site Address	County	Latitude (Degrees)	Longitude (Degrees)
Webberville Road	WETX	48-453-7000	2600-B Webberville Rd.	Travis	30.2632	-97.7131
Murchison Middle School	MUTX	48-453-7001	3724 North Hills Dr.	Travis	30.3544	-97.7602
Travis High School	TRTX	48-453-7002	1211 East Oltorf St.	Travis	30.2322	-97.7444
Pickle Research Center	PITX	48-453-7003	10000 Burnet Rd.	Travis	30.3926	-97.7285
Round Rock	RRTX	48-491-7004	212 Commerce Blvd	Williamson	30.5326	-97.6849

Round Rock (RRTX) - The northernmost site, Round Rock, was about 1.5 miles north-northwest of the Round Rock central business district and less than 0.4 miles east of Interstate Highway 35 (IH-35). The site was on a vacant lot, on a cul-de-sac, at the end of Commerce Boulevard (Figure 2-1). The site was next to the Round Rock Public Works Department Annex.

Pickle Research Center (PITX) – The Pickle Research Center Site was on the University of Texas Pickle Research Center Campus in north Austin, less than 0.3 miles east of Mo Pac Boulevard (Loop 1). Mo Pac Boulevard is one of Austin’s major north-south traffic arteries (Figure 2-2).

Murchison Middle School (MUTX) – The Murchison Middle School Site was in residential neighborhood of northwest Austin, less than 0.7 miles west of Mo Pac Boulevard (Figure 2-3). The air toxics sampling station was collocated with a Texas Commission on Environmental Quality (TCEQ) ozone monitor, between the school parking lot and athletic field.

Webberville Road (WETX) – The Webberville Road site was in a residential neighborhood east of downtown Austin (Figure 2-4). This site was collocated with a TCEQ air toxics and particulate matter monitoring site.

Travis High School (TRTX) – The southernmost site, Travis High School, was about two miles south of downtown Austin. The site was between a parking lot and an athletic field, less than 200 yards from the frontage road of IH-35 (Figure 2-5).

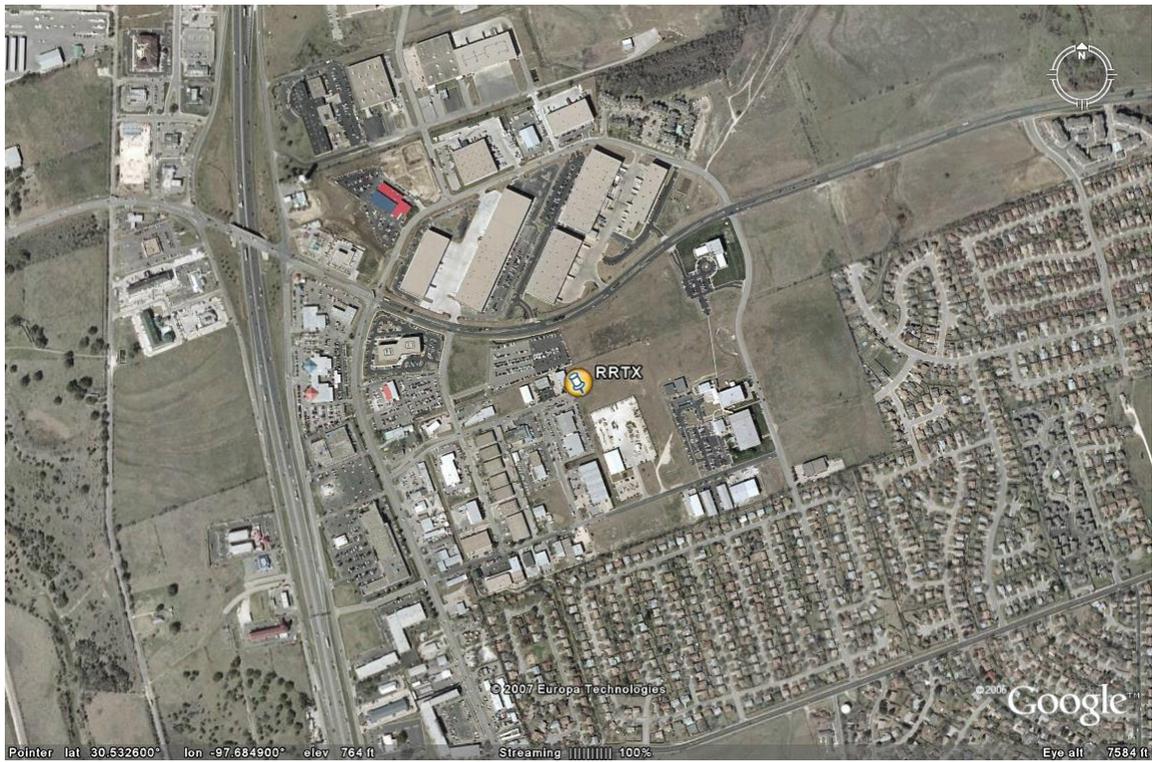


Figure 2-1. Aerial Photograph Showing the Round Rock Sampling Site

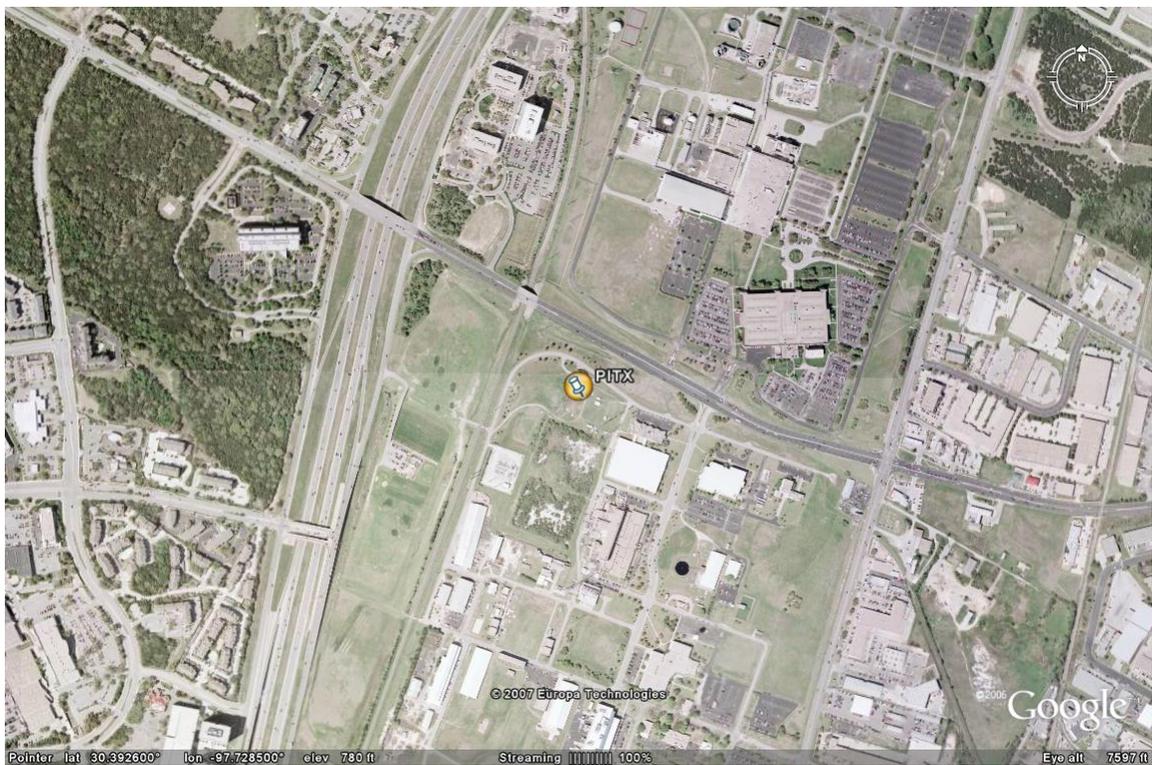


Figure 2-2. Aerial Photograph Showing the Pickle Research Center Sampling Site

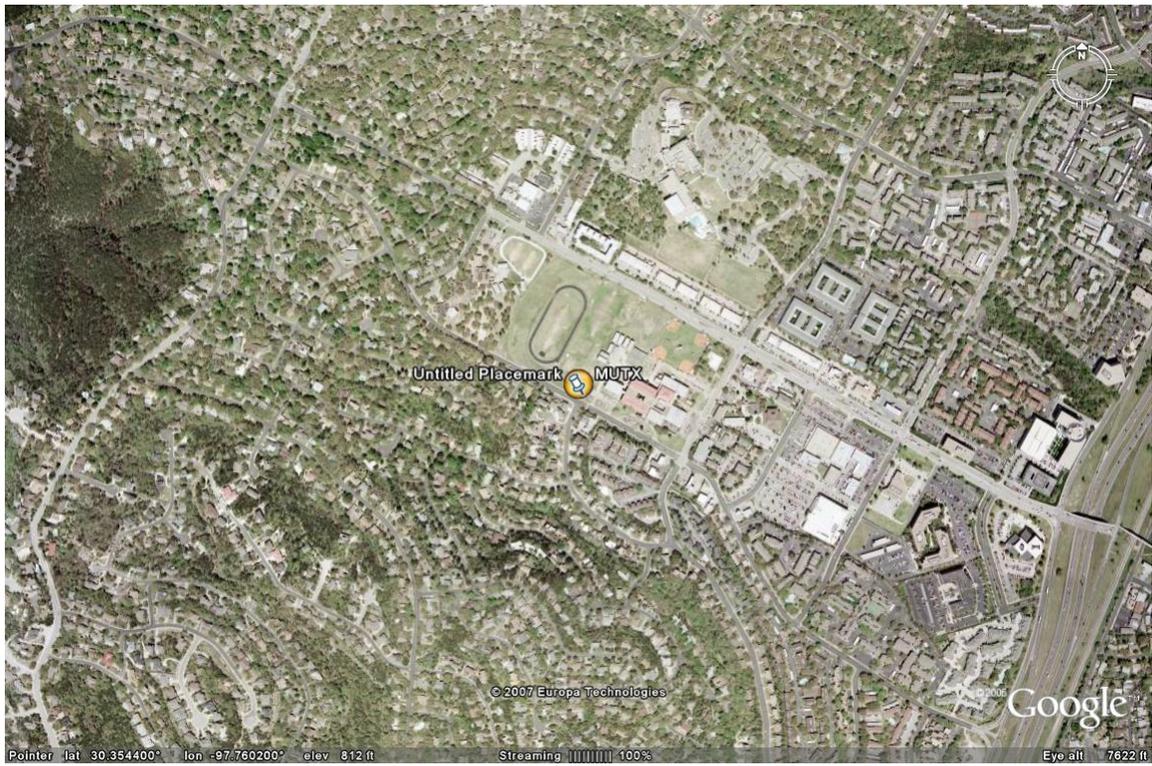


Figure 2-3. Aerial Photograph Showing the Murchison Middle School Sampling Site

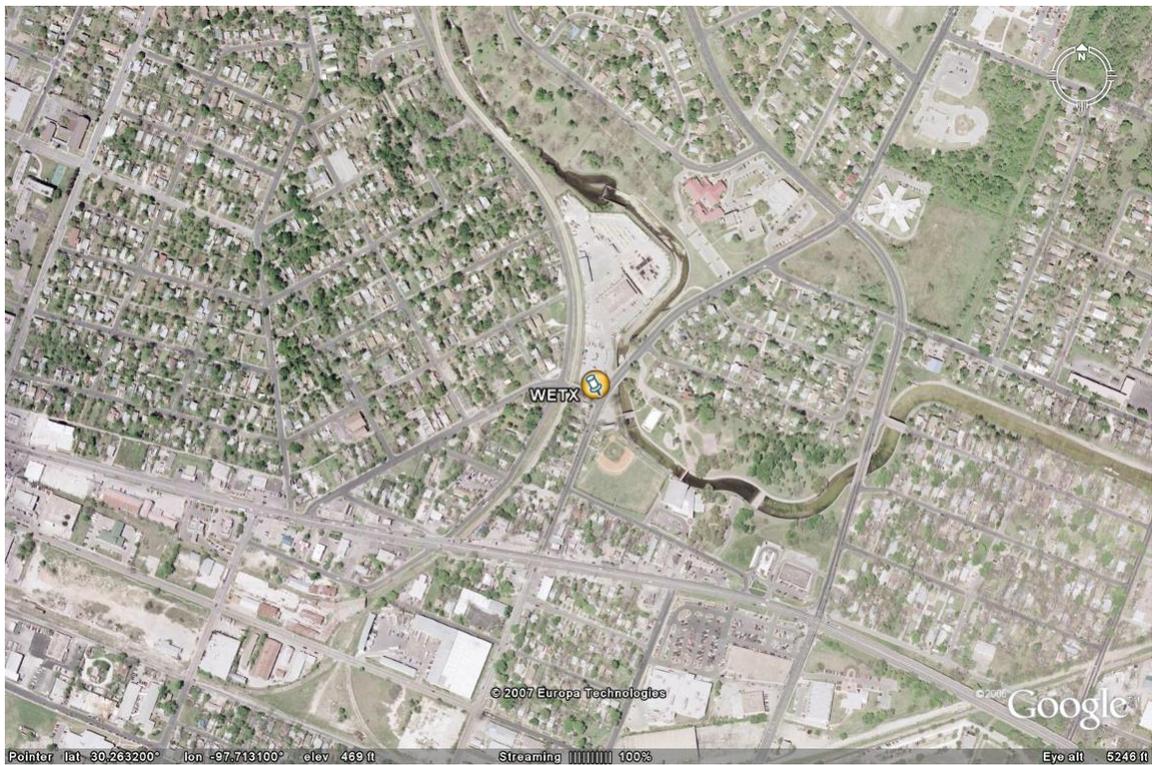


Figure 2-4. Aerial Photograph Showing the Webberville Road Sampling Site

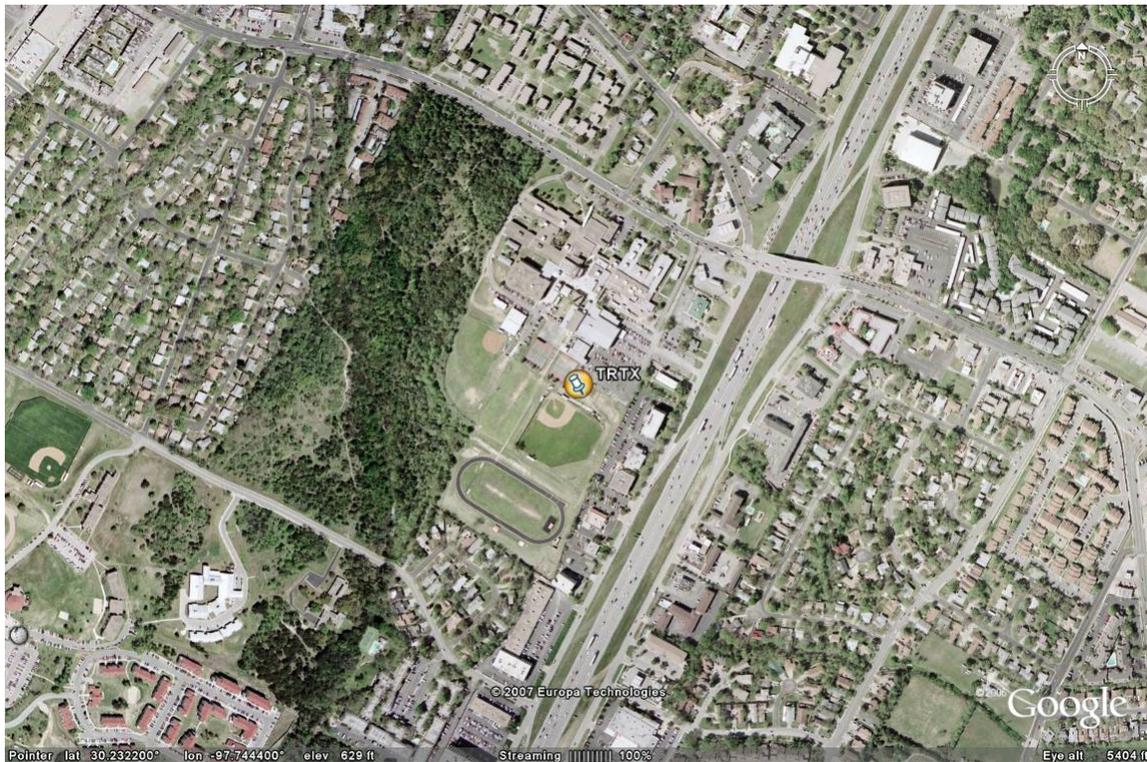


Figure 2-5. Aerial Photograph Showing the Travis High School Sampling Site

Measurements were made for 19 hazardous air pollutants (HAPs) that compose the core target list for the National Air Toxics Trend Stations (NATTS) Network plus an additional 64 HAPs that may be present in the ambient air and can be measured using the same methods as the 19 core pollutants. The NATTS core list is a subset of the 33 common urban HAPs that are believed to pose the greatest risks to public health in U.S. cities (EPA, 2004). Table 2-2 lists the 19 core air toxics and summarizes their measurement approaches. The complete list of ARTS target chemicals is given in Appendix A.

To perform these measurements, each sampling site was equipped with an ATEC Model 2200 Toxic Air Sampler and a Tisch Environmental, Inc. TE-6000 Series PM10 sampler. The ATEC Model 2200 is a microcomputer controlled instrument that can be programmed to draw ambient air simultaneously into TO-15 canisters and TO-11A cartridges for measuring volatile organic compounds (VOC) and carbonyl compounds, respectively. These samplers, which were housed in Shelter One K-5 insulated weatherproof enclosures, were configured with mass flow controllers, pressure transducers, and a vacuum pump to draw in ambient air at controlled rates and monitor sample flows and pressures. Separate sampling inlets for canisters and TO-11A cartridges, each constructed of chromatography grade stainless steel tubing and an inverted glass funnel to keep out precipitation, were attached to the Toxic Air Sampler intake ports. One of the ATEC samplers, placed at the Webberville Road site, was outfitted with dual canister and TO-11A channels for collecting duplicate samples.

**Table 2-2
Summary of Target Chemicals and Sampling/Analytical Methods**

ARTS Target Chemicals	Sampling/Analysis Method	Method Description
59 volatile organic compounds (VOC), including: Benzene Carbon tetrachloride Vinyl chloride Trichloroethylene Acrolein Chloroform 1,3-Butadiene 1,2-Dichloropropane Methylene chloride Tetrachloroethylene	EPA Method TO-15	Sample collection in stainless steel canister with subsequent laboratory analysis by gas chromatography using mass spectroscopy
12 carbonyl compounds, including: Acetaldehyde Formaldehyde	EPA Method TO-11A	Sample collection using DNPH-treated cartridges followed by laboratory analysis using high pressure liquid chromatography
11 metals, including: Arsenic Beryllium Cadmium Lead Manganese Nickel	EPA Method IO-3.5	Sample collection using high volume PM10 samplers with subsequent laboratory analysis using inductively coupled plasma/mass spectrometry (ICP/MS)
Hexavalent chromium (Cr ⁶⁺) (measured only at one site, Webberville Road)	Modified CARB Method 039	Sample collection using bicarbonate-impregnated cellulose filters followed by laboratory analysis using ion chromatography

The Tisch Environmental, Inc. sampler is a conventional volumetric flow controlled high volume PM10 sampler that has been designated by EPA as a Federal Reference Method (FRM) sampler for collecting particulate matter as PM10. Figure 2-6 shows photographs of the canister/cartridge and PM10 sampling equipment.

One of the five sampling sites, Webberville Road, was also equipped with a separate particulate matter sampler to support measurements of hexavalent chromium (Cr⁶⁺). The Cr⁶⁺ sampler, which was designed and built by ERG, is a dual channel, programmable, flow controlled sampler designed to draw ambient air through 47-milimeter filters loaded into externally mounted Teflon filter holders. Figure 2-7 shows photographs of the Cr⁶⁺ sampler and filter holders.



Figure 2-6. Photographs of the PM10 and Enclosed Toxic Air Sampler at PITX



Figure 2-7. Photographs of the ERG Cr⁶⁺ Sampler and Externally Mounted Filter Holders

Air sampling was conducted for 24-hour periods at each site, once every 12th day beginning June 15, 2005. This sampling frequency provided for approximately 30 samples at each site from which to estimate annual average levels of the target air pollutants. Sampling followed the EPA one-in-six-day national monitoring schedules for 2005 and 2006, with samples collected on alternating national sampling days to maintain the once every 12th day frequency. In June 2006 the sampling frequency was increased to once every 6th day to make up for some samples that were missed earlier on due to equipment malfunctions or operator errors.

Sample setup procedures, which were performed on the day before each sampling day, included installation of the sampling media (i.e., VOC canisters, carbonyl cartridges, and particulate matter filters) in the sampling equipment, performing sampler leak checks and flow rate checks, documenting the sample setup parameters, and programming the samplers to run for 24 hours beginning one minute after midnight. The canister sample flows were controlled at a rate that would leave the samples under slight vacuum at the end of each sampling period. The cartridge flow rates were controlled at 0.9 liters per minute, in accordance with the TO-11A method. After the completion of each sampling period, a chemist or instrument technician would return to each sampling site to record the final canister vacuum, carbonyl cartridge volume, and



particulate matter flow rates before collecting the sampling media for shipment to the ERG laboratory. ERG analyzed the samples using the equipment and protocols it uses for the EPA Urban Air Toxics Monitoring Program (ERG, 2006).

Duplicate samples for assessing VOC, carbonyl, and hexavalent chromium measurement precision were collected at the Webberville Road site. Trip blanks for assessing carbonyl cartridge and particulate matter filter background levels were collected at each site. Canister blanks were not collected; however, each of the ATEC Toxic Air Samplers was blank certified according to TO-15 before it was installed in the field. Table 2-3 gives the numbers of duplicate sample pairs and trip blanks collected for each type of sample.

**Table 2-3
Numbers of Duplicate Sample Pairs and Trip Blanks**

Sample Type	Duplicates	Trip Blanks
TO-15 Canisters	16	0
TO-11A Cartridges	24	38
PM10 Filters	0	6
Cr ⁶⁺ Filters	2	10



3.0 Results

This section gives the ARTS results with emphasis on the core air toxics and other HAPs that had relatively high concentrations compared with common health-based reference concentrations. Section 3.1 gives the average levels of the core air toxics at each site and an assessment of the relative health risks. Section 3.2 compares the ARTS measurement results with air toxics levels measured in other U.S. cities and Section 3.3 compares the ARTS measurement results with modeled estimates of air toxics levels from the 1999 NATA.

3.1 Average Concentrations and Comparative Health Risks

The average levels detected during the one-year program for the 19 core air toxics are summarized in Table 3-1. The results for all 83 ARTS target compounds are given in Appendix A. For estimating average concentration levels, one-half the detection limit (DL) was substituted for all the values that were either not detected or detected at levels below the DL. Measurement results for carbonyl compounds and metals were blank subtracted using the average concentrations of field blank samples collected throughout the study.

The average levels measured for VOC and carbonyl compounds ranged from a few micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) down to a few hundredths of a $\mu\text{g}/\text{m}^3$ while the average levels of metals ranged from a few nanograms per cubic meter (ng/m^3 or $10^{-3} \mu\text{g}/\text{m}^3$) down to a few hundredths of a ng/m^3 . To place these results in perspective, Table 3-1 also gives the 10^{-5} cancer risk level and the reference concentrations (RfC) used in the EPA National Air Toxics Assessment (NATA) for non-cancer health effects. The 10^{-5} cancer risk level is an estimate of the average concentration of a particular air pollutant that produces a one in one hundred thousand risk of contracting cancer for individuals who are exposed to that average concentration over a lifetime (70 years). It is a convenient reference for gauging relative risk but is not used here as a benchmark for differentiating acceptable from unacceptable risks (elsewhere in this report, compounds having average levels exceeding the 10^{-6} risk level, i.e., one in a million, are highlighted). The RfC is an estimate, with uncertainty spanning perhaps a factor of 10, of a long-term inhalation exposure that is likely to be without appreciable risks of adverse non-cancer health effects (EPA, 2005).

