National Air Toxics Trends Study
Grand Junction, Colorado

January through December 2012

Colorado Department
of Public Health
and Environment

Prepared by the Air Pollution Control Division
Technical Services Program
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I. EXECUTIVE SUMMARY

The Grand Junction air toxics monitors were originally established as a part of the 2001/2002 Pilot Study for the National Air Toxics Trends Sites (NATTS). The network was created by the Environmental Protection Agency (EPA) in an effort to gather data that were suitable for identifying trends in air toxics concentration levels. Grand Junction was one of the five "rural" sites selected for the study initially. Since that time, and as the population of the Grand Junction area has grown, the EPA has reconsidered, and decided that the site is more indicative of urban concentrations, and has changed the designation of the site from rural to urban.

Most of the compounds detected at Grand Junction in 2012 are found in urban air nationwide. There do not appear to be any compounds of local significance. The majority of compounds can be related to motor vehicle sources. These include formaldehyde, benzene, toluene, ethylbenzene, xylenes, and styrene. Chloroflourocarbons are also present, including chloromethane, dichlorodifluoromethane, trichlorofluoromethane, and trichlorotrifluoroethane. Polycyclic aromatic hydrocarbon compounds naphthalene, phenanthrene and acenaphthene are frequently detected.

This report has two appendices. Appendix A, "Documentation for Grand Junction Urban Air Toxics Trends Monitoring Locations – Site Maps and Photographs" provides information concerning the two air monitoring sites discussed in this report. Appendix B, "Air Toxics Summary: Compounds Contributing to Cancer and Non-cancer Risks – Overview of Sources and Health Effects," provides a brief summary of many of the compounds monitored. That document discusses the chemical formula, sources, and uses of each compound. It also profiles potential health effects, such as carcinogenicity, the compound's potential to cause birth defects, and whether it damages target organs in the body.

II. INTRODUCTION

Background

The NATTS Network collects ambient air toxics monitoring data as a part of the Urban Air Toxic Strategy (UATS). Under Section 112 of the Clean Air Act (CAA), the EPA established a list of 188 toxic air pollutants, also known as hazardous air pollutants (HAPs). These are pollutants that are known, or suspected, to cause cancer, or other major health issues. People who are exposed to these HAPs at sufficient concentration levels may have an increased chance of getting cancer, damaging their immune system, etc. Most air toxics originate from mobile sources, like cars, trucks, or buses, as well as stationary sources, such as factories, refineries, and power plants. Some air toxics also come from indoor sources as well, like cleaning solvents, and building materials.

Since it is not practical, or possible, to monitor for each of the 188 compounds, the EPA developed a subset of HAPs that have the greatest impact on the public, as well as the environment, in urban areas. For the purposes of the NATTS Study, the list of 188 HAPs was pared down to a subset of 62 HAPs, 33 of which are on the "Urban HAP List."[1] The remaining 29 compounds were chosen because they have risk factors that were developed by the EPA. From the list of 62 compounds, a "core" list of 19 toxic air pollutants that must be monitored at all times was created. These compounds are considered to be "priority compounds" because they are major health risk drivers, based on a relative ranking performed by the EPA.[2] They are referred to as the "Method Quality Objective (MQO) Core Analytes."[3] These compounds can be seen in Table 1.

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[1] Technical Assistance Document for the National Air Toxics Trends Stations Program." US Environmental Protection Agency. April 1, 2009. http://www.epa.gov/ttnamti1/files/ambient/airtox/nattsTADRevision2_508Compliant.pdf

[2] *Ibid.*

[3] *Ibid.*

Table 1. NATTS HAPs with Mandatory Monitoring Requirements

VOCs	Carbonyls	PAHs	PM_{10} Metals	TSP Metals
1,3-Butadiene	Acetaldehyde	Benzo(a)pyrene	Arsenic	Hexavalent Chromium
Acrolein	Formaldehyde	Naphthalene	Beryllium	
Benzene			Cadmium	
Carbon Tetrachloride			Lead	
Chloroform			Manganese	
Tetrachloroethylene			Nickel	
Trichloroethylene				
Vinyl Chloride				

The Grand Junction air toxics monitoring site was established in 2004. This site will measure air toxics for at least six years, to determine the success of the National Air Toxics Strategy in reducing the U.S. population exposure to cancer-causing substances in the air. The main test will be a comparison of mean concentrations of compounds for the first three years (2004-2006), versus the mean concentrations for successive three-year periods (2007-2009, 2010-2012, etc.), starting from 2004 and continuing to the present. Data collected beyond the initial six year study scope will be used for trending analyses.

This report presents data from January 2012 through December 2012. It is separated into sections covering the various compounds of interest. Sections 3, 4, 5, 6, and 7 discuss the compounds monitored as a part of this study. Sections 8, 9 and 10 compare the PM_{10}, $PM_{2.5}$, and meteorological data collected as a part of the regular monitoring conducted in Grand Junction by the Colorado Department of Public Health and Environment (CDPHE) to the national ambient air quality standards (NAAQS). Each section begins with summary statistics for the compounds analyzed and then the percentage of samples in which each chemical was detected. Summary graphs of certain compounds are presented.

Site Information

The NATTS Study at Grand Junction collects samples at two separate locations. These two sites (Powell and Pitkin sites) are in close proximity to one another. The Powell site is located on top of the Powell Building (approximately three stories in height) at 650 South Avenue, and the Pitkin site is located approximately 50 meters to the NNW of the Powell Building, on the roof of a small shelter, near ground level, at 645-1/4 Pitkin Avenue. The hexavalent chromium and particulate/metals samplers are located on the Powell Building, and the carbon monoxide analyzer, air toxics samplers (VOC/carbonyl/PAH), and meteorological tower are located at the Pitkin site. Due to the different sampling heights, staff at Region VIII of the EPA suggested the sites be separately catalogued in the national air monitoring database [AQS IDs: 080770017 (Powell), and 080770018 (Pitkin)]. Documentation regarding these sites, including maps, photographs, and aerial views, is available as Appendix B in this document. The sites are located on the southern end of the downtown area, in an area of commercial/light industrial land use.

III. CARBONYLS

Summary Statistics

The carbonyls discussed in this section are the group of organic chemicals that contain a carbon atom double bonded to an oxygen atom. The generalized symbol for the carbonyl group is R-C=O, where the “R” is some other carbon compound. Thirteen compounds were measured for this study in 2012. A listing of these compounds, as well as a summary of the collected data, is shown in Table 3 and Table 2. Of the thirteen carbonyl compounds analyzed for, two are included on the mandatory monitoring list of 19 core HAPs. They are bolded in Table 2. New to the carbonyl testing list in 2012 is 2-butanone. It has previously been analyzed for via the volatile organic compound (VOC) tests. It was moved to the carbonyl testing list because that method provides better results at lower levels for this compound. The previous years’ values from the VOC analytical method are indicated with an asterisk.

Table 2. Carbonyl Sample Summary - 2012

Compound	CAS Number	# of ND's	% ND
2-Butanone	78-93-3	0	0%
Acetaldehyde	**75-07-0**	**0**	**0%**
Acetone	67-64-1	0	0%
Benzaldehyde	100-52-7	0	0%
Butyraldehyde	123-72-8	0	0%
Crotonaldehyde	123-73-9	0	0%
Formaldehyde	**50-00-0**	**0**	**0%**
Propionaldehyde	123-38-6	0	0%
Hexaldehyde	66-25-1	2	3%
Valeraldehyde	110-62-3	5	8%
Tolualdehydes	NA	7	11%
2,5-Dimethylbenzaldehyde	5779-94-2	61	100%
Isovaleraldehyde	590-86-3	61	100%

ND = Not Detected

Bold = MQO Core Analyte

Table 3. Carbonyl Average Concentration Comparison 2004-2012

	Annual Averages (μg/m^3)								
Analyte	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**
2,5-Dimethylbenzaldehyde	*0.08*	*0.06*	*0.02*	*0.03*	*0.03*	*0.00*	*0.01*	*0.01*	*0.01*
2-Butanone	2.56*	0.43*	1.23*	0.99*	0.98*	1.03*	1.46*	1.08*	0.54
Acetaldehyde	**10.53**	**5.39**	**4.25**	**5.03**	**4.48**	**2.89**	**1.95**	**2.43**	**2.85**
Acetone	18.39	11.08	9.69	12.45	12.35	5.57	5.13	4.92	5.46
Benzaldehyde	1.11	0.95	1.45	1.41	1.30	0.34	0.31	0.41	0.39
Butyraldehyde	0.91	1.18	1.00	1.06	0.92	0.35	0.34	0.39	0.33
Crotonaldehyde	0.67	0.62	0.50	0.57	0.55	0.22	0.20	0.16	0.16
Formaldehyde	**3.45**	**3.83**	**4.94**	**4.94**	**5.04**	**4.01**	**2.74**	**2.74**	**2.98**
Hexaldehyde	0.56	0.43	0.46	0.43	0.52	0.12	0.13	0.10	0.11
Isovaleraldehyde	*0.04*	*0.07*	*0.15*	*0.08*	*0.08*	*0.01*	*0.01*	*0.00*	*0.01*
Propionaldehyde	0.39	0.75	0.74	0.73	0.91	0.39	0.35	0.35	0.34
Tolualdehydes	0.61	0.63	1.11	0.98	0.77	0.18	0.19	0.19	0.18
Valeraldehyde	0.18	0.71	0.59	0.06	0.52	0.15	0.11	0.08	0.09

Bold = MQO Core Analyte

Italic = less than 90% detection rate

* = Results obtained by different analytical method

Carbonyl compounds were sampled on an every-sixth-day basis for the year, for a total of 61 samples attempted. There were no missed samples. The data recovery rate of 100% exceeds the EPA goal for over 85% sample recovery.

The annual mean concentrations for each carbonyl compound, from 2004 through 2012, are listed in Table 3. The annual means were calculated by replacing all "non-detect" values with one-half of the sample minimum detection limit. This is an accepted conservative technique for calculating annual values when some of the samples were less than the laboratory's ability to detect. The most prevalent carbonyls in the ambient air in Grand Junction are formaldehyde, acetone, and acetaldehyde. The other nine compounds measured in this study occurred at concentration levels significantly below those of the top three compounds. Since 2004, the annual average concentrations for many of the carbonyl compounds have dropped.

All of the carbonyls, except for isovaleraldehyde and 2,5-dimethylbenzaldehyde were present in over 85% of the samples. Isovaleraldehyde has not been detected since 2010. Note that the true annual mean of 2,5-dimethylbenzaldehyde may be well below the number reported in the table due to the fact that this compound was never detected, and one-half of the detection limit was used for the estimated concentration of the non-detects. Actual concentrations could have been at lower levels than these estimates. During the pilot phase of this study in 2001-2002, 2,5-dimethylbenzaldehyde was detected 34 percent of the time. That number dropped to 4.8 percent in 2005, and the compound has not been detected since 2006.

Graphs

The summary data for carbonyl compounds measured during 2012 are graphed in Figure 1. The compounds in these graphs are ordered by ranking their average concentrations. The graphs show that acetaldehyde, acetone, and formaldehyde had the highest maxima. The maximums observed in 2012 were similar to those in 2011. In comparison, the national average concentrations for acetaldehyde, and formaldehyde, at all NATTS stations, from 2003 through 2010, were 1.78, and 2.98 micrograms per meter cubed, respectively.[4] The formaldehyde and acetaldehyde values in Grand Junction were similar to the national averages across the NATTS network. The data obtained from the 2011 National Monitoring Programs (NMP) report indicates that the annual mean concentrations observed for acetone, acetaldehyde, and formaldehyde were 2.57, 2.00, and 2.86 micrograms per meter cubed, respectively.[5]

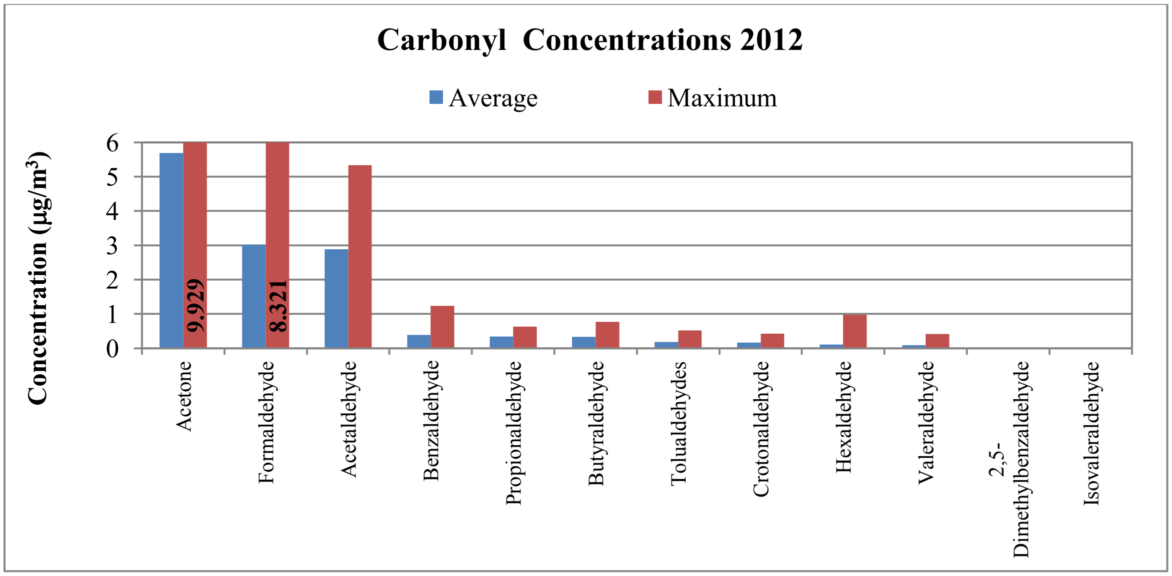

Figure 1. Annual Mean and Maximum Carbonyl Concentrations for 2012

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[4] "National Air Toxics Trends Stations (NATTS) Network Assessment. Revised Draft." US EPA. September 2012.

[5] "2011 National Monitoring Programs Annual Report (UATMP, NATTS, CSATAM). US EPA. August 2013. http://www.epa.gov/ttnamti1/files/ambient/airtox/2011nmpreport.pdf.

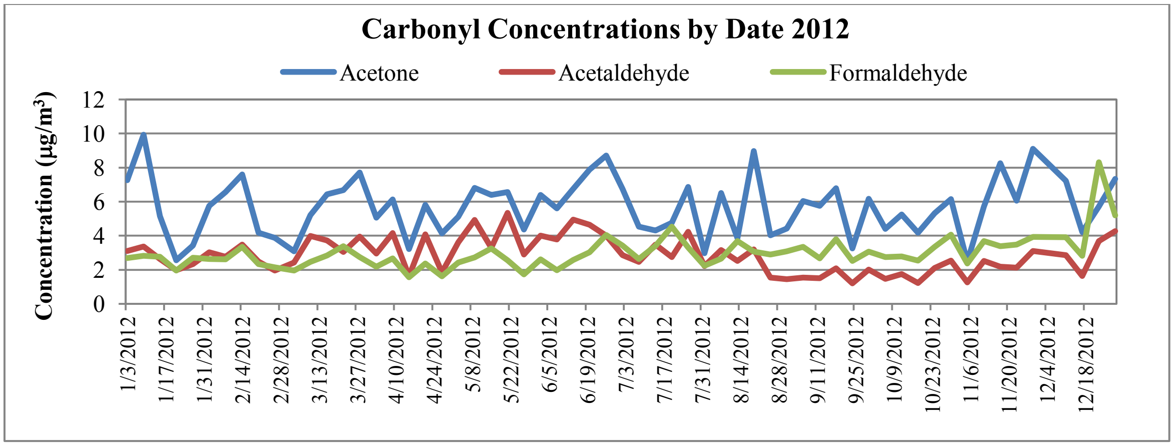

Figure 2. **Carbonyl Sample Day Comparisons for 2012**

Figure 2 shows the concentrations for select carbonyl compounds during the year. The compounds did not show much seasonal variation. This was also the case in 2011 as well. This is interesting, because it is generally believed that more formaldehyde is formed photochemically during the summer period of higher solar radiation. Formaldehyde plays a role in the formation of ozone, a chemical that usually peaks during the summer.

Figure 3 is a graph of the weekday versus weekend average carbonyl concentrations in 2012. As was expected, the average weekday concentrations were slightly higher than the average weekend concentrations, with a few exceptions. 2,5-dimethylbenzaldehyde, and isovaleraldehyde, have weekday and weekend average concentrations that are equal, because their concentrations are merely half the value of their respective method detection limits (MDLs) for the entire year, since they were non-detectable in all samples. Butyraldehyde, benzaldehyde, hexaldehyde, and valeraldehyde have weekend averages that are slightly higher than their weekday counterparts. Butyraldehyde is used in the manufacture of plasticizers, rubber accelerators, solvents, and high polymers.[6] It has also been found in the essential oils from flowers, fruits, leaves, and the bark of various plants. Hexaldehyde, or hexanal, is used as a food additive, in the organic synthesis of plasticizers, rubber chemicals, dyes, synthetic resins, and insecticides, as well as in perfumery.[7] It is also found naturally in many fruits, vegetables, meats, shellfish, and certain species of trees and plants.[8]

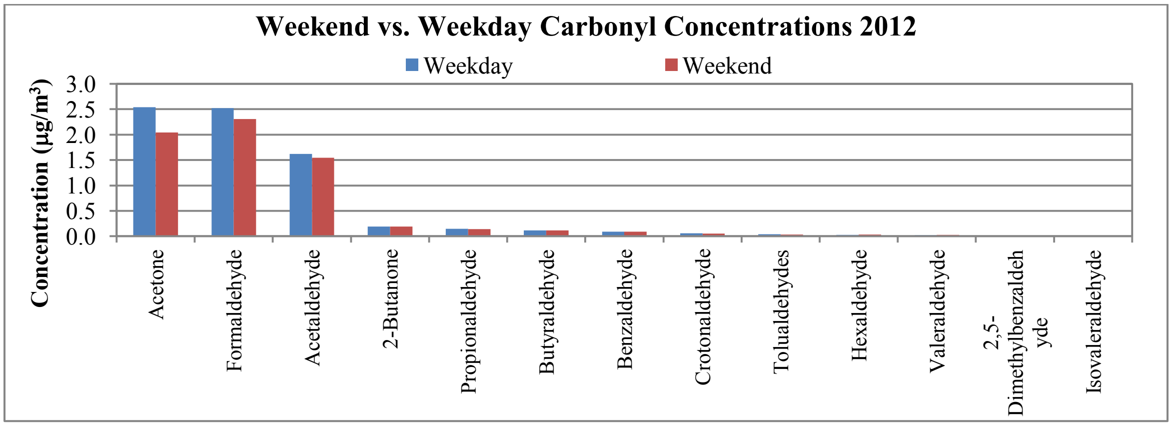

Figure 3. **Weekday vs. Weekend Carbonyl Concentrations - 2012**

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[6] "Butyraldehyde Compound Summary." PubChem Online Database. December 2013. http://pubchem.ncbi.nlm.nih.gov/summary/summary.cgi?cid=261#x351

[7] NCBI, PubChem Compound Database. December 2013. http://pubchem.ncbi.nlm.nih.gov/summary/summary.cgi?cid=6184

[8] *Ibid.*

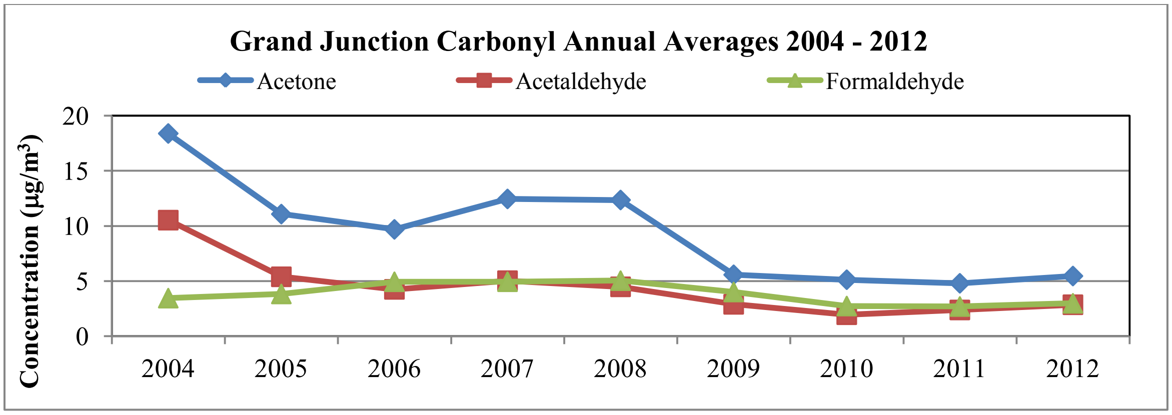

Figure 4. Carbonyl Annual Averages 2004 – 2012

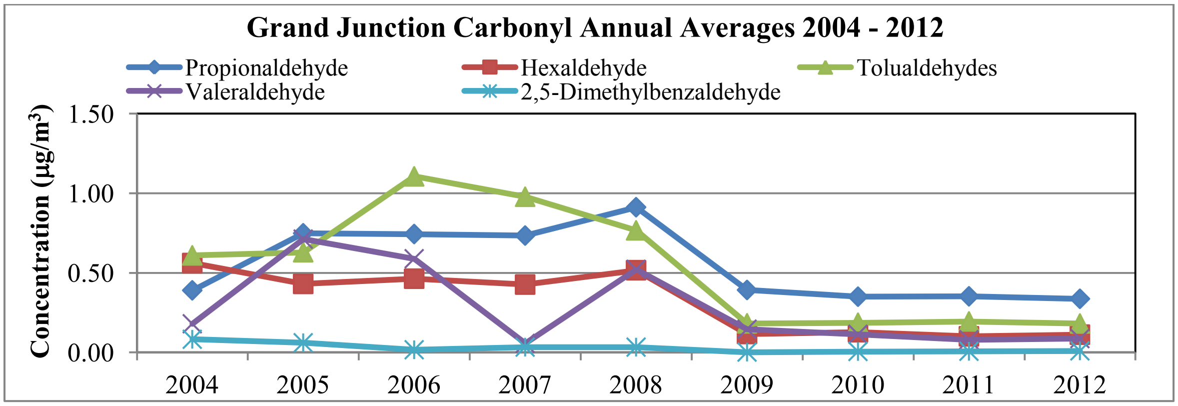

Figure 5. Carbonyl Annual Averages 2004 – 2012, ctd.

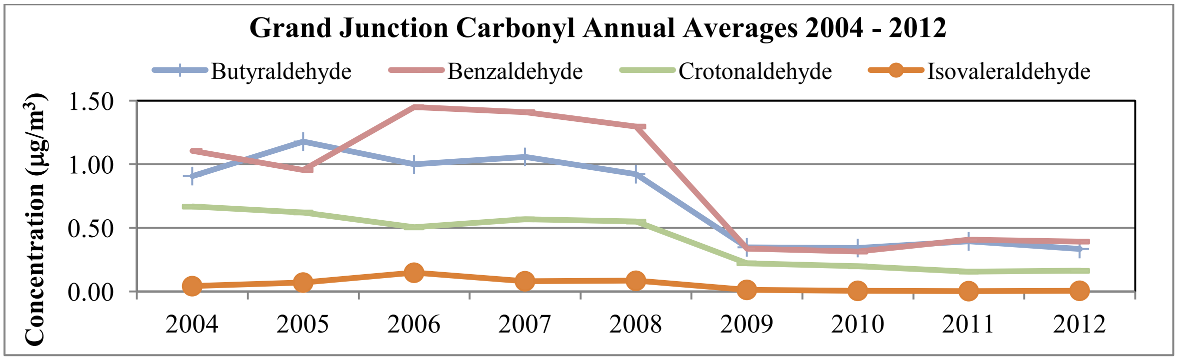

Figure 6. Carbonyl Annual Averages 2004 – 2012, ctd.

Figure 4 through Figure 6 are graphs of the annual average carbonyl concentrations at the Grand Junction site, for 2004 through 2012. The overall trend appears to be that the carbonyl concentrations are decreasing. The NATTS program was initially established to monitor the 3-year average concentrations of air toxics compounds, with the thought that successive 3-year averages would show at least a 15% drop in concentration values. Figure 7 below shows the 3 year average concentrations for acetone, acetaldehyde, and formaldehyde, from 2004 through 2006, 2007 through 2009, and 2010 through 2012. The formaldehyde average increased slightly from the first three-year average to the second, showing a 14% increase between the first two 3-year averages; but, then decreased by 40% from the 2007-2009 to the 2010-2012 average. Propionaldehyde exhibited a similar trend with an increase of 8%, followed by a decrease of 49%. Acetone, and acetaldehyde both showed decreases of 22%, and 38%, respectively, from the 2004-2006 to the 2007-2009 averages, and decreases of 49% and 42% from the 2007-2009 to the 2010-2012 averages. The averages for all other compounds continued to drop, one by as much as 92% of it's previous 3-year average.

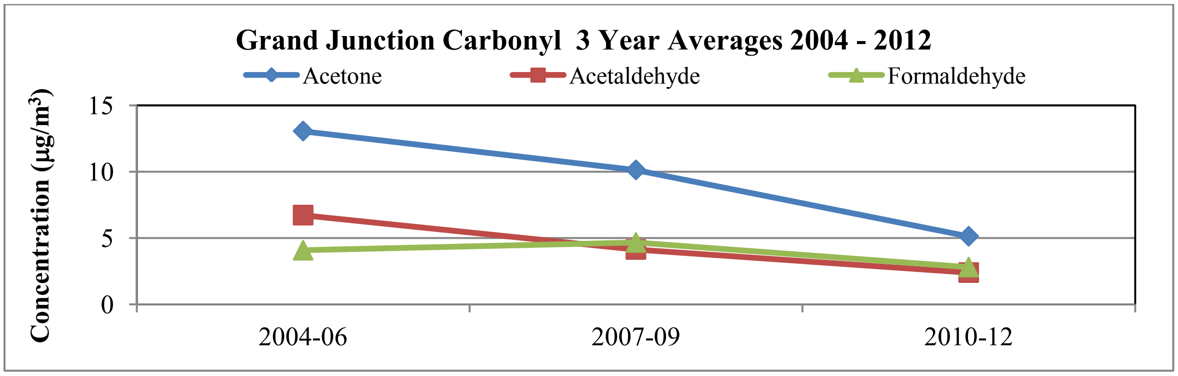

Figure 7. **Carbonyl 3-Year Averages 2004 – 2012**

Quality Assurance/Quality Control

Field Blanks

Field blanks were collected twelve times per year by attaching a blank sample cartridge to the sampler briefly, and then removing it. The purpose of these blanks was to assess contamination that might exist in the cartridge media, sample installation, or shipping. Most cartridges had very small amounts of formaldehyde, acetaldehyde, acetone, and propionaldehyde. Detailed information regarding field blank results is available upon request.

Precision of Sample Results

This project collected precision data in order to assess both sampling and analytical procedures. Six times during the year, a second carbonyl cartridge was sampled simultaneously with the primary sample. These additional samples, or duplicates, were collected to assess the precision (repeatability) of the sampling method. In general, agreement between the two samples was excellent. Detailed information regarding precision results is available upon request.