Two of the core air toxics, benzene and carbon tetrachloride, had average levels above the respective 10^{-5} cancer risk level at one or more monitoring sites. Benzene levels exceeded the 10^{-5} level only at the Webberville Road site while carbon tetrachloride exceeded the 10^{-5} level, just barely, at the Pickle Research Center and Travis High School sites. Acrolein is the only core air toxic that had average levels above the non-cancer RfC. The acrolein average levels exceeded the RfC by more than 100 times at every monitoring site. The average acrolein levels were higher than the average levels measured in most other U.S. cities in 2005 and 2006, according to data downloaded from the EPA AirData website¹; however, no known sources account for this excess. CAPCOG, TCEQ, and EPA are planning additional measurements and data quality assessments in 2007 to address the reliability of the ARTS acrolein results.

¹ <http://www.epa.gov/air/data/reports.html>



**Table 3-1
Average Levels of Core Air Toxics**

Air Pollutant	Average Concentration ($\mu\text{g}/\text{m}^3$)					10^{-5} Cancer Risk Level ($\mu\text{g}/\text{m}^3$) ^a	Non- Cancer RfC ($\mu\text{g}/\text{m}^3$) ^b
	MUTX	PITX	RRTX	TRTX	WETX		
1,2-Dichloropropane	0.08	0.08	0.09	0.08	0.08	0.53	4
1,3-Butadiene	0.07	0.07	0.07	0.14	0.33	0.33	2
Acetaldehyde	1.34	1.33	1.38	1.40	1.62	4.55	9
Acrolein	3.73	2.51	4.60	2.58	3.77	N/A	0.02
Arsenic	4.8E-04	4.5E-04	5.1E-04	9.9E-04	1.1E-03	2.3E-03	3.0E-02
Benzene	0.94	0.80	0.98	1.11	1.88	1.28	30
Beryllium	1.4E-05	1.4E-05	1.4E-05	1.4E-05	1.3E-05	4.2E-03	2.0E-02
Cadmium	9.1E-05	1.0E-04	1.0E-04	3.7E-04	1.4E-04	5.6E-03	2.0E-02
Carbon Tetrachloride	0.63	0.68	0.66	0.68	0.67	0.67	40
Chloroform	0.07	0.11	0.18	0.09	0.09	0.43	98
Formaldehyde	2.78	2.85	3.26	2.98	2.72	1818.18	9.8
Hexavalent Chromium	--	--	--	--	2.3E-05	8.3E-04	1.0E-01
Lead	1.7E-03	1.9E-03	2.4E-03	2.6E-03	3.0E-03	N/A	1.5E+00
Manganese	4.9E-03	5.9E-03	5.8E-03	5.3E-03	7.0E-03	N/A	5.0E-02
Dichloromethane	0.55	0.56	0.82	0.53	0.71	21.28	1000
Nickel	5.7E-04	6.6E-04	7.4E-04	8.3E-04	8.0E-04	6.3E-02	6.5E-02
Tetrachloroethylene	0.27	0.11	0.26	0.19	0.19	1.79	270
Trichloroethylene	0.07	0.09	0.07	0.09	0.08	5.00	600
Vinyl chloride	0.03	0.03	0.03	0.03	0.03	1.25	100

^a 10^{-5} excess cancer risk levels for all compounds except formaldehyde were derived from the upper-bound excess cancer risk estimates (URE) reported by the EPA Integrated Risk Information System (IRIS). The 10^{-5} excess cancer risk is equal to $10^{-5}/\text{URE}$. An updated URE for formaldehyde, from the EPA 1999 National Air Toxics Assessment, was used in place of the formaldehyde URE listed in IRIS.

^b Non-cancer RfC values are from IRIS.

Bold face type denotes average concentration above the 10^{-5} excess cancer risk level or non-cancer RfC.



3.1.1 Comparative Analysis of Excess Cancer Risks

Table 3-2 lists all the compounds, including non-core compounds, having average excess cancer risk estimates greater than one in a million (10^{-6}). The average excess risk estimate for each compound was calculated by taking the average concentration from all the ARTS monitoring sites and multiplying that value by the particular compound's upper-bound excess risk estimate (URE). The URE is the upper-bound excess risk estimated to result from a lifetime of continuous exposure to a carcinogenic air pollutant at a concentration of $1.0 \mu\text{g}/\text{m}^3$. Values of URE for each ARTS target compound except formaldehyde was obtained from the EPA Integrated Risk Information System (IRIS), which is accessible on the Internet at <http://www.epa.gov/iris/>. For formaldehyde, an updated URE from the EPA National Air Toxics Assessment (EPA, 2005) was used instead of the value listed in IRIS.

**Table 3-2
ARTS Target Compounds Having Estimated Excess Cancer Risk
Greater than One per Million at One or More Sampling Sites ^a**

Chemical Name	% of Values > DL	Average Concentration ($\mu\text{g}/\text{m}^3$)					URE ($\mu\text{g}/\text{m}^3$) ₋₁	Avg. Excess Risk (per million)
		MUTX	PITX	RRTX	TRTX	WETX		
1,2-Dibromoethane	<1	0.10	0.10	0.10	0.11	0.10	2.2E-04	22.7
Hexachloro-1,3-butadiene	2	0.83	0.86	0.80	0.80	0.80	2.2E-05	17.9
Carbon Tetrachloride	99	0.63	0.68	0.66	0.68	0.67	1.5E-05	9.9
Benzene	100	0.94	0.80	0.98	1.11	1.88	7.8E-06	8.9
Acrylonitrile	3	0.07	0.06	0.06	0.06	0.18	6.8E-05	5.9
1,1,2,2-Tetrachloroethane	<1	0.10	0.10	0.10	0.10	0.09	5.8E-05	5.6
1,3-Butadiene	62	0.07	0.07	0.07	0.14	0.33	3.0E-05	4.1
Acetaldehyde	100	1.34	1.33	1.38	1.40	1.62	2.2E-06	3.1
Arsenic	100	5E-04	5E-04	5E-04	1E-03	1E-03	4.3E-03	3.0
p-Dichlorobenzene	65	0.23	0.24	0.26	0.26	0.35	1.1E-05	2.9
Chloromethylbenzene	1	0.06	0.05	0.05	0.06	0.05	4.9E-05	2.6
Chloroform	19	0.07	0.11	0.18	0.09	0.09	2.3E-05	2.4
1,2-Dichloropropane	0	0.08	0.08	0.09	0.08	0.08	1.9E-05	1.6
1,2-Dichloroethane	2	0.06	0.05	0.05	0.06	0.05	2.6E-05	1.4
Tetrachloroethylene	42	0.27	0.11	0.26	0.19	0.19	5.6E-06	1.1

^a Average concentrations and cancer risk estimates are based on substituting $\frac{1}{2}$ DL for non-detected values. An alternate approach using zero $\mu\text{g}/\text{m}^3$ for non-detected values gives lower risk estimates for infrequently detected compounds. See text below for explanation and Table 3-3 for the alternate risk characterization.

Table 3-2 also gives the percentage of all ARTS samples in which each of the listed compounds was detected. Note that several of the compounds having comparatively high cancer risks were rarely detected and only appear in Table 3-2 because of the data reporting convention, which substitutes one-half the DL for non-detected levels. In addition to being rarely detected, these compounds had detection limits that were high compared with the 10^{-6} risk level. See Appendix A for a list of average detection limits.

The comparative cancer risks attributed to different ARTS target compounds, expressed as percentages of the total, are given in Figure 3-1. Note that greater than 40% of the estimated excess risk is attributed to 1,2-dibromoethane plus hexachloro-1,3-butadiene; however, neither of these compounds was detected in greater than 2% of the samples. In fact, 60% of the estimated total excess cancer risk was attributed to compounds that were each detected in no greater than 3% of the samples. The actual risks posed by exposure to these compounds might not be so high if $\frac{1}{2}$ DL is not a good estimate for the average of the non-detected concentrations.

An alternate representation of the relative risks attributed to different target compounds is given in Figure 3-2. For this case, zero $\mu\text{g}/\text{m}^3$ was substituted for non-detected values instead of $\frac{1}{2}$ DL. Based on this alternate analysis, almost 50% of the total excess cancer risk is attributed to carbon tetrachloride plus benzene while the estimated excess risks attributed to 1,2-dibromoethane and hexachloro-1,3-butadiene are comparatively small. Note that 40% of the total excess risk was attributed to three priority mobile source air toxics (benzene, acetaldehyde, and 1,3-butadiene) when zeros were assumed for non-detected values.

In assessing which of the alternate risk characterizations may be more accurate it is helpful to consider the relative emissions of the different air pollutants. For example, the Travis and Williamson County 1999 total estimated emissions of 1,2-dibromoethane and hexachloro-1,3-butadiene were 0.15 and 0.36 pounds, respectively, while the total benzene and carbon tetrachloride estimated emissions were 2,000,000 and 650 pounds, respectively (EPA, 2003). Given these proportions, the comparative risks from 1,2-dibromoethane and hexachloro-1,3-butadiene are likely to be small, even when considering that the URE for each of these compounds is several times greater than the URE for benzene. Table 3-3 gives the 1999 NEI emissions for each of the compounds listed in Table 3-2 and the estimated excess cancer risks based on both of the described approaches for treating non-detects. The excess cancer risk for all ARTS target compounds, averaged over all ARTS sites, is 40 in a million (4.0×10^{-5}) when zeros are substituted for non-detects.

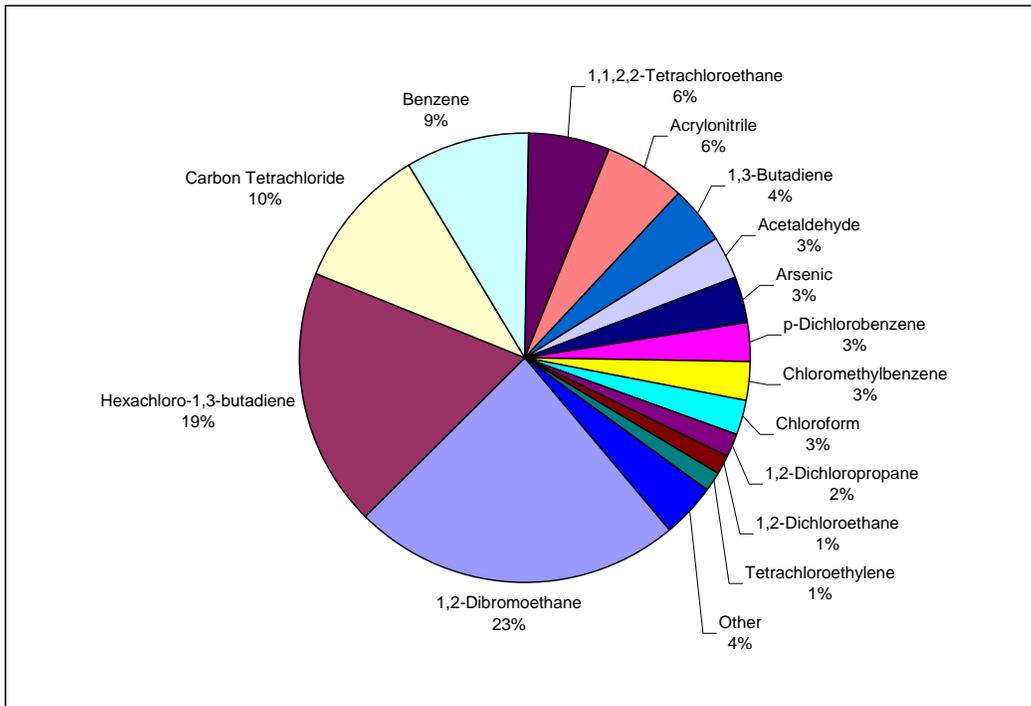


Figure 3-1. Percentages of Estimated Excess Cancer Risks Attributed to ARTS Target Compounds Using 1/2 DL for Non-Detects (Averaged for All ARTS Sites)

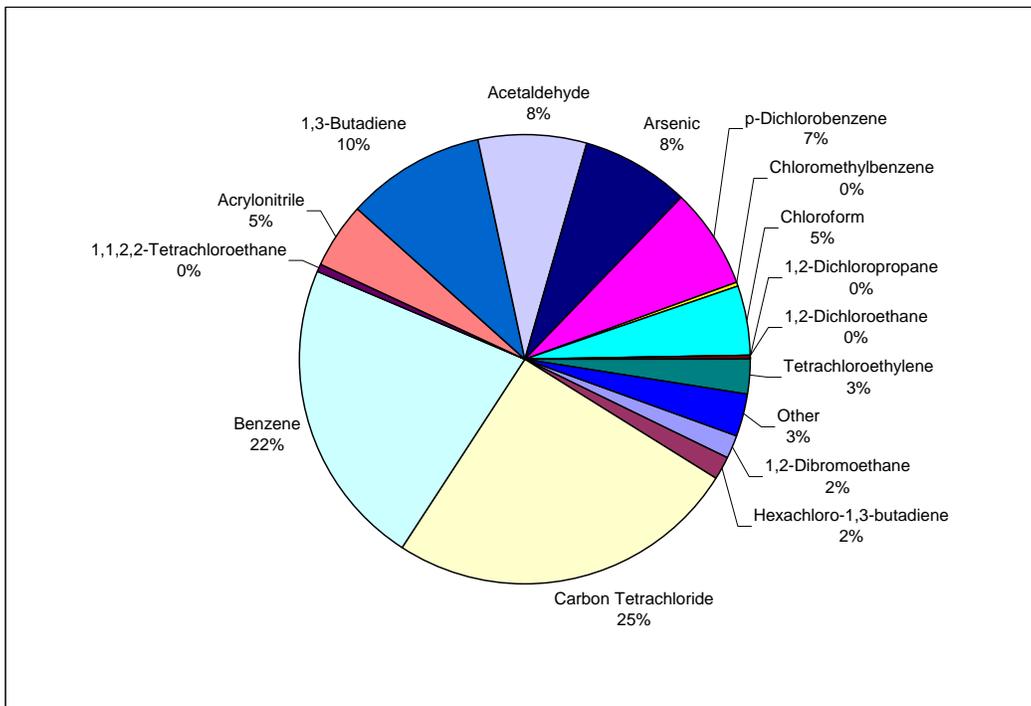


Figure 3-2. Percentages of Estimated Excess Cancer Risks Attributed to ARTS Target Compounds Using Zero µg/m³ for Non-Detects (Averaged for All ARTS Sites)

**Table 3-3
1999 Emissions and Excess Risk Estimates Based on
Alternate Approaches for Treating Non-Detected Values**

Chemical Name	% of Values > DL	1999 Emissions for Travis and Williamson Counties (Pounds) ^a	Average Excess Risk (per Million) Using ½ DL for Non-Detects	Average Excess Risk (per Million) Using zero µg/m ³ for Non-Detects
1,2-Dibromoethane	<1	0.15	22.7	0.7
Hexachloro-1,3-butadiene	2	0.355	17.9	0.6
Carbon Tetrachloride	99	540	9.9	9.9
Benzene	100	2,020,140	8.9	8.9
Acrylonitrile	3	180	5.9	2.1
1,1,2,2-Tetrachloroethane	<1	0.615	5.6	0.2
1,3-Butadiene	62	252,680	4.1	4.1
Acetaldehyde	100	443,620	3.1	3.1
Arsenic	100	25.7	3.0	3.0
p-Dichlorobenzene	65	74,840	2.9	2.9
Chloromethylbenzene	1	3.75	2.6	0.1
Chloroform	19	75,880	2.4	2.0
1,2-Dichloropropane	0	7.41	1.6	0.0
1,2-Dichloroethane	2	1,120	1.4	0.1
Tetrachloroethylene	42	243,380	1.1	1.0

^a 1999 Emissions data downloaded from <http://www.epa.gov/air/data/reports.html>

3.1.2 Comparative Analysis of Non-Cancer Effects

Table 3-4 lists the top 10 ARTS target compounds ranked by the likelihood of producing non-cancer adverse health effects. The rankings are based on each compound's average hazard quotient (HQ), which, for a particular compound, is equal to the average concentration divided by the compound's RfC. HQ values less than one indicate no adverse health effects are expected while HQ values greater than one indicate that adverse health effects are possible (EPA, 2006).

Acrolein is the only ARTS target compound with a hazard quotient greater than one. The acrolein measurements are of particular interest and concern because of the high HQ and because they are among the highest annual average acrolein levels reported in the EPA AQS database for 2005 and 2006 (Figure 3-3). The highest acrolein levels were measured in samples collected during July-November 2005 and during May-June 2006. The measurement precision appears reasonably good, based on analyses of collocated samples; however, the data are questionable because no known sources of acrolein account for the differences in the measured levels relative to the average concentrations reported for most other areas and because potential positive biases in the measurement approach used in ARTS have been observed elsewhere (Heaton, 2006). CAPCOG, TCEQ, and EPA are planning additional measurements and data quality assessments in 2007 to address the reliability of the ARTS acrolein results.

**Table 3-4
ARTS Target Compounds Having the Top 10 Non-Cancer Hazard Quotients**

Analyte	Average Concentrations ($\mu\text{g}/\text{m}^3$)					RfC ($\mu\text{g}/\text{m}^3$) ^a	Average Hazard Quotient
	MUTX	PITX	RRTX	TRTX	WETX		
Acrolein ^b	3.73	2.51	4.60	2.58	3.77	0.02	172
Formaldehyde	2.78	2.85	3.26	2.98	2.72	9.8	0.30
Acetaldehyde	1.34	1.33	1.38	1.40	1.62	9	0.16
1,3-Butadiene	0.07	0.07	0.07	0.14	0.33	2	0.07
Manganese	0.00	0.01	0.01	0.01	0.01	0.05	0.12
1,2-Dibromoethane	0.10	0.10	0.10	0.11	0.10	0.8	0.13
Acrylonitrile	0.07	0.06	0.06	0.06	0.18	2	0.04
Benzene	0.94	0.80	0.98	1.11	1.88	30	0.04
1,2-Dichloropropane	0.08	0.08	0.09	0.08	0.08	4	0.02
Arsenic	0.00	0.00	0.00	0.00	0.00	0.03	0.02

^a Non-cancer RfC values are from the EPA Integrated Risk Information System (IRIS).

^b Reliability of the ARTS acrolein measurements will be addressed in a summer 2007 follow up study.

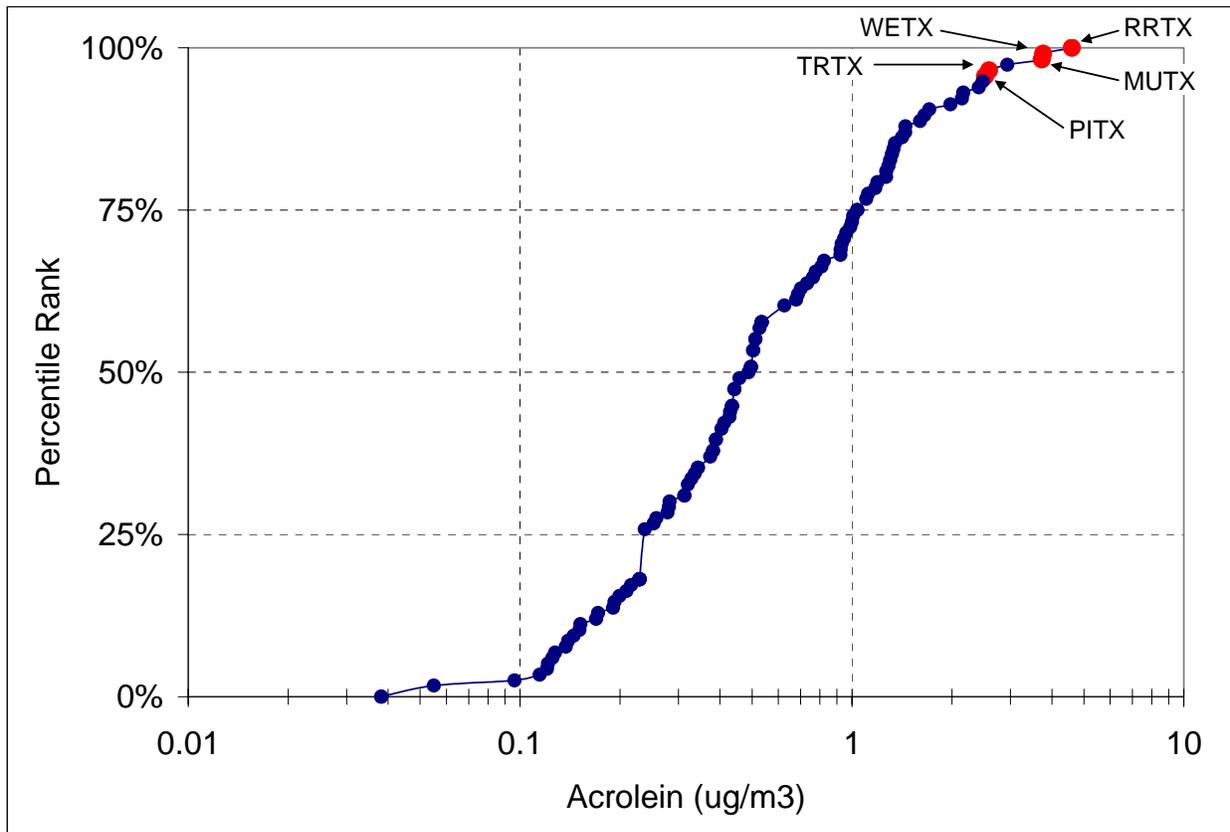


Figure 3-3. Percentile Chart of 2005 Acrolein Averages from EPA AQS with 2005-2006 ARTS Site Averages Superimposed

Acrolein is a byproduct of combustion and, based on the EPA 1999 NATA, it is the most significant HAP with regard to potential for causing non-cancer adverse health effects (EPA, 2006). Nationally, the key sources for acrolein are open burning, prescribed fires and wildfires, and on road and nonroad mobile sources. In Travis and Williamson counties, nonroad and on road mobile sources accounted for 82% and 63% of the estimated emissions, respectively, according to the 1999 NEI (Figure 3-4). With 57,880 and 21,860 pounds of total emissions in 1999, Travis and Williamson counties ranked higher than 92% and 78% of 1207 U.S. urban counties, respectively, but significantly lower than Harris and Dallas counties as well as other urban counties with much lower reported ambient air concentrations (EPA, 2003).

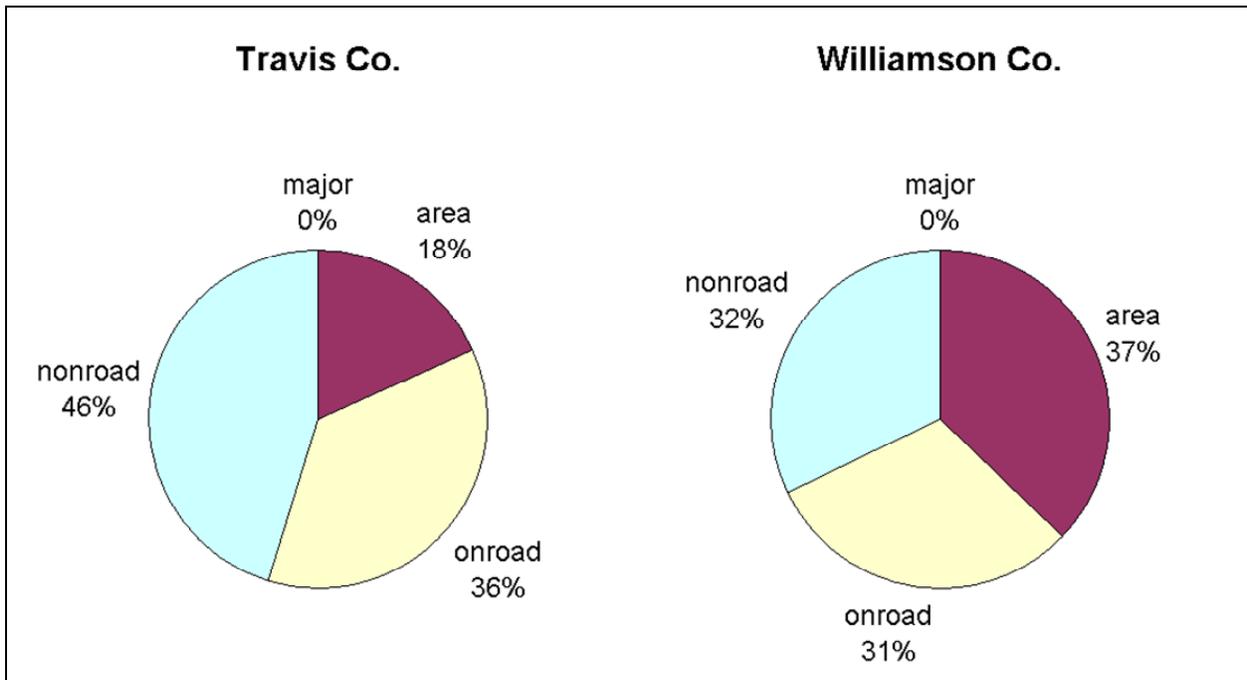


Figure 3-4. Acrolein 1999 NEI Emissions by Source Sector in Travis and Williamson Counties

Acrolein was measured in ARTS using EPA Compendium Method TO-15, which differs from how acrolein had usually been measured in the past. ERG began using TO-15, after extensive performance tests in 2005, because method TO-11A, which was the basis for much of the earlier measurement data throughout U.S, had been shown to underestimate the true levels (ERG, 2005). However, research conducted by the Rhode Island Department of Health shows that TO-15 can produce unrealistically high measurement values for acrolein under some conditions, perhaps by production of acrolein from the decay of other sample constituents inside the TO-15 canisters (Heaton, 2006). More work is needed to verify the acrolein levels measured in ARTS.

3.1.3 Spatial Variations

Most of the ARTS target compounds had average concentrations that varied by less than a factor of two (i.e., 100%) from the lowest to highest site (Figure 3-5). Core target compounds having comparatively low between-site variability include carbon tetrachloride, formaldehyde, and acetaldehyde. None of these compounds had average concentrations that differed between sites by more than 21%. This is probably an indication that the sources of these compounds are either uniformly distributed throughout the Austin-Round Rock area or that the measured levels are highly impacted by background concentrations.

The compounds that varied by greater than a factor of two in average concentration between sites included several constituents of motor vehicle emissions. Generally, these compounds, which include 1,3-butadiene, benzene, trimethylbenzene, xylene, and acetylene, were greatest at the Webberville Road site (WETX); however, toluene and styrene were greatest at the Round Rock site (RRTX). There is no obvious reason why the Webberville Road site would be more heavily impacted by mobile source emissions than the other sites. In fact, it is the ARTS site that is furthest from a major highway. Perhaps, these results indicate that exposure to mobile source emissions may be greater near densely populated neighborhood surface streets, where traffic moves more slowly, than near freeways having greater traffic counts.

Figure 3-6 gives the VOC average concentration profile for each site, to more clearly illustrate the differences in VOC average concentrations at Webberville Road compared with other sites. In this figure, the VOC species are sorted in order of decreasing average concentration at Webberville Road. Note that while the other sites have similar profiles, WETX stands out from the rest with respect to the mobile source air toxics and other constituents of motor vehicle emissions noted above. Figures 3-7 and 3-8 give the average concentration profiles for carbonyl compounds and metals, respectively. No single site stands out from the rest as WETX does with respect to VOC; however, cadmium and antimony were notably higher at Travis High School (TRTX) compared with the other sites.

The higher levels of benzene and 1,3-butadiene found on average at WETX contributed to higher excess cancer risk estimates for that site. Table 3-5 gives the excess cancer risk estimates for each site using zero $\mu\text{g}/\text{m}^3$ in place of non-detects, while Figures 3-9 through 3-13 give pie graphs showing the composition of total cancer risk by target compound.

**Table 3-5
Total Excess Cancer Risk Estimates from All ARTS Target Compounds**

Monitoring Site	Excess Cancer Risk (per Million)
Round Rock	34
Pickle Research Center	29
Murchison Middle School	31
Webberville Road	61
Travis High School	43

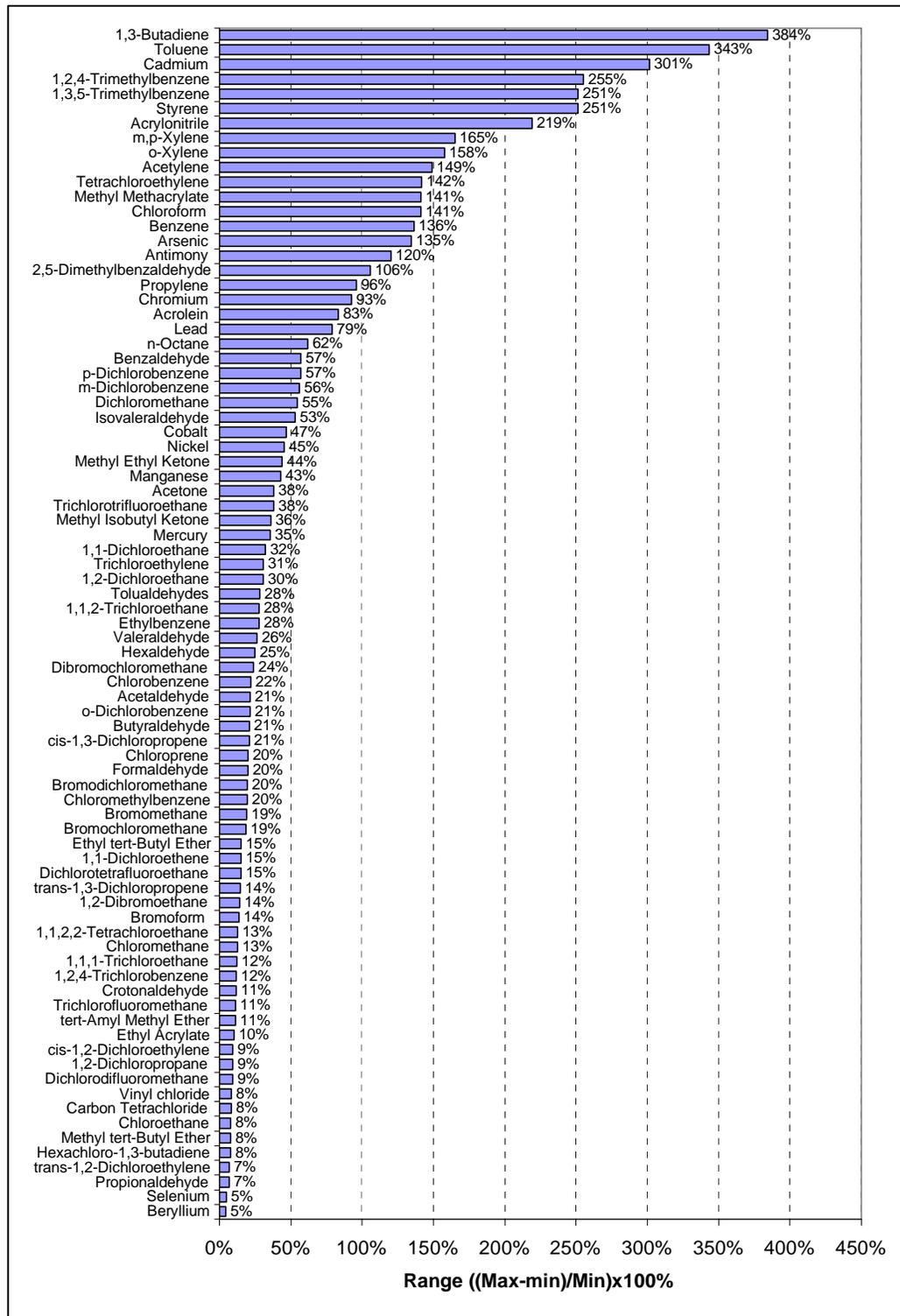


Figure 3-5. Maximum Spatial Variations in Average Concentrations (Expressed as the Difference between the Highest and Lowest Site Average, Divided by the Lowest Site Average)

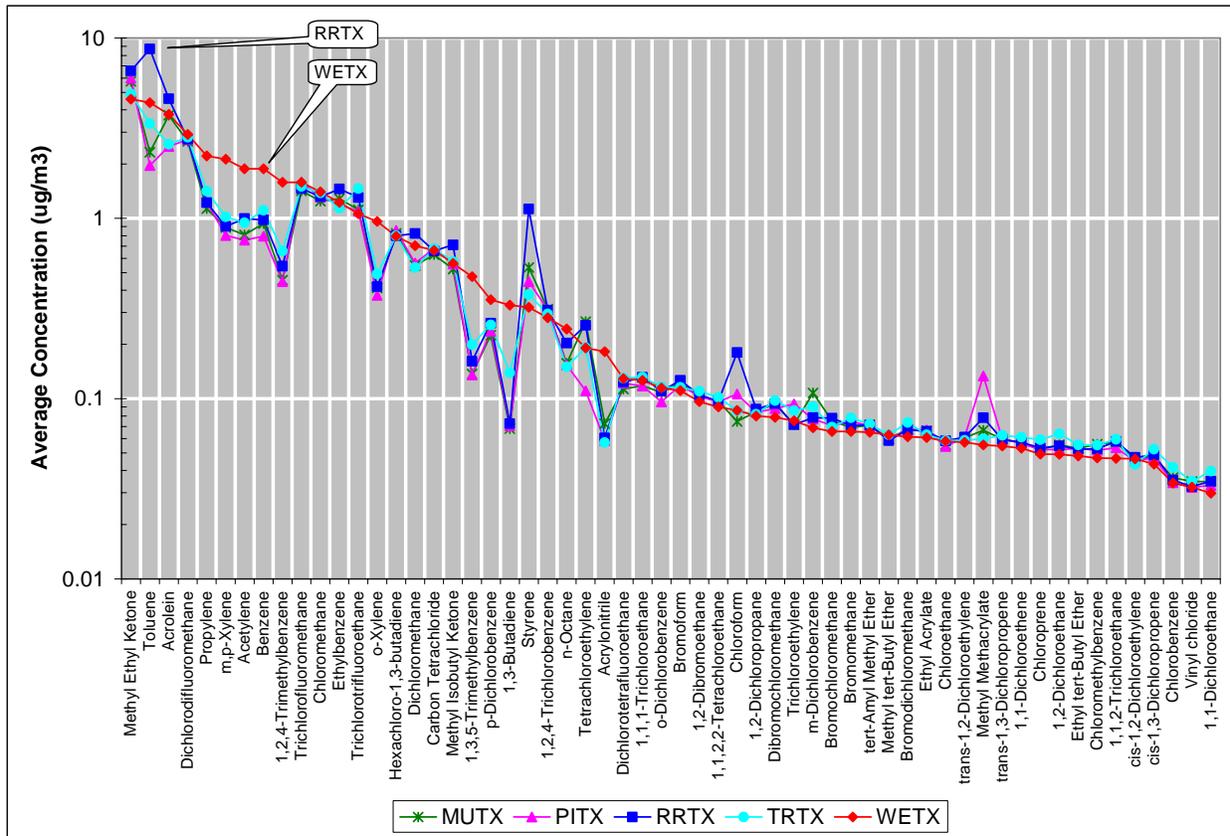


Figure 3-6. Average Concentration Profiles for VOC at ARTS Sites

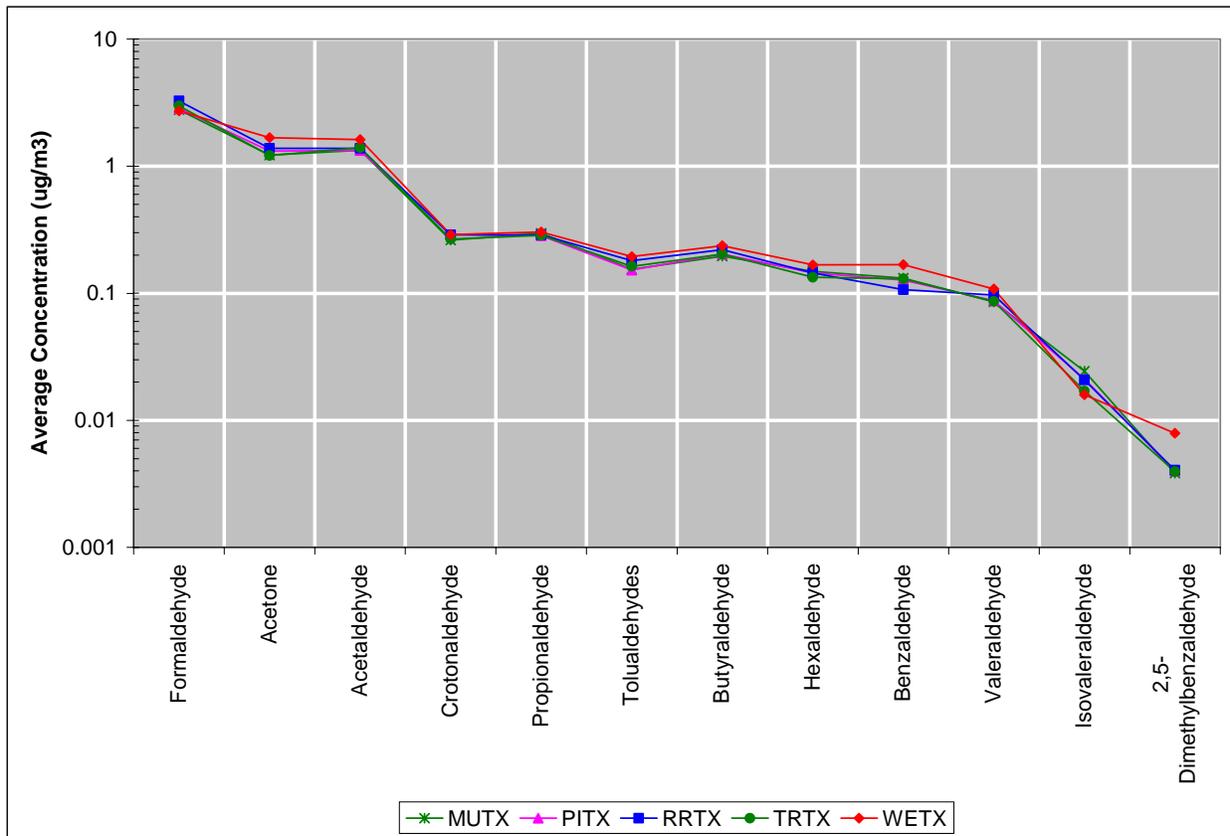


Figure 3-7. Average Concentration Profiles for Carbonyl Compounds at ARTS Sites

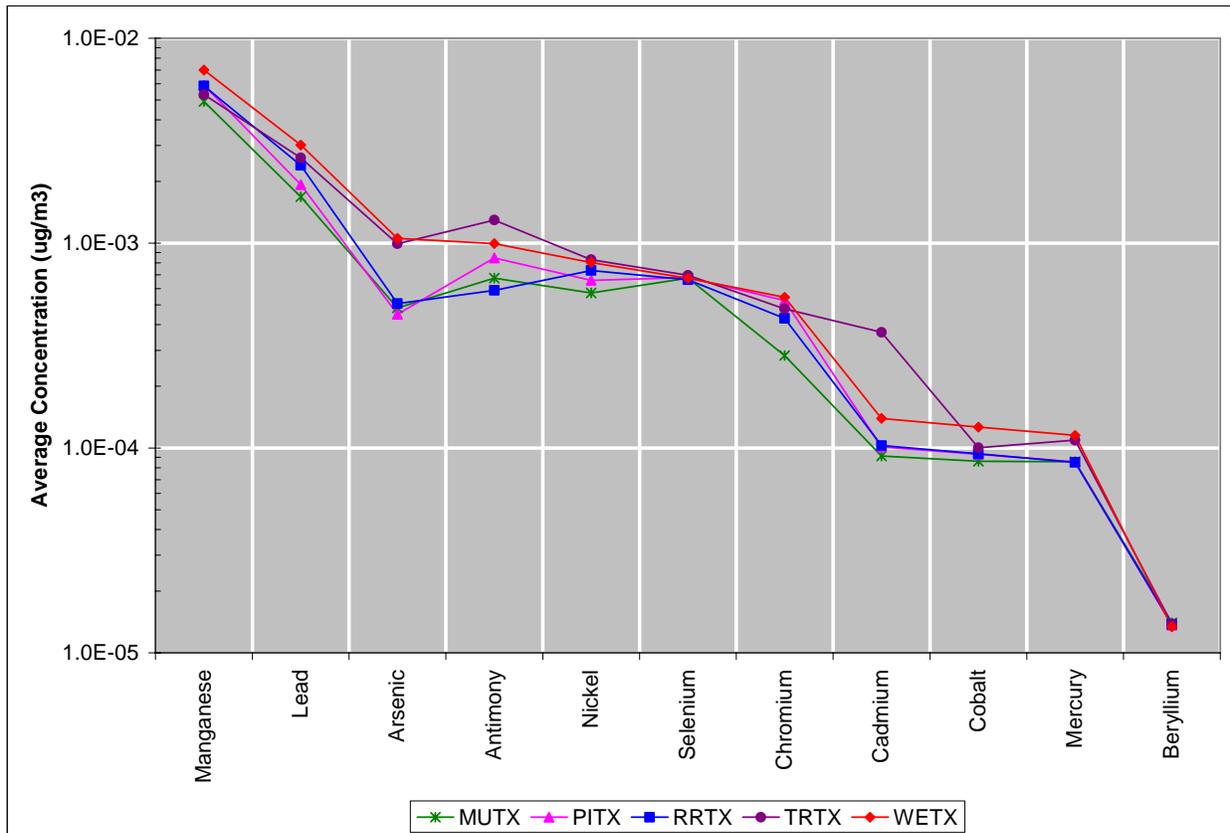


Figure 3-8. Average Concentration Profiles for Metals at ARTS Sites

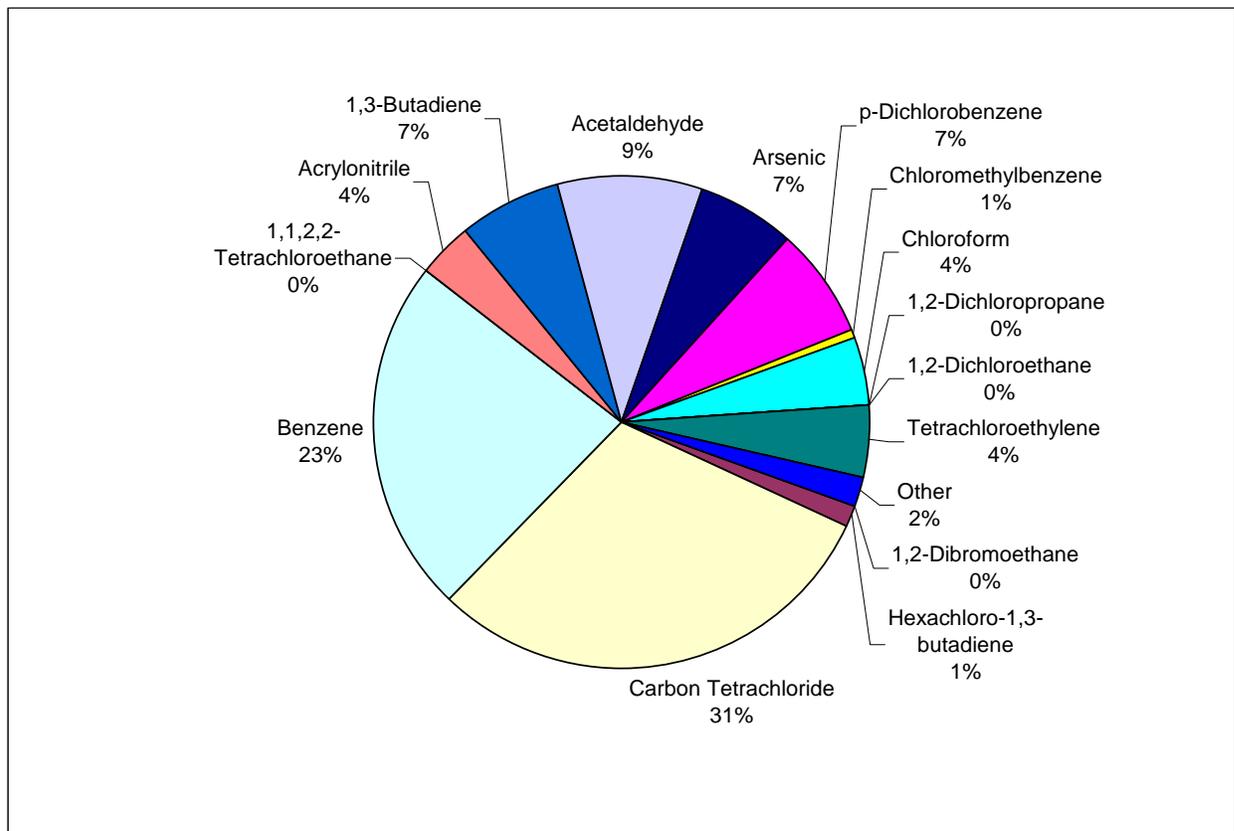


Figure 3-9. Percentages of Estimated Excess Cancer Risks Attributed to ARTS Target Compounds at Murchison Middle School Using Zero $\mu\text{g}/\text{m}^3$ for Non-Detects

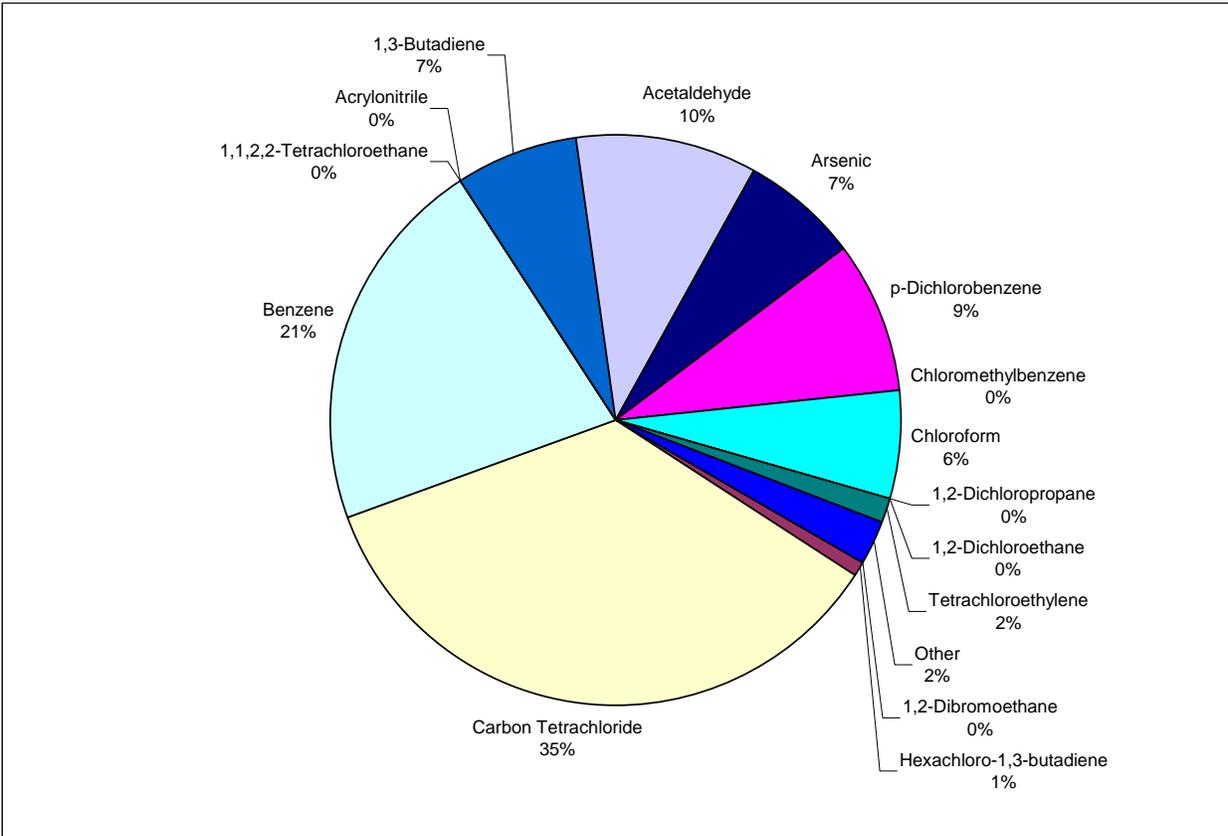


Figure 3-10. Percentages of Estimated Excess Cancer Risks Attributed to ARTS Target Compounds at Pickle Research Center Using Zero $\mu\text{g}/\text{m}^3$ for Non-Detects