IV. VOLATILE ORGANIC COMPOUNDS

Summary Statistics

Volatile organic compound (VOC) data collected at the Grand Junction – Powell station from January through December 2012 are presented in this section. There were 60 VOCs analyzed for this study. The list of these VOCs and the number of times each was detected in samples during the study is found in Table 4. Bolded compounds are MQO Core Analytes. These are the same VOCs collected by all of the sites participating in the national air toxics study. VOCs are typically sampled on an every-sixth-day basis, for a total of 61 possible days. During 2012, however, this was not the case. For a short period of time, the Grand Junction site was without a VOC sampler, due to mechanical failure issues. Upon receipt of a different sampler, the site began sampling on an every-third-day basis to attempt to meet a total sample tally of 61 for the year. In all, 62 samples were attempted, with no samples voided, for a 100% sample recovery rate. However, due to the mechanical problems, no samples were collected in August, or for the first half of September.

Table 4. VOC List with 2012 Detection Rates

Compound	CAS Number	# of ND's	% ND
1,2,4-Trimethylbenzene	95-63-6	0	0%
1,3,5-Trimethylbenzene	108-67-8	0	0%
1,3-Butadiene	**106-99-0**	**0**	**0%**
Acetonitrile	75-05-8	0	0%
Acetylene	74-86-2	0	0%
Acrolein	**107-02-8**	**0**	**0%**
Benzene	**71-43-2**	**0**	**0%**
Carbon Disulfide	75-15-0	0	0%
Carbon Tetrachloride	**56-23-5**	**0**	**0%**
Chloromethane	74-87-3	0	0%
Dichlorodifluoromethane	75-71-8	0	0%
Dichloromethane	75-09-2	0	0%
Dichlorotetrafluoroethane	76-14-2	0	0%
Ethylbenzene	100-41-4	0	0%
m,p-Xylene	100-01-6	0	0%
n-Octane	111-65-9	0	0%
o-Xylene	95-47-6	0	0%
Propylene	115-07-1	0	0%
Styrene	100-42-5	0	0%
Tetrachloroethylene	**127-18-4**	**0**	**0%**
Toluene	108-88-3	0	0%
Trichlorofluoromethane	75-69-4	0	0%
Trichlorotrifluoroethane	76-13-1	0	0%
Methyl Isobutyl Ketone	108-10-1	1	2%
Bromomethane	74-83-9	5	8%
1,2-Dichloroethane	107-06-2	6	10%
1,1,1-Trichloroethane	71-55-6	7	11%
1,1,1-Trichloroethane	71-55-6	7	11%
p-Dichlorobenzene	106-46-7	9	15%
Chloroform	**67-66-3**	**17**	**27%**
Trichloroethylene	**79-01-6**	**39**	**63%**
Dibromochloromethane	124-48-1	40	65%
Methyl Methacrylate	80-62-6	45	73%
m-Dichlorobenzene	541-73-1	52	84%
o-Dichlorobenzene	95-50-1	52	84%
Hexachloro-1,3-butadiene	87-68-3	53	85%
Acrylonitrile	107-13-1	55	89%
Bromoform	75-25-2	55	89%
1,1,2,2-Tetrachloroethane	79-34-5	56	90%
1,1,2,2-Tetrachloroethane	79-34-5	56	90%
1,2-Dibromoethane	106-93-4	57	92%
1,2,4-Trichlorobenzene	120-82-1	58	94%

Compound	CAS Number	# of ND's	% ND
Ethyl tert-Butyl Ether	637-92-3	58	94%
Vinyl chloride	**75-01-4**	**58**	**94%**
Chlorobenzene	108-90-7	59	95%
Chloroethane	75-00-3	59	95%
1,1-Dichloroethene	75-35-4	60	97%
Bromodichloromethane	75-27-4	60	97%
Ethyl Acrylate	140-88-5	60	97%
Methyl tert-Butyl Ether	1634-04-4	60	97%
1,1,2-Trichloroethane	79-00-5	61	98%
tert-Amyl Methyl Ether	994-05-8	61	98%
trans-1,2-Dichloroethylene	156-60-5	61	98%
1,1-Dichloroethane	75-34-3	62	100%
1,2-Dichloropropane	78-87-5	62	100%
Bromochloromethane	74-97-5	62	100%
Chloroprene	126-99-8	62	100%
cis-1,2-Dichloroethylene	156-59-4	62	100%
cis-1,3-Dichloropropene	10061-01-5	62	100%
trans-1,3-Dichloropropene	10061-02-6	62	100%

ND = Not Detected,
Bold = MQO Core Analyte

In 2012, there were 26 compounds detected in at least 90% of the samples taken, two more than in 2011. Two compounds dropped off the 90% detection list, but four more compounds were added. The compounds that dropped off the list are 1,1,1-trichloroethane, and 2-butanone (MEK). The trichloroethane compound was detected in just under 90% of the samples taken, at a rate of 89%. MEK was removed from the VOC analysis, and added to the carbonyl analysis, as the latter is more sensitive to the lower levels of MEK being detected. The four additional compounds that made the 2012 list are 1,2-dichloroethane, 1,3-butadiene, bromomethane, and tetrachloroethylene. Eight of the VOC compounds are on the core list of 19 HAPs. Only five of those eight compounds were detected in greater than 90% of the samples taken in 2012. The three compounds not detected in enough samples were chloroform, trichloroethylene, and vinyl chloride. They were detected in 73%, 37%, and 6% of the samples in 2012, respectively. Table 5 is an alphabetical listing of the 26 compounds most frequently detected in 2012. Italicized compounds are on the list of 19 core HAPs.

Table 5. VOCs Detected in Greater Than 90% of 2012 Samples

90% Detection Rate		
1,2,4-Trimethylbenzene	Carbon Disulfide	n-Octane
1,2-Dichloroethane	*Carbon Tetrachloride*	o-Xylene
1,3,5-Trimethylbenzene	Chloromethane	Propylene
1,3-Butadiene	Dichlorodifluoromethane	Styrene
Acetonitrile	Dichloromethane	*Tetrachloroethylene*
Acetylene	Dichlorotetrafluoroethane	Toluene
Acrolein	Ethylbenzene	Trichlorofluoromethane
Benzene	m,p-Xylene	Trichlorotrifluoroethane
Bromomethane	Methyl Isobutyl Ketone	

Italicized compounds are on the list of 19 core HAPs

There were seven compounds that were not detected at all during 2012, which is down from the 11 non-detect compounds in 2011. There were 16 compounds that were detected in five percent, or less, of the samples in 2011. This is a decrease from 2011, where 20 compounds were detected in five percent, or less, of the samples. This list of 16 compounds includes many compounds that are chiefly emitted by stationary sources. It appears that these source types are not present in the immediate vicinity of the station.

Table 6 summarizes the annual mean concentrations for each of the 60 VOCs measured during the study, from 2004 through 2012. Compounds that have bolded values are MQO Core Analytes. Compounds with italicized values were detected in less than 90% of the samples for the year. It should be noted that the annual means were calculated by replacing all "non-detect" values with one-half of the sample method detection limit. This is an accepted conservative technique for calculating annual values when some of the samples were less than the laboratory's ability to measure. As a result of this technique, the average and maximum concentrations are the same if the compound was never detected. The compounds are listed in alphabetical order. There are several things to note about this table. First, the acetonitrile values for all of 2004, and the first three-and-a-half months of 2005 were voided due to a contamination in the sampler. Acrolein was not analyzed until 2005, and carbon disulfide was added to the list of analytes in 2006. Removed from this list were the compounds of chloromethylbenzene, and methyl ethyl ketone (MEK). MEK was added to the carbonyl analysis. Chloromethylbenzene was never detected in greater than 90% of samples.

Table 6. VOC Data Summary 2012

	µg/m³								
Analyte	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**
1,1,1-Trichloroethane	*0.136*	*0.148*	0.120	0.095	0.092	0.092	*0.086*	0.065	*0.053*
1,1,2,2-Tetrachloroethane	*0.172*	*0.155*	*0.045*	*0.057*	*0.031*	*0.010*	*0.034*	*0.082*	*0.064*
1,1,2-Trichloroethane	*0.218*	*0.145*	*0.016*	*0.050*	*0.022*	*0.009*	*0.044*	*0.068*	*0.057*
1,1-Dichloroethane	*0.101*	*0.074*	*0.012*	*0.034*	*0.014*	*0.006*	*0.031*	*0.016*	*0.030*
1,1-Dichloroethene	*0.099*	*0.090*	*0.028*	*0.045*	*0.010*	*0.014*	*0.023*	*0.019*	*0.028*
1,2,4-Trichlorobenzene	*0.668*	*0.582*	*0.057*	*0.153*	*0.111*	*0.019*	*0.071*	*0.130*	*0.082*
1,2,4-Trimethylbenzene	1.212	1.011	0.814	0.639	0.499	0.468	0.517	0.699	0.587
1,2-Dibromoethane	*0.192*	*0.158*	*0.069*	*0.052*	*0.027*	*0.009*	*0.041*	*0.069*	*0.065*
1,2-Dichloroethane	*0.121*	*0.096*	*0.030*	*0.044*	*0.018*	*0.015*	*0.034*	*0.040*	0.082
1,2-Dichloropropane	*0.162*	*0.120*	*0.076*	*0.046*	*0.023*	*0.010*	*0.052*	*0.053*	*0.044*
1,3,5-Trimethylbenzene	0.408	*0.332*	0.251	0.205	0.161	0.153	0.187	0.234	0.225
1,3-Butadiene	***0.208***	***0.199***	**0.197**	**0.159**	**0.145**	**0.166**	**0.136**	***0.135***	**0.180**
Acetonitrile	*VOID*	*17.182**	*0.594*	1.698	6.609	1.244	20.326	0.538	6.028
Acetylene	2.258	2.051	1.804	1.461	2.021	2.053	1.547	1.375	1.444
Acrolein	**----**	***0.809***	***0.615***	**0.631**	**0.683**	**1.019**	**1.368**	**0.735**	**1.091**
Acrylonitrile	*0.113*	*0.074*	*0.088*	*0.038*	*0.126*	*0.140*	*0.044*	*0.069*	*0.032*
Benzene	**2.248**	**1.946**	**1.850**	**1.460**	**1.616**	**1.928**	**1.414**	**1.333**	**1.276**
Bromochloromethane	*0.238*	*0.155*	*0.050*	*0.049*	*0.016*	*0.013*	*0.044*	*0.021*	*0.037*
Bromodichloromethane	*0.134*	*0.119*	*0.023*	*0.063*	*0.023*	*0.009*	*0.063*	*0.084*	*0.072*
Bromoform	*0.310*	*0.217*	*0.088*	*0.078*	*0.026*	*0.013*	*0.051*	*0.126*	*0.104*
Bromomethane	*0.107*	*0.083*	*0.039*	0.048	0.059	0.056	*0.079*	*0.043*	0.111
Carbon Disulfide	----	----	8.510	8.706	10.935	13.610	1.191	1.500	1.416
Carbon Tetrachloride	***0.515***	***0.488***	**0.585**	**0.528**	**0.679**	**0.663**	**0.534**	**0.536**	**0.665**
Chlorobenzene	*0.092*	*0.071*	*0.013*	*0.032*	*0.018*	*0.018*	*0.029*	*0.048*	*0.057*
Chloroethane	*0.136*	*0.086*	*0.028*	*0.032*	0.034	0.041	*0.023*	*0.016*	*0.025*
Chloroform	***0.101***	***0.113***	***0.084***	***0.090***	**0.105**	**0.122**	***0.087***	***0.087***	***0.091***
Chloromethane	1.269	1.322	1.214	1.220	1.424	1.465	1.338	1.268	1.237

Analyte	**µg/m^3**								
	2004	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**
Chloroprene	*0.091*	*0.074*	*0.040*	*0.028*	*0.015*	*0.012*	*0.023*	*0.014*	*0.022*
cis-1,2-Dichloroethylene	*0.119*	*0.090*	*0.032*	*0.036*	*0.014*	*0.011*	*0.067*	*0.018*	*0.036*
cis-1,3-Dichloropropene	*0.113*	*0.083*	*0.032*	*0.038*	*0.016*	*0.005*	*0.031*	*0.050*	*0.034*
Dibromochloromethane	*0.298*	*0.203*	*0.043*	*0.063*	*0.021*	*0.016*	*0.041*	*0.087*	*0.071*
Dichlorodifluoromethane	3.069	3.179	2.777	2.702	2.789	3.215	2.902	2.761	2.565
Dichloromethane	*0.489*	*0.429*	0.414	0.383	3.432	1.956	91.647	1.313	40.119
Dichlorotetrafluoroethane	*0.108*	*0.124*	0.123	0.118	0.111	0.135	0.131	0.133	0.123
Ethyl Acrylate	*0.123*	*0.114*	*0.023*	*0.034*	*0.043*	*0.007*	*0.021*	*0.041*	*0.030*
Ethyl tert-Butyl Ether	*0.104*	*0.095*	*0.015*	*0.021*	*0.010*	*0.035*	*0.018*	*0.017*	*0.023*
Ethylbenzene	1.195	1.355	0.662	0.614	0.474	0.531	0.507	0.619	0.692
Hexachloro-1,3-butadiene	*0.853*	*0.987*	*0.072*	*0.191*	*0.091*	*0.005*	*0.063*	*0.185*	*0.115*
m,p-Xylene	3.730	4.622	2.289	2.047	1.529	1.697	1.548	1.968	2.104
m-Dichlorobenzene	*0.210*	*0.170*	*0.012*	*0.049*	*0.045*	*0.024*	*0.028*	*0.097*	*0.070*
Methyl Isobutyl Ketone	*0.265*	*0.179*	*0.212*	*0.169*	*0.172*	0.153	*0.174*	0.156	0.174
Methyl Methacrylate	*1.285*	*0.786*	*0.260*	*1.337*	*0.491*	*0.049*	*0.050*	*0.049*	*0.064*
Methyl tert-Butyl Ether	*0.134*	*0.118*	*0.012*	*0.019*	*0.009*	*0.007*	*0.017*	*0.015*	*0.020*
n-Octane	*0.330*	*0.340*	0.243	0.238	0.204	0.231	0.296	0.373	0.423
o-Dichlorobenzene	*0.120*	*0.147*	*0.015*	*0.053*	*0.045*	*0.021*	*0.033*	*0.101*	*0.062*
o-Xylene	1.554	1.967	0.831	0.730	0.558	0.602	0.550	0.713	0.794
p-Dichlorobenzene	*0.180*	*0.143*	*0.090*	0.069	*0.040*	*0.071*	*0.035*	*0.089*	*0.079*
Propylene	1.406	1.319	1.110	0.911	0.881	1.008	0.879	0.861	0.948
Styrene	2.185	1.053	0.373	0.583	1.256	0.626	2.572	1.450	2.960
tert-Amyl Methyl Ether	*0.146*	*0.128*	*0.025*	*0.025*	*0.027*	*0.029*	*0.026*	*0.033*	*0.034*
Tetrachloroethylene	***0.306***	***0.272***	***0.342***	**0.318**	**0.328**	**0.427**	**0.398**	***0.263***	**0.318**
Toluene	5.584	5.525	4.064	4.222	2.905	3.820	3.231	4.006	3.663
trans-1,2-Dichloroethylene	*0.099*	*0.090*	*0.036*	*0.034*	*0.010*	*0.008*	*0.025*	*0.016*	*0.026*
trans-1,3-Dichloropropene	*0.120*	*0.103*	*0.020*	*0.038*	*0.016*	*0.009*	*0.033*	*0.057*	*0.036*
Trichloroethylene	***0.134***	***0.120***	***0.053***	***0.055***	***0.033***	***0.108***	***0.055***	***0.086***	***0.136***
Trichlorofluoromethane	2.174	1.626	1.517	1.456	1.506	1.707	1.604	1.518	1.594
Trichlorotrifluoroethane	0.778	0.807	0.758	0.825	0.680	0.847	0.722	0.752	0.655
Vinyl chloride	***0.051***	***0.051***	***0.011***	***0.030***	***0.007***	***0.006***	***0.015***	***0.011***	***0.014***

2004 NOTE: Acetonitrile VOID due to contamination in sampler.

2005 NOTE: Acetonitrile VOID thru 4/10/2005 due to contamination in sampler.

Bold = MQO Core Analyte

Italic = Less than 90% detection rate

In general, the concentrations from 2012 compared well with the 2011 data. However, some compounds did show average concentrations that were significantly higher than their 2011 values. For instance, dichloromethane and acetonitrile showed much larger annual average concentrations in 2012 as opposed to 2011. In 2011, their respective annual average concentrations were 1.31, and 0.54 µg/m^3. In 2012, they were 40.12, and 6.03 µg/m^3. The large increase in concentrations arises from significantly elevated concentrations of these compounds on several sample days throughout a 6 week period. The MDL levels did change slightly for some of the compounds, but this is to be expected as the laboratory calculates new MDLs every year.

Graphs

Figure 8 through Figure 10 are graphs showing the 24 hour maximum, and annual mean concentrations for each of the 26 compounds that were detected in greater than 90% of the samples in 2012, as well as the remaining VOC compounds that are on the mandatory monitoring list of 19 core HAPs. These graphs are ordered from highest to lowest annual mean concentration. Note that the graphs' scales vary from a full-scale level at 20 micrograms per meter cubed to a full-scale value of four micrograms per meter cubed. The compounds with the five largest annual average concentrations are dichloromethane, acetonitrile, toluene, styrene, and dichlorodifluoromethane. Their values are 40.12, 6.03, 3.66, 2.96, and 2.57 micrograms per meter cubed, respectively. In comparison, the same respective concentration values from the 2011 NMP report are 3.51, 24.68, 2.70, 0.25, and 1.23 micrograms per meter cubed, respectively.[9]

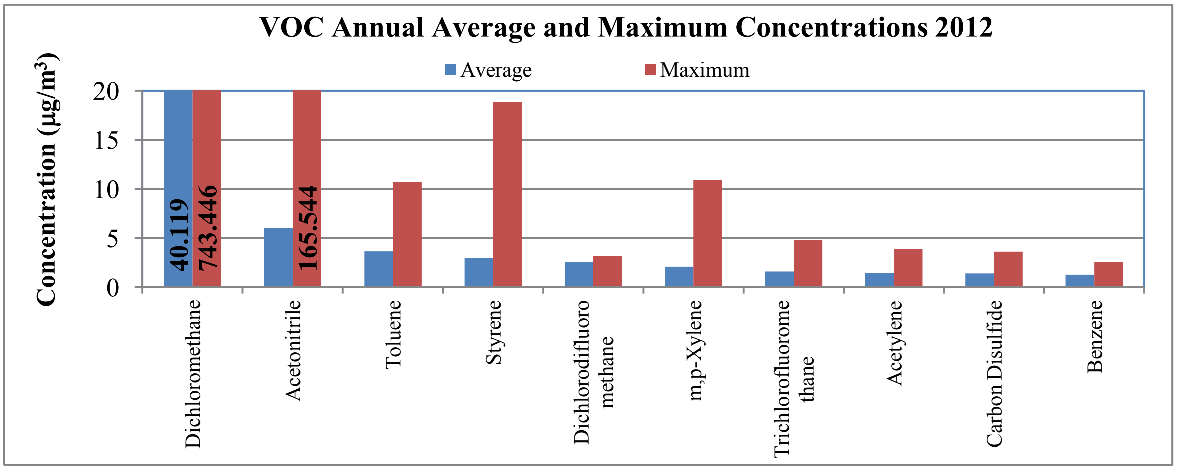

Figure 8. VOC Annual and Maximum Concentrations 2012

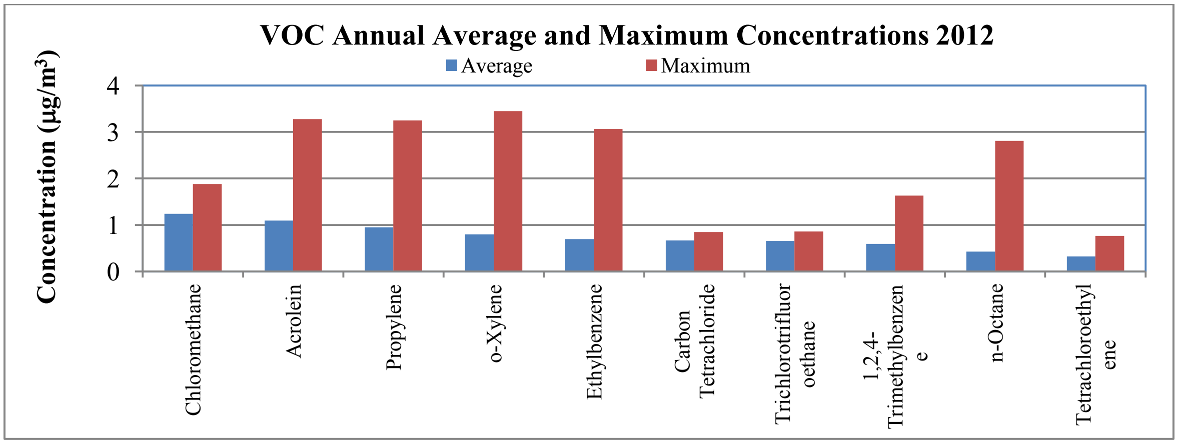

Figure 9. VOC Annual and Maximum Concentrations 2012, ctd.

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[9] "2011 National Monitoring Programs Annual Report (UATMP, NATTS, CSATAM). US EPA. August 2013. http://www.epa.gov/ttnamti1/files/ambient/airtox/2011nmpreport.pdf.

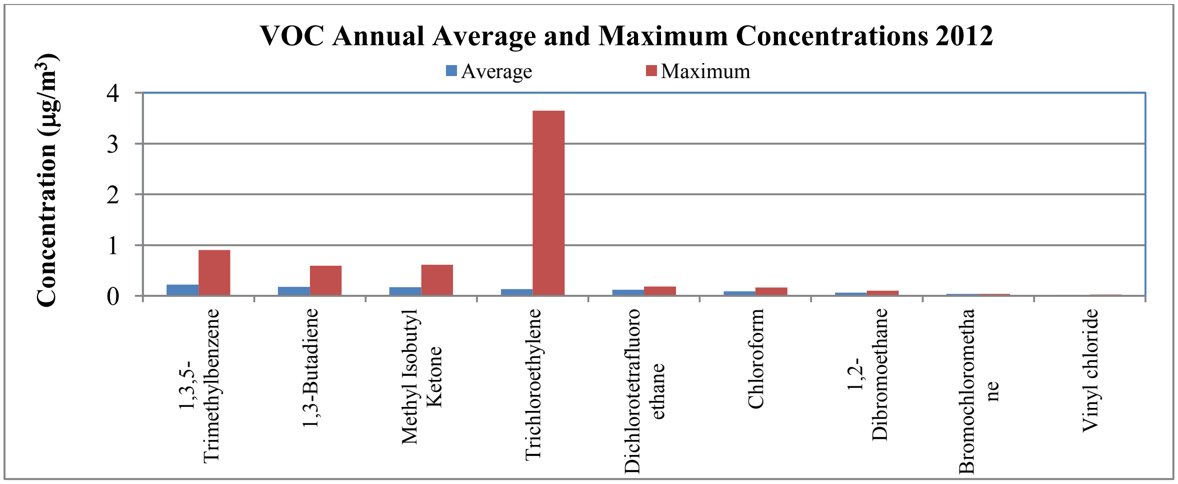

Figure 10. VOC Annual and Maximum Concentrations 2012, ctd.

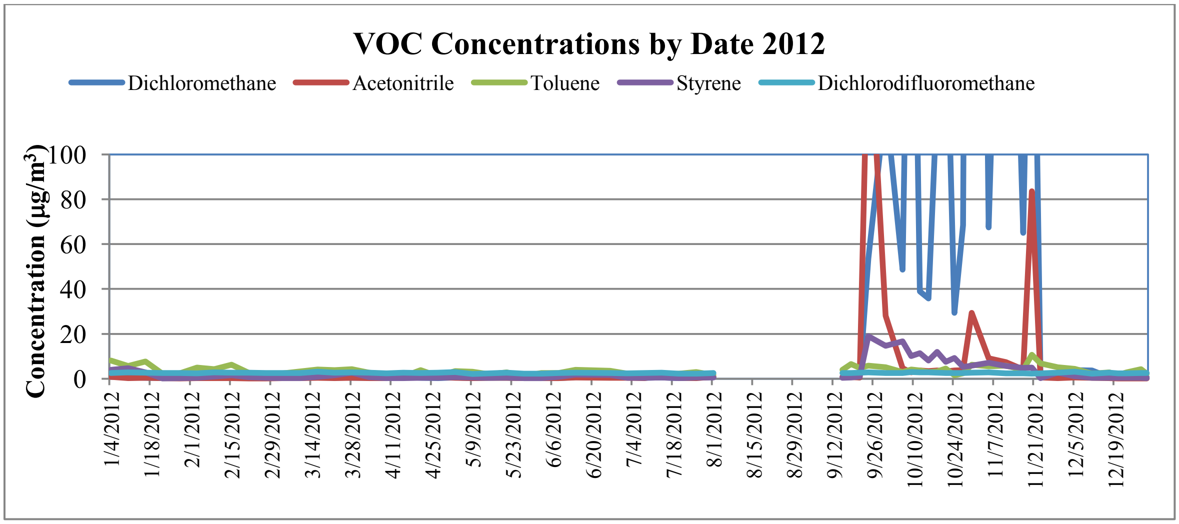

Figure 11. VOC Concentrations by Date 2012

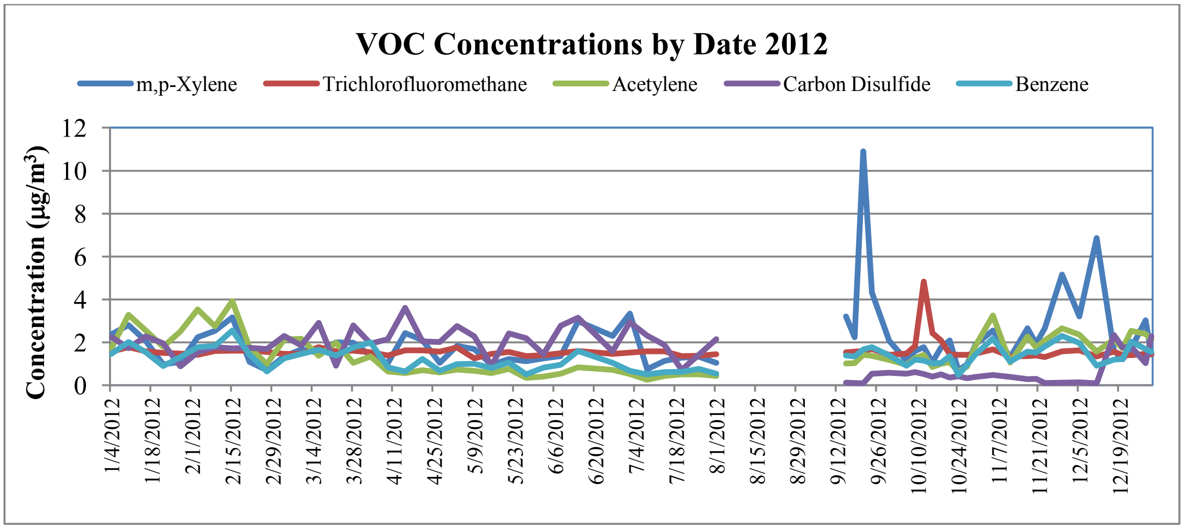

Figure 12. VOC Concentrations by Date 2012, ctd.