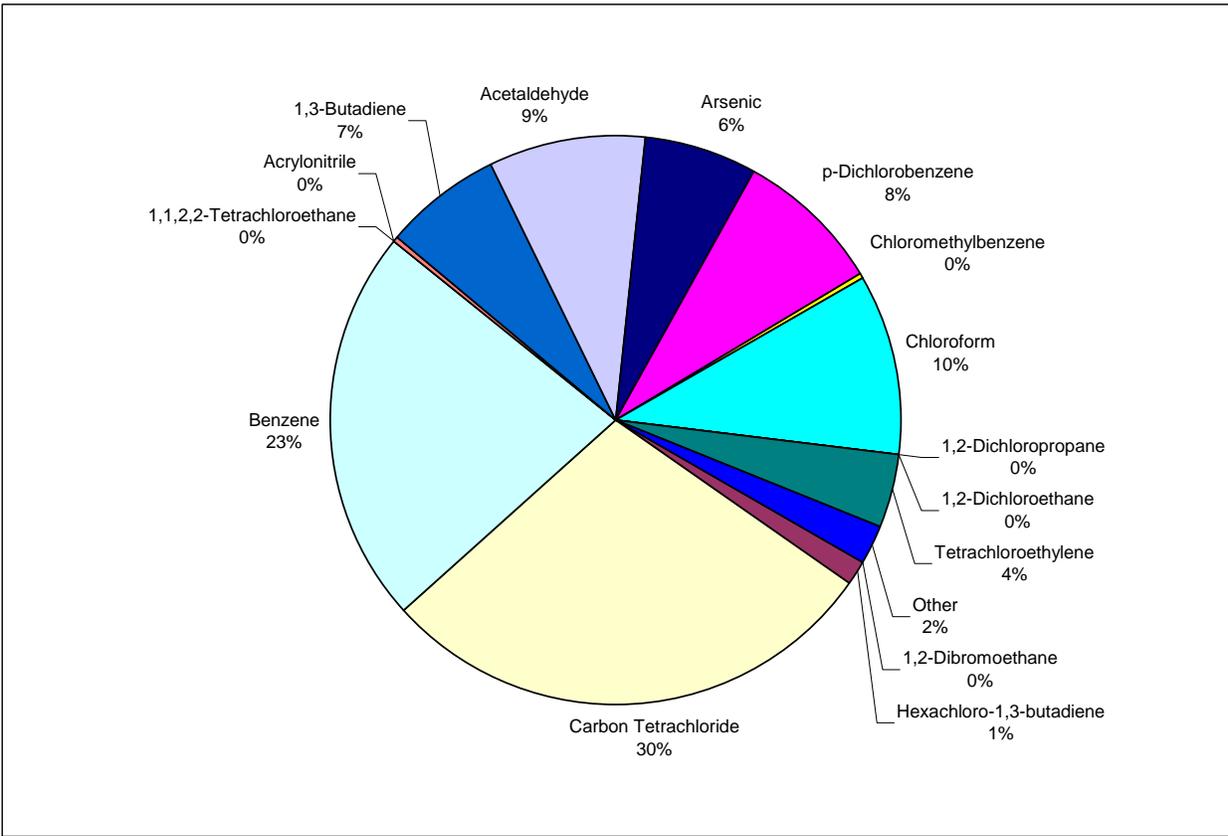


Figure 3-11. Percentages of Estimated Excess Cancer Risks Attributed to ARTS Target Compounds at Round Rock Using Zero $\mu\text{g}/\text{m}^3$ for Non-Detects

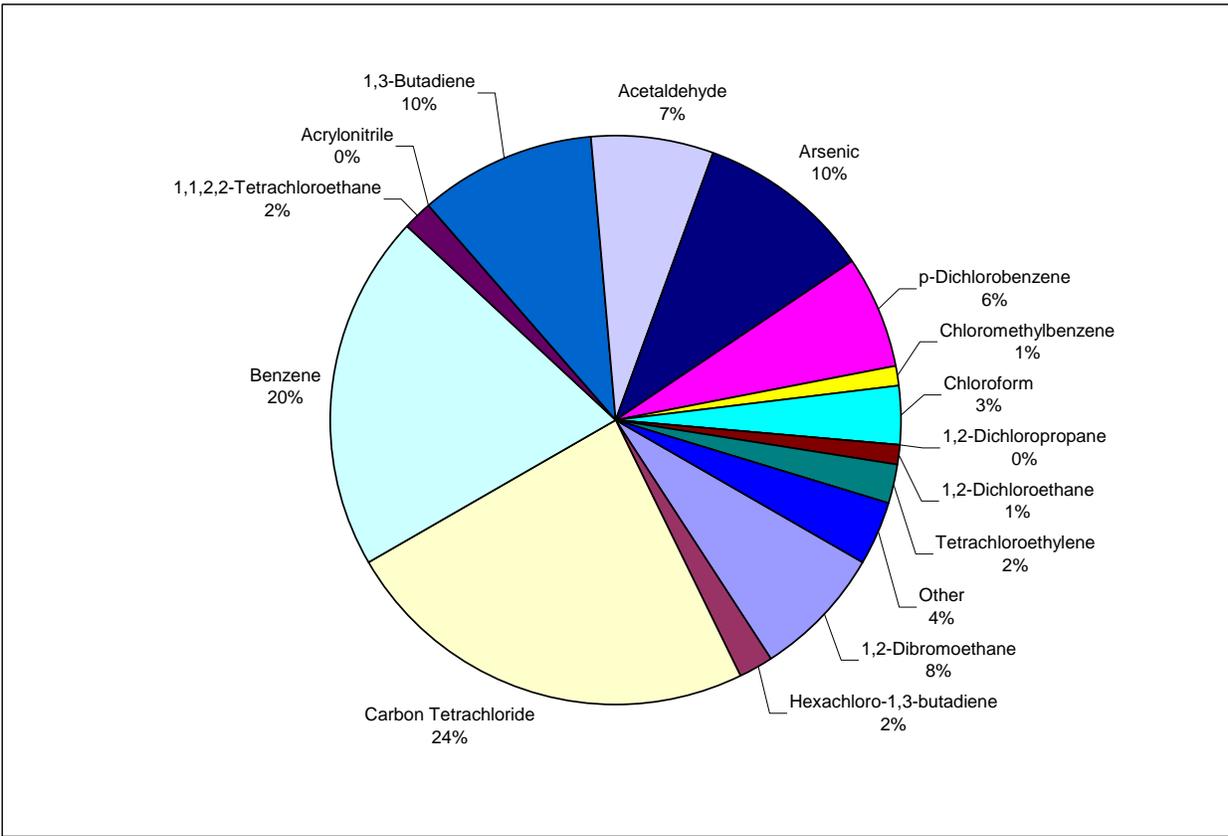


Figure 3-12. Percentages of Estimated Excess Cancer Risks Attributed to ARTS Target Compounds at Travis High School Using Zero $\mu\text{g}/\text{m}^3$ for Non-Detects

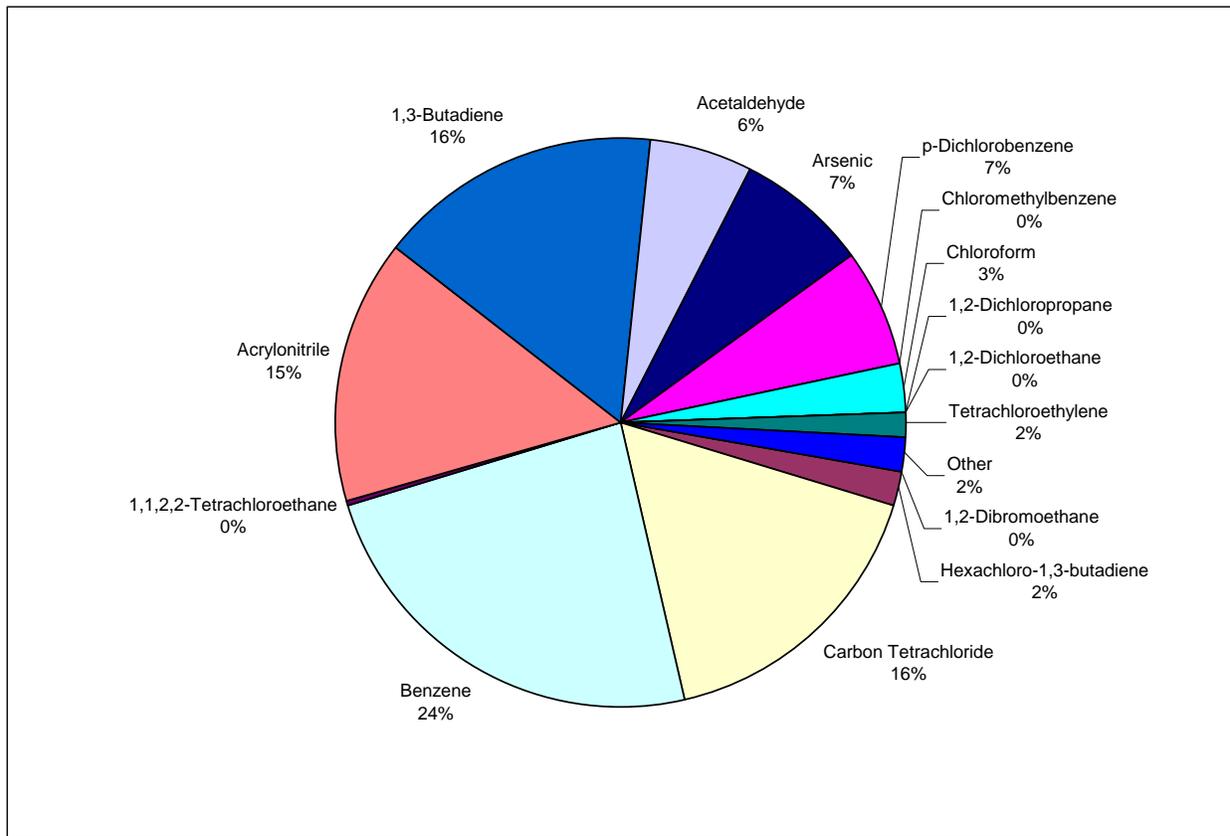


Figure 3-13. Percentages of Estimated Excess Cancer Risks Attributed to ARTS Target Compounds at Webberville Road Using Zero $\mu\text{g}/\text{m}^3$ for Non-Detects

3.2 Comparison with Other Cities

Air toxics measurements from other cities provide additional reference points with which to gauge the quality of the Austin-Round Rock air. To perform this assessment, the average concentrations of the NATTS core compounds from hundreds of locations across the U.S. were downloaded from the EPA Air Quality System (AQS) database, which is available online at <http://www.epa.gov/air/data/index.html>. Table 3-6 summarizes these measurements in terms of the number of sites reporting data for a particular compound and the median of the site-averages. The average concentrations measured in ARTS are also provided for comparison.

Except for acrolein, which was discussed in Section 3.1.2, the median site-averages for core air toxics measured in ARTS were approximately equal to or less than the corresponding medians of the 2005 site-averages reported in AQS. For most compounds, the differences were less than a factor of two (Figure 3-14).



**Table 3-6
ARTS Core Compound Average Concentrations and
Summary of 2005 Data from Other U.S. Monitoring Sites**

Compound Name	ARTS 2005 - 2006 Average ($\mu\text{g}/\text{m}^3$)						Other U.S. Sites (2005 Averages)	
	MUTX	PITX	RRTX	TRTX	WETX	Median	Median ($\mu\text{g}/\text{m}^3$)	Count
1,2-Dichloropropane	0.08	0.08	0.09	0.08	0.08	0.08	0.08	266
1,3-Butadiene	0.07	0.07	0.07	0.14	0.33	0.07	0.14	317
Acetaldehyde	1.34	1.33	1.38	1.40	1.62	1.38	1.71	218
Acrolein	3.73	2.51	4.60	2.58	3.77	3.73	0.44	111
Arsenic	4.8E-04	4.5E-04	5.1E-04	9.9E-04	1.1E-03	5.1E-04	1.0E-03	34
Benzene	0.94	0.80	0.98	1.11	1.88	0.98	0.98	445
Beryllium	1.4E-05	1.4E-05	1.4E-05	1.4E-05	1.3E-05	1.4E-05	2.0E-05	33
Cadmium	9.1E-05	1.0E-04	1.0E-04	3.7E-04	1.4E-04	1.0E-04	4.9E-04	33
Carbon Tetrachloride	0.63	0.68	0.66	0.68	0.67	0.67	0.63	312
Chloroform	0.07	0.11	0.18	0.09	0.09	0.09	0.24	296
Formaldehyde	2.78	2.85	3.26	2.98	2.72	2.85	3.01	220
Hexavalent Chromium	--	--	--	--	2.3E-05	2.3E-05	2.0E-05	63
Lead	1.7E-03	1.9E-03	2.4E-03	2.6E-03	3.0E-03	2.4E-03	5.0E-03	36
Manganese	4.9E-03	5.9E-03	5.8E-03	5.3E-03	7.0E-03	5.9E-03	5.7E-03	33
Dichloromethane	0.55	0.56	0.82	0.53	0.71	0.56	0.84	306
Nickel	5.7E-04	6.6E-04	7.4E-04	8.3E-04	8.0E-04	7.4E-04	2.5E-03	36
Tetrachloroethylene	0.27	0.11	0.26	0.19	0.19	0.19	0.23	325
Trichloroethylene	0.07	0.09	0.07	0.09	0.08	0.08	0.14	310
Vinyl chloride	0.03	0.03	0.03	0.03	0.03	0.03	0.06	269

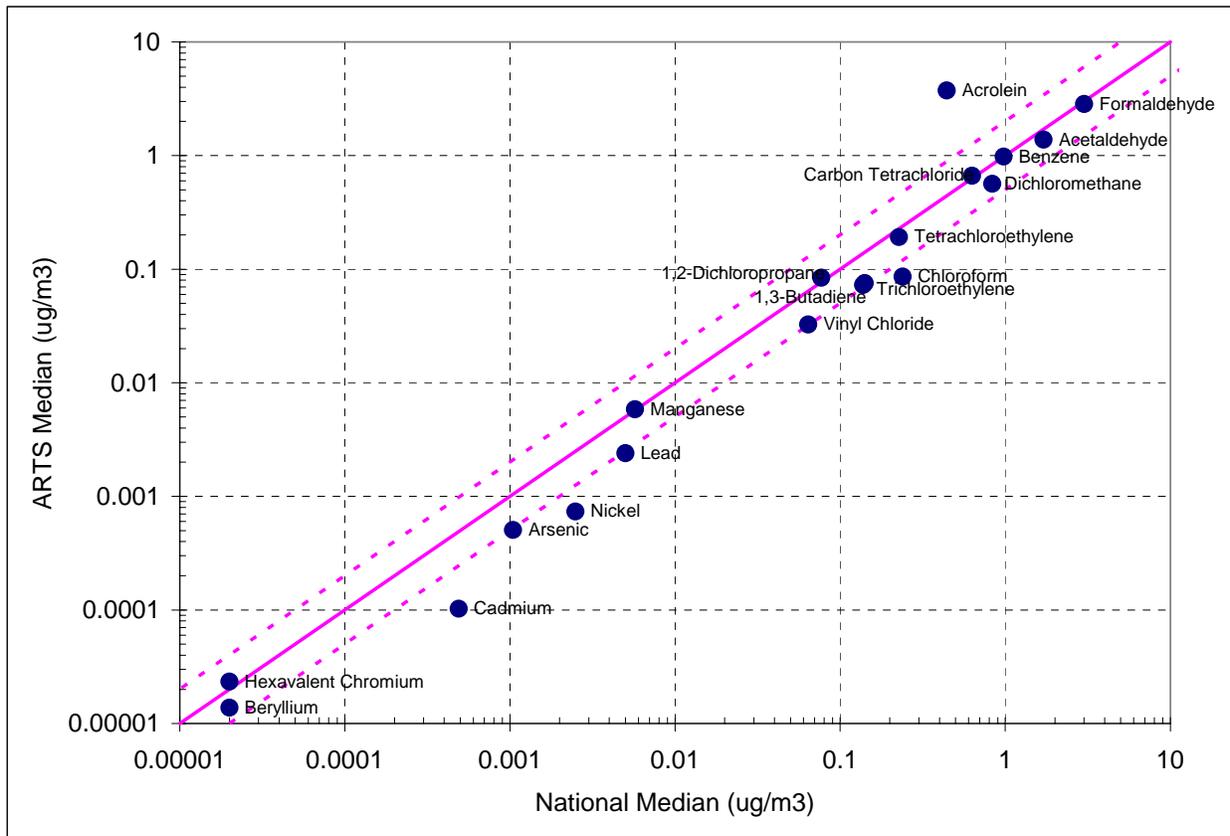


Figure 3-14. Comparison of Core Air Toxics Average Levels Measured in ARTS and the Median of 2005 Average Levels Reported for Other U.S. Monitoring Sites

3.3 Comparison of Monitoring Results with NATA Modeled Estimates

In 2006 EPA reported modeled estimates of ambient air toxics levels at the county and census tract levels across the U.S. as part of its National Air Toxics Assessment. Figure 3-15 shows a comparison of the average modeled estimates for Travis County with the average levels measured during ARTS for the NATTS core compounds. The agreement is within about a factor of two for 10 of the 19 core compounds, including benzene, acetaldehyde, and butadiene, which are three of the compounds that pose the greatest estimated health risks. Compounds for which the modeled-monitored agreements were comparatively poor include acrolein, trichloroethylene, arsenic, and cadmium. With a few exceptions, better agreements between modeled and monitored estimates were found for VOC and carbonyl core compounds than for metals.

Remarkably good agreements were found between the NATA total excess cancer risk estimates and the total excess risk estimates derived from the ARTS measurements. See, for example, Figure 3-16 which compares the monitored risk estimate for each monitoring site with the modeled estimate from the census tract in which the monitor was placed. The modeled risk estimates agreed with the monitor-derived estimates to within $\pm 50\%$ at each site. Note that the average modeled risk estimate for Travis County is identical to the average risk estimate derived from the four ARTS Travis County monitors.

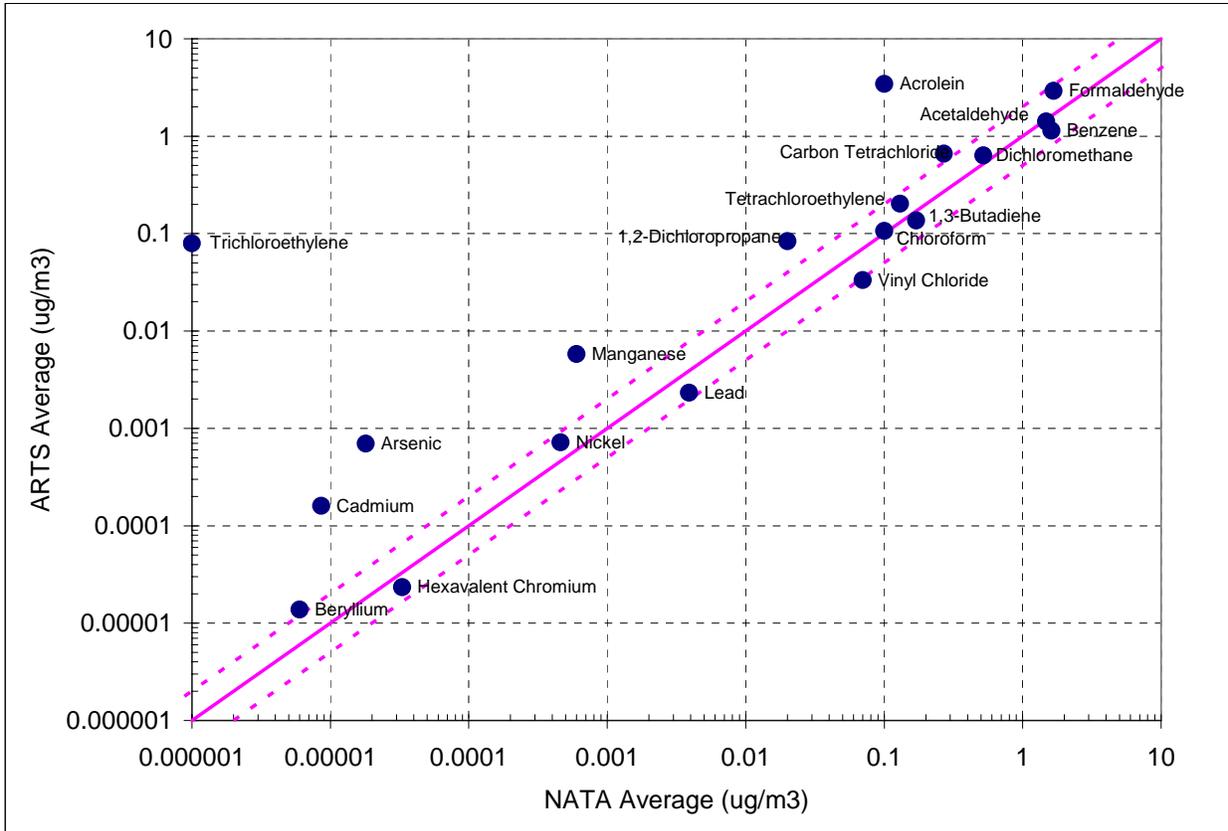


Figure 3-15. Comparison of Travis County Modeled Estimates of Core Air Toxics Concentrations with the Average Levels Measured in ARTS (Solid Line Represents One-to-One Agreement; Dashed Lines Represent a Factor of Two Disagreement)

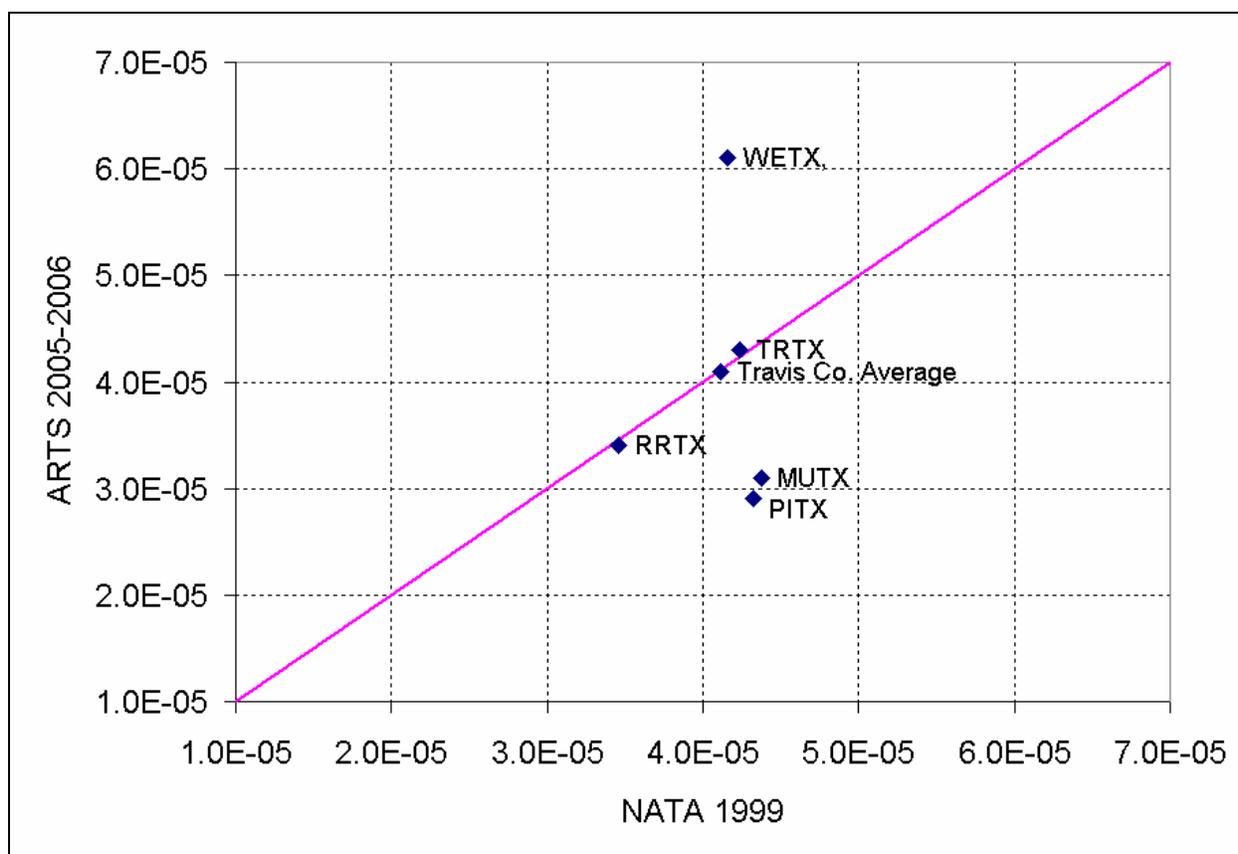


Figure 3-16. Comparison of 1999 NATA Excess Cancer Risk Estimates With ARTS 2005-2006 Measurement-Derived Estimates

4.0 Source Apportionment

Source apportionment of ARTS target compounds was performed using EPA Positive Matrix Factorization 1.1 (EPA PMF 1.1)², which is a statistical model based on factor analysis. To run EPA PMF 1.1, the user provides a file of measurement data where each column contains a different air pollutant species and each row contains a different time, typically an hour or a day. Then EPA PMF uses a constrained weighted least squares approach to decompose the file of concentrations into a set of computed source profiles and times series of contributions to the measured concentrations from each of the profiles.

One of the advantages of using EPA PMF compared with other source apportionment models is that it requires no a priori assumptions about which sources are important contributors to the measured concentrations. Instead, the model computes source profiles and their contributions to the measured concentrations based on the best fit to the data. The user then interprets the computed source profiles based on the presence of key species that are indicative of certain source types, and familiarity with the monitoring site environment. The user must, however, specify the number of source profiles to compute. This can be done by iteration, using multiple model runs to achieve the best statistical fit to the data and most sensible set of source profiles.

The primary objective of applying source apportionment to the ARTS data was to identify the sources most responsible for the levels of benzene at Webberville Road and to apportion their contributions. To achieve this goal, a subset of the ARTS target compounds, containing 31 of the VOC and carbonyl compounds that were most frequently detected, was analyzed. Streamlining the dataset in this way provides a better fit to the compounds of greatest interest. The EPA PMF inputs included the average detection limits for the 31 chemical species and estimates of uncertainty for each compound computed as the average relative percent difference from duplicate field samples.

EPA PMF was run for scenarios having 3 to 9 source factors. The six-factor solution, which produced a comparatively good fit to the benzene data (Figure 4-1) and the most meaningful set of source profiles, is described below. Table 4-1 lists the six source profiles and their key constituents. Three of the computed source profiles (numbers 3, 4, and 5), are identified as motor vehicle emissions, background air, and secondary carbonyl production. It is perhaps not surprising for an area with comparatively low major source emissions that these would be among the most significant contributors to the ambient air toxics levels. The other three source profiles (numbers 1, 2, and 6 in Table 4-1) are more difficult to interpret and may, in fact, reflect uncertainty in either the measurement process or the source apportionment modeling. All the source profiles were detected at all the ARTS sites; however, the toluene and motor vehicle emissions profiles were significantly more important at Round Rock and Webberville Road, respectively (Figure 4-2).

² <http://www.epa.gov/heads/products/pmf/pmf.htm>

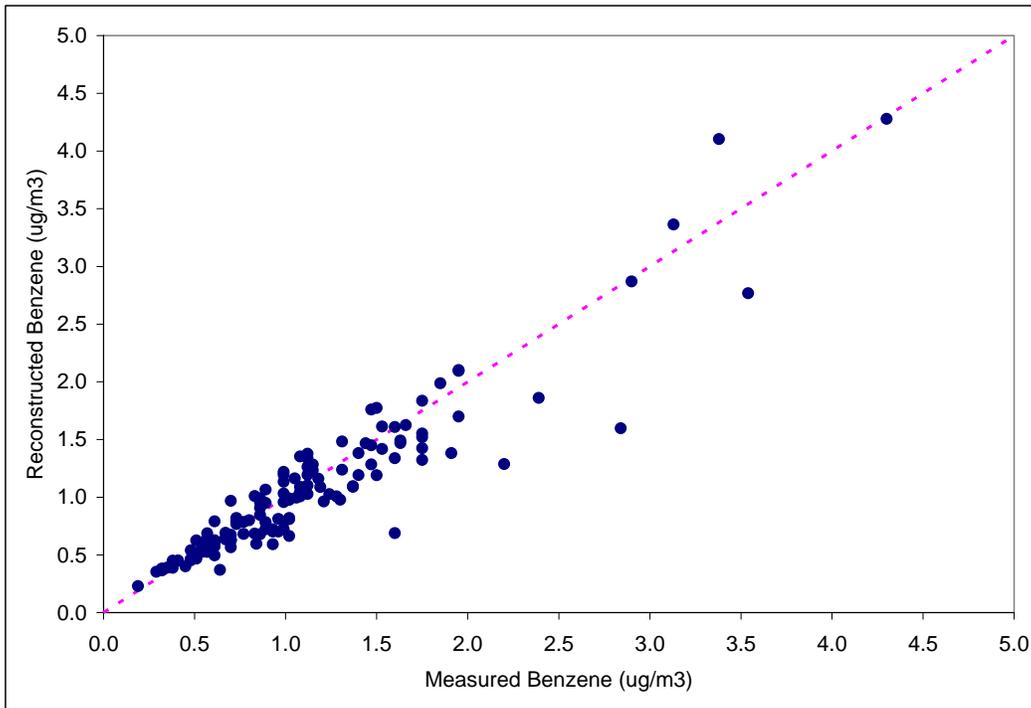


Figure 4-1. Scatter Plot Showing the Agreement between the Measured Benzene Level and the Benzene Level Reconstructed from the Sum of Six Source Profile Contributions for Each ARTS Sample (R-Square = 0.87)

**Table 4-1
ARTS Source Profiles**

Source Profile No.	Description	Key Constituents	Key Months/Sites
1	Acrolein/MEK	Acrolein, MEK	Jun.-Sep./All sites
2	Toluene	Toluene	Mar.-Nov./RRTX
3	Motor Vehicles	Benzene, toluene, ethyl benzene, xylene, trimethylbenzene, acetylene, propylene, butadiene	All months/WETX
4	Background	Carbon tetrachloride, chloromethane, dichlorofluoromethane, trichlorofluoromethane	All months/All sites
5	Carbonyl	Formaldehyde, acetaldehyde, acetone	Jun.-Sep./All sites
6	Undefined	Ethyl benzene, MEK, styrene, xylene, MIBK	Jun.-Sep. 2005/All sites

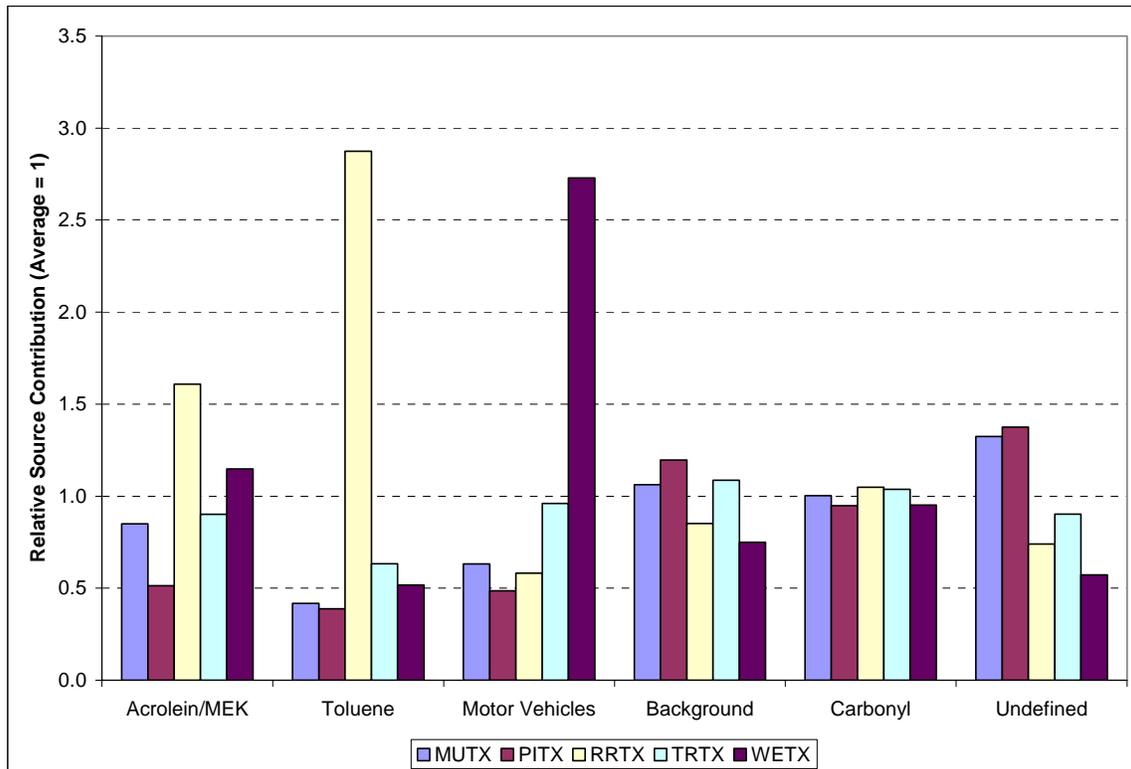


Figure 4-2. Relative Source Contributions by ARTS Site

4.1 Source Profile 1 – Acrolein/Methyl Ethyl Ketone (MEK)

This source factor is comprised almost entirely of acrolein and methyl ethyl ketone (MEK) plus smaller amounts of propylene, toluene, acetylene, and formaldehyde (Figure 4-3). Ninety-eight percent of the acrolein and 86% of the MEK that was measured in ARTS was attributed to this source factor. This source factor was strongest during June-September 2005 and May-June 2006 and was found at all ARTS sites (Figure 4-4).

No known sources appear to account for this source profile or the levels of acrolein that were measured in ARTS. Primary sources of acrolein include motor vehicles, electricity generating units, wood combustion, and other combustion processes. Acrolein is also produced in the atmosphere from other VOCs that are emitted by motor vehicles, including propylene and 1,3-butadiene. Concern has been raised elsewhere (Heaton, 2006) that acrolein may sometimes be produced in TO-15 canisters from decay of other sample constituents.

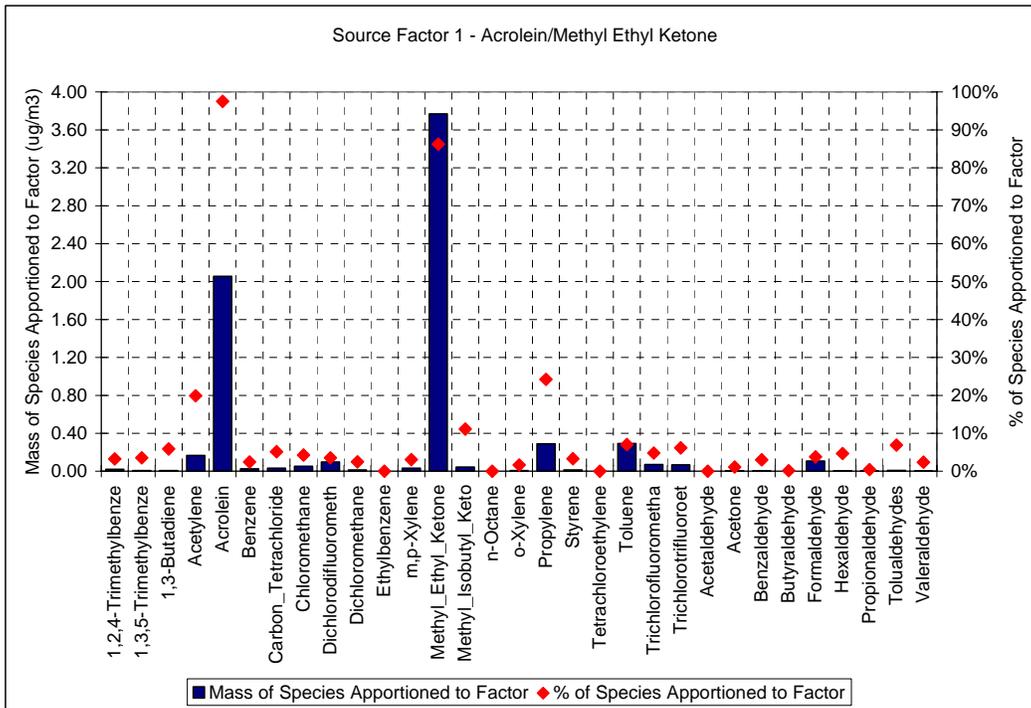


Figure 4-3. Acrolein/Methyl Ethyl Ketone Source Profile

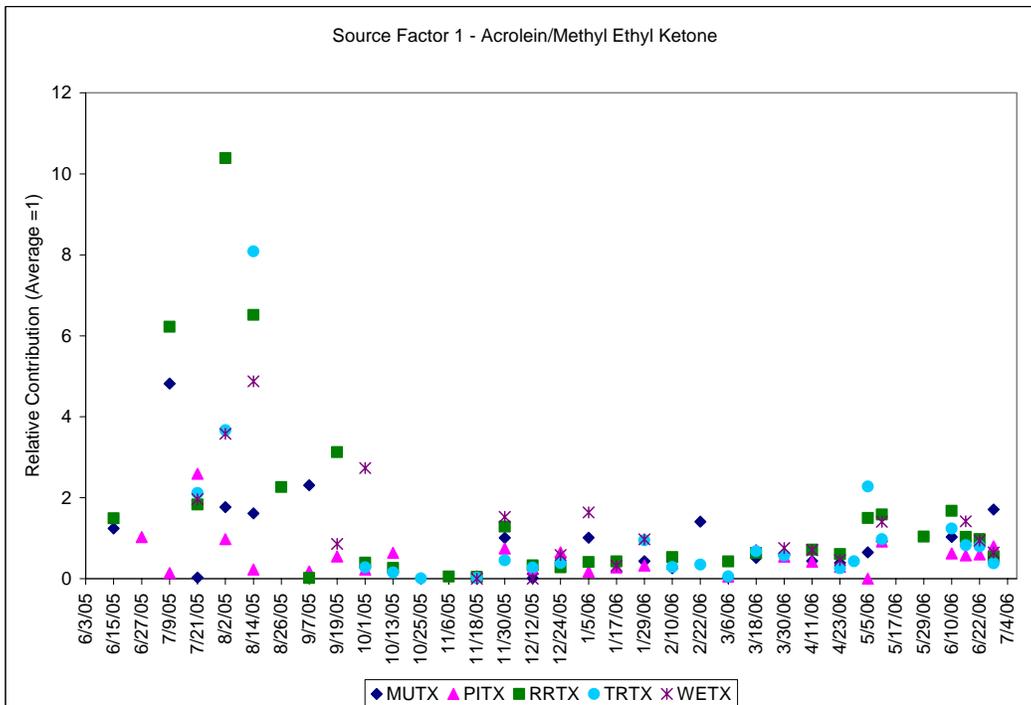


Figure 4-4. Time Series of Acrolein/MEK Source Profile Contributions

4.2 Source Profile 2 – Toluene

This source factor is comprised almost entirely of toluene (Figure 4-5) and was found primarily at the Round Rock Site where it accounted for 85% of the toluene that was measured. Recall that toluene levels were greatest at RRTX, where they averaged $8.7 \mu\text{g}/\text{m}^3$ over the 12-month field study. Average toluene levels at the other ARTS sites ranged from 2.0 to $4.7 \mu\text{g}/\text{m}^3$. Contributions from this source factor were greatest during June-November 2005 and March-June 2006 (Figure 4-6). This source factor most likely represents a local toluene source close to the RRTX site.

4.3 Source Profile 3 – Motor Vehicles

This source factor is comprised of benzene, toluene, ethyl benzene, xylene, 1,3-butadiene, and several other constituents of motor vehicle exhaust (Figure 4-7). It was found throughout the year at all the ARTS sites but most significantly at Webberville Road (Figure 4-8). On average, 53% and 86% of the benzene and 1,3-butadiene, respectively, was attributed to this source factor. At Webberville Road, 79% and 95% of the benzene and 1,3-butadiene, respectively, was attributed to this source factor.

4.4 Source Profile 4 – Background

This source factor is comprised mainly of dichlorodifluoromethane (Freon 12), trichlorofluoromethane (Freon 11), trichlorotrifluoroethane (Freon 113), chloromethane, and carbon tetrachloride (Figure 4-9). This source profile was found throughout the year at all ARTS sites (Figure 4-10) and had comparatively low spatial and temporal variability. It probably represents the Freons and other halocarbons that have accumulated in the atmosphere from prior use. Approximately 50-70% of all the mass of each of these halocarbons measured in ARTS was attributed to this source factor. Uncertainty in the source apportionment modeling due to the relatively minor temporal variability of these compounds is perhaps the best explanation of why no greater than 50-70% of these compounds were attributed to this source factor. Formaldehyde, acetaldehyde, and benzene were also associated with this source factor, probably as background contributions from area sources.

4.5 Source Profile 5 – Carbonyl Compounds

This source factor is comprised mainly of formaldehyde, acetaldehyde, and acetone (Figure 4-11). Greater than 70% of the mass of these chemicals were attributed to this source profile. Approximately 50% or greater of other carbonyl compounds measured in ARTS was also attributed to this source factor. The contributions from this source factor were greatest during June-November 2005 and March-June 2006 (Figure 4-12) but this source factor had the least spatial variability of all the source factors. The strength of this source factor at Murchison Middle School correlated with daily maximum 8-hour ozone levels, suggesting that this factor is associated with photochemical production (Figure 4-13).