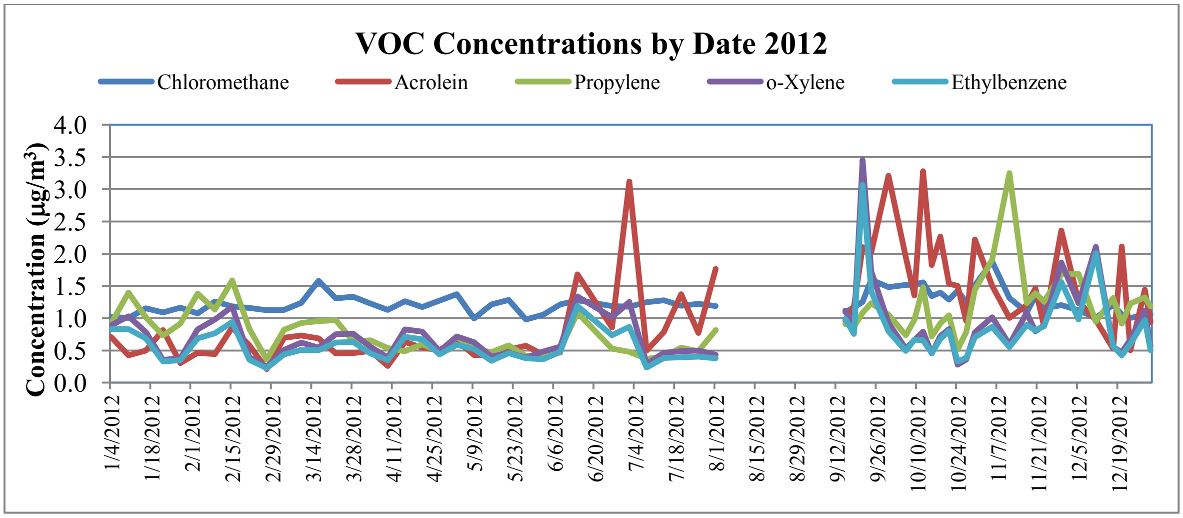

Figure 13. VOC Concentrations by Date 2012, ctd.

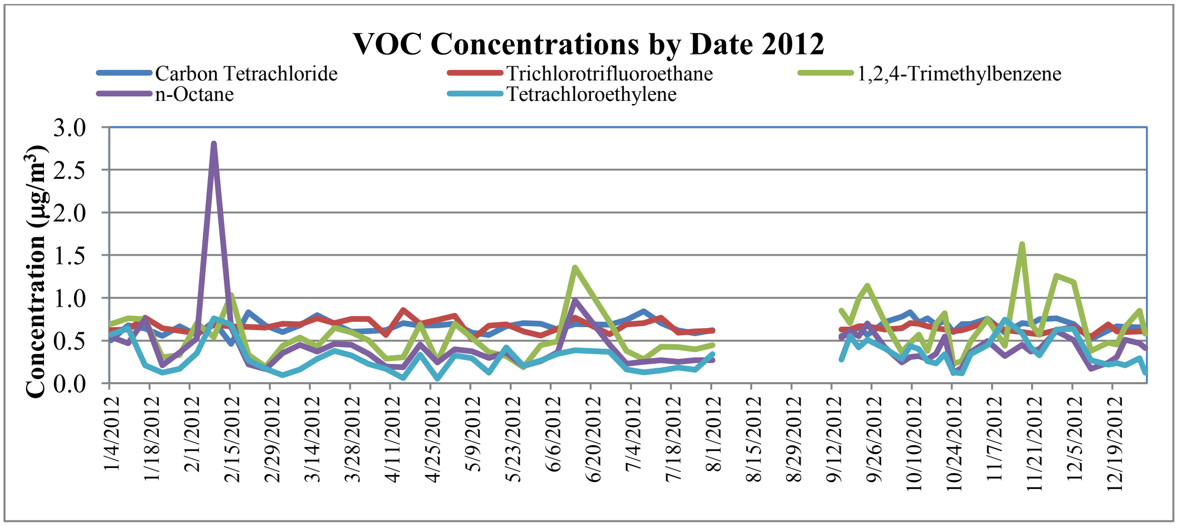

Figure 14. VOC Concentrations by Date 2012, ctd.

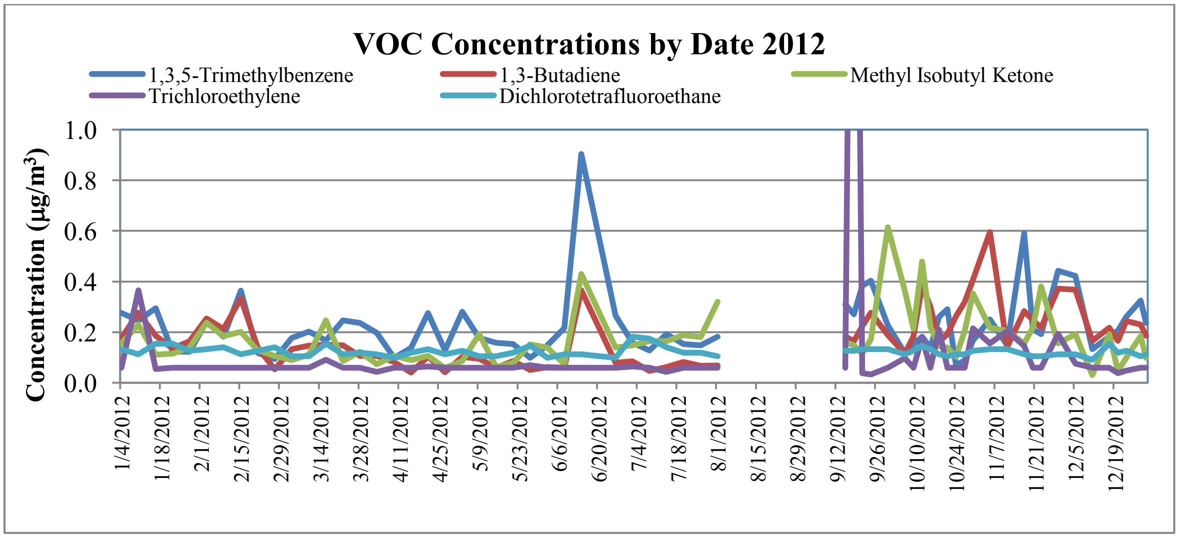

Figure 15. VOC Concentrations by Date 2012, ctd.

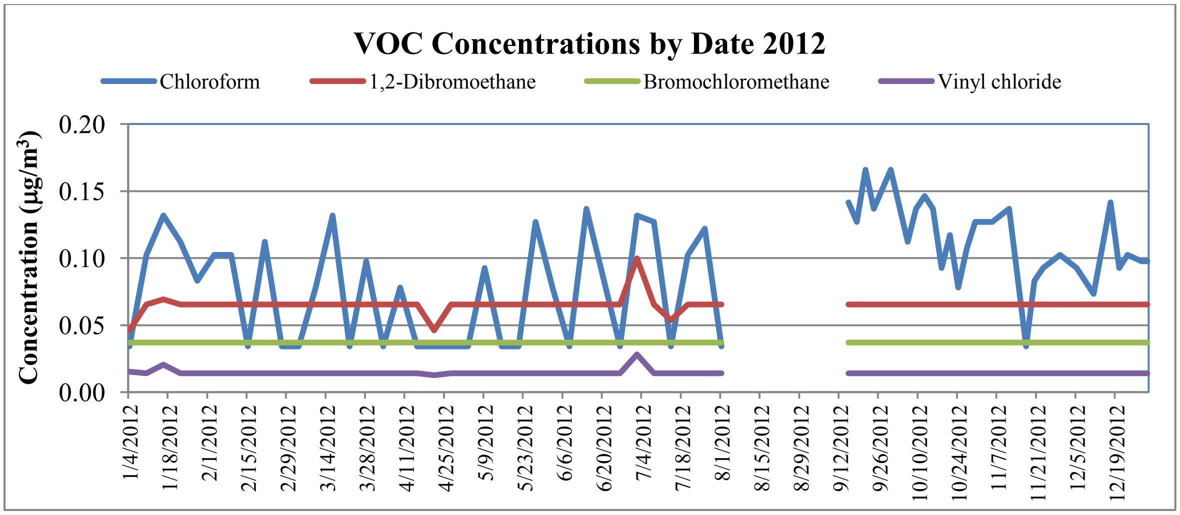

Figure 16. VOC Concentrations by Date 2012, ctd.

Figure 11 through Figure 16 show the concentrations of the 26 most detected VOCs, as well as the three other VOC compounds on the core 19 list, by date. The concentrations tended to trend well with each other. Some of the compounds do show a seasonal variation in their concentrations. This is most easily seen in the graphs of acetylene and propylene in Figure 12 and Figure 13. VOC concentrations are typically higher in the summer due to the higher temperatures, and longer availability of ultraviolet rays for the photolytic process.

Figure 11also shows that the concentration of dichloromethane was off the charts from approximately mid-September through mid-November, with a maximum value of near 750 micrograms per cubic meter, during that time period. On September 16, 2012, the ERG supplied air toxics analyzer was returned to service at the site. The first three samples taken showed normal concentrations for dichloromethane, as did the final four samples taken with that same sampler. Between the December 11, and December 17 sample dates, the sampler was replaced with the repaired sampler that was previously installed at the site, as there were concerns of possible contamination in the other sampler. No evidence of contamination was ever found, which moved the discussion to a possible new source in the area. A search of the area near the site did not provide any clues as to a possible source. It is still unclear why the concentration values for this compound were so large during that time period.

Figure 17 through Figure 23 graphically illustrate the weekday versus weekend VOC concentrations in 2012 for all 60 compounds. It should be noted here that compounds showing the same weekday and weekend averages are reflecting concentrations that are equal to one-half of the MDL; that is, they were never detected. The compounds are separated into four groups: alkanes, alkenes, alkynes, and aromatics. The alkane compounds have carbon atoms with only one single bond. The alkenes have carbon atoms with double bonds, and the alkynes have triple bonds. The aromatics are ring structures, like benzene, with other substituents bonded to the ring.

In general, the weekday concentrations for most compounds were larger than those on the weekend. This is expected, as many of the compounds emitted are associated with automobile emissions, and traffic in the area is usually decreased on the weekends. There were, however, a few exceptions to this. Six of the compounds had higher weekend concentrations than weekday concentrations. These compounds are trichlorofluoromethane, dichloromethane, carbon tetrachloride, acetonitrile, and 1,2-dichloroethane. Of these, 1,2-dichloroethane was detected in only 27% of the samples taken. For the compounds that were not detected consistently, their concentrations are heavily based on their respective MDLs, and not much should be read into their weekend versus weekday concentrations. The dichloromethane had two large concentration spikes on weekend days (1/15/2011 and 4/3/2011), which is the reason for the larger weekend concentration values.

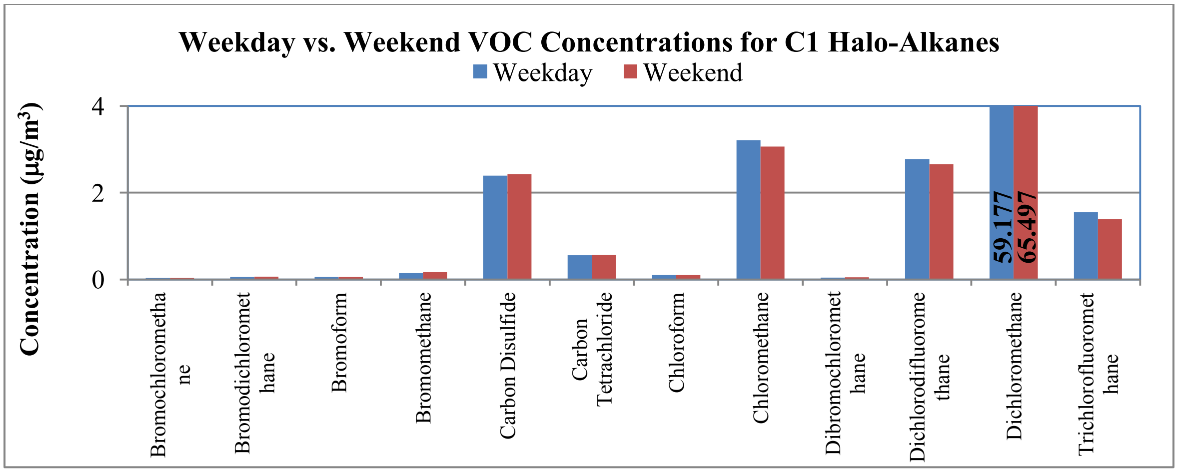

Figure 17. VOC Weekday vs. Weekend Comparison for C1 Alkanes

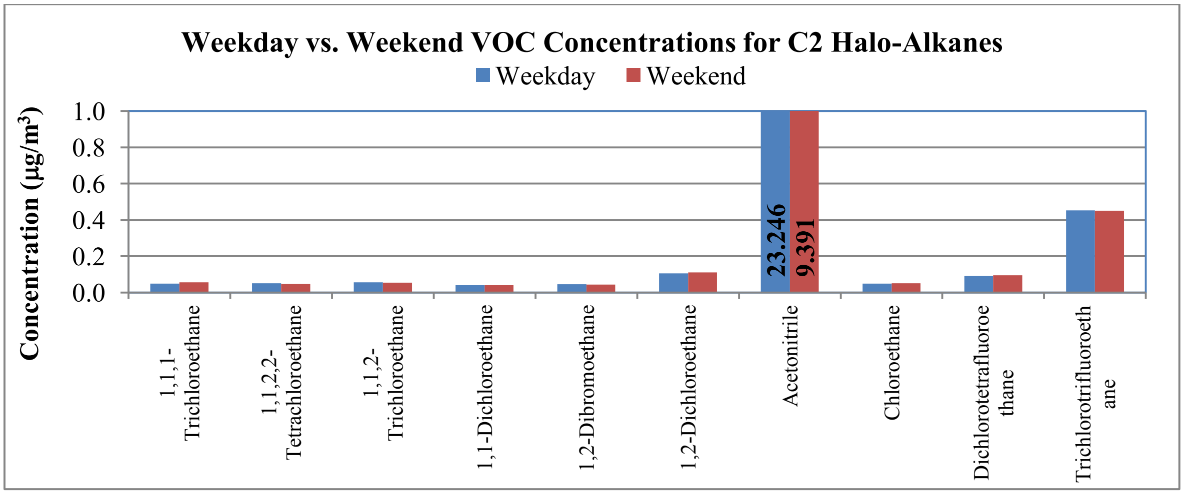

Figure 18. VOC Weekend vs. Weekday Concentrations for C2 Alkanes

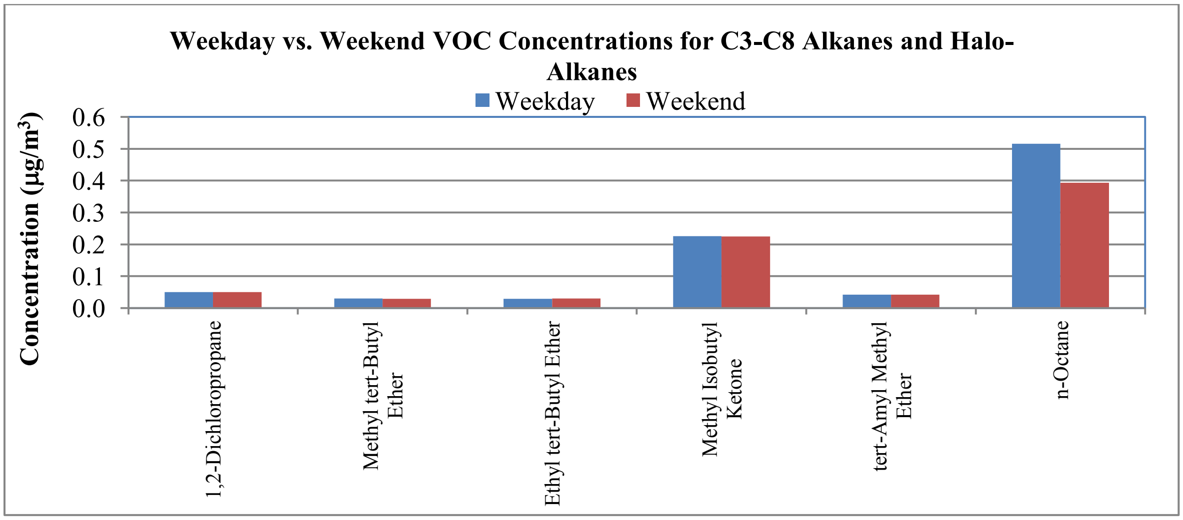

Figure 19. VOC Weekend vs. Weekday Concentrations for C3 – C8 Alkanes

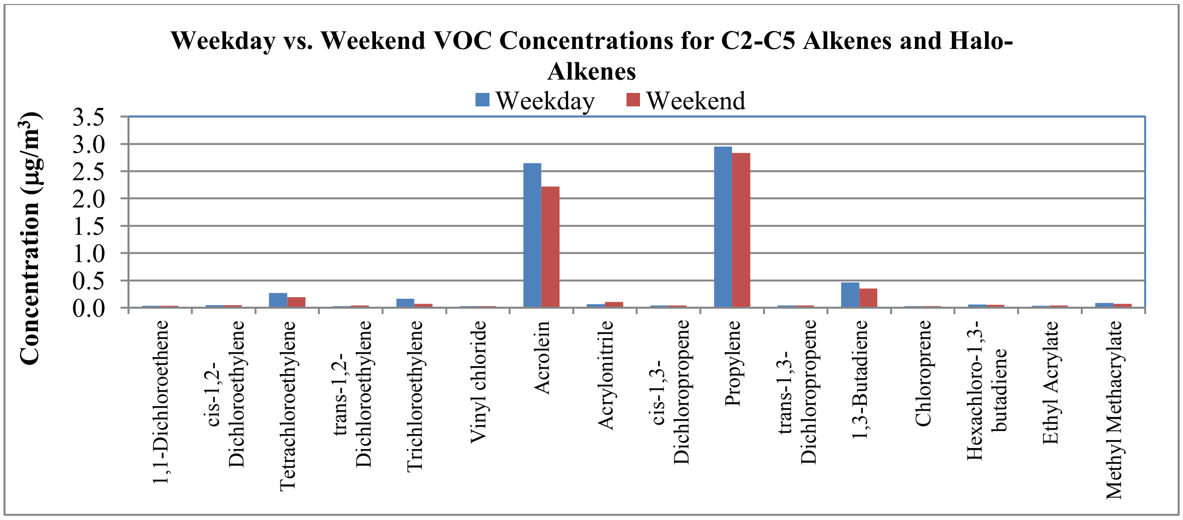

Figure 20. VOC Weekend vs. Weekday Concentrations for C2-C5 Alkenes

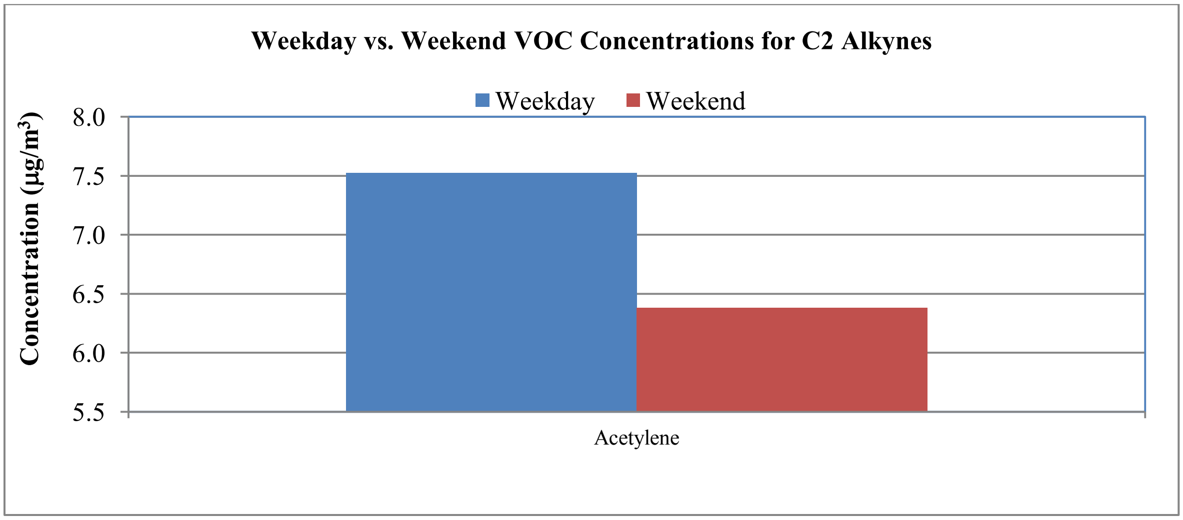

Figure 21. VOC Weekend vs. Weekday Concentrations for Alkynes

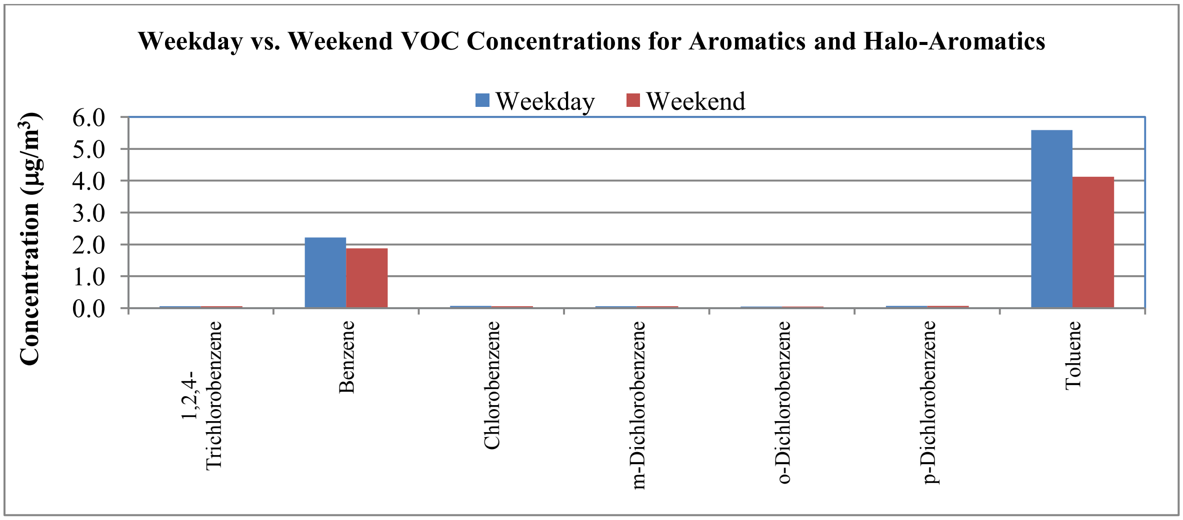

Figure 22. VOC Weekend vs. Weekday Concentrations for Aromatics

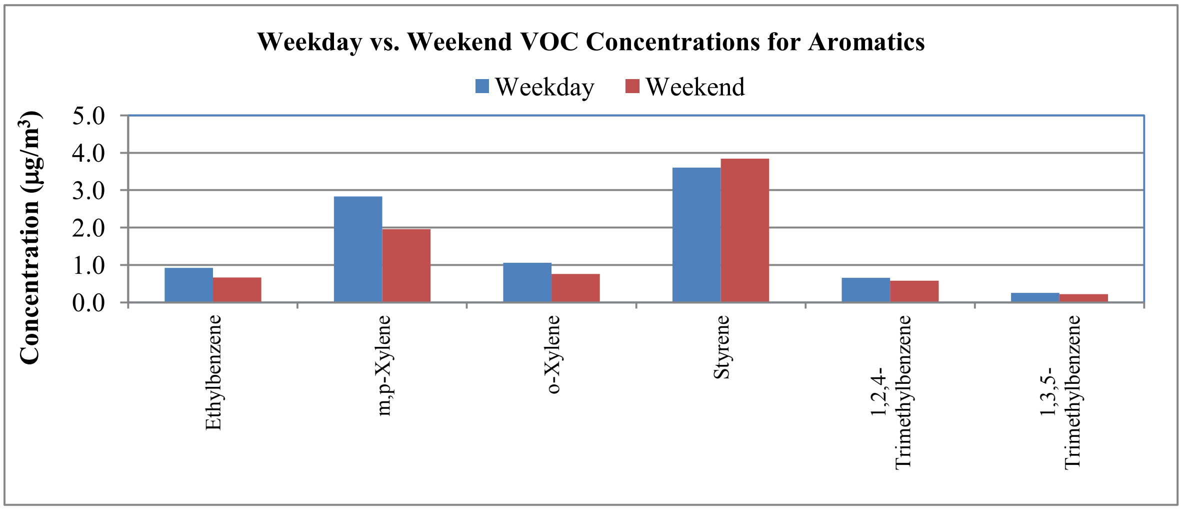

Figure 23. VOC Weekend vs. Weekday Concentrations for Aromatics, ctd.

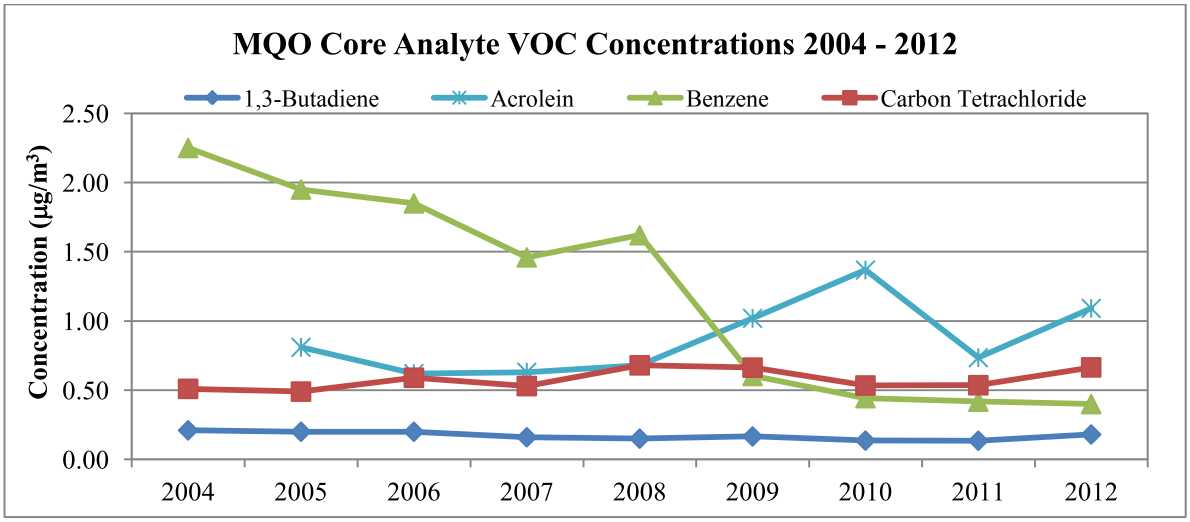

Figure 24. MQO Core Analyte VOC Concentrations 2004 – 2012

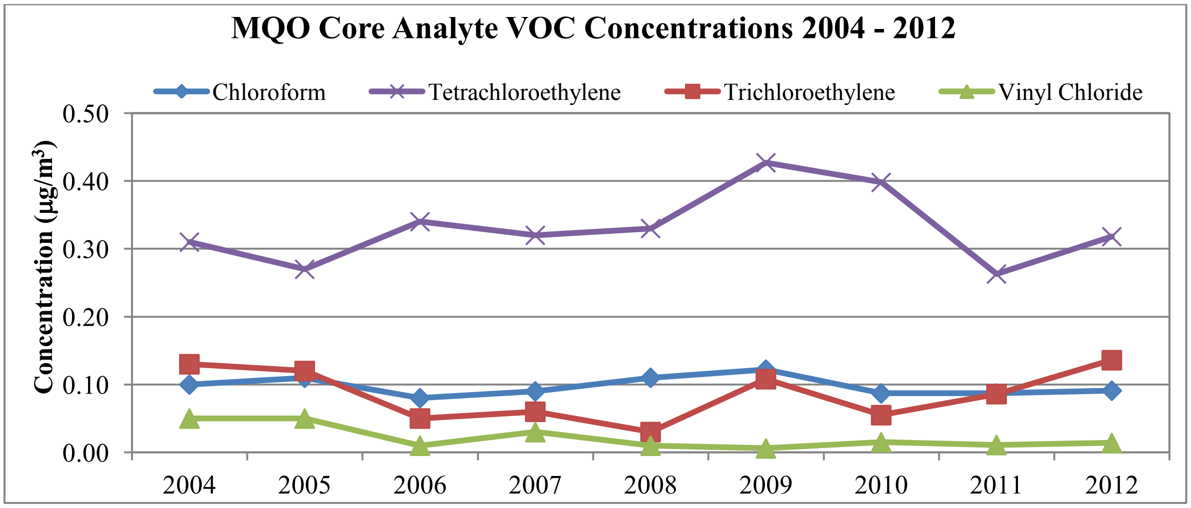

Figure 25. MQO Core Analyte VOC Concentrations 2004 – 2012, ctd.