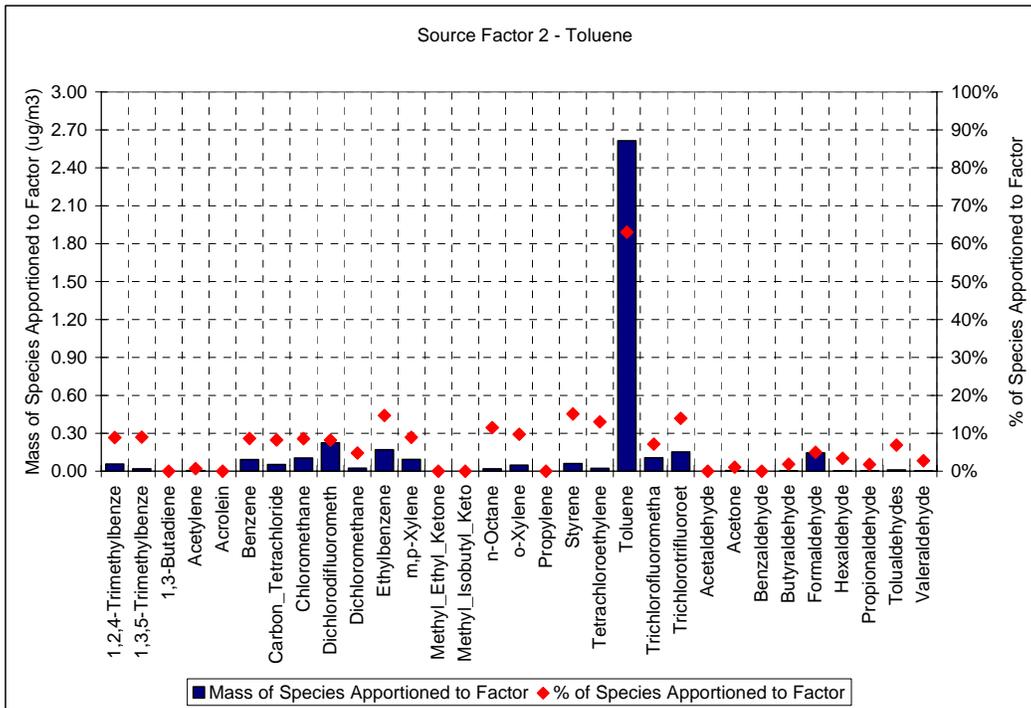


Figure 4-5. Toluene Source Profile

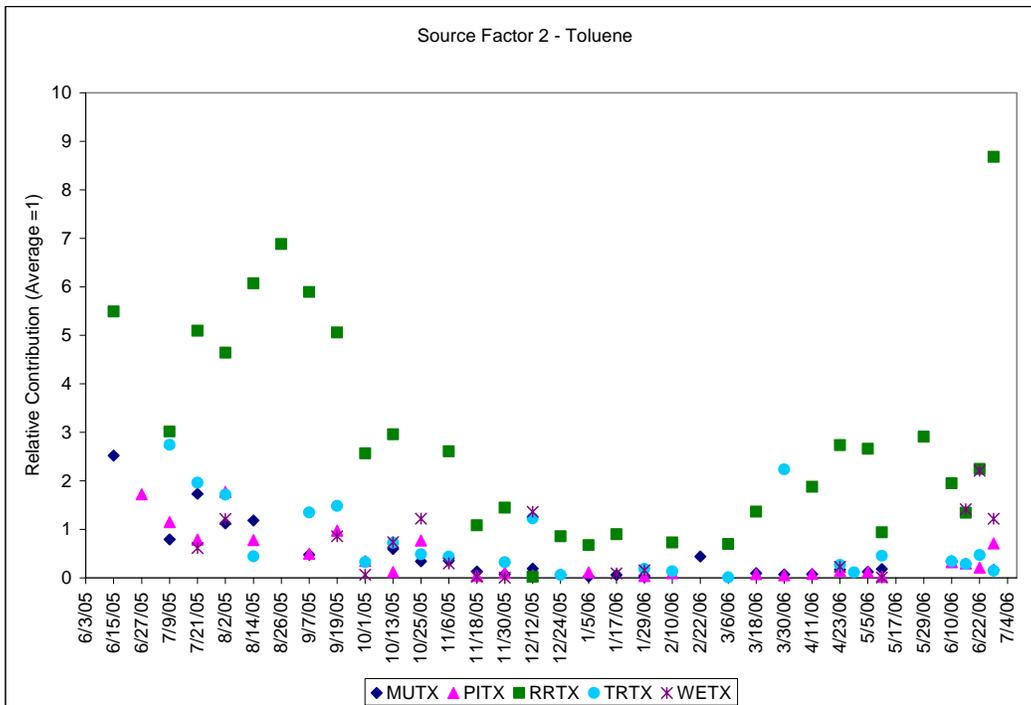


Figure 4-6. Time Series of Toluene Source Profile Contributions

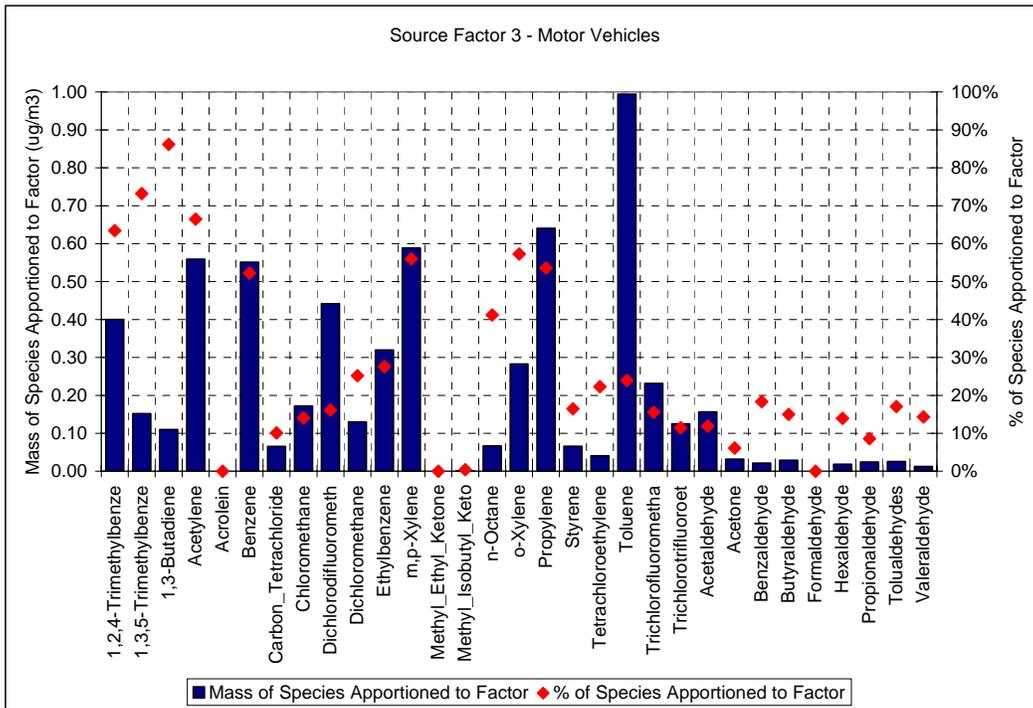


Figure 4-7. Motor Vehicle Source Profile

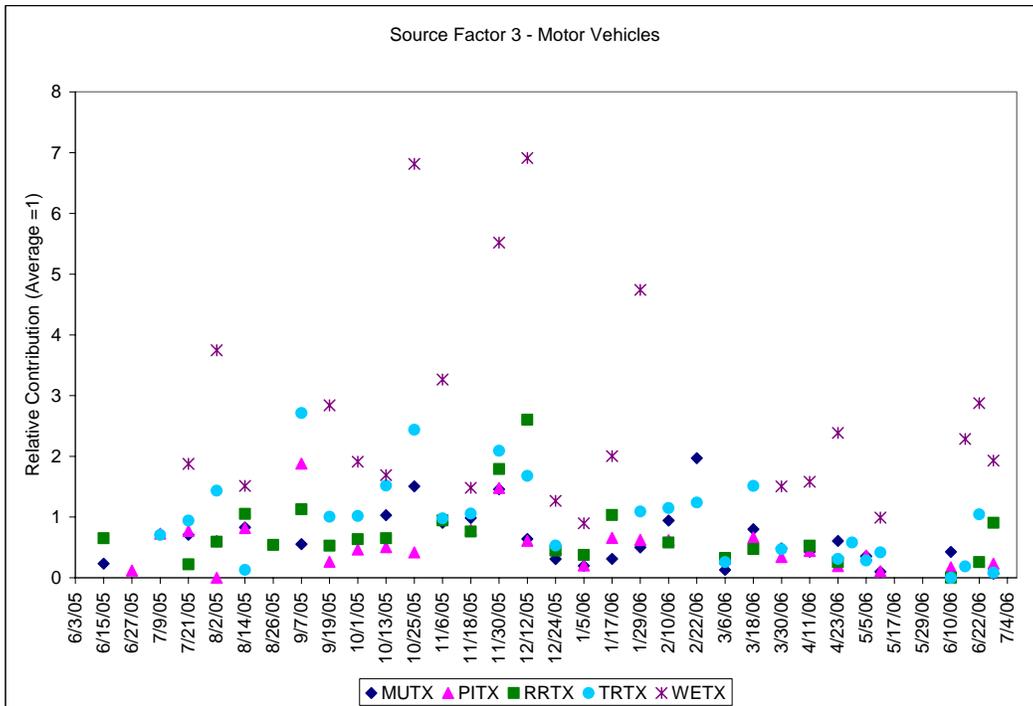


Figure 4-8. Time Series of Motor Vehicle Source Profile Contributions

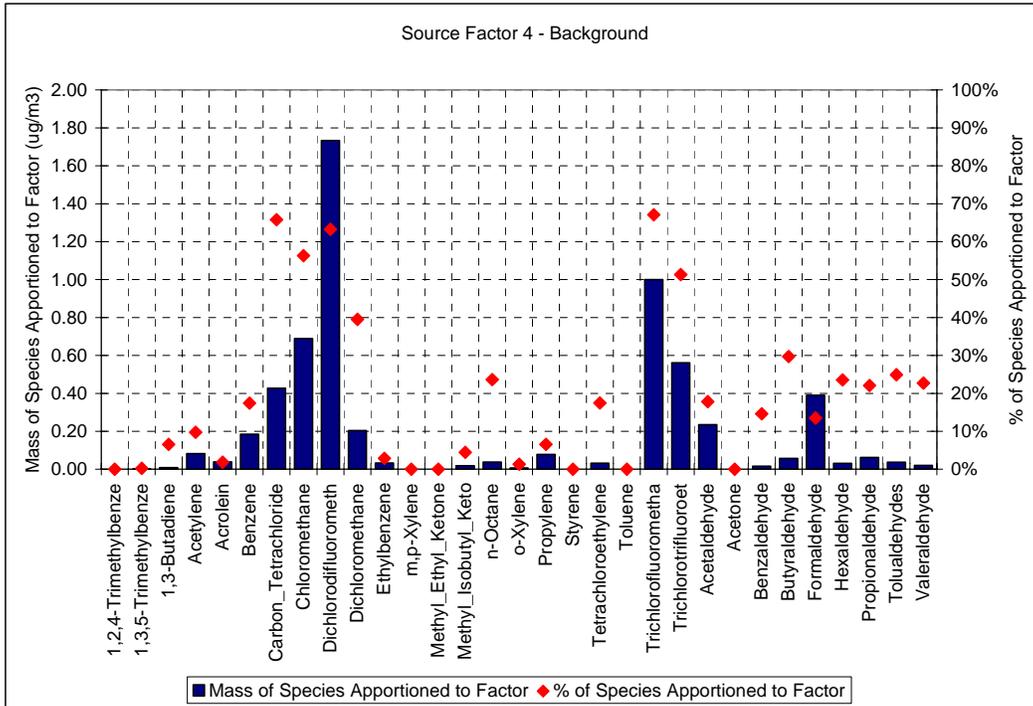


Figure 4-9. Background Source Profile

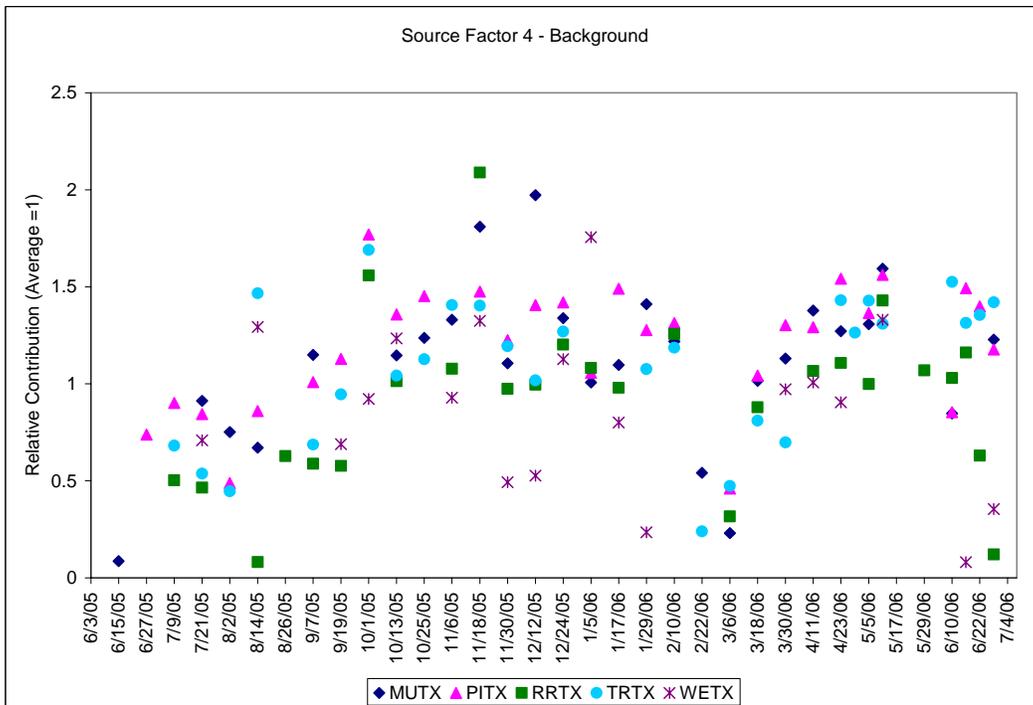


Figure 4-10. Time Series of Background Source Profile Contributions

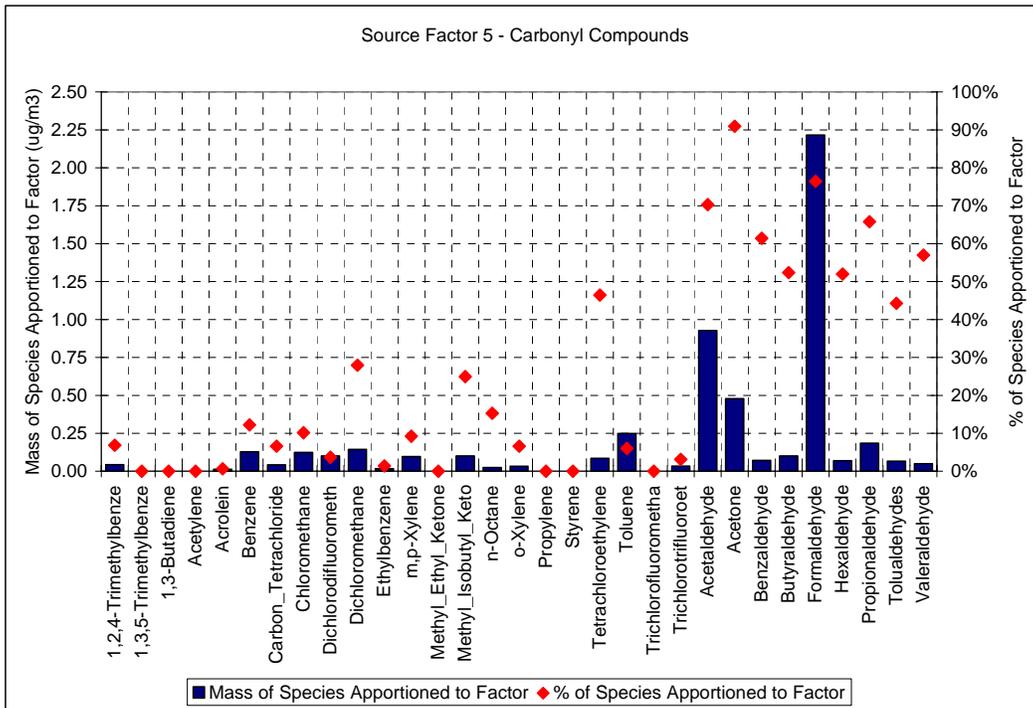


Figure 4-11. Carbonyl Compound Source Profile

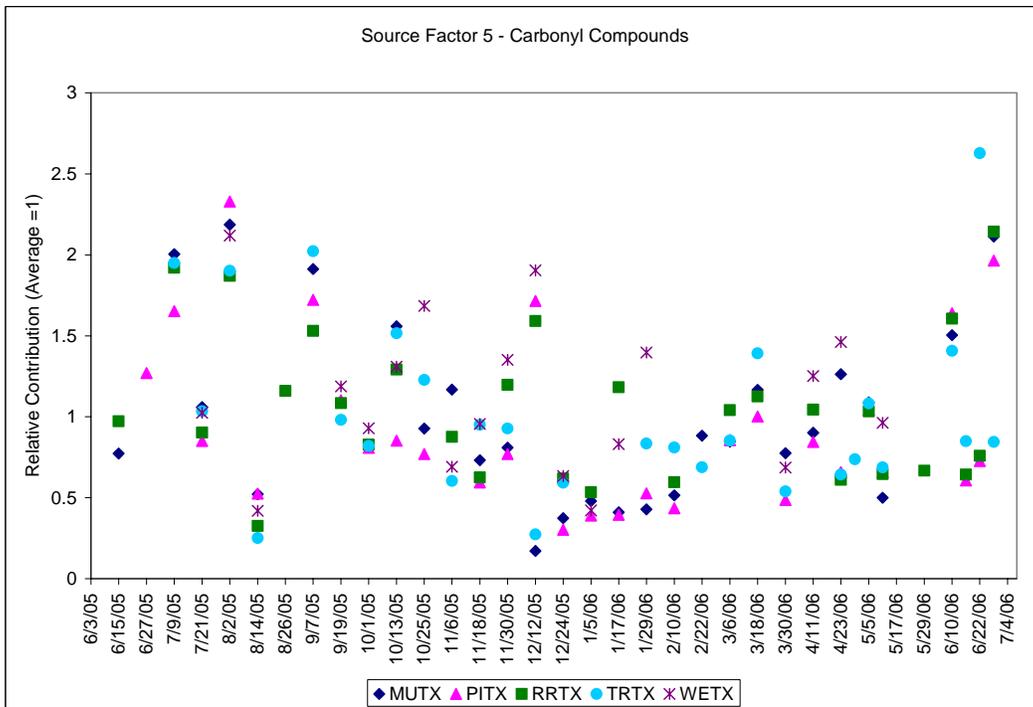


Figure 4-12. Time Series of Carbonyl Compound Source Profile Contributions

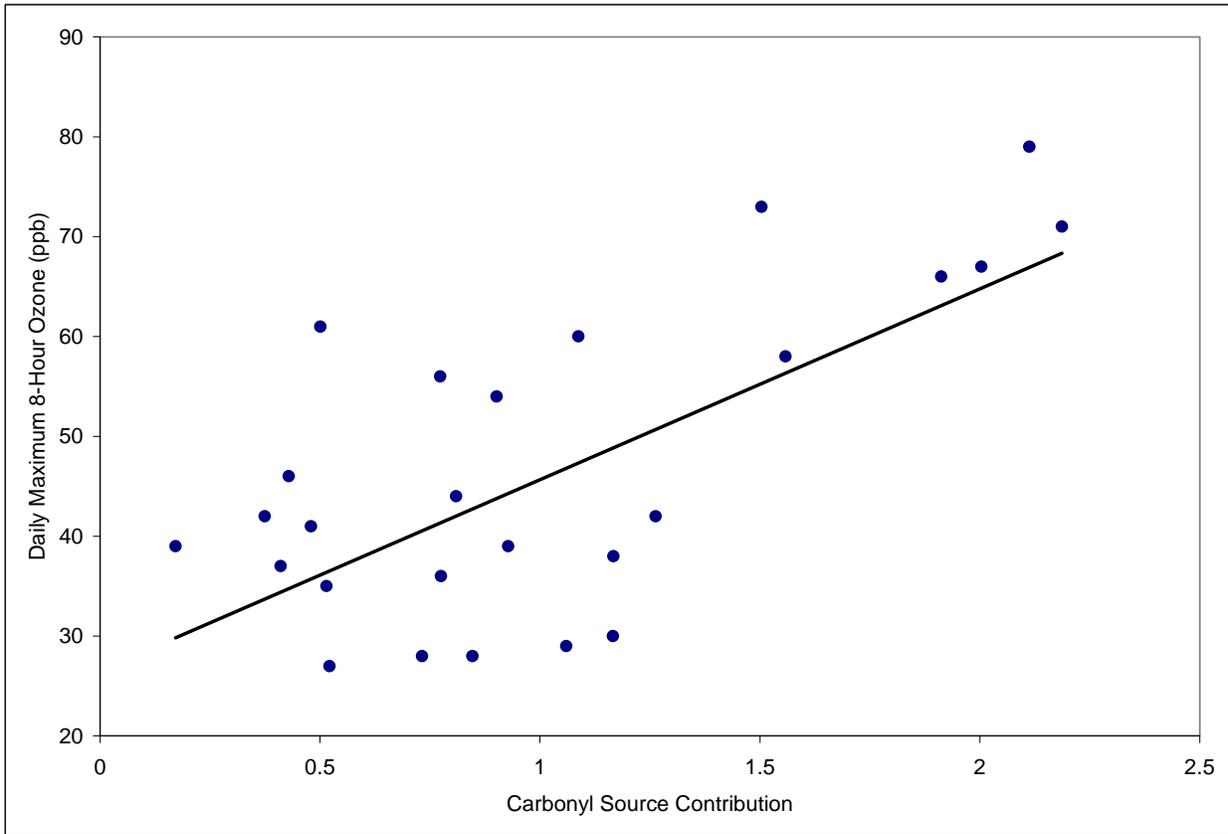


Figure 4-13. Scatter Plot Showing the Relationship Between the Carbonyl Source Factor Contribution and the Daily Maximum 8-Hour Ozone Level at Murchison Middle School (R-Square = 0.4)

4.6 Source Profile 6 – Undefined

This source profile is comprised mainly of ethyl benzene, methyl ethyl ketone, styrene, xylene, and methyl isobutyl ketone (Figure 4-14). The contributions from this source factor were greatest at the start of ARTS and dropped off rapidly during June-October 2005 (Figure 4-15). Several of the key constituents of this source profile are used in solvents; however, no known source appears to account for this source factor or its marked decay from June-October 2005. Most likely this source factor results from some artifact of the measurement process, for example contamination of the canisters, the sampling systems, or the laboratory equipment. Most notably, approximately 50-60% of the ethyl benzene, styrene, and methyl isobutyl ketone measured in ARTS were attributed to this source factor.

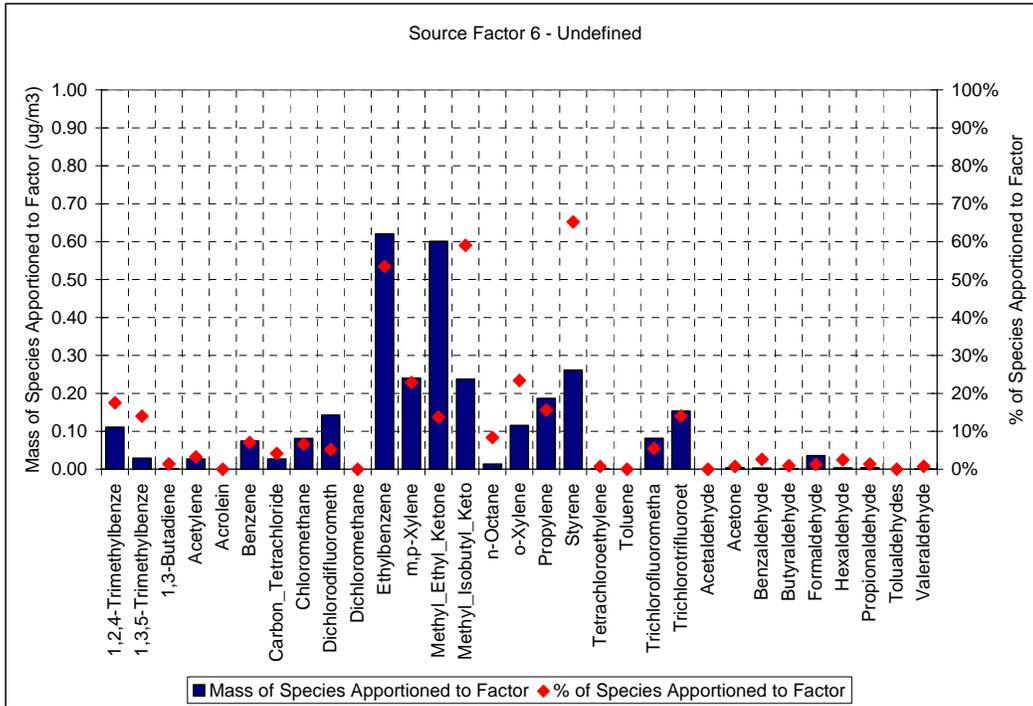


Figure 4-14. Undefined Source Profile

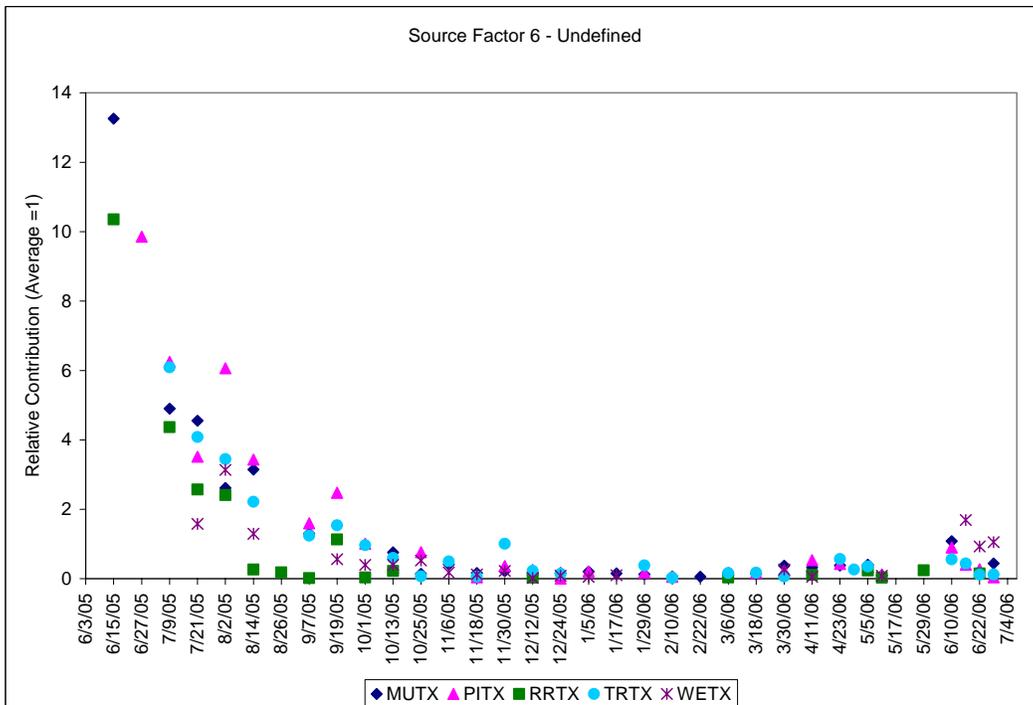


Figure 4-15. Time Series of Undefined Source Profile Contributions

4.7 Source Apportionment of Benzene and Other Core ARTS Compounds

Figures 4-16 and 4-17 summarize the benzene source apportionment averaged for all ARTS sites and separately for Webberville Road, respectively. On average, 53% of the benzene was attributed to motor vehicle emissions while at Webberville Road the benzene contribution from motor vehicles was estimated to be 79%. This 53% average contribution is identical to the percentage of the Travis County average benzene concentration attributed to on road mobile sources by NATA.

Figures 4-18 and 4-19 give the source apportionment results for 1,3-butadiene. The percentage of 1,3-butadiene attributed to motor vehicle emissions was 86%, on average, and 95% at Webberville Road. The NATA model attributed only 45% of the Travis County 1,3-butadiene average to mobile sources and 40% to background.

Figures 4-20 and 4-21 give the source apportionment results for formaldehyde and acetaldehyde, respectively. Seventy-seven percent of the formaldehyde and 70% of the acetaldehyde was attributed to the secondary carbonyl source profile while 13% and 18% of formaldehyde and acetaldehyde was attributed to background, respectively. Twelve percent of acetaldehyde was attributed to motor vehicle emissions while, surprisingly, none of the formaldehyde was attributed to motor vehicles.