Figure 24 and Figure 25 graph the annual average concentrations of the eight VOCs that are a part of the mandatory monitoring subset of 19 HAPs. The graphs do not appear to indicate a general trend in concentration values since 2004. A calculation of the 3-year average concentrations (2007 – 2009) for all compounds also shows that the overall concentration average is dropping compared to the previous 3 year average (2004 – 2006).

Quality Assurance/Quality Control

Field Blanks

The volatile organic compound sampling method involves sampling in stainless steel canisters with specially treated interior surfaces. The canisters are re-used. After a full canister is analyzed, it is pumped out repeatedly to a high vacuum. This procedure cleans it for the next use. Periodically, one canister from each cleaning batch is tested to make sure the method is performing adequately. The test canister is filled with ultra-pure air, and then analyzed. If it shows no contamination, the batch is released for use. If contamination is found, the entire batch is sent through the cleaning process for a second time. The canisters arrive in the field closed, and under a vacuum of 20 to 30 inches of mercury. Therefore, field blanks are not used in this method. The canisters are "blanked" at the laboratory prior to shipping to the field.

Precision of Sample Results

On six random sampling dates per year, a second canister was sampled simultaneously with the primary sample. These additional samples, known as duplicates, were collected in order to assess the precision (repeatability) of the canister sampling method. In general, repeatability for the two collocated samples was excellent. Information regarding precision and accuracy results is available upon request to the Air Pollution Control Division.

V. POLYCYCLIC AROMATIC HYDROCARBONS

Summary Statistics

In April 2008, the Grand Junction National Air Toxics Trends Site added a sampler for polycyclic aromatic hydrocarbon (PAH) compounds. A good definition of these chemicals is:

> *Polycyclic aromatic hydrocarbons (also known as polynuclear aromatic hydrocarbons) are composed of two or more aromatic (benzene) rings which are fused together when a pair of carbon atoms is shared between them. The resulting structure is a molecule where all carbon and hydrogen atoms lie in one plane. Naphthalene ($C_{10}H_8$, MW = 128.16 g), formed from two benzene rings fused together, has the lowest molecular weight of all PAHs. The environmentally significant PAHs are those molecules which contain two (e.g., naphthalene) to seven benzene rings (e.g., coronene with a chemical formula $C_{24}H_{12}$; MW = 300.36 g). In this range, there are a large number of PAHs which differ in number of aromatic rings, position at which aromatic rings are fused to one another, and number, chemistry, and position of substituents on the basic ring system.* (Source: Ambient Water Quality Criteria for Polycyclic Aromatic Hydrocarbons (PHAs) Ministry of Environment, Lands and Parks, Province of British Columbia. By N. K. Nagpal, Ph.D., Water Quality Branch, Water Management Division, British Columbia, Canada, Ministry of Environment, February, 1993).

In all, 61 PAH samples were attempted, and 60 were collected for analysis (98.4% sample recovery rate). Twenty-two compounds were measured for this study. The list of these compounds and the summary of the collected data are shown in Table 7 and Table 8. Fourteen of the 22 compounds analyzed for were detected in greater than 90% of the samples, and 19 were detected in greater than 50% of the samples. Nine compounds were detected in every sample taken. These are: 9-fluorenone, acenaphthene, benzo(b)fluoranthene, chrysene, fluoranthene, fluorene, naphthalene, phenanthrene, and pyrene.

Table 7. PAH Sample Summary Data 2012

Compound	CAS Number	# of ND's	% ND
9-Fluorenone	486-25-9	0	0%
Acenaphthene	83-32-9	0	0%
Benzo (b) fluoranthene	205-99-2	0	0%
Chrysene	218-01-9	0	0%
Fluoranthene	206-44-0	0	0%
Fluorene	86-73-7	0	0%
Naphthalene	**91-20-3**	**0**	**0%**
Phenanthrene	85-01-8	0	0%
Pyrene	129-00-0	0	0%
Anthracene	120-12-7	1	2%
Retene	483-65-8	2	3%
Benzo (e) pyrene	192-97-2	3	5%
Benzo (a) anthracene	56-55-3	6	10%
Benzo (g,h,i) perylene	191-24-2	6	10%
Indeno(1,2,3-cd)pyrene	193-39-5	14	23%
Acenaphthylene	208-96-8	15	25%
Coronene	191-07-1	18	30%
Benzo (a) pyrene	**50-32-8**	**20**	**33%**
Benzo (k) fluoranthene	207-08-9	23	38%
Perylene	198-55-0	37	62%
Cyclopenta[cd]pyrene	27208-37-3	39	65%
Dibenz (a,h) anthracene	53-70-3	45	75%

ND = Not Detected
Bold = MQO Core Analyte

Table 8 summarizes the annual mean concentrations for each PAH measured during the study, from 2008 through 2012. The compounds that were detected in less than 90% of the samples taken are italicized to show that their averages are dependent upon their respective MDL values. Bolded compounds are listed among those on the list of 19 core HAPs to be be monitored. The annual means were calculated by replacing all "non-detect" values with one-half of the sample minimum detection limit. This is an accepted conservative technique for calculating annual values when some of the samples were less than the laboratory's ability to detect. Naphthalene had the largest annual average of the PAH compounds with a value of 204 nanograms per meter cubed in 2012. This is over ten times greater than the next closest average concentration, which is acenaphthene, with 20.5 nanograms per meter cubed. Naphthalene is found in tobacco smoke, mothballs, coal tar production, and from the combustion of coal and oil.

Table 8. PAH Annual Average Values 2008 - 2012

Analyte	2008 Average (ng/m^3)	2009 Average (ng/m^3)	2010 Average (ng/m^3)	2011 Average (ng/m^3)	2012 Average (ng/m^3)
9-Fluorenone	*1.53*	2.67	2.34	2.13	2.74
Acenaphthene	8.41	11.34	7.30	10.54	20.5
Acenaphthylene	*2.12*	*3.68*	*2.50*	*2.22*	*2.28*
Anthracene	*0.63*	1.65	0.89	0.77	0.83
Benzo (a) anthracene	*0.20*	*0.39*	*0.25*	0.26	0.22

Analyte	**2008 Average (ng/m^3)**	**2009 Average (ng/m^3)**	**2010 Average (ng/m^3)**	**2011 Average (ng/m^3)**	**2012 Average (ng/m^3)**
Benzo (a) pyrene	***0.18***	***0.33***	***0.20***	***0.22***	***0.18***
Benzo (b) fluoranthene	0.36	0.72	0.50	0.48	0.41
Benzo (e) pyrene	*0.19*	*0.39*	*0.24*	0.23	0.19
Benzo (g,h,i) perylene	*0.26*	0.43	0.28	0.25	0.21
Benzo (k) fluoranthene	*0.10*	*0.21*	*0.14*	*0.14*	*0.12*
Chrysene	0.35	0.68	0.49	0.48	0.42
Coronene	*0.15*	*0.23*	*0.13*	*0.11*	*0.09*
Cyclopenta[cd]pyrene	*0.16*	*0.19*	*0.10*	*0.13*	*0.12*
Dibenz (a,h) anthracene	*0.06*	*0.06*	*0.03*	*0.05*	*0.04*
Fluoranthene	2.52	3.79	3.30	3.35	3.55
Fluorene	5.15	9.20	6.44	7.67	12.6
Indeno(1,2,3-cd)pyrene	*0.21*	*0.37*	*0.24*	*0.23*	*0.19*
Naphthalene	**112**	**189**	**147**	**158**	**204**
Perylene	*0.07*	*0.08*	*0.09*	*0.07*	*0.06*
Phenanthrene	11.98	17.91	13.92	14.02	18.7
Pyrene	1.81	2.87	2.28	2.19	2.20
Retene	0.67	1.37	1.04	0.85	0.77

Bold = MQO Core Analyte
Italic = less than 90% detection rate

Graphs

Graphs of the concentration data from the fifteen PAH compounds that were detected in greater than 90% of the samples taken are shown in Figure 26 through Figure 29. Naphthalene is the most variable, with concentrations ranging from 45.5 to 822 nanograms per meter cubed. Naphthalene had the largest annual average concentration, followed by acenaphthene, and phenanthrene, with values of 204, 20.5, and 18.7 nanograms per meter cubed. In comparison, the National Monitoring Program (NMP) national averages for these compounds in 2011 were 81.7, 9.92, and 4.64 nanograms per meter cubed, respectively.[10] The phenanthrene, fluorene, and fluoranthene concentrations tended to follow the same general trend that naphthalene did. Acenaphthylene, pyrene, retene, benzo (b) fluoranthene, and benzo (g,h,i) perylene exhibited a seasonal variation, with larger concentrations in the winter months, and lower concentrations in the summer months. This makes sense, since the primary source of many PAHs in air is the incomplete combustion of wood and fuel.[11] PAHs are a product of combustion from common sources like automobiles, wood-burning stoves and furnaces, cigarette smoke, etc. The natural sources of PAHs include volcanoes, forest fires, crude oil, and shale oil.[12]

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[10] "2011 National Monitoring Programs Annual Report (UATMP, NATTS, CSATAM). US EPA. August 2013. http://www.epa.gov/ttnamti1/files/ambient/airtox/2011nmpreport.pdf.

[11] "Toxicological Profile for Polycyclic Aromatic Hydrocabons." US Department of Health and Human Services, Agency for Toxic Substances and Disease Resigtry. August 1995. http://www.atsdr.cdc.gov/ToxProfiles/tp69.pdf

[12] *Ibid*.

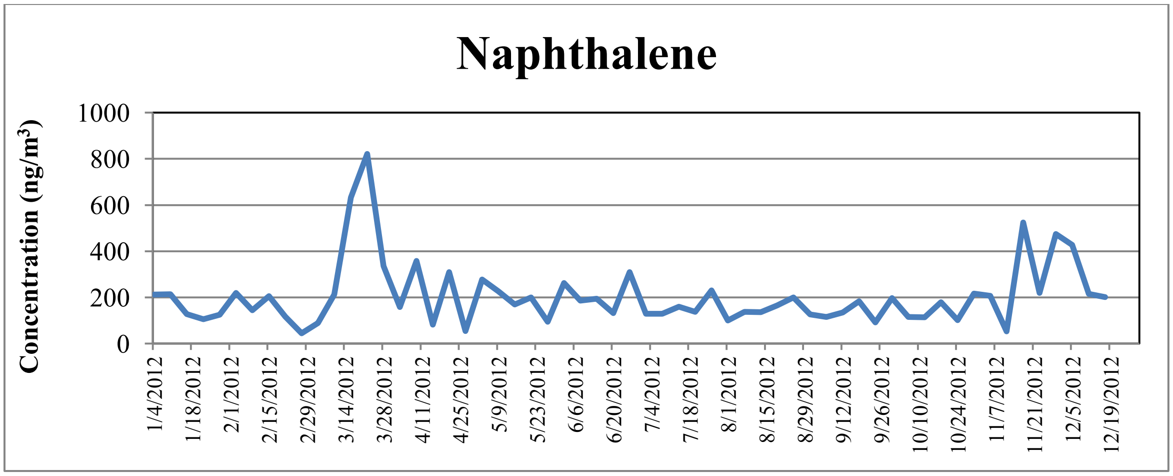

Figure 26. Naphthalene Concentration by Date 2012

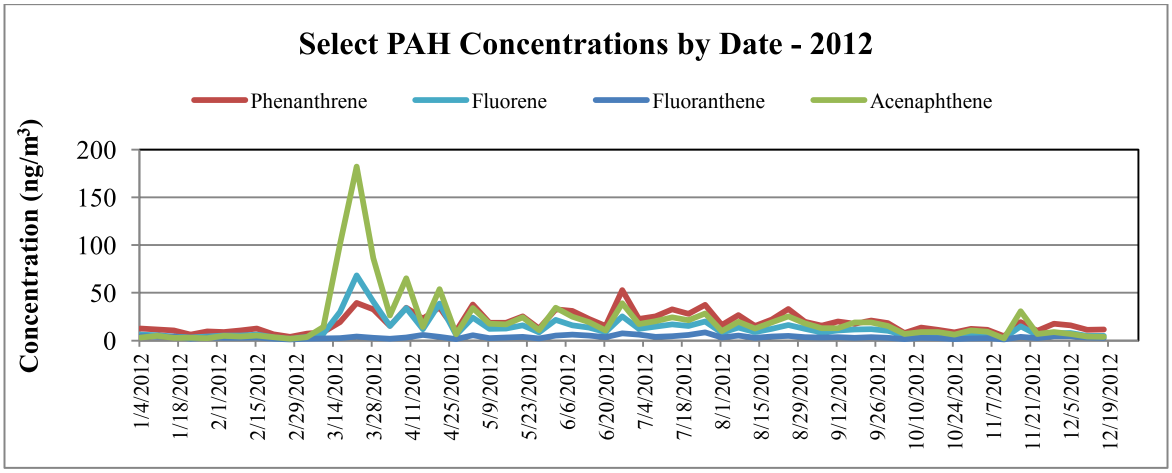

Figure 27. Select PAH Concentrations by Date 2012

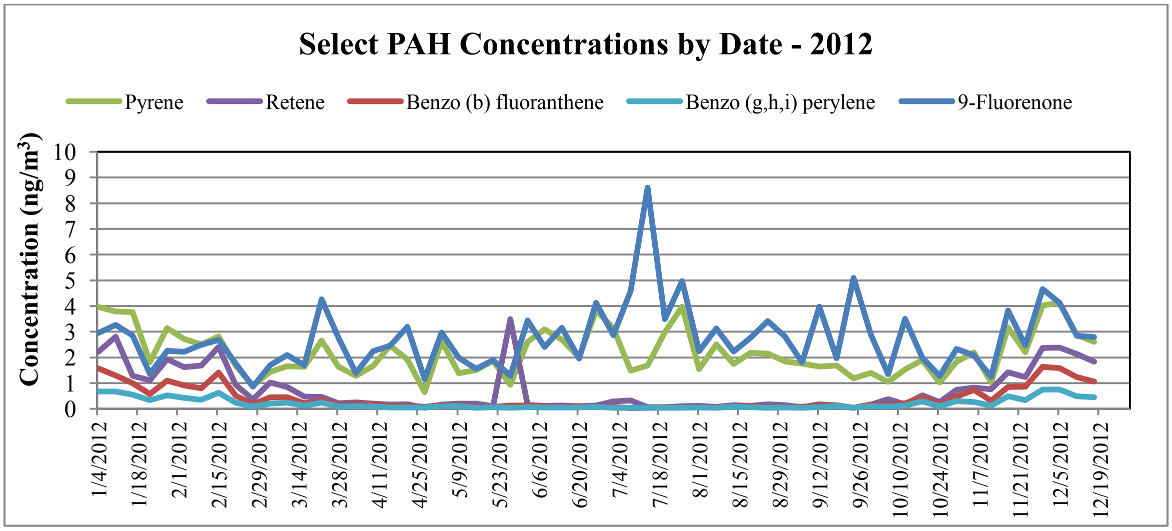

Figure 28. Select PAH Concentrations by Date 2012, ctd.

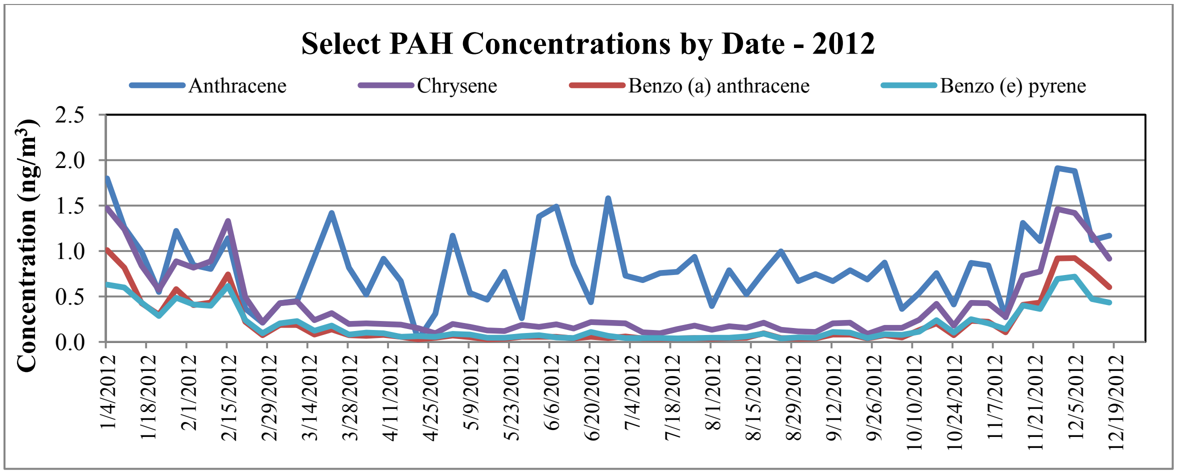

Figure 29. Select PAH Concentrations by Date 2012, ctd.

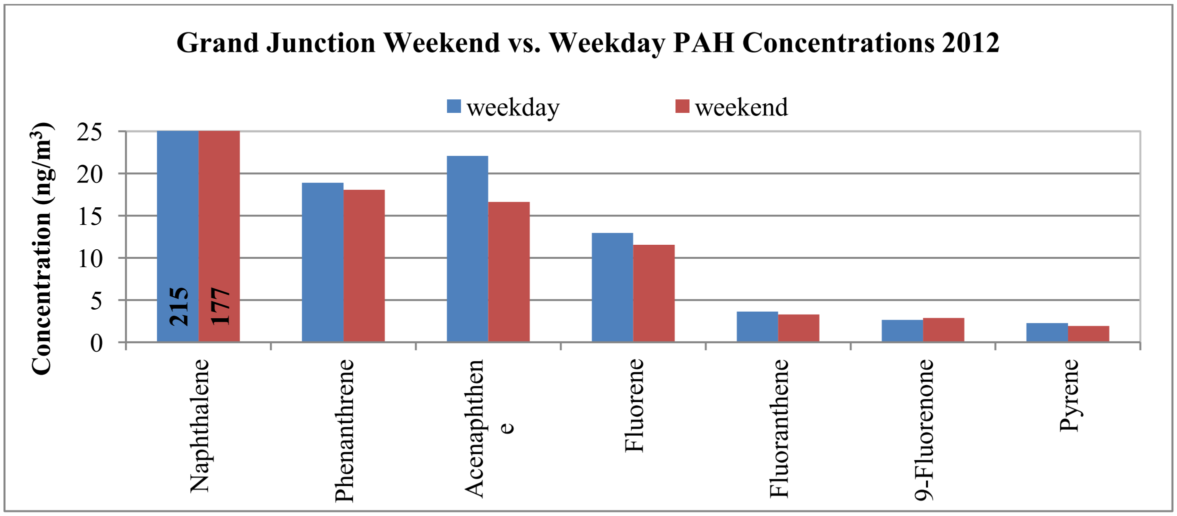

Figure 30. PAH Weekend vs. Weekday Concentrations 2012

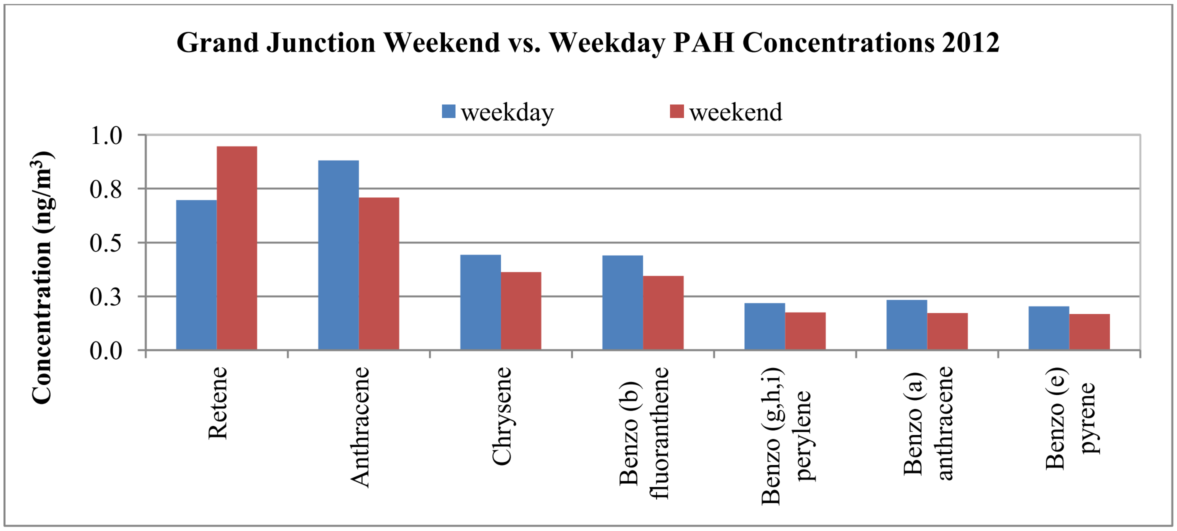

Figure 31. PAH Weekend vs. Weekday Concentrations 2012, ctd.

Figure 30 and Figure 31 are graphs of the weekend and weekday concentrations for the fourteen PAH compounds detected in greater than 90% of the samples taken in 2012. The weekday averages were larger than the weekend values for all compounds, except retene, and 9-fluorenone. Those compounds had larger weekend values than weekday values. The values for naphthalene are off the chart with a weekday average of 215 nanograms per meter cubed, and a weekend average of 177 nanograms per meter cubed. Figure 32 through Figure 34 are graphs of the annual average concentrations for the fourteen compounds detected in greater than 90% of the samples taken in 2012. The graphs show that many of the compound concentrations are increasing since 2010.

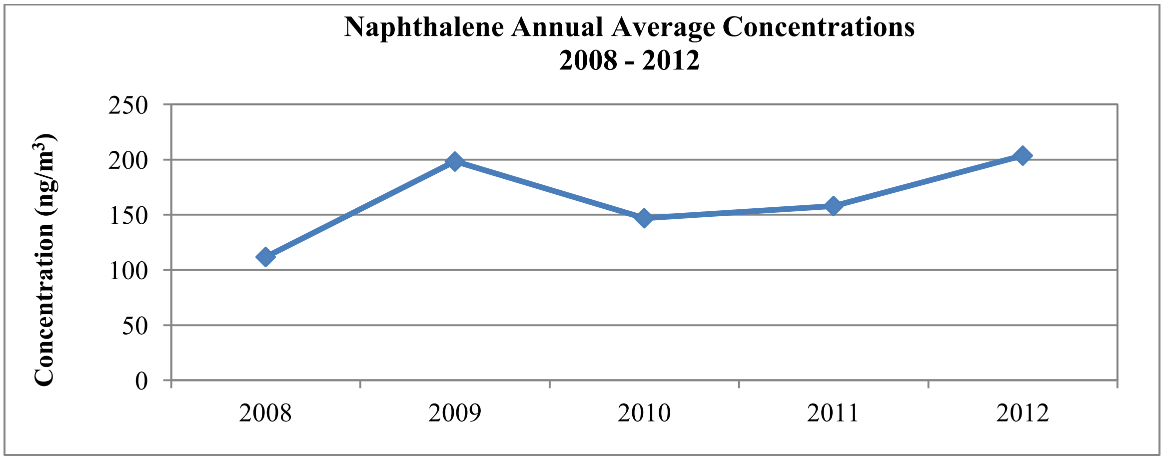

Figure 32. Naphthalene Annual Average Concentrations 2008 – 2012

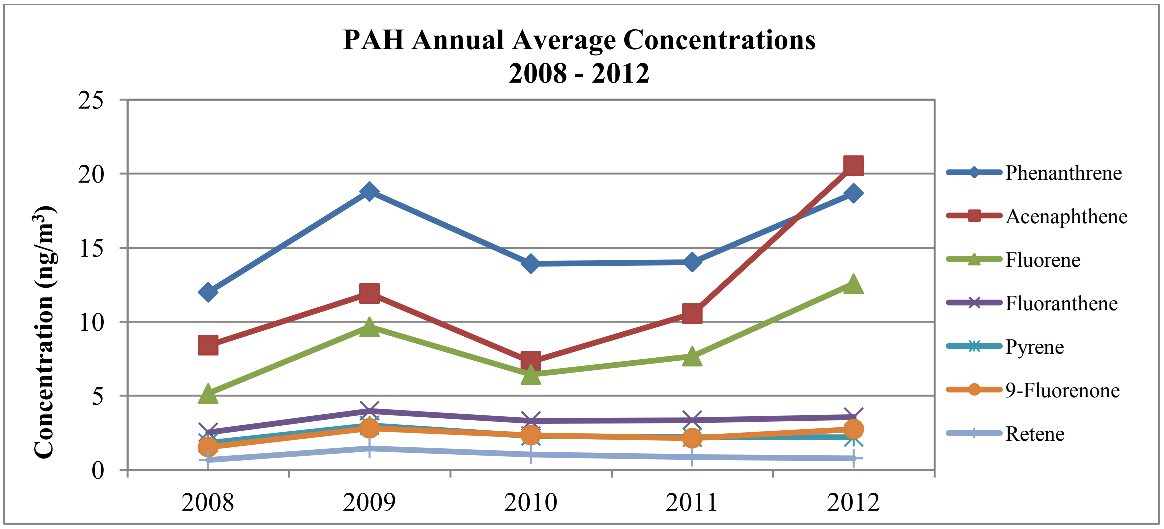

Figure 33. Select PAH Annual Average Concentrations 2008 – 2012

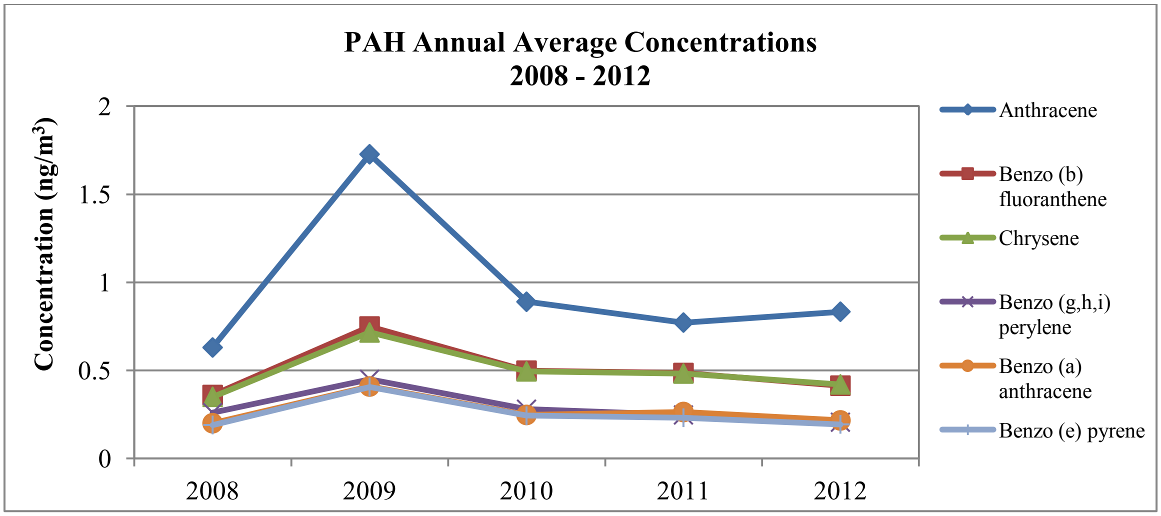

Figure 34. **Select PAH Annual Average Concentrations 2008 – 2012, ctd.**

Quality Assurance/Quality Control

Field Blanks

Periodically, the laboratory analyzes a “blank,” or unused, filter for PAH compounds. The purpose of this extra analysis is to determine if there was any contamination of the filter during manufacturing, or during laboratory processing. In 2012, the laboratory analyzed 12 “filter blanks,” filters which never left the lab. Several compounds were detected at very low levels in many of the filter blanks.