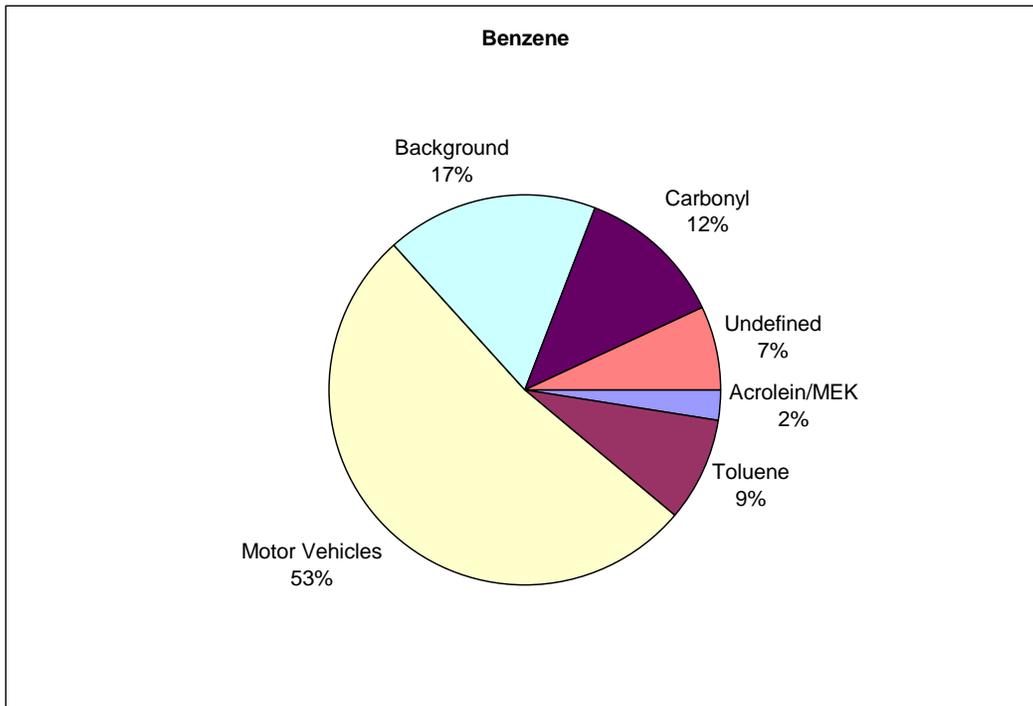


Figure 4-16. Benzene Source Apportionment for All ARTS Sites

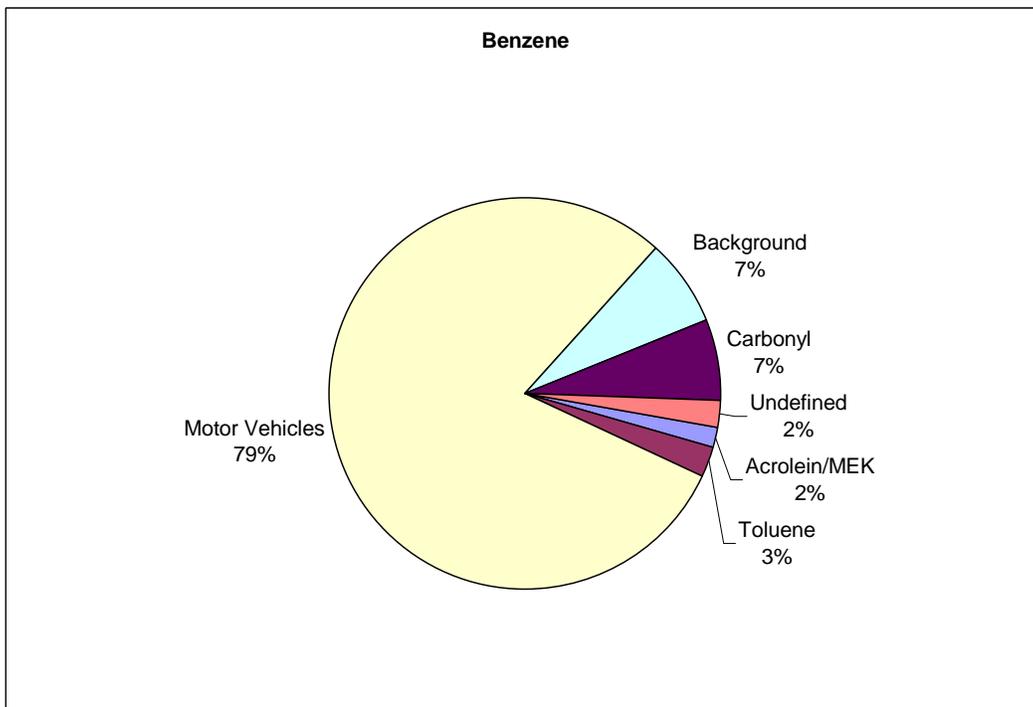


Figure 4-17. Benzene Source Apportionment for Webberville Road

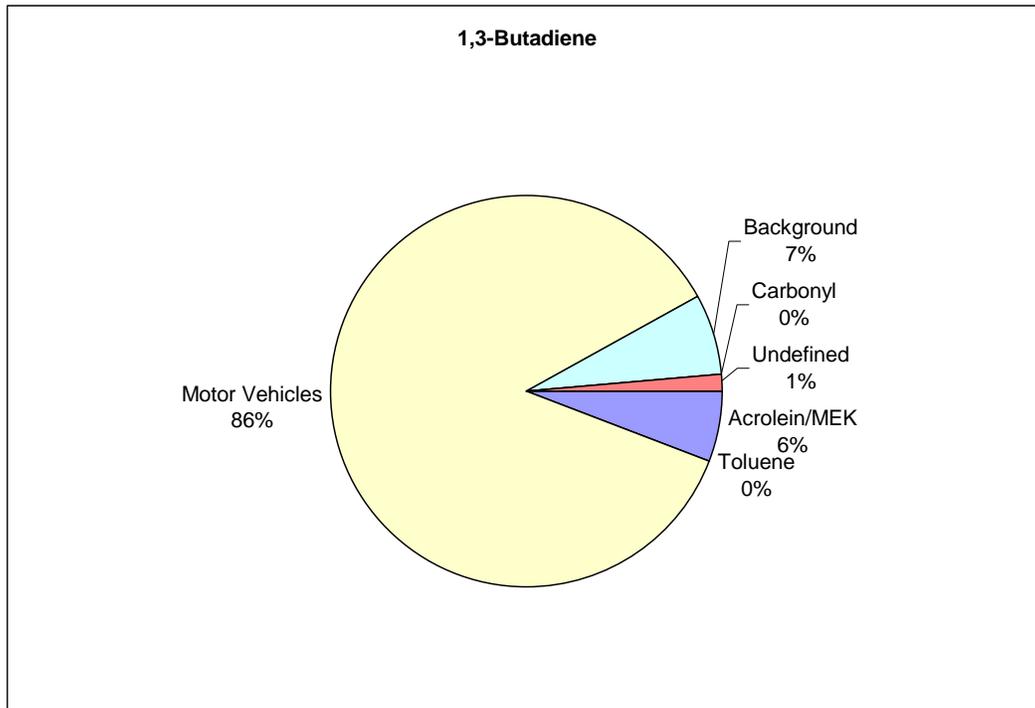


Figure 4-18. 1,3-Butadiene Source Apportionment for All ARTS Sites

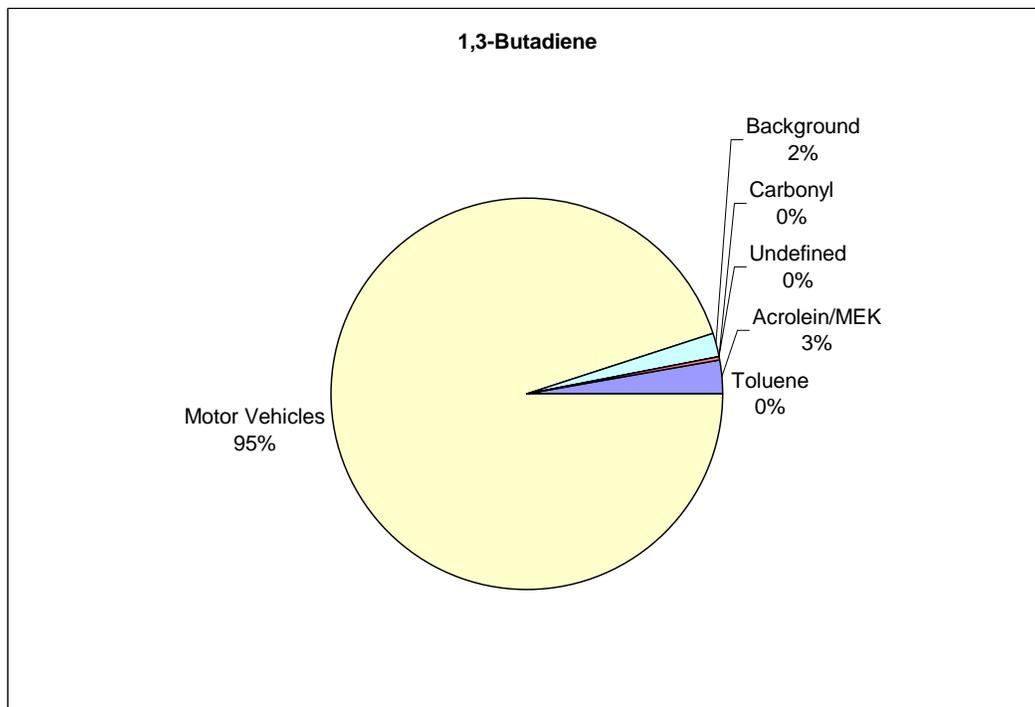


Figure 4-19. 1,3-Butadiene Source Apportionment for Webberville Road

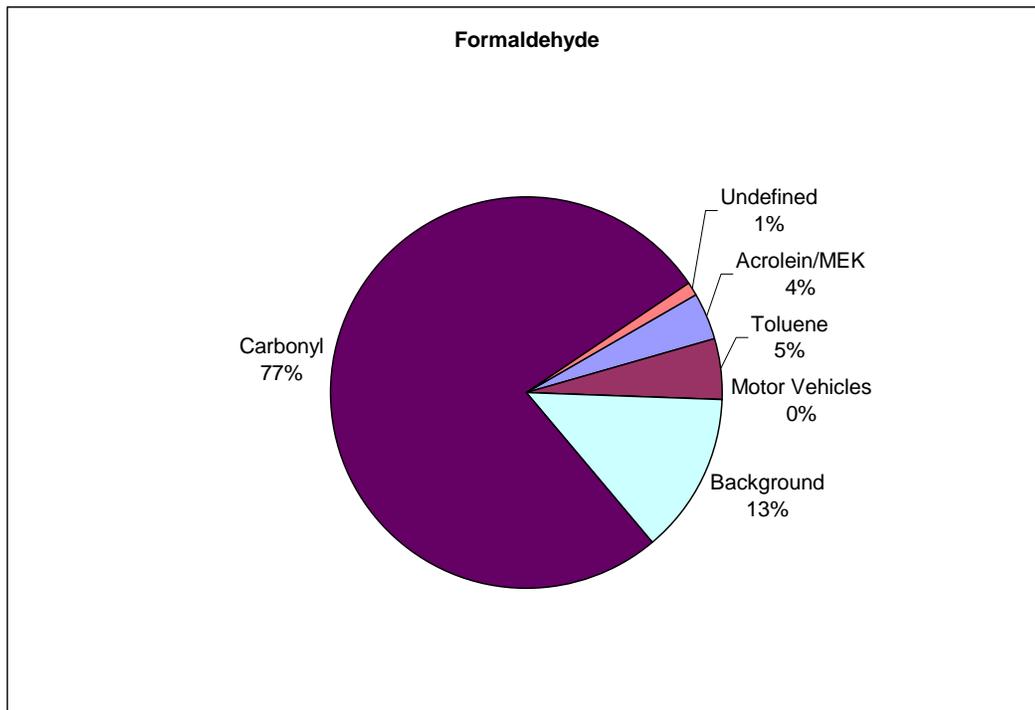


Figure 4-20. Formaldehyde Source Apportionment for All ARTS Sites

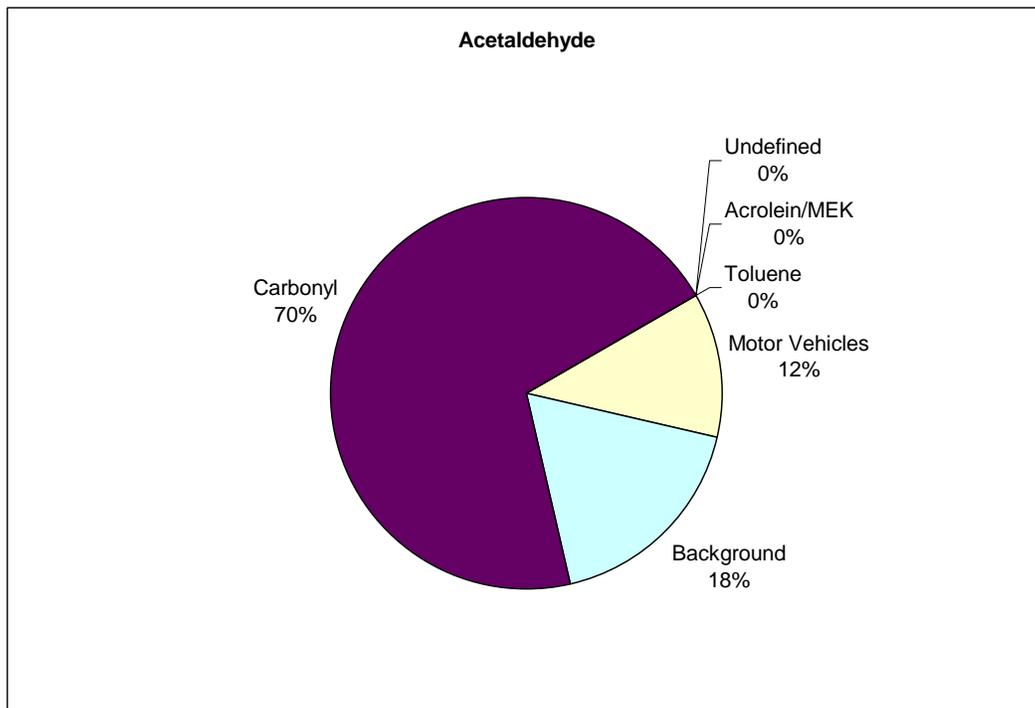


Figure 4-21. Acetaldehyde Source Apportionment for All ARTS Sites



5.0 Data Quality

The quality of the data generated by ARTS is expressed in terms of completeness, precision, and accuracy. Completeness is the percentage of samples collected at each site relative to the number that was scheduled at the start of the measurement program. Precision is a measure of agreement between two measurements made side by side. Accuracy is a measure of the bias in a measurement result relative to the true value.

5.1 Completeness

Thirty-one TO-15 VOC canisters, TO-11A carbonyl cartridges, and PM10 filters for metals analyses were originally scheduled to be collected at each site from June 15, 2005 through June 10, 2006. Additionally, 31 particulate matter filters for hexavalent chromium analysis were scheduled for collection at Webberville Road. The total numbers collected and completeness at each site are given in Table 5-1. The completeness exceeded the 75% project objective for each sample type, at each site.

To compensate for missed samples early during the field program and achieve the levels of completeness reported in Table 5-1, the field sampling was extended to June 28, 2006 and the nominal every 12th day sampling frequency was increased to every sixth day during the entire month of June 2006. In some cases, the extra sampling dates resulted in greater than 31 total samples collected and therefore greater than 100% completeness.

**Table 5-1
Summary of ARTS Data Completeness**

Sample Type	Number Scheduled (Per Site)	Number Collected					Completeness (%)				
		MUTX	PITX	RRTX	TRTX	WETX	MUTX	PITX	RRTX	TRTX	WETX
VOC Canisters	31	31	31	30	31	26	100	100	97	100	84
Carbonyl Cartridges	31	30	31	32	30	29	97	100	103	97	94
Metals PM10 Filters	31	30	33	31	30	33	97	106	100	97	106
Cr ⁶⁺ Filters	31	--	--	--	--	24	--	--	--	--	77
Average	31	30	32	31	30	28	98	102	100	98	90



5.2 Precision

For each pair of duplicate samples, the relative percent difference (RPD) was calculated as:

$$RPD = \frac{|X_1 - X_2|}{\bar{X}} \times 100\%$$

Where:

- X_1 is the ambient air concentration of a given pollutant measured in one sample;
- X_2 is the concentration of the same pollutant measured in the duplicate sample; and
- \bar{X} is the arithmetic mean of X_1 and X_2 .

Precision for each TO-15 and TO-11A compound was then calculated as the average RPD based on all the valid duplicate sample sets that were collected. Over the 12-month study, 16 valid pairs of TO-15 canisters and 24 valid pairs of TO-11A cartridges were collected, all at Webberville Road. Duplicate PM10 samples for assessing metals precision were not collected.

The precision estimates from TO-11A cartridges and TO-15 canisters are given in Tables 5-2 and 5-3, respectively. Note that only compounds that were detected in at least one set of duplicate samples are listed in these tables. Most of the reported compounds had measurement precision estimates within 20%, with notable exceptions being acetonitrile and acrolein. Essentially, no agreement was found between primary and duplicate sample results for acetonitrile (Figure 5-1), causing all the data for that compound to be invalidated. A possible source of uncertainty in the acetonitrile measurements may be re-entrainment into the ATEC sampling system of acetonitrile used in the preparation TO-11A cartridges. Although this would seem unlikely given that separate sampling inlets were used for TO-15 canisters (in which acetonitrile was measured) and TO-11A cartridges, no other explanation appears plausible. In contrast to acetonitrile, reasonably good agreement between primary and duplicate samples was found in 13 of the 16 sample pairs for acrolein (Figure 5-2). Therefore, the acrolein data were not invalidated but are questionable, nevertheless, for other reasons discussed below.

Three sets of duplicate canister samples collected during June 16-28, 2006 were not used in the precision assessments. What would have been the primary samples collected at Webberville Road on those dates had uncharacteristically high levels of ethyl benzene, xylene, styrene, and methyl methacrylate and very poor agreement with the duplicate sample results. These samples were invalidated and replaced with the duplicates. Other options for treating these outliers might have been: (1) reporting them as valid data and incorporating their uncertainties into the overall precision estimates, or (2) invalidating both samples in the duplicate set. The first of these alternative options would have increased the reported levels of styrene and methyl methacrylate by about a factor of 10 while approximately doubling the reported levels of p/m-xylene and o-xylene; however, this option would not have raised the average levels above the respective non-cancer RfC and none of the affected compounds are suspected carcinogens. Additionally, none of the outlier compounds were on the core target list. The second alternative would not have affected the reported average concentrations significantly for the outlier compounds but would have invalidated about 10% of the reported data and all the detected



values for acrylonitrile at Webberville Road (see Section 5.3.3 for a discussion of the acrylonitrile data quality and the effect of invalidating the detected values.

Table 5-2
Summary of ARTS Measurement Precision for TO-11A Compounds

Compound Name	Precision (Relative Percent Difference)
Acetaldehyde	27%
Acetone	13%
Benzaldehyde	21%
Butyraldehyde	18%
Crotonaldehyde	4%
Formaldehyde	12%
Hexaldehyde	15%
Isovaleraldehyde	6%
Propionaldehyde	15%
Tolualdehydes	11%
Valeraldehyde	13%

5.3 Bias

The accuracy of the ARTS monitoring data was not assessed directly but it is assumed equal, in general, to the accuracy of air toxics monitoring data achieved by the EPA Urban Air Toxics Monitoring Program (UATMP) (ERG, 2006). ARTS used the same sampling and analytical methods used in the UATMP (i.e., Compendium Methods TO-11A, TO-15, and IO-3.5), which have been approved by EPA for accurately measuring ambient levels of VOC, carbonyl compounds, and metals, respectively, and the samples were analyzed by the same laboratory used in the UATMP. Despite these measures, and the absence of any known biases, some of the ARTS measurement data appear questionable for reasons cited below.

5.3.1 Acrolein Data Quality

Already noted in this report, the acrolein levels measured in ARTS are considerably higher than levels reported for most other U.S. monitoring sites. Although ERG has demonstrated reliable performance of the TO-15 method for measuring acrolein, no known sources account for differences in the acrolein levels measured in ARTS relative to measurements reported for most other U.S. cities. While reasonably good agreements in acrolein levels were found in 13 of 16 duplicate canister pairs, very poor agreements were found in the other three (Figure 5-2). Additionally, positive biases in acrolein measurements by TO-15 have been reported elsewhere (Heaton, 2006). The acrolein levels measured in ARTS are reported as valid but are held with some skepticism until they can be verified by follow up measurements and additional quality assurance. CAPCOG, TCEQ, and EPA plan to conduct additional acrolein measurements and data quality assessments in summer 2007.

**Table 5-3
Summary of ARTS Measurement Precision for TO-15 Compounds**

Compound Name	Precision (Relative Percent Difference)
1,1,1-Trichloroethane	17%
1,2,4-Trimethylbenzene	28%
1,3,5-Trimethylbenzene	31%
1,3-Butadiene	13%
Acetonitrile	170%
Acetylene	16%
Acrolein	49%
Benzene	16%
Bromomethane	13%
Carbon Tetrachloride	6%
Chlorobenzene	8%
Chloroethane	34%
Chloroform	7%
Chloromethane	7%
Dichlorodifluoromethane	5%
Dichloromethane	24%
Dichlorotetrafluoroethane	4%
Ethylbenzene	19%
Hexachloro-1,3-butadiene	11%
m,p-Xylene	17%
Methyl Ethyl Ketone	34%
Methyl Isobutyl Ketone	33%
n-Octane	18%
o-Xylene	15%
p-Dichlorobenzene	39%
Propylene	17%
Styrene	20%
Tetrachloroethylene	15%
Toluene	16%
Trichloroethylene	4%
Trichlorofluoromethane	5%
Trichlorotrifluoroethane	36%
Vinyl Chloride	3%

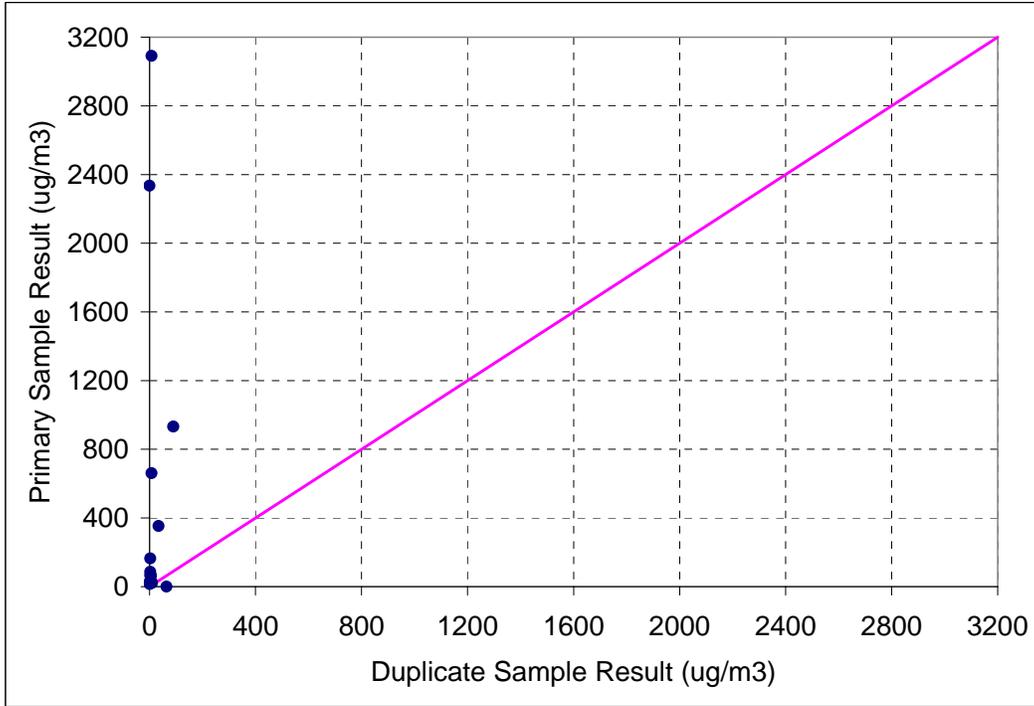


Figure 5-1. Comparison of Primary and Duplicate Sample Results for Acetonitrile

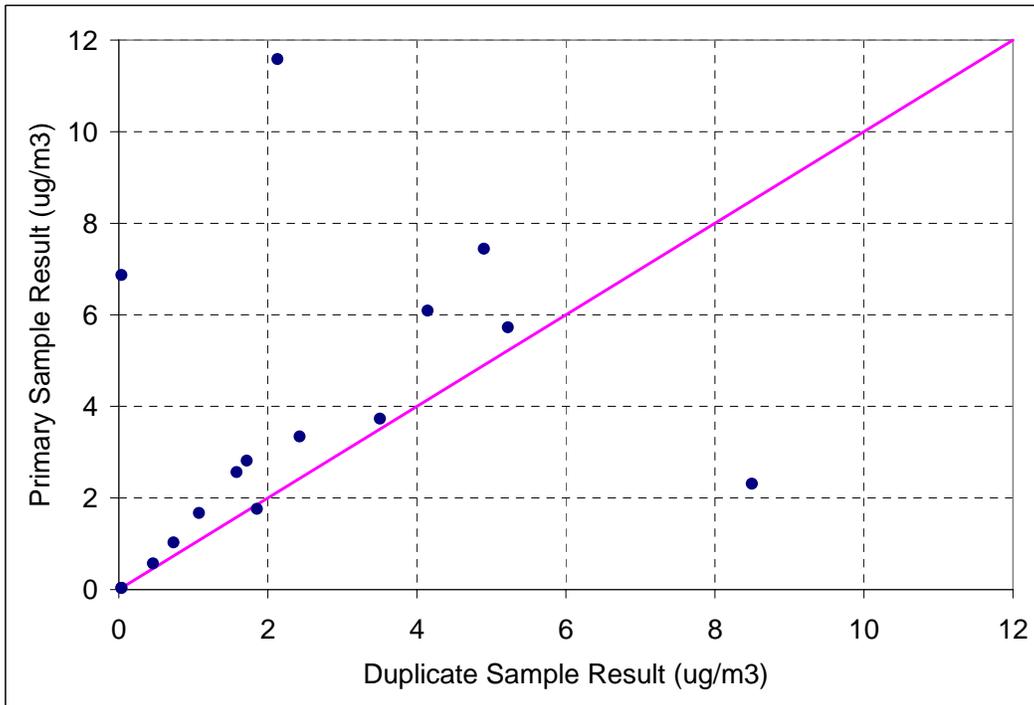


Figure 5-2. Comparison of Primary and Duplicate Sample Results for Acrolein

5.3.2 Styrene, Ethyl benzene, and Methyl Isobutyl Ketone Data Quality

Source apportionment using EPA PMF found an unidentifiable source factor that accounted for greater than 50% of the styrene, ethyl benzene, and methyl isobutyl ketone measured in ARTS. The unidentifiable source factor also accounted for 10-20% of the trimethylbenzene, xylene, methyl ethyl ketone, propylene, and trichlorotrifluoroethane. The signal from this source factor was strongest in June 2005 and decayed rapidly over time through October 2005 (see, for example, Figures 5-3 and 5-4). Many of the compounds detected in this source factor are common solvents; however, no specific source of these chemical appears to account for its presence at every ARTS site or its observed temporal trend. Therefore, data collected for these compounds, particularly from June-October 2005 appear questionable. Benzene was also detected in this source factor but only 7% of the benzene measured in ARTS, averaged over all the sites was attributed to it. At Webberville Road, where the benzene levels were highest, only 2% of the observed benzene was attributed to the unidentified source factor.