Precision of Sample Results

Precision air samples were not run in 2012. Assessing precision requires a collocated sampler at the site, and the NATTS group chose to take precision samples at other locations in the nationwide network.

VI. PM_{10} METALS

The metals data included in the initial version of this report were found to have various errors due to the contracted laboratory not following correct procedures for establishing the method detection limits (MDLs). The concentrations for some of the metals rely heavily on the MDL values, as one-half the value of the MDL is substituted for the concentration in instances where the metal is not detected during the analysis. Because it is impossible to go back and calculate the MDLs being used for the 2012 data, a new MDL study was performed by the lab in 2014. The values obtained as a result of this study will be used for the analysis of 2010-2013 metals data, in an effort to keep from losing several years’ worth of valuable data.

In previous years, antimony and total chromium were also a part of the suite of compounds CDPHE had the lab analyze for. These two compounds are not required as a part of the NATTS program. As such, when the new MDL study was performed they were dropped from the list of compounds. Any data associated with those two compounds will not be in this, or future, reports.

Summary Statistics

During the study, metals were sampled on the every sixth day schedule, for a total of 61 samples attempted.

Of those 61 samples, five were missed or voided, leaving a total of 56 samples collected (91.8% sample recovery). Table 9 shows the percentage of the samples in which each metal was detected. Arsenic, lead, manganese, and nickel were detected in 90% or more of the samples. Beryllium was never detected, while cadmium was detected in 36% of the samples.

Table 9. Metals List with 2012 Detection Rates

Compound	CAS Number	# of ND's	% ND
Manganese	**7439-96-5**	**0**	**0%**
Nickel	**7440-02-0**	**0**	**0%**
Arsenic	**7440-38-2**	**1**	**2%**
Lead	**7439-92-1**	**1**	**2%**
Cadmium	**7440-43-9**	**36**	**64%**
Beryllium	**7440-41-7**	**56**	**100%**

Bold = MQO Core Analyte

Table 10 summarizes the annual mean concentrations for each of the metals measured during the study, from 2004 through 2012, and is organized from the highest 2012 annual average concentration value to the lowest. The compounds that are listed in bold type are on the list of 19 core HAPs. The italicized compounds are those that were detected in less than 90% of the samples taken. Annual means were calculated by using one-half of the detection limits in place of the non-detect samples. Results show that manganese wasthe compound with the highest annual average. The other metals were present at lower concentrations. The manganese, nickel, and lead concentrations were higher than their 2011 values.

Table 10. Metals Data Summary 2012

Analyte	2004 Average ($\mu g/m^3$)	2005 Average ($\mu g/m^3$)	2006 Average ($\mu g/m^3$)	2007 Average ($\mu g/m^3$)	2008 Average ($\mu g/m^3$)	2009 Average ($\mu g/m^3$)	2010 Average ($\mu g/m^3$)	2011 Average ($\mu g/m^3$)	2012 Average ($\mu g/m^3$)
Manganese	**0.013**	**0.01199**	**0.01504**	**0.01523**	**0.01474**	**0.00870**	**0.00834**	**0.00882**	**0.01085**
Lead	**0.0049**	**0.00401**	**0.00433**	**0.00426**	**0.00248**	**0.00209**	**0.00205**	**0.00279**	**0.00303**
Nickel	**0.0006**	**0.00091**	**0.00119**	**0.00144**	**0.00143**	**0.00088**	**0.00180**	**0.00211**	**0.00226**
Arsenic	**0.0003**	**0.00213**	**0.00288**	**0.00422**	**0.00243**	**0.00087**	**0.00132**	**0.00067**	**0.00057**
Beryllium	***0.0001***	***0.00091***	***0.00059***	***0.00069***	***0.00019***	***0.00013***	***0.00014***	***0.00014***	***0.00013***
Cadmium	***0.0001***	***0.00035***	***0.00026***	***0.00024***	***0.00014***	***0.00023***	***0.00020***	***0.00021***	***0.00008***

Bold = MQO Core Analyte
Italic = less than 90% detection rate

Graphs

The metal compounds measured during the study are graphed in Figure 35. This figure shows that manganese, lead, and nickel were the metals with the largest average concentrations, having values of 10.85, 3.03, and 2.26 nanograms per meter cubed, respectively. In comparison, the NMP national average concentrations for these compounds in 2011 were 8.81, 3.82, and 1.27 nanograms per meter cubed, respectively.[13] Figure 36 and Figure 37 indicate that most of the metals were at low concentration levels throughout the year. There does not appear to be any seasonal trending in the metals values based on the 2012 data. Nickel has the largest amount of variability in the concentration values recorded, with values ranging from just slightly over zero to near 27 nanograms per meter cubed.

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[13] "2011 National Monitoring Programs Annual Report (UATMP, NATTS, CSATAM). US EPA. August 2013. http://www.epa.gov/ttnamti1/files/ambient/airtox/2011nmpreport.pdf.

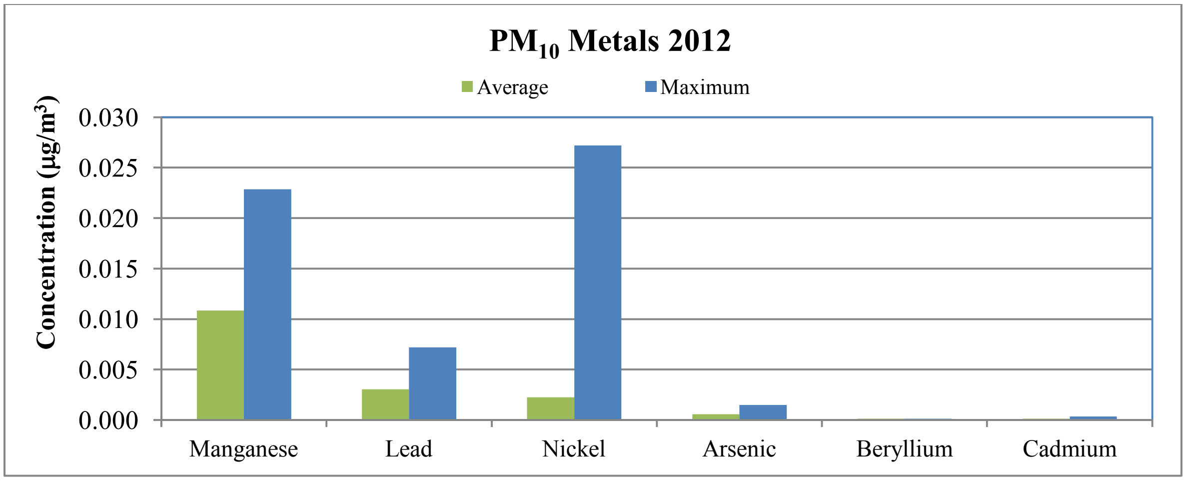

Figure 35. PM_{10} Metals Average and Maximum Concentrations 2012

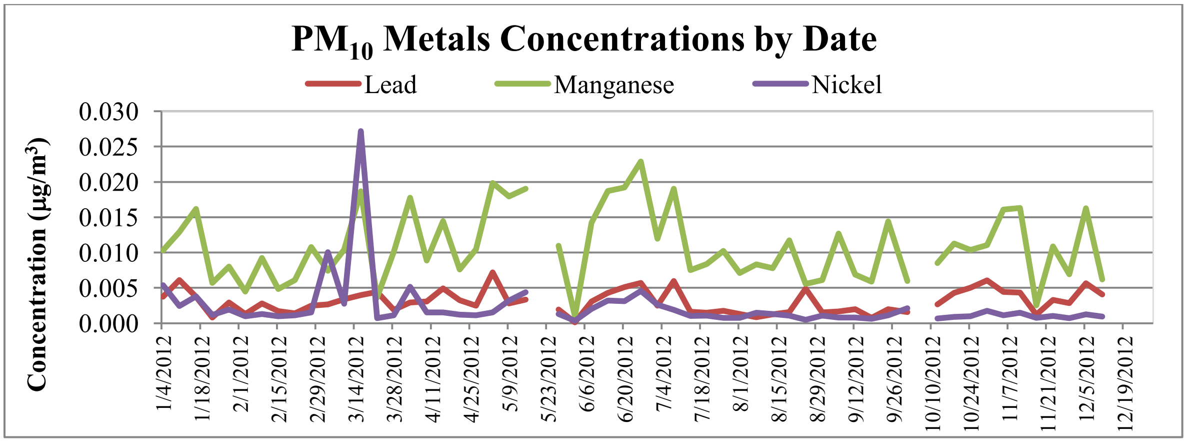

Figure 36. PM_{10} Metals Concentrations by Date 2012

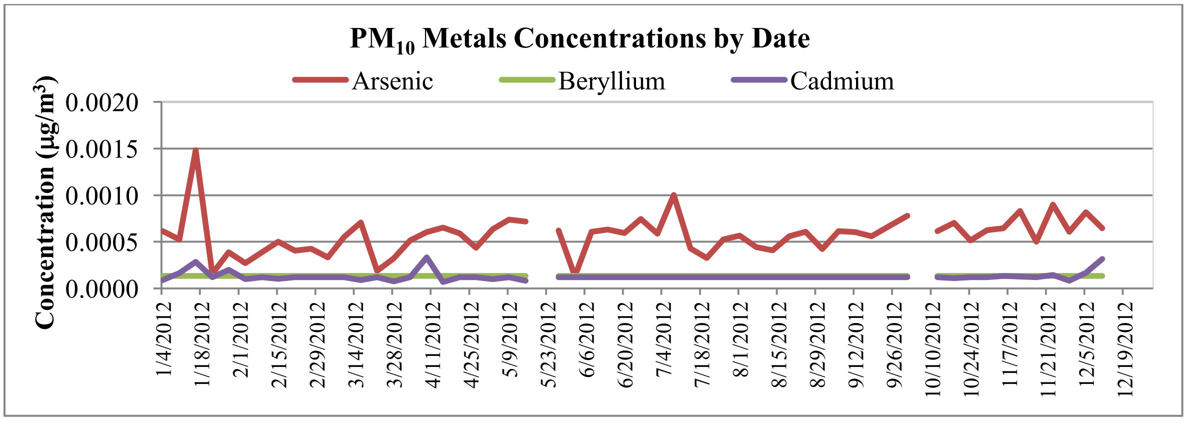

Figure 37. PM_{10} Metals Concentrations by Date 2012, ctd.

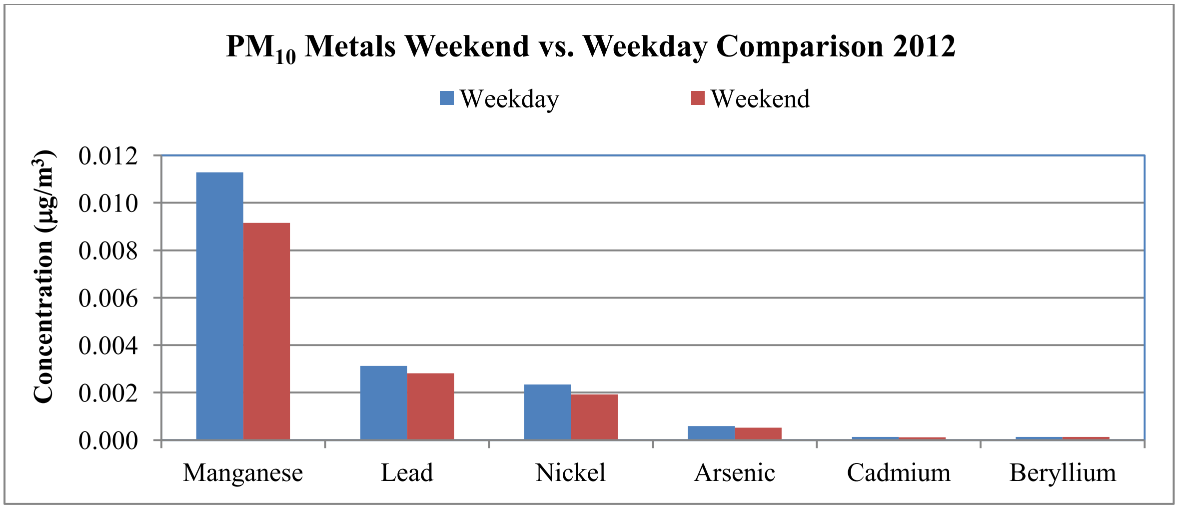

Figure 38. PM$_{10}$ Metals Weekend versus Weekday Comparison 2012

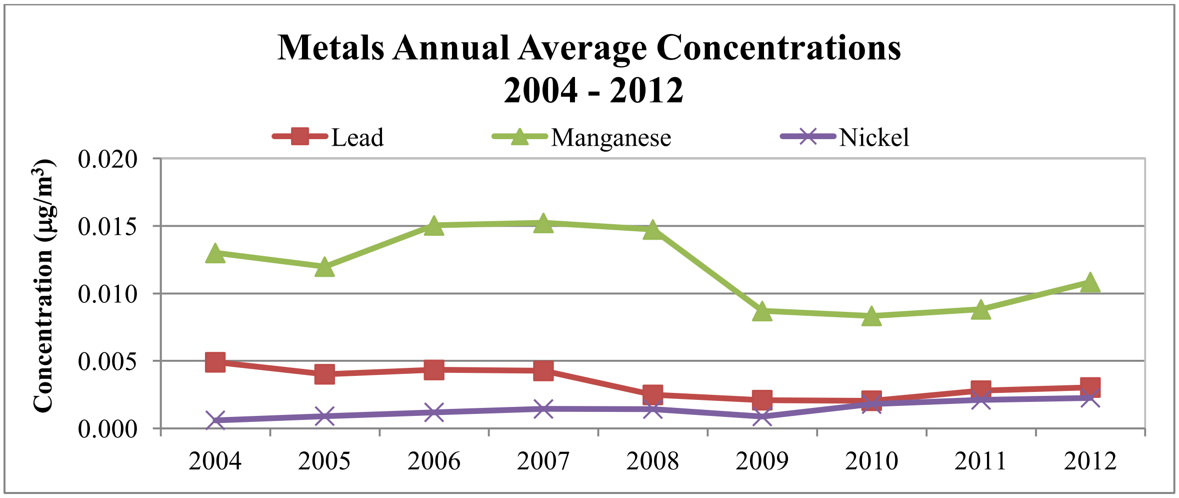

Figure 39. PM$_{10}$ Metals Annual Average Concentrations 2004 – 2012

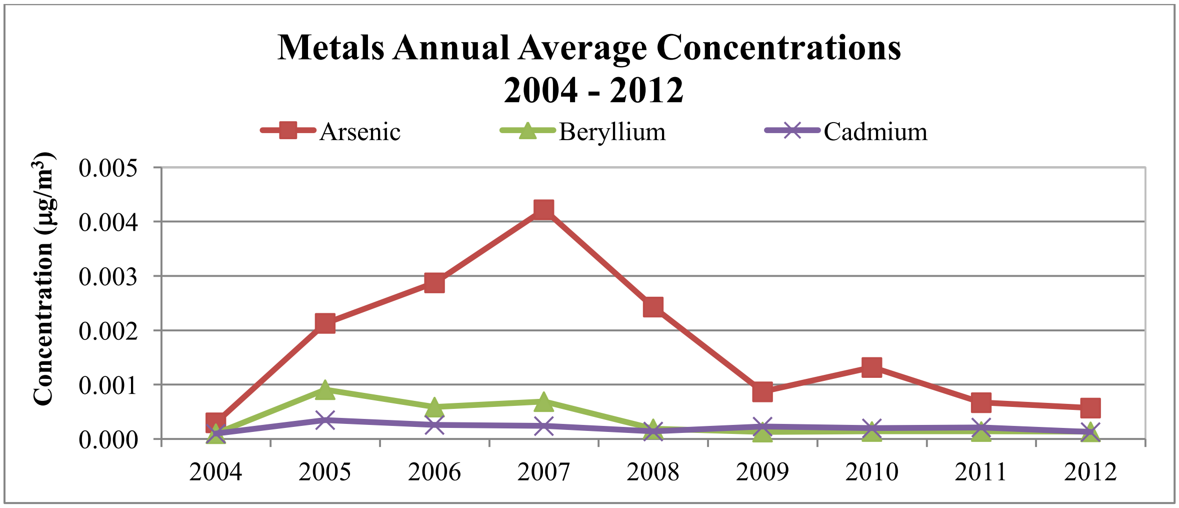

Figure 40. PM$_{10}$ Metals Annual Average Concentrations, 2004 – 2012

Figure 38 is a chart of the weekend versus weekday concentrations for the PM_{10} metals. All of the compounds had weekend averages that were less than the weekday averages. Cadmium, and beryllium were rarely detected, meaning the concentration values are heavily dependent on their MDL values, thus giving weekend versus weekday concentrations that are equal. Figure 39 and Figure 40 are graphs of the annual average concentrations for each of the PM_{10} metals from 2004 through 2012. The graphs appear to show a general downward trend in the concentration values for all the compounds but nickel. A calculation of the 3-year averages from 2004 to 2006, 2007 to 2009, and 2010 to 2012, shows a decrease in concentrations (going from the first 3-year average to the last 3-year average) for all compounds except nickel, which showed increases of 39% (1st 3-year average to 2nd 3-year average), and 67% (2nd 3-year average to 3rd 3-year average). At this time, it is unclear what is behind this phenomenon.

Quality Assurance/Quality Control

Field and Filter Blanks

Periodically, the laboratory analyzes a “blank,” or unused, filter for metals. The purpose of this extra analysis is to determine if there was any contamination of the filter during manufacturing or during laboratory processing. In 2010, CDPHE switched to using a different analytical laboratory. As a result of this switch, no blank filters were analyzed, and therefore, no data was available from the lab for year 2010. In 2004, total chromium contamination was a problem for the national air toxics network. These chromium contamination findings were believed to be related to the use of metal knives in cutting individual filters from the giant sheets prepared at the factory. At the extremely low levels of metals in ambient air that the national air toxics network is assessing, such filter contamination is a concern. The national project team evaluated new filter materials and sampling methods, and recommended changing to Teflon filters, and low volume PM_{10} samplers in early 2005.

Precision of Sample Results

Twelve duplicate precision samples were run in 2012. The agreement between samples was not good, with annual average percent differences ranging from 42% for arsenic to 253% for nickel. The annual average percent difference was obtained by taking the average of the percent differences between the primary and duplicate sample concentration values for each compound in each of the 12 duplicate samples taken. These large differences are likely due to inefficient extraction methods being used by the lab.

VII. HEXAVALENT CHROMIUM

Summary Statistics

Hexavalent chromium data collected at the Grand Junction – Powell station in 2012 are presented in this section. In 2005, a new hexavalent chromium sampler was added to the Grand Junction site. The technical steering committee made this decision for the nationwide air toxics monitoring network. The previous method only measured total chromium and could not distinguish between the trivalent (Cr^{3+}) and the hexavalent (Cr^{6+}) forms. These two forms are quite different in their health effects. The Cr^{6+} form is a carcinogen, while the Cr^{3+} form is not. This new method is described in the document, “Hexavalent Chromium Method Development: Final Report, Work Assignment 5-03,” by Eastern Research Group in Morrisville, North Carolina on September 30, 2005. Note that, due to its sensitivity, this method gives results in nanograms per cubic meter of air (ng/m^3), a unit one thousand times lower than the micrograms per cubic meter ($\mu g/m^3$) used elsewhere in this report.

During the year long period, hexavalent chromium was sampled on an every sixth day basis, with several make-up samples taken throughout the year to replace missed samples. A total of 61 samples were attempted, with 60 being analyzed (98.4% sample recovery). Table 11 shows that hexavalent chromium was detected in 60 percent of the samples taken in 2012. Table 12 shows the average hexavalent chromium concentrations recorded from 2005 through 2012. The annual mean was calculated by using one-half of the minimum detection limit in place of the non-detect samples. This is an accepted conservative technique for calculating annual values when some of the samples were less than the laboratory's ability to measure. The average values in 2012 are less than those from 2011.

Table 11. Hexavalent Chromium Sample Summary 2009-2012

Compound	CAS Number	2009		2010		2011		2012	
		# of ND's	% ND	# of ND's	# of ND's	# of ND's	% ND	# of ND's	% ND
Hexavalent Chromium	1854-02-99	38	61%	18	38%	17	29%	24	40%

Table 12. Hexavalent Chromium Average and Maximum Concentrations 2009-2012

Analyte	2005 Average (ng/m^3)	2006 Average (ng/m^3)	2007 Average (ng/m^3)	2008 Average (ng/m^3)	2009 Average (ng/m^3)	2010 Average (ng/m^3)	2011 Average (ng/m^3)	2012 Average (ng/m^3)
Hexavalent Chromium	0.0234	0.0270	0.0155	0.0208	0.0082	0.0125	0.0160	0.0128

Graphs

Figure 41 shows the annual average and maximum hexavalent chromium concentrations for 2005 through 2012. Figure 42 shows hexavalent chromium concentrations during the 2012 calendar year. All but three concentrations were less than 0.050 ng/m^3 for the year. In comparison, the NMP national average concentration for hexavalent chromium in 2011 was 0.024 nanograms per meter cubed.[14] The maximum concentrations in 2009, 2010, 2011, and 2012 occurred on September 28, 2009, June 1, 2010, December 29, 2011, and May 3, 2012.

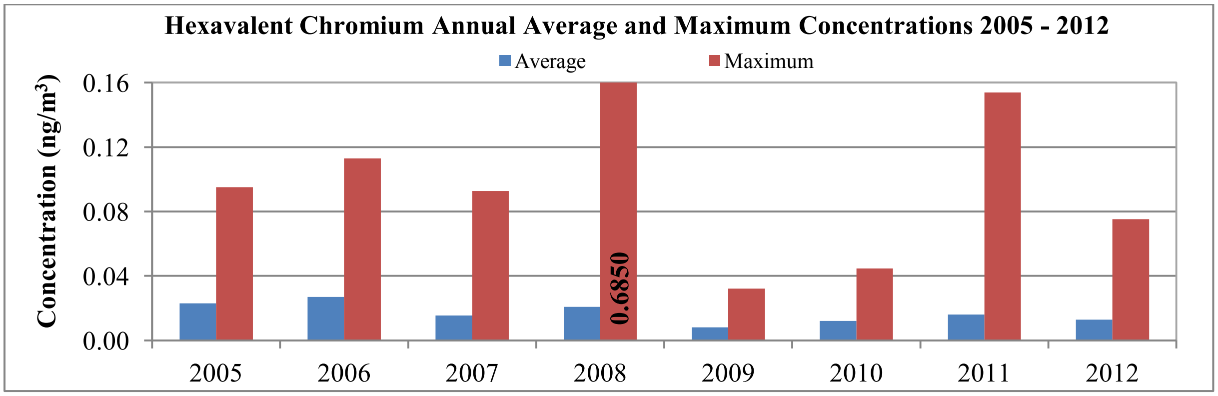

Figure 41. Hexavalent Chromium Annual Average and Maximum 2009-2012

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[14] "2011 National Monitoring Programs Annual Report (UATMP, NATTS, CSATAM). US EPA. August 2013. http://www.epa.gov/ttnamti1/files/ambient/airtox/2011nmpreport.pdf.