5.3.3 Acrylonitrile Data Quality

Acrylonitrile was detected in only four canister samples but because of its relatively high upper-bound risk estimate acrylonitrile accounts for 5% of the estimated total excess cancer risk, averaged for all ARTS sites, even when zeros are substituted for the non-detects. For Webberville Road, where three of the four detected concentrations were found, acrylonitrile accounts for 15% of the total excess cancer risk, even when zeros are substituted for the non-detects. All the detected concentrations for acrylonitrile were measured in samples collected during June 2006. No obvious reason exists to disqualify these measurement results; however, it is noteworthy that had sampling ended on June 10, 2006 as originally planned, instead of on June 28, 2006, the acrylonitrile contributions to the estimated risk (substituting zero $\mu\text{g}/\text{m}^3$ for non-detects) would have been essentially zero percent (see Table 5-4 and Figures 5-5 and 5-6). The total excess risk estimate for Webberville Road, in this case, would have been 52 per million instead of the reported 61 per million.

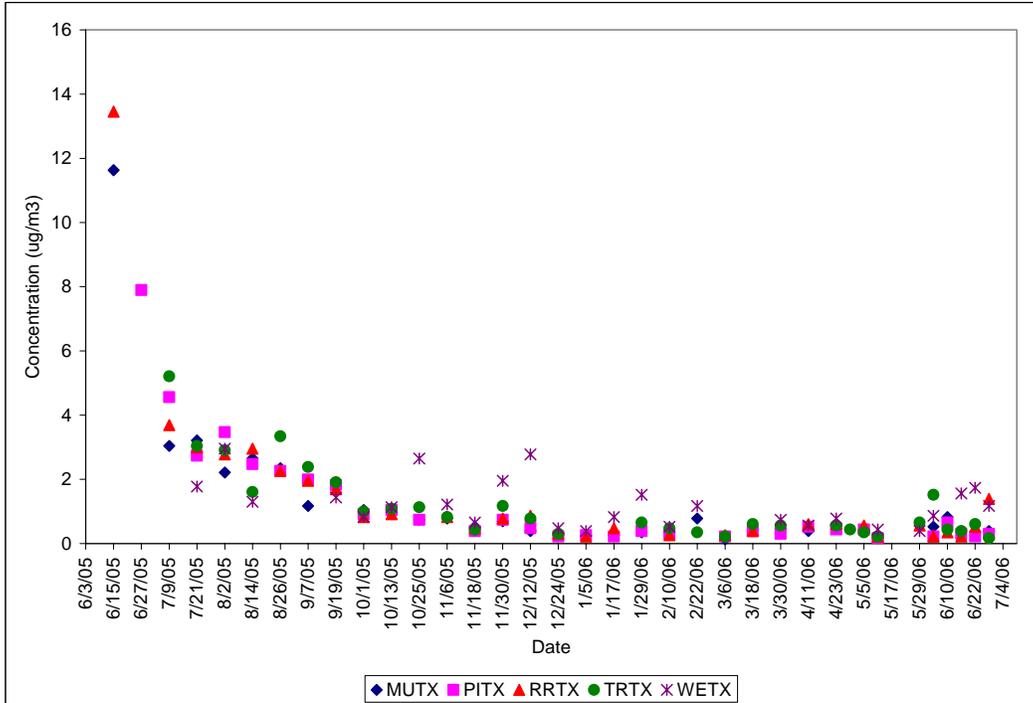


Figure 5-3. Time Series of Measured Ethyl Benzene Showing Decreasing Trend During June-October 2005

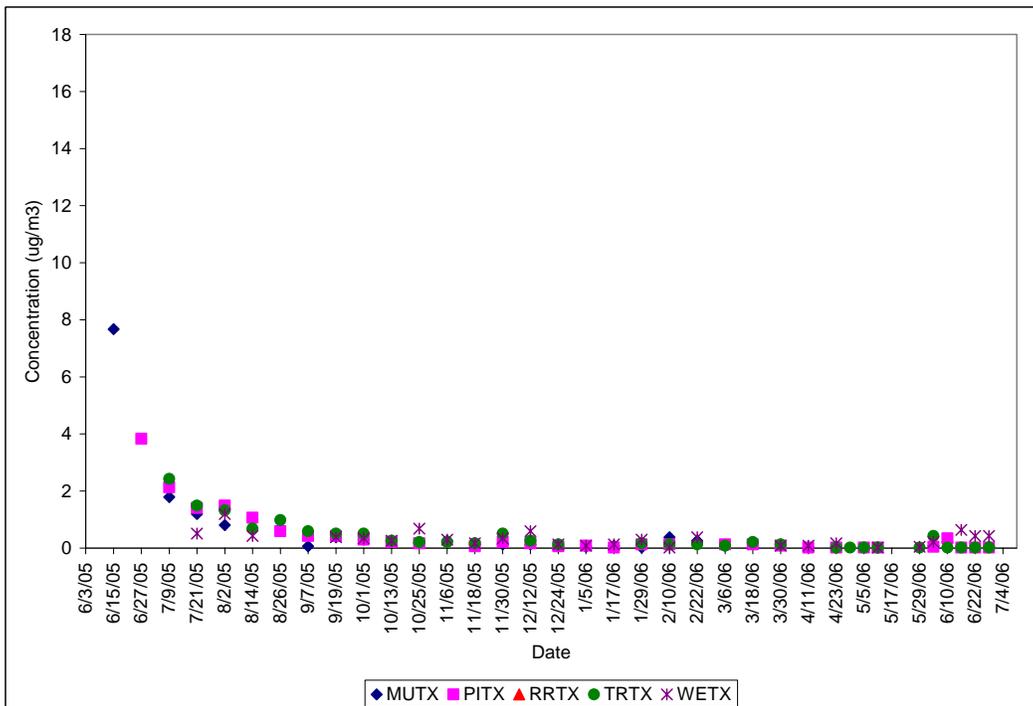


Figure 5-4. Time Series of Measured Styrene Showing Decreasing Trend During June-October 2005



Table 5-4

1999 Emissions and Excess Risk Estimates Based on Alternate Approaches for Treating Non-Detected Values for Samples Collected Through June 10, 2006

Chemical Name	% of Values > DL	1999 Emissions for Travis and Williamson Counties (Pounds) ^a	Average Excess Risk (per Million) Using ½ DL for Non-Detects	Average Excess Risk (per Million) Using zero µg/m³ for Non-Detects
1,2-Dibromoethane	<1	0.15	23.3	0.7
Hexachloro-1,3-butadiene	2	0.355	19.5	0.7
Carbon Tetrachloride	99	540	9.7	9.8
Benzene	100	2,020,140	9.0	8.0
1,1,2,2-Tetrachloroethane	<1	0.615	5.9	0.2
1,3-Butadiene	60	252,680	4.2	4.2
Acrylonitrile	<1	180	4.1	0.3
Acetaldehyde	100	443,620	3.2	3.2
Arsenic	100	25.7	3.0	3.0
p-Dichlorobenzene	62	74,840	2.9	2.9
Chloromethylbenzene	1	3.75	2.8	0.1
Chloroform	20	75,880	2.6	2.1
1,2-Dichloropropane	0	7.41	1.6	0.0
1,2-Dichloroethane	2	1,120	1.5	0.1
Tetrachloroethylene	40	243,380	1.1	1.0

^a 1999 Emissions data downloaded from <http://www.epa.gov/air/data/reports.html>

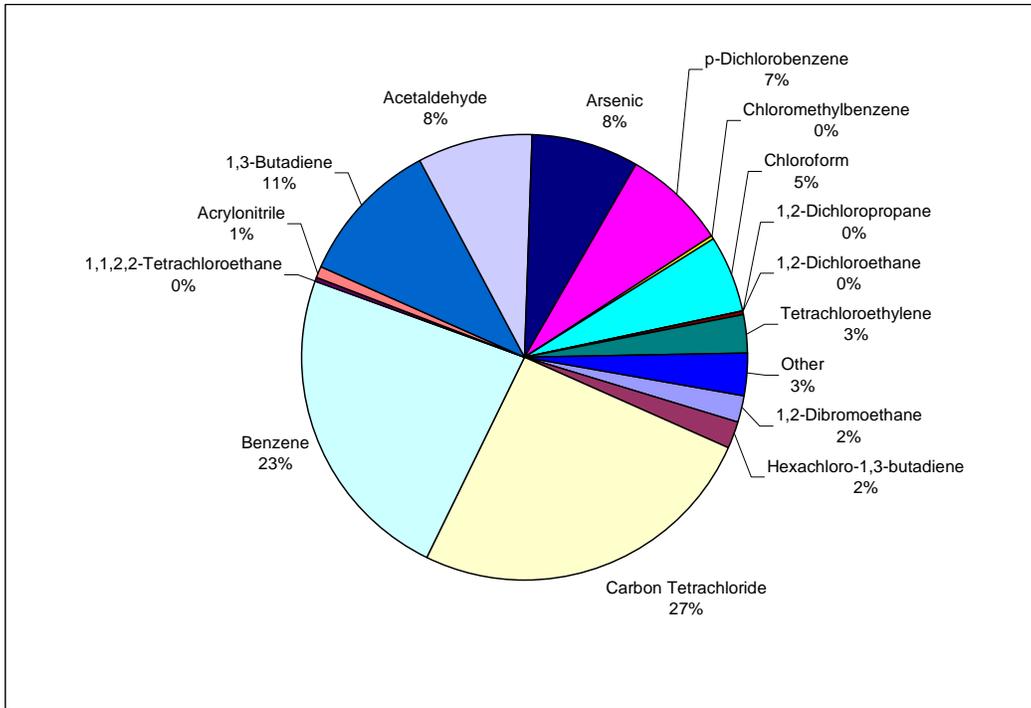


Figure 5-5. Percentages of Estimated Excess Cancer Risks Attributed to ARTS Target Compounds through June 10, 2006, Using Zero $\mu\text{g}/\text{m}^3$ for Non-Detects (Averaged for All ARTS Sites)

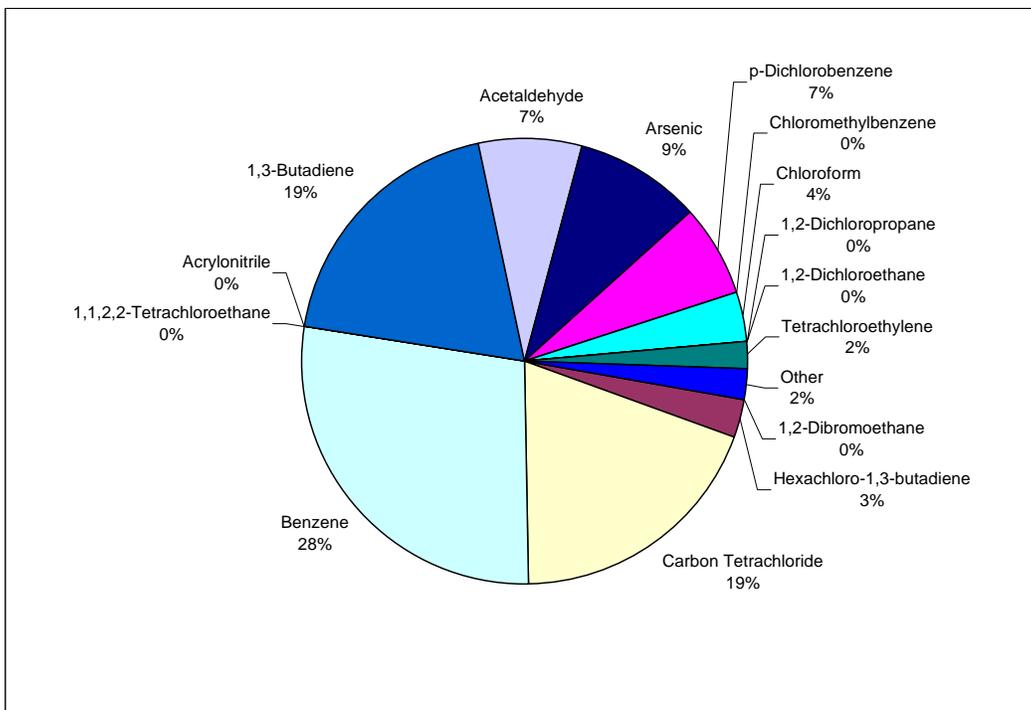


Figure 5-6. Percentages of Estimated Excess Cancer Risks Attributed to ARTS Target Compounds through June 10, 2006 at Webberville Rd. Using Zero $\mu\text{g}/\text{m}^3$ for Non-Detects



6.0 Summary and Conclusions

With one exception, the levels of the 19 core air toxics averaged over all ARTS monitoring sites were comparable to or less than the average levels in most other U.S. cities where similar measurements have been made. Acrolein is the one core compound that was found at significantly higher concentrations in ARTS compared with most other U.S. cities. Acrolein was found to have the greatest potential for producing non-cancer health effects of all ARTS target compounds and it is also the most significant non-cancer air toxics risk driver on a national scale, according to the EPA 1999 National Air Toxics Assessment (EPA, 2006). Acrolein is emitted by motor vehicles, electricity generating units, wildfires, and other combustion processes including smoking cigarettes; however, no known sources account for the differences between the ARTS data and measurements collected elsewhere. Acrolein is also produced in the atmosphere from chemical reactions and some suspect it can be produced inside the sampling vessels used for its measurement, perhaps rendering the measurements unreliable (Heaton, 2006). CAPCOG, TCEQ, and EPA are planning additional measurements and data quality assessments in summer 2007 to address the reliability of the ARTS acrolein results.

The greatest risks of contracting cancer from inhalation exposure to measured HAPs in the Austin-Round Rock area come from carbon tetrachloride and benzene. Carbon tetrachloride exists primarily as a background air pollutant resulting from prior widespread uses including in fire extinguishers, as a propellant for aerosol spray cans, as a cleaning fluid, and in the production of Freon refrigerants. Carbon tetrachloride production and use for consumer products has been phased out over concern for its toxicity and harm to the earth's ozone layer but it remains a background constituent of outdoor air because of its long half-life of 30-100 years (Argonne National Laboratory, 2005). The average levels of carbon tetrachloride measured in ARTS varied by less than 10% from the lowest to highest site and were within $\pm 10\%$ of the 2005 national median at all ARTS sites.

Benzene is a constituent of motor vehicle emissions and is also found in emissions from burning coal and oil, evaporative emissions from gasoline refueling, and in industrial solvents. About half the benzene measured in ARTS appears to come from motor vehicles. The average benzene levels were within $\pm 13\%$ of the 2005 national median at four ARTS sites but were almost twice the national median at Webberville Road where the highest levels of other motor vehicle emissions constituents were also measured. After carbon tetrachloride and benzene, the next greatest risks of contracting cancer from inhalation exposure to HAPs come from 1,3-butadiene and acetaldehyde, which along with benzene are classified by EPA as priority mobile source air toxics.

The ARTS measurement results agreed remarkably well with results of the 1999 National Air Toxics Assessment (NATA), based on its identification of key air pollutants, estimations of air toxics levels, and estimations of total risks due to inhalation exposure to toxic air pollutants. The NATA modeled estimate of total cancer risk for Travis County, 41 in a million, is equal to the total excess cancer risk estimated from ARTS measurement data. The NATA estimate for Williamson County, 28 in a million, differs by less than 20 percent from the 34 in a million estimated from the ARTS monitoring data collected in Round Rock. To place these risk estimates in perspective, note that one out of every three Americans (330,000 in one million) will contract cancer during a lifetime, when all causes are taken into account (EPA, 2006).



7.0 References

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Appendix A
ARTS Average Concentrations and Detection Limits



**Table A-1
Average Concentrations and Detection Limits for TO-11A Compounds**

Compound Name	Average Concentration ($\mu\text{g}/\text{m}^3$)					Average DL ($\mu\text{g}/\text{m}^3$)	# values > DL
	MUTX	PITX	RRTX	TRTX	WETX		
2,5-Dimethylbenzaldehyde	0.00	0.00	0.00	0.00	0.01	0.008	1
Acetaldehyde	1.34	1.33	1.38	1.40	1.62	0.013	152
Acetone	1.22	1.31	1.39	1.22	1.68	0.014	152
Benzaldehyde	0.13	0.13	0.11	0.13	0.17	0.009	151
Butyraldehyde	0.20	0.20	0.22	0.20	0.24	0.008	151
Crotonaldehyde	0.26	0.29	0.29	0.27	0.29	0.006	148
Formaldehyde	2.78	2.85	3.26	2.98	2.72	0.011	152
Hexaldehyde	0.15	0.14	0.14	0.13	0.17	0.006	151
Isovaleraldehyde	0.02	0.02	0.02	0.02	0.02	0.007	77
Propionaldehyde	0.30	0.28	0.29	0.29	0.30	0.007	151
Tolualdehydes	0.15	0.15	0.18	0.16	0.19	0.013	150
Valeraldehyde	0.09	0.09	0.10	0.09	0.11	0.007	150

**Table A-2
Average Concentrations and Detection Limits for PM10 Compounds and Cr⁶⁺**

Compound Name	Average Concentration ($\mu\text{g}/\text{m}^3$)					Average DL ($\mu\text{g}/\text{m}^3$)	# values > DL
	MUTX	PITX	RRTX	TRTX	WETX		
Antimony	6.7E-04	8.5E-04	5.9E-04	1.3E-03	9.9E-04	3.2E-05	158
Arsenic	4.8E-04	4.5E-04	5.1E-04	9.9E-04	1.1E-03	2.2E-05	158
Beryllium	1.4E-05	1.4E-05	1.4E-05	1.4E-05	1.3E-05	2.8E-05	4
Cadmium	9.1E-05	1.0E-04	1.0E-04	3.7E-04	1.4E-04	2.0E-05	158
Chromium	2.8E-04	5.2E-04	4.3E-04	4.8E-04	5.4E-04	3.8E-04	158
Cobalt	8.6E-05	9.3E-05	9.4E-05	1.0E-04	1.3E-04	2.7E-05	158
Lead	1.7E-03	1.9E-03	2.4E-03	2.6E-03	3.0E-03	8.3E-04	141
Manganese	4.9E-03	5.9E-03	5.8E-03	5.3E-03	7.0E-03	1.7E-04	158
Mercury	8.6E-05	8.6E-05	8.5E-05	1.1E-04	1.2E-04	2.1E-04	5
Nickel	5.7E-04	6.6E-04	7.4E-04	8.3E-04	8.0E-04	2.1E-04	158
Selenium	6.8E-04	6.8E-04	6.6E-04	7.0E-04	6.7E-04	2.5E-05	158
Hexavalent Chromium	--	--	--	--	2.3E-05	1.2E-05	16



**Table A-3
Average Concentrations and Detection Limits for TO-15 Compounds**

Compound Name	Average Concentration ($\mu\text{g}/\text{m}^3$)					Average DL ($\mu\text{g}/\text{m}^3$)	# values > DL
	MUTX	PITX	RRTX	TRTX	WETX		
1,1,1-Trichloroethane	0.12	0.12	0.13	0.13	0.13	0.044	99
1,1,2,2-Tetrachloroethane	0.10	0.10	0.10	0.10	0.09	0.145	1
1,1,2-Trichloroethane	0.06	0.05	0.06	0.06	0.05	0.056	1
1,1-Dichloroethane	0.03	0.03	0.03	0.04	0.03	0.041	1
1,1-Dichloroethene	0.06	0.06	0.06	0.06	0.05	0.087	1
1,2,4-Trichlorobenzene	0.31	0.31	0.31	0.29	0.28	0.390	0
1,2,4-Trimethylbenzene	0.45	0.45	0.54	0.66	1.59	0.099	138
1,2-Dibromoethane	0.10	0.10	0.10	0.11	0.10	0.166	1
1,2-Dichloroethane	0.06	0.05	0.05	0.06	0.05	0.079	3
1,2-Dichloropropane	0.08	0.08	0.09	0.08	0.08	0.148	0
1,3,5-Trimethylbenzene	0.14	0.14	0.16	0.20	0.47	0.058	112
1,3-Butadiene	0.07	0.07	0.07	0.14	0.33	0.042	93
Acetylene	0.81	0.76	1.00	0.95	1.88	0.030	149
Acrolein	3.73	2.51	4.60	2.58	3.77	0.192	119
Acrylonitrile	0.07	0.06	0.06	0.06	0.18	0.113	4
Benzene	0.94	0.80	0.98	1.11	1.88	0.030	149
Bromochloromethane	0.08	0.07	0.08	0.07	0.07	0.102	0
Bromodichloromethane	0.07	0.07	0.07	0.07	0.06	0.093	1
Bromoform	0.12	0.12	0.13	0.12	0.11	0.185	0
Bromomethane	0.07	0.07	0.07	0.08	0.07	0.085	17
Carbon Tetrachloride	0.33	0.08	0.14	0.12	0.67	0.115	147
Chlorobenzene	0.63	0.68	0.66	0.68	0.03	0.044	3
Chloroethane	0.04	0.03	0.04	0.04	0.06	0.054	42
Chloroform	0.06	0.05	0.06	0.06	0.09	0.058	28
Chloromethane	0.07	0.11	0.18	0.09	1.40	0.058	149
Chloromethylbenzene	1.24	1.31	1.32	1.38	0.05	0.065	2
Chloroprene	0.06	0.05	0.05	0.06	0.05	0.088	1
cis-1,2-Dichloroethylene	0.05	0.05	0.05	0.06	0.05	0.068	1
cis-1,3-Dichloropropene	0.05	0.05	0.05	0.04	0.04	0.072	1
Dibromochloromethane	0.05	0.05	0.05	0.05	0.08	0.111	1
Dichlorodifluoromethane	0.09	0.09	0.09	0.10	2.92	0.032	149
Dichloromethane	2.67	2.74	2.75	2.82	0.71	0.170	127
Dichlorotetrafluoroethane	0.55	0.56	0.82	0.53	0.13	0.036	128
Ethyl Acrylate	0.11	0.12	0.12	0.13	0.06	0.093	0