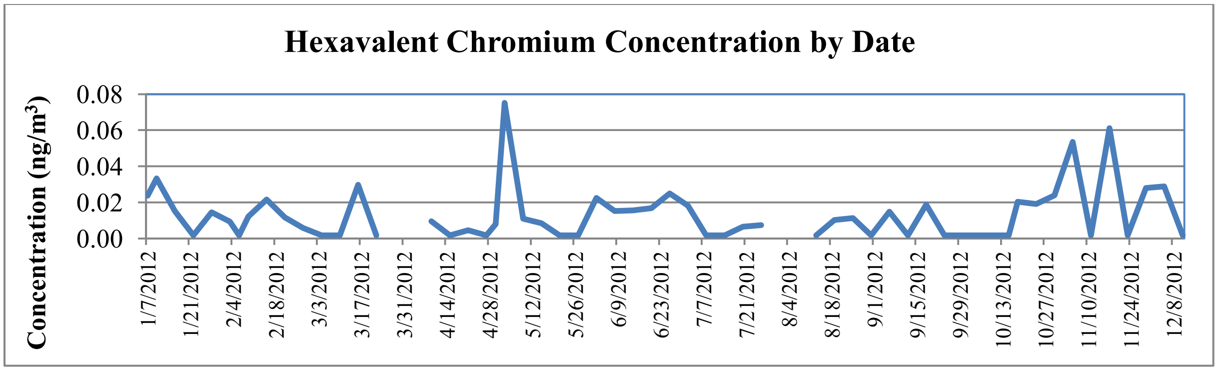

Figure 42. **Hexavalent Chromium Concentrations by Date 2012**

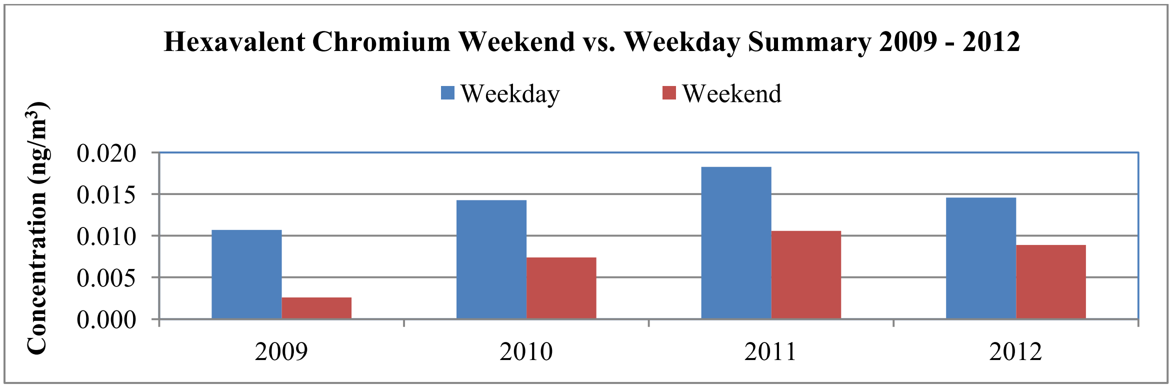

Figure 43. **Hexavalent Chromium Weekend vs. Weekday Summary**

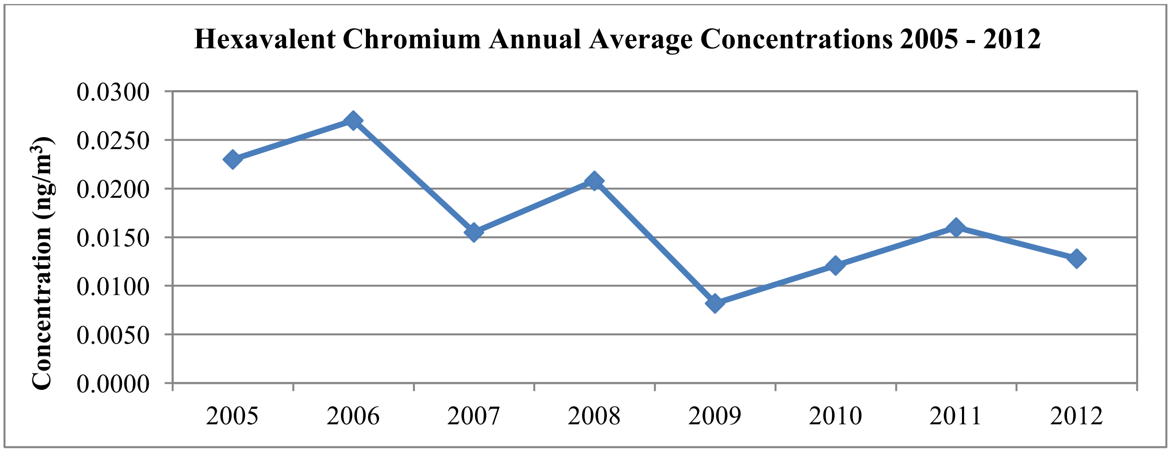

Figure 44. **Hexavalent Chromium Annual Average Concentrations 2005 – 2012**

Figure 43 is a summary of the weekday versus weekend hexavalent chromium concentrations for 2009 through 2012. The average weekday concentration is larger than the weekend concentration. This is expected, as hexavalent chromium is primarily used in industrial processes and would be used during the week. Figure 44 is a graph of the annual average hexavalent chromium concentrations from 2005 through 2012. The graph indicates a general downward trend in the concentrations for this compound. A calculation of the 3-year averages from 2005 through 2007, and 2008 through 2010, shows a decrease from 0.022 to 0.014 ng/m^3, which is a decrease of nearly 40%.

Quality Assurance/Quality Control

Field Blanks

Once a month, a filter was transported to the field, placed on the sampler, and immediately removed, without having any air passed through it. These "field blanks" were taken to assess whether contamination in the field or the sampling materials is significant. Out of 12 blanks taken, none showed detectable levels of hexavalent chromium. Unlike total chromium samples discussed in the previous section, hexavalent chromium samples are not potentially compromised by high blank levels. This is good, because the concentrations of hexavalent chromium are more relevant in risk assessment studies than total chromium.

Precision of Sample Results

Six times during the year, a laboratory split sample was analyzed. An incoming sample was split into two separate samples, and then analyzed by the lab. A comparison of the results obtained gave an idea of the precision of the analytical method. In general, the duplicate samples showed good agreement, varying from a minimum percent difference of -9% to a maximum of 17%.

VIII. PM$_{10}$

Sample Statistics Summary

The Colorado Department of Public Health and Environment operates samplers for particulate matter 10 microns or less in diameter (PM$_{10}$) at the Grand Junction – Powell station. These samplers serve to indicate the status of Grand Junction regarding the National Ambient Air Quality Standards (NAAQS) for PM$_{10}$ and PM$_{2.5}$. Results of the statewide particulate matter monitoring network are discussed in "Colorado: 2011 Air Quality Data Report" by the Air Pollution Control Division. In 2012, 131 samples were attempted, and 128 were collected on the primary sampler. However, 26 samples from the primary sampler were voided at the lab due to equipment failure, and/or lab errors. For 14 of the 26 missed/voided sample dates, the collocated sampler was in operation, and those values replaced the missing values for the primary sampler. This brings the final data recovery rate to 88.5%.

Table 13. PM$_{10}$ Average Concentrations 2004 – 2012

Analyte	2004 Average (µg/m^3)	2005 Average (µg/m^3)	2006 Average (µg/m^3)	2007 Average (µg/m^3)	2008 Average (µg/m^3)	2009 Average (µg/m^3)	2010 Average (µg/m^3)	2011 Average (µg/m^3)	2012 Average (µg/m^3)
PM$_{10}$ (every 3rd day)	29.0	25.6	30.1	29.6	29.5	24.8	22.4	18.4	22.2
PM$_{10}$ (every 6th day)	29.2	25.4	29.8	28.9	29.6	25.9	19.2	18.4	20.3

Table 14. PM$_{10}$ Maximum Concentrations 2004 – 2012

Analyte	2004 Max (µg/m^3)	2005 Max (µg/m^3)	2006 Max (µg/m^3)	2007 Max (µg/m^3)	2008 Max (µg/m^3)	2009 Max (µg/m^3)	2010 Max (µg/m^3)	2011 Max (µg/m^3)	2012 Max (µg/m^3)
PM$_{10}$ (every 3rd day)	102.1	197.5*	98.3	84.7	116.1	68.4	155.0	41.0	77.0
PM$_{10}$ (every 6th day)	31.6	61.5	65.7	68.8	83.5	68.4	57.0	39.0	44.0

Table 13 lists the average concentrations observed at the Grand Junction site from 2004 through 2012. The table lists average concentrations for the entire every third day sampling period, as well as concentrations obtained on the same days that the air toxics analyzers were in operation (every sixth day), from 2005 through 2012. The averages are similar for the third and sixth day sampling, and are less than half of the former annual standard level of 50 micrograms per meter cubed. The maximum value observed in 2012 was 77.0 micrograms per meter cubed.

Table 14 lists the maximum concentrations observed at the Grand Junction site from 2004 through 2012. The table lists the maximum concentrations for the entire every third day sampling period, as well as concentrations obtained on the same days that the air toxics analyzers were in operation (every sixth day), from 2009 through 2012. The maximums are similar for some years, but quite different for others. To date, the highest concentration observed during the every third day sampling period was 197.5 micrograms per meter cubed in 2005.

Graphs

Figure 45 is a graph of the PM_{10} concentration data recorded every sixth sampling day. The graph does not appear to indicate any seasonal variation. A large part of the data set was voided due to laboratory processing errors.

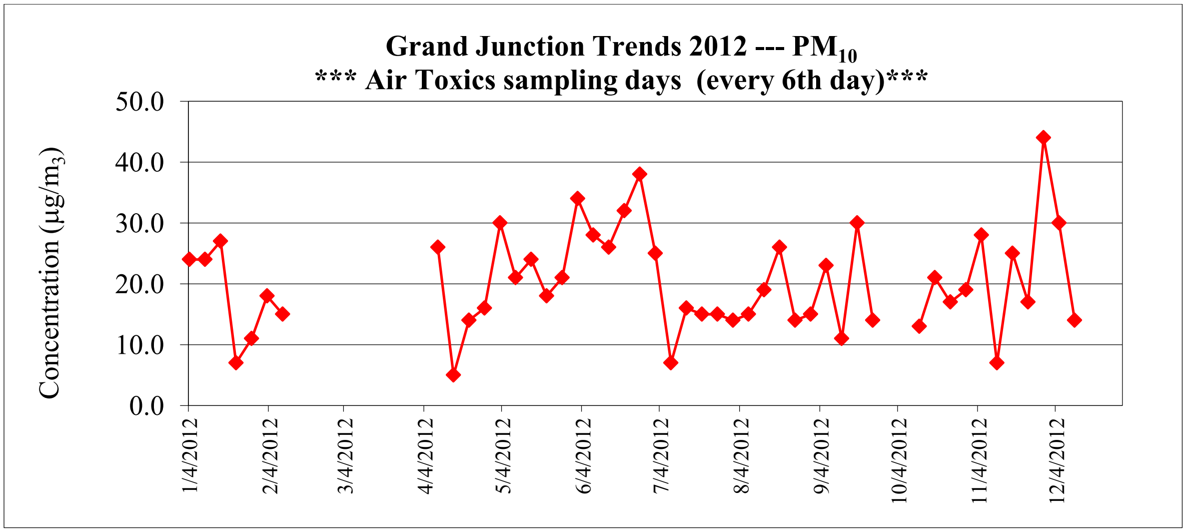

Figure 45. **PM_{10} Concentrations by Date (every 6th Day)**

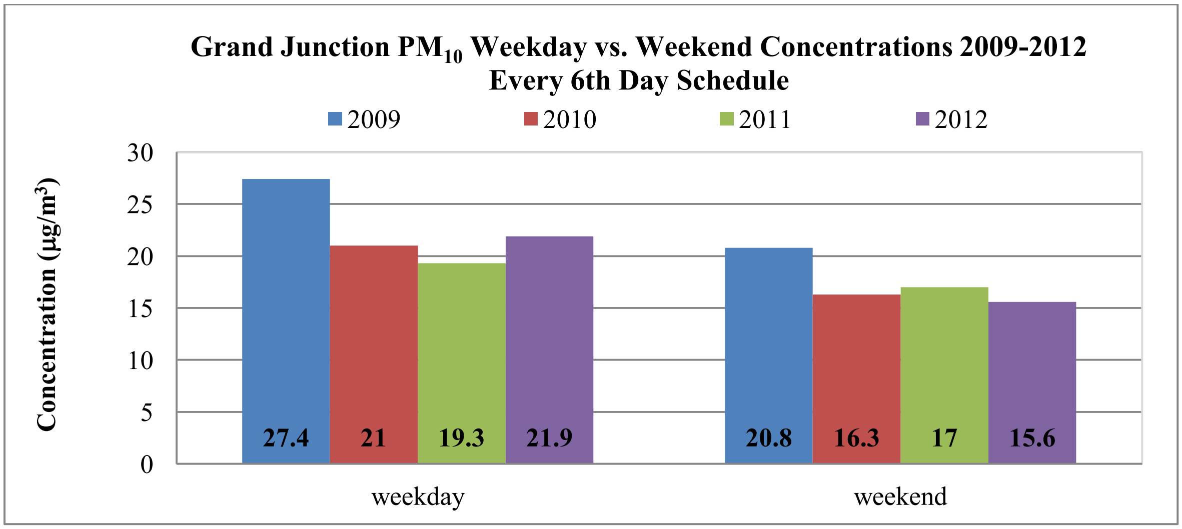

Figure 46. **PM_{10} Weekend vs. Weekday Comparison 2009-2012, every 6th day**

Figure 46 is a graph of the weekend versus weekday concentrations for PM_{10} on the every sixth day sampling schedule. The weekday average is larger than the weekend average. PM_{10} is dominated by surface disturbance of earth materials (street sand, windblown dust). The PM_{10} levels are subject to change due to daily weather conditions. Figure 47 is a graph of the annual average PM_{10} concentrations from 2004 through 2012, for the every third day sampling period. Figure 48 is a graph of the 24-hour maximum PM_{10} concentrations from 2004 through 2012, for the every third day sampling period.

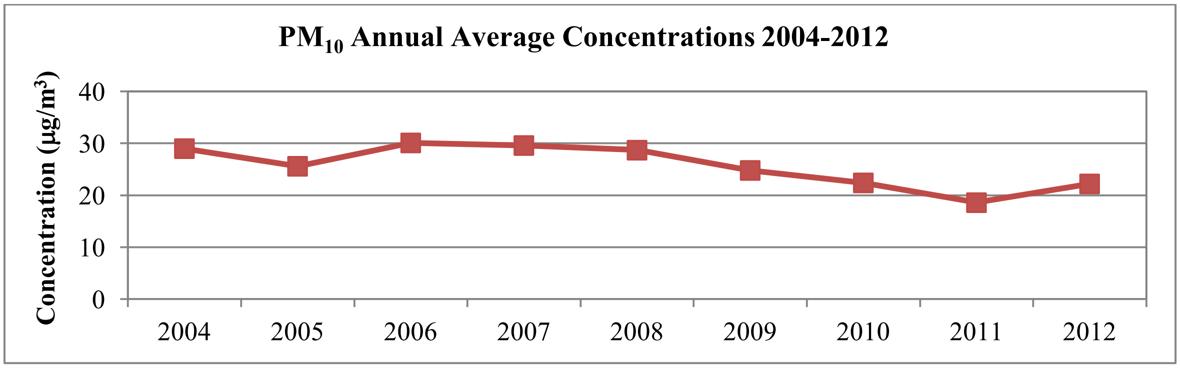

Figure 47. **PM_{10} Annual Average Concentrations 2004 – 2012**

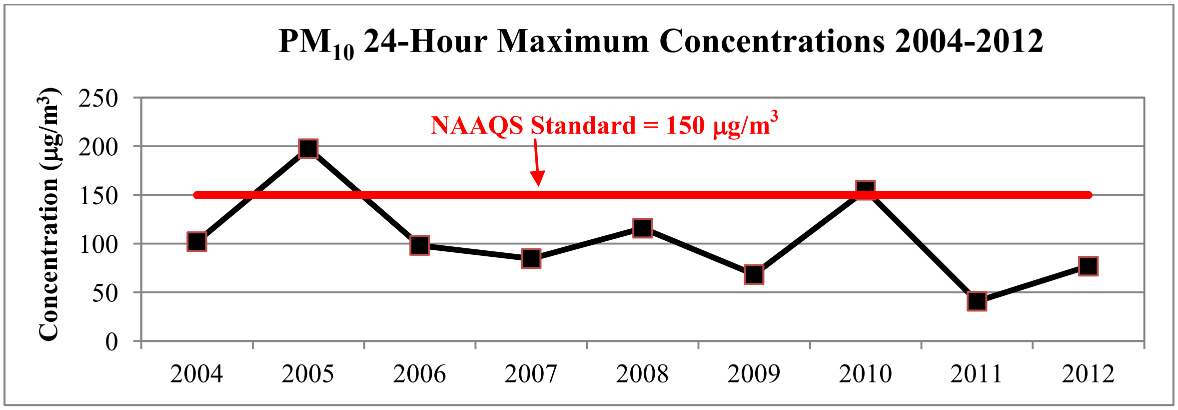

Figure 48. **PM_{10} Annual Maximum Concentrations 2004 – 2012**

Quality Assurance/Quality Control

Field Blanks

There were six field blanks taken for PM_{10}.

Precision of Sample Results

Collocated samples were run once every sixth day, half as frequently as the primary samples were run. This is done in an effort to validate the collected data. There is good agreement between the primary and collocated sampler concentrations.

IX. $PM_{2.5}$

Sample Statistics Summary

The Colorado Department of Public Health and Environment operates samplers for particulate matter 2.5 microns or less in diameter ($PM_{2.5}$) at the Grand Junction – Powell station. This sampler serves to indicate the status of Grand Junction regarding the National Ambient Air Quality Standards (NAAQS) for and $PM_{2.5}$. Results of the statewide particulate matter monitoring network are discussed in "Colorado: 2012 Air Quality Data Report" by the Air Pollution Control Division. The National Air Toxics Trends Study chose to monitor air toxics in Grand Junction because of the availability of $PM_{2.5}$ speciation data, which gives insight into air toxics in particulate matter. It should be noted here, however, that the speciation sampler previously located in Grand Junction was removed, and relocated to the state's NCore site in Denver at the end of 2009. The $PM_{2.5}$ data discussed here is the gravimetric filter data only, and does not include any speciated results. In 2012, 131 samples were attempted, and 125 were collected. Twenty-three of these samples were voided at the lab, however, due to equipment malfunctions, and/or lab errors, bringing the final data recovery percentage to 77.9%.

Table 15. $PM_{2.5}$ Average Concentrations 2004-2012

Analyte	2004 Average (µg/m^3)	2005 Average (µg/m^3)	2006 Average (µg/m^3)	2007 Average (µg/m^3)	2008 Average (µg/m^3)	2009 Average (µg/m^3)	2010 Average (µg/m^3)	2011 Average (µg/m^3)	2012 Average (µg/m^3)
$PM_{2.5}$ (3rd day)	10.4	8.4	9.7	9.5	9.1	9.8	9.0	7.1	7.3
$PM_{2.5}$ (6th day)	10.4	8.0	9.8	9.0	8.9	10.5	8.4	6.8	7.2

Table 16. $PM_{2.5}$ 24-Hour Maximum Concentrations 2004-2012

Analyte	2004 Max (µg/m^3)	2005 Max (µg/m^3)	2006 Max (µg/m^3)	2007 Max (µg/m^3)	2008 Max (µg/m^3)	2009 Max (µg/m^3)	2010 Max (µg/m^3)	2011 Max (µg/m^3)	2012 Max (µg/m^3)
$PM_{2.5}$ (1st max)	36.3	19.0	28.5	30.7	27.8	59.1	43.3	23.9	28.3
$PM_{2.5}$ (98th percentile)	31.6	18.0	24.0	26.0	25.0	41.0	37.0	22.0	24.0

Table 15 lists the annual average $PM_{2.5}$ concentrations at the Grand Junction sites for 2004 through 2012. $PM_{2.5}$ emissions are generated by agriculture, and the combustion of automobile fuels, coal, wood, etc., as well as by secondary formation from other available atmospheric compounds. The table lists concentrations for the entire every third day sampling period, for 2004 through 2012, as well as the subset of concentrations obtained on the same days that the air toxics analyzers were in operation (every sixth day), for 2006 through 2012. The averages are very similar for the third and sixth day sampling in 2012, and are less than half of the annual standard level of 15 micrograms per meter cubed. lists the 24-hour first maximum, and 98th percentile maximum values for 2004 through 2012. The maxima for the third and sixth day sampling in 2012 are the same, at 28.3 micrograms per cubic meter, and below the 24-hour maximum standard of 35 micrograms per meter cubed.

Graphs

A graph of the daily concentration values for the every sixth day sampling subset is shown in Figure 49. They show that the $PM_{2.5}$ concentrations are generally pretty consistent throughout the year, but tend to vary more during the winter months, when there is more smoke in the air from agricultural burning, and household wood burning. There is a large section of data that was voided due to lab processing errors.

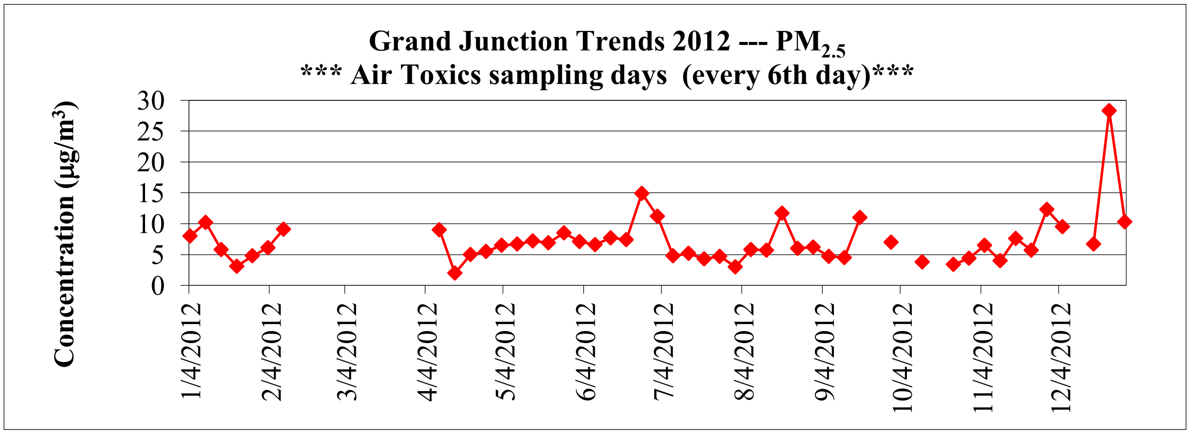

Figure 49. **$PM_{2.5}$ Concentration by Date, Every 6th Day Sampling 2012**

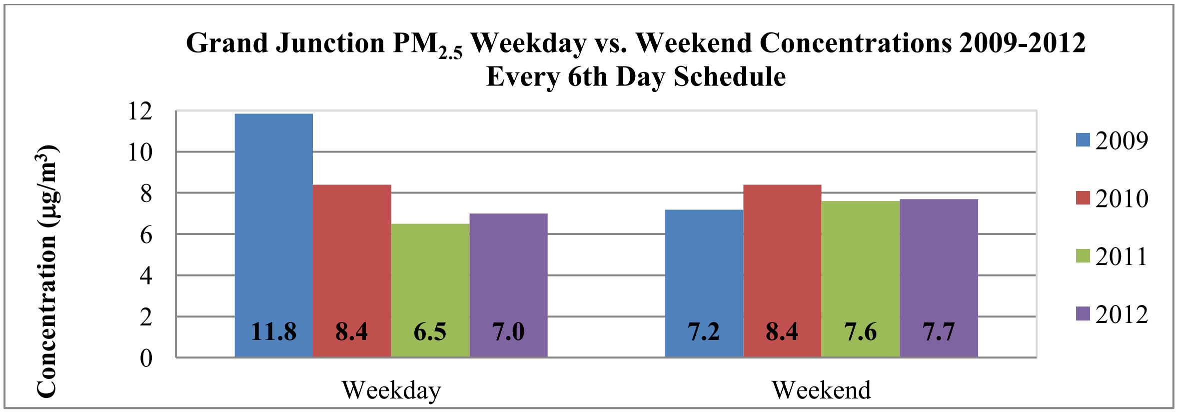

Figure 50. **$PM_{2.5}$ Weekend vs. Weekday Comparison 2009-2012, every 6th day**

Figure 50 shows how the weekend versus weekday average concentrations compare for 2009-2012, for the every 6th day sampling schedule. In 2009, weekday averages were larger than the weekend averages, since then, the weekend values have tended to be higher than the weekday values. The 2012 weekday averages have increased slightly since 2011. The weekend averages have been variable since 2009. Figure 51 shows the annual average concentrations for $PM_{2.5}$ for 2004 through 2012. The average trend seems to be decreasing since 2009.

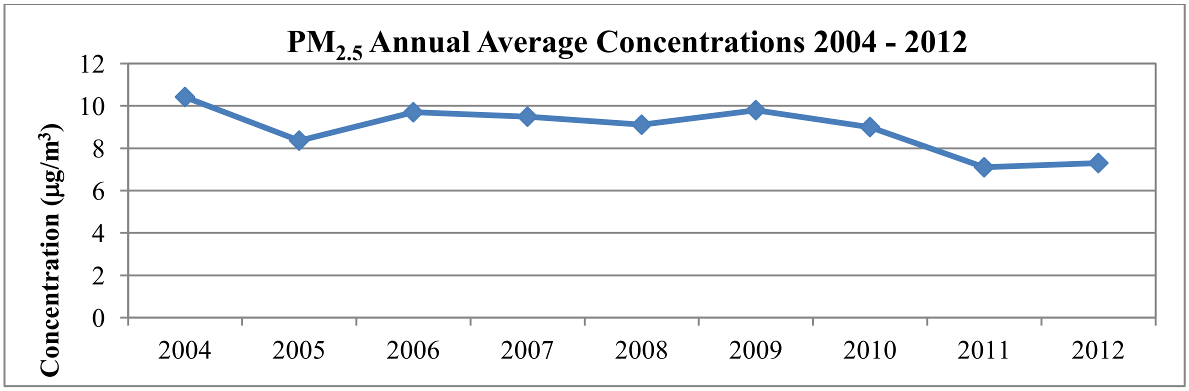

Figure 51. **$PM_{2.5}$ Annual Average Concentrations 2004 – 2012**

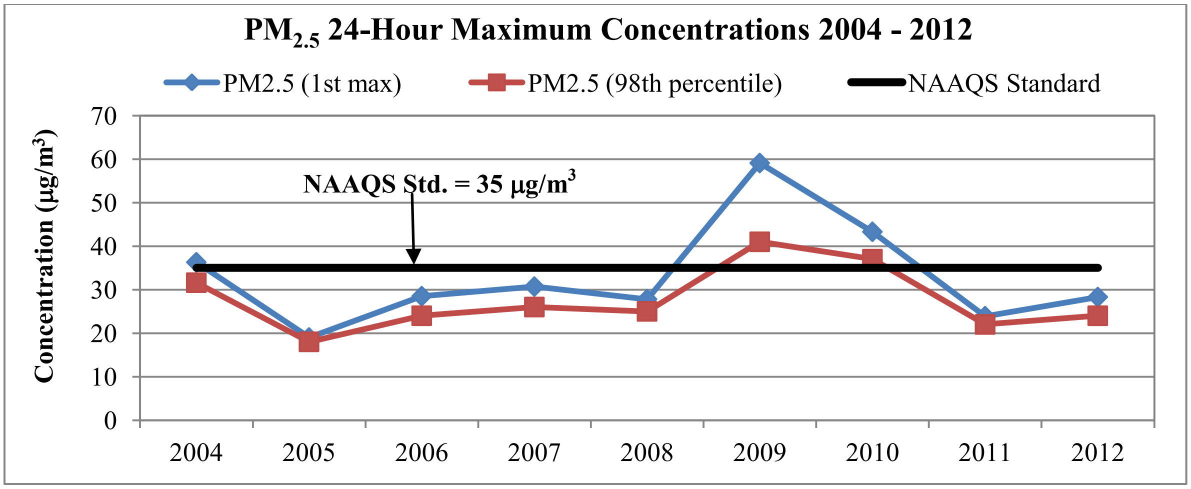

Figure 52. **$PM_{2.5}$ Annual Average Concentrations 2004 – 2012**

Figure 52 is a graph of the maximum 24-hour fine particulate concentration values. The line with the diamond markers is the first maximum concentration value, while the line with the squares is the 98th percentile value. The straight black line indicates the level of the standard, 35 micrograms per meter cubed.

Quality Assurance/Quality Control

Field Blanks

There were three field blanks taken for $PM_{2.5}$.

Precision of Sample Results

No collocated samples were run for $PM_{2.5}$.

X. METEOROLOGY

A meteorological tower at the Pitkin shelter site measures wind speed, wind direction, relative humidity, and temperature. The 2012 wind rose is shown below. The "arms" of this diagram show the percentage of the time that the wind blew from each direction. The shading on each arm indicates the wind speeds associated with each direction. Each of the concentric rings, moving outward, signifies an additional four percent of the time. For example, about 15% of the winds are from the east. Wind speeds in the ranges of 0.5 to 2.1 meters per second (m/s) or 2.1 to 3.6 m/s are the most frequent.

The wind rose shows that winds follow a daily pattern typical of river valleys. At night, the winds come from the southeast quarter, flowing down river. During the day, heating of the air causes flow reversals, and flow comes from the northwest.

A look at the highest concentrations days for each pollutant indicated that some days showed maxima for more than one air pollutant. Many of these dates are in the fall or winter period, which indicates possible local temperature inversions and limited air mixing, thus allowing pollutants of all types to build up in the area.

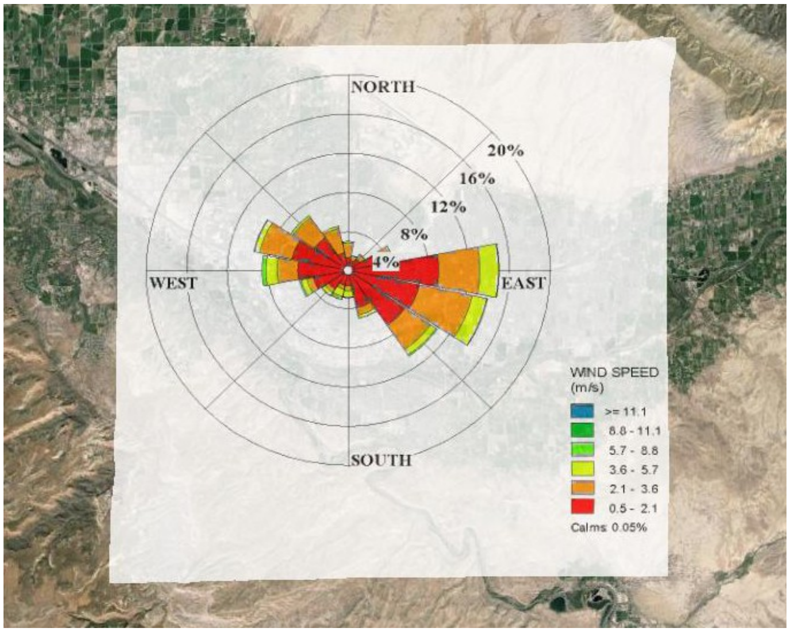

Figure 53. Wind Rose for Grand Junction 2012

XI. DATA CORRELATIONS AND DISCUSSION

The data presented below are the results of several correlation comparisons between the particulate concentrations, and various other air toxics compound concentrations.

Carbonyl Correlations and Sample Composition

Carbonyl compounds are known to have adverse effects on human health. They can be emitted directly from primary sources (motor vehicle emissions, and incomplete combustion), or can be formed secondarily via atmospheric photo-oxidation reactions.[15] They play an important role in the formation of ozone in the atmosphere, and are of great interest to atmospheric researchers, as is particulate matter. Particulates are a mixture of solid particles and liquid droplets found in the air. Of interest to researchers are two different classes of particulates: coarse (having a diameter of 10 micrometers or less), and fine (having a diameter of 2.5 micrometers or less). These particles are small enough to be inhaled deep into the lungs, and cause serious health problems. Fine particulates are the major cause of visibility issues in many parts of the U.S. A correlation of the annual average carbonyl concentration data was performed with both the PM_{10}, and $PM_{2.5}$ annual average data sets. The results of the correlation are presented in Table 17.

Table 17. Correlation Coefficient Values for Carbonyls-Particulates

Analyte	**r - PM_{10}**	**r-$PM_{2.5}$**
Acetone	0.778	0.515
Acetaldehyde	**0.633**	**0.512**
Formaldehyde	**0.879**	**0.523**
Butyraldehyde	0.774	0.293
Benzaldehyde	0.869	0.402

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[15] Wang et al., "Seasonal Variation and Source Apportionment of Atmospheric Carbonyl Compounds in Urban Kaohsiung, Taiwan." *Aerosol and Air Quality Research,* 10: 559–570, 2010. http://aaqr.org/VOL10_No6_December2010/5_AAQR-10-07-OA-0059_559-570.pdf

Analyte	**r - PM_{10}**	**r-$PM_{2.5}$**
Crotonaldehyde	0.838	0.467
Propionaldehyde	0.703	0.171
Hexaldehyde	0.866	0.477
Tolualdehydes	0.833	0.395
Valeraldehyde	0.473	0.124

Bold = MQO Core Analyte

Several of the carbonyl compounds tended to correlate well with the PM_{10} data. It should be noted here that the correlation was performed only for the carbonyl compounds that were detected in 90% or more of the samples taken. Formaldehyde shows the strongest correlation with an "r" value of 0.879, which is up from 0.862 in 2011. The other two of the "big three" carbonyls, acetaldehyde, and acetone, did show some correlation with the course particulate concentrations. There was little correlation between any of the carbonyls and the fine particulate concentrations. Formaldehyde had the highest "r" value of the group at 0.523. A graph of the two carbonyls with the highest "r" value for the PM_{10} correlation is shown in Figure 54.

The final graph presented in this section is a snapshot of the chemical make-up of the carbonyls group from 2004 through 2012. Figure 55 shows the percentage each carbonyl compound contributed to the overall total carbonyl concentration from year to year. Clearly, acetone, acetaldehyde, and formaldehyde dominate the carbonyl concentrations yearly.

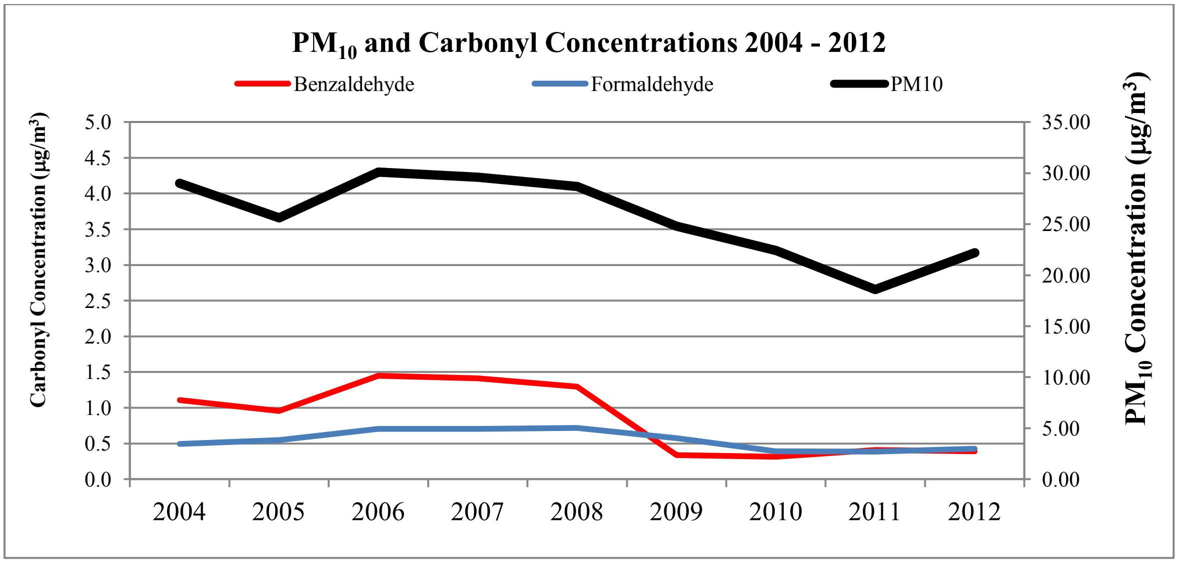

Figure 54. PM_{10} – Carbonyl Concentration Comparison

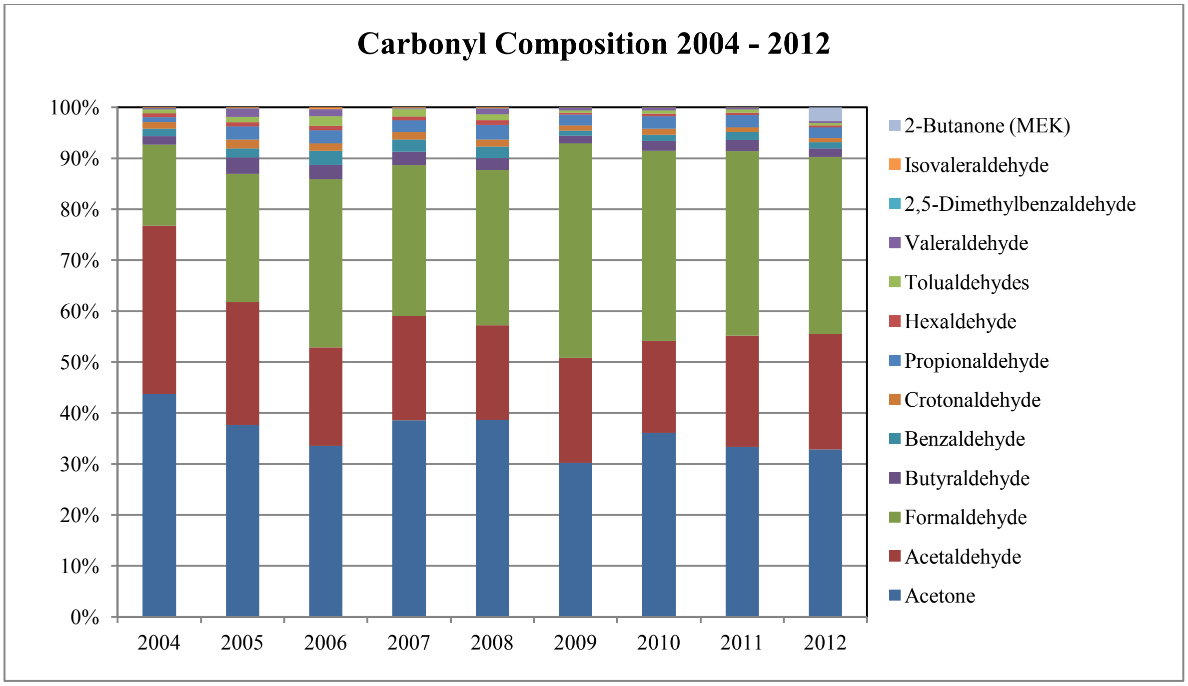

Figure 55. Annual Carbonyl Composition

VOC Correlations and Sample Composition

VOCs are organic compounds which have a high vapor pressure at room temperature. Because of this high vapor pressure, which is the result of a low boiling point, large numbers of VOC molecules can evaporate, or sublimate, from a liquid, or solid form and enter the ambient air. The NATTS program monitors for 60 of these compounds, many of which are never detected in any samples. The VOC correlation data used and discussed in this section is based upon the subset of 24 compounds that were detected in greater than 90% of the samples taken, for at least five of the nine years of data, between 2004 and 2012. It does not include three of the eight mandatory monitoring compounds (chloroform, trichloroethylene, and vinyl chloride), because they were not detected in enough samples. The other five mandatory compounds (1,3-butadiene, acrolein, benzene, carbon tetrachloride, and tetrachloroethylene) are included as they were detected in greater than 90% of the samples taken. They are bolded in the table below.

Table 18 is a listing of the correlation coefficients (r) for each of the 24 VOC compound data sets, with both $PM_{2.5}$, and PM_{10} data sets. For the VOC - PM_{10} correlation, only carbon disulfide and benzene correlated fairly well with the course particulate concentrations, with correlation coefficient values of 0.840 and 0.832, respectively. Figure 56 is a graph of the carbon disulfide, benzene, and PM_{10} concentrations.

Table 18. VOC – Particulate Correlation Coefficient Values

Analyte	**r-PM_{10}**	**r-$PM_{2.5}$**
1,1,1-Trichloroethane	0.631	0.532
1,2,4-Trimethylbenzene	0.316	0.191
1,3,5-Trimethylbenzene	0.203	0.104
1,3-Butadiene	**0.536**	**0.428**
Acetonitrile	-0.327	-0.242
Acetylene	0.615	0.624
Acrolein	**-0.668**	**-0.129**
Benzene	**0.832**	**0.504**
Carbon Disulfide	0.840	0.866

Analyte	r-PM_{10}	r-$PM_{2.5}$
Carbon Tetrachloride	**0.079**	**0.106**
Chloromethane	0.087	0.408
Dichlorodifluoromethane	0.208	0.514
Dichloromethane	-0.621	-0.289
Dichlorotetrafluoroethane	-0.440	-0.461
Ethylbenzene	0.187	0.048
m,p-Xylene	0.228	0.050
n-Octane	-0.779	-0.798
o-Xylene	0.217	0.043
Propylene	0.607	0.295
Styrene	-0.599	-0.414
Tetrachloroethylene	**0.045**	**0.559**
Toluene	0.261	0.190
Trichlorofluoromethane	0.204	0.500
Trichlorotrifluoroethane	0.332	0.476

Bold = MQO Core Analyte

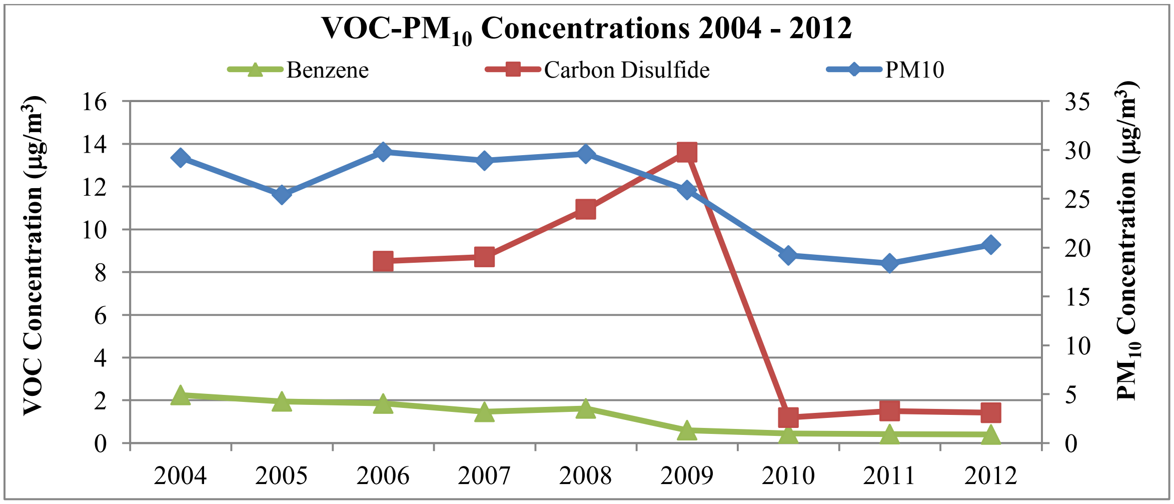

Figure 56. VOC – PM_{10} Concentration Comparison

The VOC – $PM_{2.5}$ correlation showed only one compound with a strong correlation. Carbon disulfide correlated well with the fine particulate matter concentrations, showing a positive r-value of 0.866. Figure 57 shows the concentration graphs for carbon disulfide, and $PM_{2.5}$ concentrations.

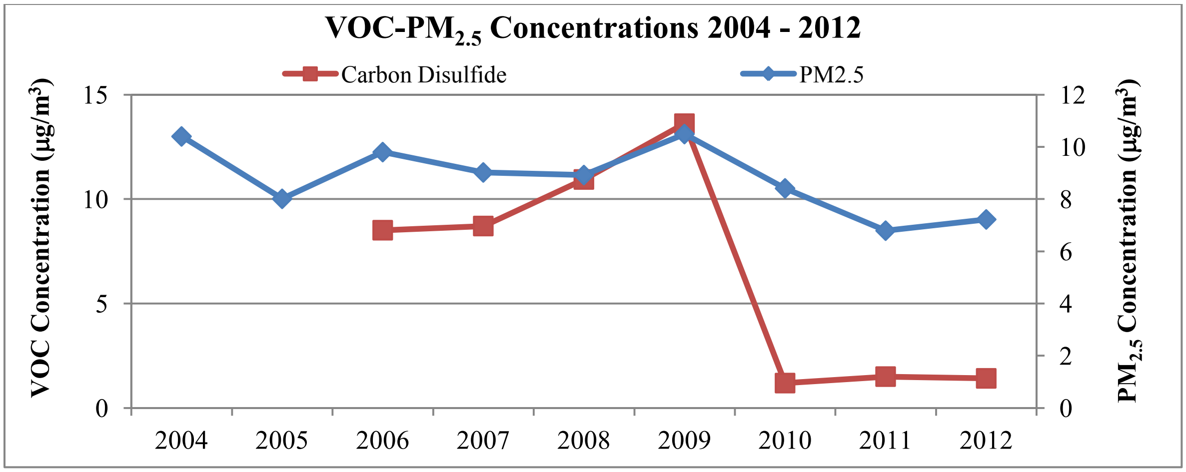

Figure 57. **VOC – $PM_{2.5}$ Concentration Comparison**

The chemical make-up of the VOC compounds tends to be much more variable from year to year than the carbonyl compounds are, for the C1 through C4 carbon chains. This can be seen in Figure 58. The graph shows data from 2004 through 2012. The year to year variability is easily seen.

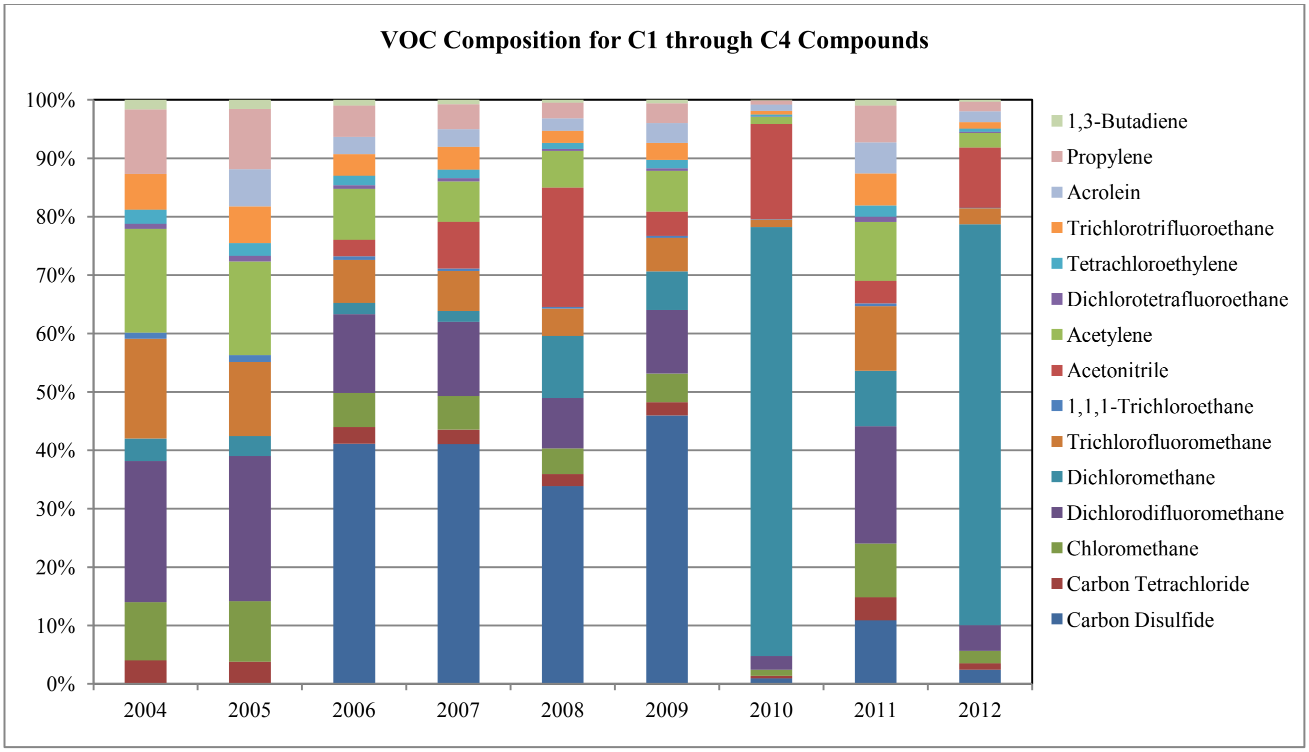

Figure 58. **Total VOC Composition for C1 through C4 Compounds**

Figure 59 shows the chemical composition of the C6 though C8 carbon chain compounds. These compounds tend to show a more consistent make-up from year to year, as opposed to the lighter end alkanes of the C1 through C4 chains. It should be noted that this grouping contains straight chain alkanes, as well as aromatic compounds. It seems likely that the major source for these C6 through C9 compounds is from motor vehicle traffic, due to the consistent nature of the chemical makeup, and the site's nearness to a major road.

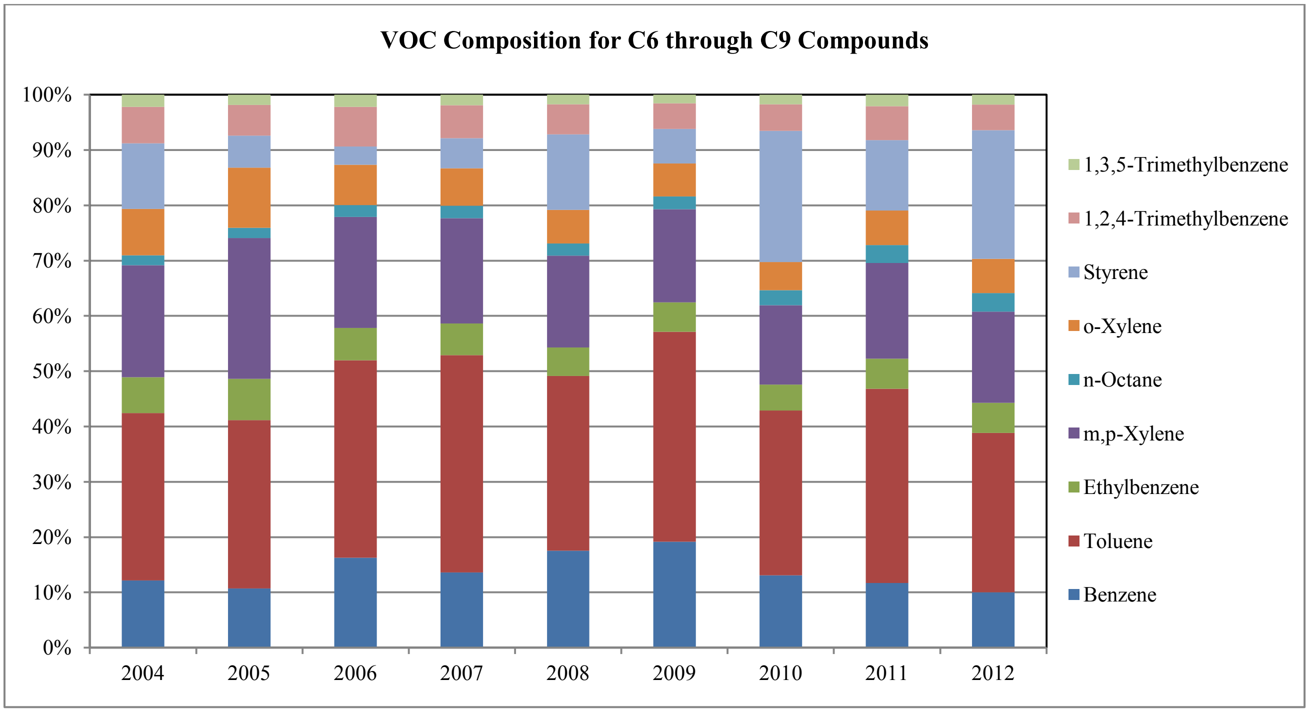

Figure 59. Total VOC Composition for C6 through C9 Compounds

PAH Correlations and Sample Composition

Polycyclic Aromatic Hydrocarbons are often found naturally in the environment, but are also man-made. They can enter the air through the incomplete combustion of fuels and garbage. They are a concern because of their persistence in the atmosphere. Because they don't burn completely, they can stay in the environment for long periods of time. Table 19 lists the correlation coefficient values for each of the PAH compounds that were detected in greater than 90% of the samples taken in each of the years from 2008 through 2012. Most of the compounds show a negative correlation with the PM_{10} values. This is reasonable, since PM_{10} is largely from geologic sources.

This particular set of compounds did tend to trend better with the fine particulate matter concentrations. Most compounds showed positive correlations with the $PM_{2.5}$ concentrations, with the lowest positive value being 0.032 for naphthalene. The strongest correlation between the PAH and $PM_{2.5}$ concentrations was seen with Benzo(g,h,i)perylene. A correlation coefficient of 0.880 was obtained for this compound. Overall, the PAHs appear to correlate with the $PM_{2.5}$ concentrations. PAHs can exist in liquid or solid phases, so their positive relationship with the smallest diameter particles, which develop from gaseous condensation, is easily explained. PAHs and $PM_{2.5}$ are also both direct combustion products. The compounds with the two largest correlation coefficient values are graphed in Figure 60.

Table 19. PAH – Particulate Correlation Coefficient Values

PAH correlations	r - PM_{10}	r - $PM_{2.5}$
9-Fluorenone	-0.415	0.133
Acenaphthene	-0.225	-0.322
Anthracene	0.183	0.740
Benzo (b) fluoranthene	0.038	0.655

PAH correlations	**r - PM_{10}**	**r - $PM_{2.5}$**
Benzo (e) pyrene	0.270	0.797
Benzo (g,h,i) perylene	0.398	0.880
Chrysene	-0.022	0.612
Fluoranthene	-0.389	0.207
Fluorene	-0.326	-0.168
Naphthalene	**-0.352**	**0.032**
Phenanthrene	-0.158	0.202
Pyrene	-0.043	0.589
Retene	0.031	0.704

Bold = MQO Core Analyte

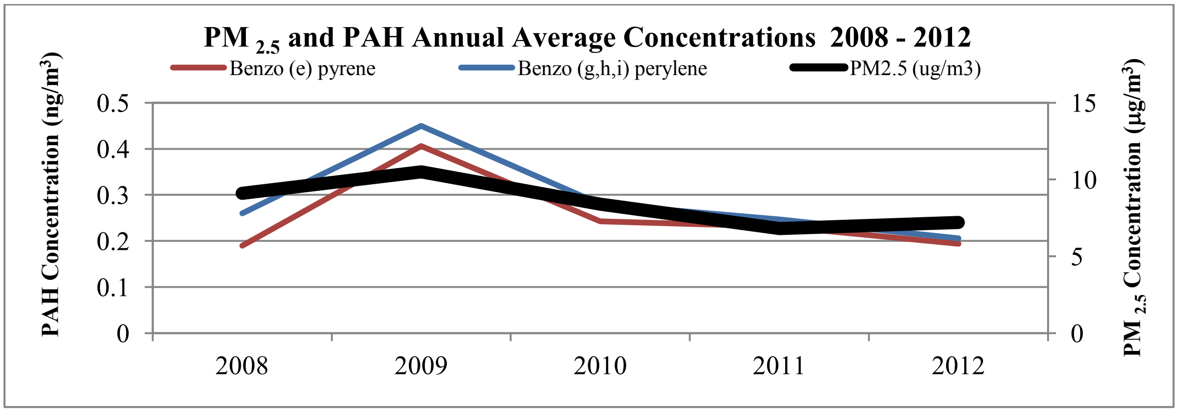

Figure 60. PAH – $PM_{2.5}$ Concentration Comparison

Figure 61 is a graph showing the percentage contribution each of the PAH compounds (detected in greater than 90% of the samples taken) to the total PAH concentration. Clearly, naphthalene is the dominant compound of the group. The composition of the PAH group does not appear to vary much from year to year. This may imply that PAH sources are consistent over time.

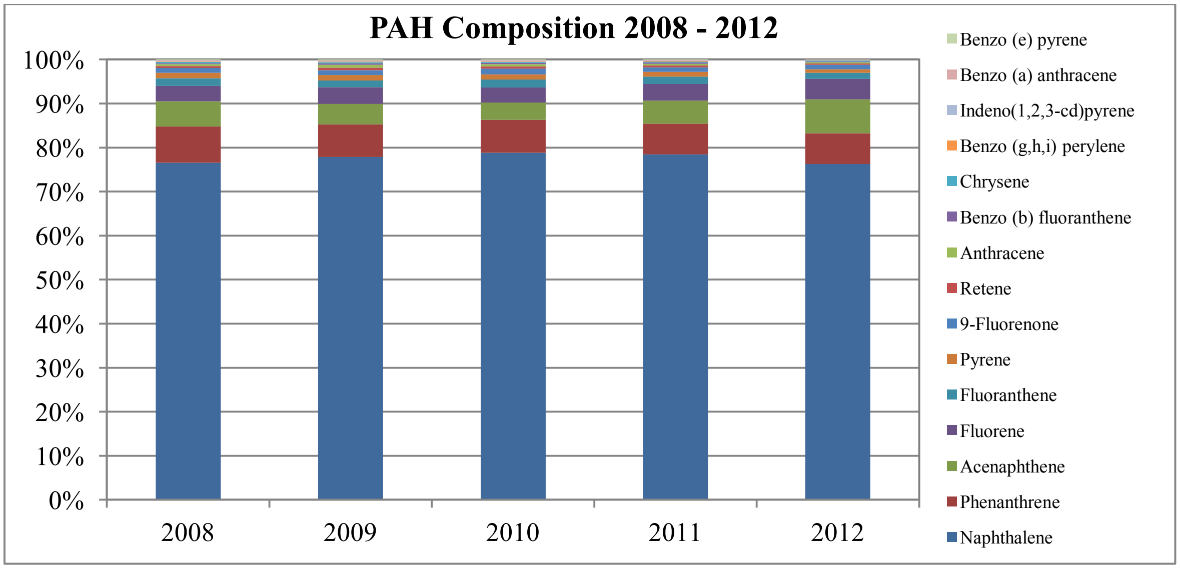

Figure 61. PAH Chemical Composition 2008 – 2012

Metals Correlations and Sample Composition

The metals in this group are sampled via a PM_{10} filter based monitor. Only four of the six metals analyzed for were detected in at least 90% of the samples taken. The correlation coefficients of these four compounds with the two different particulate classes are shown in Table 20. Manganese concentrations correlated well with the PM_{10} concentrations, having an r-value of 0.837. There were no significant correlations between any of the metals compounds and the $PM_{2.5}$ concentrations, other than nickel, which showed rather strong negative correlations with both types of particulate matter. This suggests that select metals may be coming from geologic crustal, rather than combustion or secondary formation, sources. It is odd that the nickel concentrations exhibit such a strong negative correlation with both PM_{10} and $PM_{2.5}$ concentrations. Nickel sources include various metal alloys, electroplating, motor vehicle exhaust, and geologic crustal material.[16] A graph of the PM_{10} and manganese concentrations is seen in Figure 62.

Table 20. Metals – Particulates Correlation Coefficients

Analyte	r-PM_{10}	r-$PM_{2.5}$
Arsenic	**0.544**	**0.140**
Lead	**0.565**	**0.266**
Manganese	**0.837**	**0.328**
Nickel	**-0.735**	**-0.818**

Bold = MQO Core Analyte

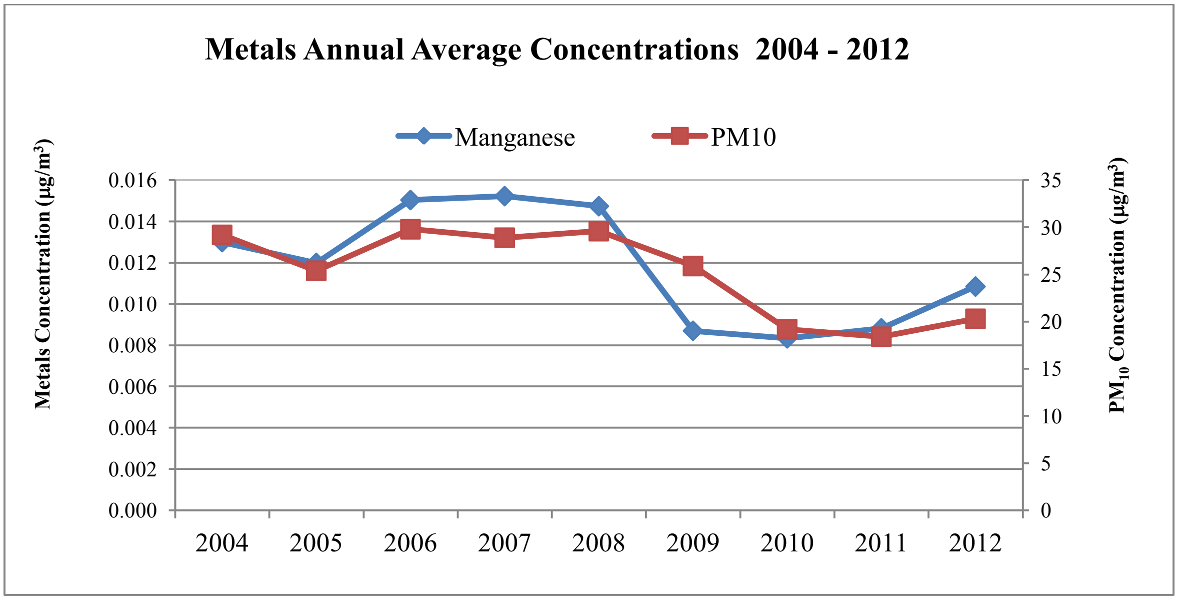

Figure 62. Metals – PM_{10} Concentration Comparison

Figure 63 is a graph showing the percentage contribution of each of the individual metals compounds to the overall total. The concentrations vary somewhat from year to year, but not as much as the C1 through C4 compounds of the VOC section.

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[16] http://scorecard.goodguide.com/chemical-profiles/html/nickel.html

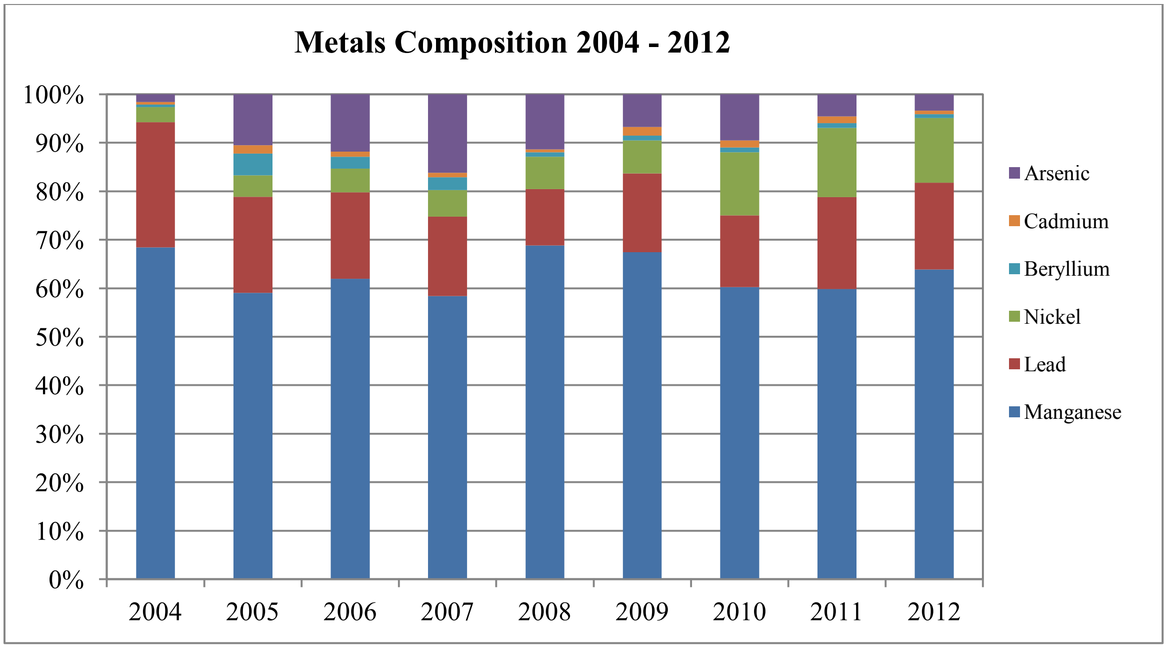

Figure 63. **Metals Chemical Composition 2004 – 2012**

XII. SUMMARY AND CONCLUSIONS

The National Air Toxics Trends Study in Grand Junction for 2012 showed similar results to prior years. The highest carbonyls in air were formaldehyde, acetaldehyde, and acetone. A correlation analysis was run between the particulate concentrations and the carbonyl concentrations. PM_{10} concentrations tended to correlate with many of the carbonyl compounds. A correlation value (r) of 0.879 was obtained when comparing PM_{10} to formaldehyde concentrations. This value was the highest obtained for the PM_{10}-carbonyl correlation. The lowest value was seen upon a comparison with valeraldehyde, with a correlation coefficient of 0.473. A comparison of the $PM_{2.5}$ concentrations with the carbonyls again showed that formaldehyde correlated the best, but had a moderate coefficient value of 0.523. Many of the carbonyls showed no correlation at all with the $PM_{2.5}$ values.

Twenty-six volatile organic compounds are ubiquitous, having been detected in 90% of the air samples for 2012. Going back to 2004, there were 24 compounds detected in at least 90% of the samples, in at least five of the nine years' worth of data acquired since then. From 2004 to 2012, the makeup of the C1 to C4 group was highly variable, with large concentrations of carbon disulfide in 2009, but not in 2010, 2011, or 2012; as well as large concentrations of dichloromethane in 2010 and 2012, but not in 2009 or 2011. The C6 through C8 group showed more consistency in the constituent concentrations from 2004 to 2012. Correlations with particulate data showed that carbon disulfide and benzene tracked most closely with the PM_{10} concentrations, with r-values of 0.840 and 0.832, respectively. Carbon disulfide and acetylene correlated best with the fine particulate concentrations, having r-values of 0.866 and 0.624, respectively.

The highest polycyclic aromatic hydrocarbons concentrations were naphthalene, acenaphthene, and phenanthrene, none of which correlated well with $PM_{2.5}$ concentrations. Their respective r-values were 0.032, -0.322, and 0.202. The compounds that did correlate well with the fine particulate matter were benzo(g,h,i)perylene, and benzo(e)pyrene, with r-values of 0.880 and 0.797, respectively. Several of the other PAH compounds also correlated somewhat with $PM_{2.5}$ values. None of the PAH compounds showed any correlation with the coarse particulate matter.

For the metals, nickel, lead and manganese showed the highest average concentrations. Manganese also had the highest correlation value with the course particulate matter at 0.837. An interesting note from the metals data are the strong negative correlations exhibited by the nickel data set when compared to both the fine and coarse particulate matter. The respective r-values obtained were -0.735, and -0.818. It is unclear what is behind this phenomenon. None of the other metals compounds showed any correlation with the fine particulate matter. Hexavalent chromium is an extremely small fraction of the chromium in air, comprising less than one percent of the total chromium concentration.

In general, it appears that the concentrations of many of the compounds of interest are dropping since the inception of the NATTS program in Grand Junction. The study will continue in 2013, as one of the major goals is to run the site long term, for comparison of the mean concentrations for each pollutant during the first three years to the means for successive three year intervals, and this is not yet possible for PAHs. Calculation of the three year average concentrations to date has shown a decrease in the majority of the concentrations of the compounds of interest. Three successive three year averages have been able to be calculated to this point, and the numbers indicate that concentration values for many of the compounds of interest are dropping.

Appendix A: Compounds Contributing to Cancer and Non-cancer Risks - Overview of Sources and Health Effects

Chemicals can be released to the environment as a result of their use and manufacture. Some chemicals may also form, as other chemicals react with sunlight and one another in outdoor air. A brief summary of the potential sources and health effects of some prevalent chemicals in the ambient air is provided below. This information is adopted from the following main sources: EPA Air Toxic Website, EPA Office of Pollution Prevention and Toxics (OPPT), EPA Integrated Risk Information System (IRIS), Agency for Toxic Substances and Disease Registry (ATSDR), New Jersey Department of Health and Senior Services, Occupational Safety and Health Administration (OSHA), National Institute of Occupational Safety and Health (NIOSH), and the California Air Resources Board (CARB).

CARBONYLS

Three of the twelve carbonyl compounds sampled are discussed below. These three are believed to be significant health risk drivers, at the nation-wide level.

ACETALDEHYDE

Acetaldehyde is a hydrocarbon with the formula CH_3CHO. It is thus closely related to formaldehyde, HCHO. Like formaldehyde, it exists in the atmosphere as a gas with a pungent odor. Acetaldehyde is ubiquitous in the ambient environment. It is mainly used as an intermediate in the synthesis of other chemicals, such as acetic acid, acetic anhydride, chloral, and glyoxal. It is employed in the food processing industry as a food and fish preservative, a flavoring agent, and in gelatin fibers. The tanning and paper industries use acetaldehyde, as do the perfume and dye manufacturers (CARB Acetaldehyde Fact Sheet).

Acetaldehyde can be released to the environment as a product of incomplete combustion in fireplaces and wood stoves, forest and wild fires, pulp and paper production, stationary internal combustion engines and turbines, vehicle exhaust, and petroleum refineries. Waste water processing is also a source. It is important to note that residential fireplaces and woodstoves are the two highest sources of emissions, followed by various industrial emissions.

Although it is used in industry, the California Air Resource Board believes that the largest sources in outdoor air are combustion and production from photochemical reactions (CARB Acetaldehyde Fact Sheet). Acetaldehyde itself can break down in these complex reactions between air pollutants and sunlight, forming formaldehyde.

The health effects of acetaldehyde are very similar to those of its chemical relative formaldehyde. It irritates the eyes and mucous membranes. It can paralyze the respiratory muscles, act as a narcotic to prevent coughing, and speed up pumping of the heart. Exposure can lead to headaches and sore throat. (Kirk Othmer, Vol 1, page 107). It should be noted that most of these health effects have been observed in factory workers, who are exposed to acetaldehyde concentrations thousands of times greater than those occurring in outdoor air. Acetaldehyde is believed to be a probable human carcinogen, leading to cancer of the nose and throat. Acetaldehyde has been shown to cause birth defects in animals, but no human research is available. (CARB Acetaldehyde Fact Sheet).

EPA's Technology Transfer Network Air Toxic Website provides information on the potential health effects of acetaldehyde. According to this source , the primary acute effects of acetaldehyde are irritation of the eyes, skin, and respiratory tract in humans. At higher exposure levels, erythema, coughing, pulmonary edema, and necrosis may happen. Chronic toxicity symptoms in humans resemble those of alcoholism.

The EPA has established a Reference Concentration (RfC) for inhalation exposure to acetaldehyde based on degeneration of the olfactory epithelium in rats. No information is available on the reproductive and developmental effects of acetaldehyde in humans. Animal studies data indicate that acetaldehyde may be a potential developmental toxin. EPA has classified acetaldehyde as a Group B2, probable human carcinogen, based on increased incidence of nasal tumors in male and female rats and laryngeal tumors in male and female hamsters after inhalation exposure.

The California Air Resources Board observed an annual mean of 1.33 ppb acetaldehyde in its state-wide network during 1996 (CARB Acetaldehyde Fact Sheet). The mean observed in this Grand Junction study, 3.2 ppb, is a bit above the California data, but acetaldehyde in Grand Junction occurs at levels typical of large urban areas. Acetaldehyde levels are therefore a national problem related primarily to the use of motor vehicles.

CROTONALDEHYDE

Crotonaldehyde with the chemical formula of C_4H_6O is also known as propylene aldehyde, betamethyl-acrolein, crotinin aldehyde and butenal. Crotonaldehyde is a colorless liquid with a pungent, suffocating odor.

Crotonaldehyde can be emitted to the environment from the combustion of gasoline, the burning of wood, paper, cotton, plastic, and tobacco. It can also be released through industrial use. It is found naturally in emissions of some vegetables and volcanoes.

According to the ATSDR Medical Management Guidelines inhaled crotonaldehyde is highly toxic. It is irritating to the upper respiratory tract even at low concentrations. Crotonaldehyde vapor is heavier than air. Therefore, higher levels of crotonaldehyde vapors would be found nearer to the ground. The mechanism of toxicity of crotonaldehyde is not known, but it is highly reactive. Crotonaldehyde is also a skin irritant and can cause eye irritation and damage to the cornea. After an acute, relatively high concentration exposure, people may become sensitized to crotonaldehyde. Except for rare cases of sensitization, no health effects have been reported in humans exposed to relatively low concentrations of crotonaldehyde. No studies have been found that address reproductive or developmental effects of crotonaldehyde in humans. The compound has been shown to cause degeneration of spermatocytes in mice. No teratogenic effects from acute exposures have been reported.

The Department of Health and Human Services has determined that crotonaldehyde may be a possible carcinogen. The EPA IRIS has classified crotonaldehyde as a possible carcinogen based on the fact that there is no human data, but an increased incidence of hepatic tumors in male rats. The possible carcinogenicity of crotonaldehyde is supported by genotoxic activity and the expected reactivity of croton oil and aldehyde. The EPA IRIS, however, has not derived a cancer toxicity value for the compound. The EPA HEAST (Health Effects Summary Tables) has established an oral cancer toxicity value for crotonaldehyde. The Agency for Research on Cancer has determined that crotonaldehyde is not classifiable as to its carcinogenicity to humans.

Information concerning typical concentrations of crotonaldehydes in air could not be located.

FORMALDEHYDE

Formaldehyde is a hydrocarbon compound with the formula HCHO. It exists in the atmosphere as a colorless gas with a pungent odor. It is used in the manufacture of urea-formaldehyde resins which are used in particleboard and plywood products. Therefore, high levels of airborne formaldehyde can also be found in indoor air as a result of release from various consumer products such as building materials and home furnishings. Another source of formaldehyde in indoor air is smoking. It is also employed in chemical manufacturing of pharmaceuticals, herbicides, and sealants. Textile finishes, such as used for "permanent press" clothes, contain formaldehyde (Kirk-Othmer, Vol 11, pages 245 - 246).

EPA's Technology Transfer Network Air Toxic Website provides information on the potential sources and health effects of formaldehyde. According to this source, the major sources of formaldehyde emissions to the ambient air include power plants, manufacturing facilities, incinerators, forest and wild fires, stationary internal combustion engines and turbines, pulp and paper plants, petroleum refineries, and automobile traffic. In urban areas, combustion of automotive fuel is the dominant source for much of the year. However, formaldehyde can also form photochemically in the air, as other hydrocarbons and oxides of nitrogen from automobile traffic break down to form ozone. Complicating the situation is the fact that the complex ozone-producing atmospheric reactions may both create and destroy formaldehyde, as the chains of chemical reactions proceed along various pathways.

The Agency for Toxic Substances and Disease Registry (ATSDR), lists a number of possible health effects that may occur from inhalation of formaldehyde. Formaldehyde is an irritant. The major acute toxic effects via inhalation exposure are eye, nose, and throat irritation and effects on the nasal cavity. At 0.4 – 3 ppm, it may cause the eyes to tear. Other effects observed in humans from exposure to high levels of formaldehyde are coughing, wheezing, chest pain, and bronchitis (EPA's Technology Transfer Network Air Toxic Website). Formaldehyde is believed to be carcinogenic (cancer-causing) to humans. However, the body can quickly break down formaldehyde, so it does not accumulate in fatty tissue. Currently, ATSDR believes that formaldehyde does not cause birth defects in humans (ATSDR Toxicological Profile for Formaldehyde). Thus, the main concerns with this compound are its irritant properties and its potential ability to cause cancer of the nose and throat.

Chronic inhalation exposure to formaldehyde in humans has been associated with respiratory symptoms and eye, nose, and throat irritation. EPA has not established an inhalation Reference Concentration (RfC) for formaldehyde. However, the ATSDR has established an inhalation reference concentration called a Minimal Risk Level (MRL) for formaldehyde based on respiratory effects in humans. Developmental effects, such as birth defects, have not been observed in animal studies. EPA has classified formaldehyde as a Group B1, probable human carcinogen, based on limited evidence in humans and sufficient evidence in animals. Occupational studies have shown statistically significant increases in incidence of lung and nasopharyngeal cancer. This evidence is considered limited because of possible exposure to other agents. Animal studies have reported an increased incidence of nasal squamous cell carcinoma by inhalation exposure. Please see EPA IRIS for a detailed discussion on the carcinogenicity of formaldehyde.

ATSDR states that typical levels of formaldehyde in urban air are 10 – 20 ppb. ATSDR cites concentrations of 0.2 ppb for rural areas, and 2-6 ppb for suburban areas (ATSDR Toxicological Profile for Formaldehyde). The mean level observed in Grand Junction during this study, 2.3 ppb, is within the "suburban" range.

VOLATILE ORGANIC COMPOUNDS

Volatile organic compounds commonly present included 1,3 – butadiene, benzene, carbon tetrachloride, tetrachloroethylene, 1,3,5 – trimethylbenzene and 1,2,4 - trimethylbenzene. Some health summary and source information regarding these compounds is given below.

BENZENE

Benzene is a hydrocarbon compound with the formula C_6H_6. It exists in the atmosphere as a colorless gas with a sweet odor. It is used in chemical manufacturing of medicines, detergents, explosives, shoes, dyes, leather, resins, paints, plastics and inks (CARB Fact Sheet on Benzene). It is also present in gasoline.

The largest sources of benzene in ambient air are automobiles, gasoline service stations, refineries, and chemical plants. Burning of vegetative matter in forest fires and woodstoves is also a source. In ambient air, benzene reacts with hydroxyl (OH^-) radicals within a few hours. Since hydroxyl radicals are common in outdoor air, this chemical transformation prevents the build-up of large concentrations of benzene.

Benzene is a serious concern from a toxicological standpoint. Unlike many of the compounds discussed here, benzene is a proven human carcinogen. It damages the blood-forming capacity of the body, leading to anemia or leukemia. Like the other volatile organic compounds, breathing large amounts can cause lightheadedness, headache, vomiting, convulsions, coma and death. It also irritates the skin and eyes, exerting a drying effect.

However, these health effects are usually seen in workplaces, where levels are thousands of times higher than those in outdoor air. Experiments with laboratory animals suggest that benzene exposure may be associated with numerous cancers. It may cause bone marrow damage and bone formation problems for a developing fetus (ATSDR Toxicological Profile for Benzene). Thus, EPA has had concern about whether levels of benzene in outdoor air are associated with cancer and leukemia. While no link with outdoor air concentrations has been unequivocally proven, EPA has acted to reduce air concentrations of this pollutant.

The EPA has established a Reference Concentration for inhalation exposure to benzene based on decreased lymphocyte count in an occupational epidemiologic study. Benzene is classified as a "known" human carcinogen for all routes of exposure by the EPA IRIS based on the increased incidence of leukemia in epidemiologic and case studies.

The Agency for Toxic Substances and Disease Registry (ATSDR) cites national 1984 to 1986 data from 300 cities, which indicate an average benzene level of 1.8 ppb for urban and suburban areas (ATSDR Toxicological Profile for Benzene). The Grand Junction – Powell site mean of 0.7 ppb observed in this study is somewhat lower.

1,3-BUTADIENE

1,3-Butadiene is a hydrocarbon compound with the formula C_4H_6. It exists in the atmosphere as a colorless gas with an odor similar to gasoline. It is used in making rubber and plastics. The most important use is in tire production. It is also used in the production of chemicals such as 1,4-hexadiene (NIOSH Current Intelligence Bulletin 41).

According to the California Air Resources Board, most emissions of 1,3-butadiene come from combustion of fuels in diesel and gas-powered motor vehicles. Other sources that they list include petroleum refining, tire wear, residential wood heating, and forest fires. Rubber and chemical production plants also have emissions. Breathing of cigarette smoke is another source of 1,3-butadiene exposure (ATSDR Fact Sheet)

1,3-Butadiene is of concern toxicologically because it is characterized as carcinogenic to humans based on the new EPA guidelines for cancer risk assessment and it also has adverse effects on reproduction and fetal development. Exposure to high concentrations can cause irritation and central nervous system effects such as eye irritation, cough, sore throat, headache, drowsiness, nausea, unconsciousness, and death. Rats and mice exposed to this compound in laboratory tests developed multiple cancers within single individuals. The animals had damaged testes and ovaries, and offspring of the animals had skeletal problems. Other effects seen in animals at low levels of inhalation exposure for one year include kidney and liver disease, and damaged lungs (ATSDR Fact Sheet). Generally, the acute health effects have not been seen at concentrations existing in outdoor air. However, EPA considers that the levels of 1,3-butadiene in air may represent a significant portion of the cancer risk related to ambient airborne chemicals.

The EPA has established a Reference Concentration for inhalation exposure to 1,3-butadiene based on ovarian atrophy in mice. The EPA has characterized 1,3-butadiene as carcinogenic to humans by inhalation based on the following total evidence: sufficient evidence from epidemiologic studies showing increased lymphohematopoietic cancers and leukemia; tumors at multiple sites in animal studies, and strong evidence suggesting that the carcinogenic effects are mediated by genotoxic metabolites of 1,3-butadiene.

ATSDR estimates that urban and suburban areas have an average concentration of 0.3 ppb 1,3-butadiene, while rural areas have 0.1 ppb (ATSDR Toxicological Profile for 1,3-Butadiene). The annual average at Grand Junction - Powell is 0.09 ppb.

CARBON TETRACHLORIDE

Carbon tetrachloride, also known as tetrachloromethane or methane tetrachloride, is a chlorinated hydrocarbon with the formula CCl_4. It exists in the atmosphere as a gas. It has a sweet odor. The primary uses of carbon tetrachloride were as a dry cleaning solvent, a grain fumigant, as a refrigerant, and as an aerosol propellant. Carbon tetrachloride has a long atmospheric half-life, so it can travel to the higher reaches of the atmosphere and damage the earth's ozone layer. Due to its toxicity and ozone-damaging qualities, most uses of carbon tetrachloride have been banned. It is still in use in industrial settings for producing refrigerants.

Carbon tetrachloride is emitted to the air from industrial sources and from petroleum refineries (California Air Resources Board Toxic Air Contaminant Identification List Summary for Carbon Tetrachloride). Carbon tetrachloride is also a common indoor air contaminant due to releases from building materials and products, such as cleaning agents, used in homes (Air Toxic Website). There are no natural sources of carbon tetrachloride; it is produced by man (ATSDR Toxicological Profile for Carbon Tetrachloride).

As is true for many of the chlorinated hydrocarbons, breathing large concentrations of carbon tetrachloride has central nervous system effects including lightheadedness, coma, convulsions, double vision, intoxication, and death. It can also cause vomiting. In animal studies, it had effects on the liver and kidney. Male rats exposed to carbon tetrachloride had lower sperm production. Female rats exposed to it had stunted offspring with birth defects. These health effects are generally observed in occupational settings, where people had exposure to very high levels over a number of years.

EPA has not established a Reference Concentration for carbon tetrachloride. The CalEPA has established a Reference Exposure Level for carbon tetrachloride based on liver effects in guinea pigs. Carbon tetrachloride has been associated with liver and kidney cancer in animals. EPA considers it a Class B2 Carcinogen (probable human carcinogen) based on liver tumors in animals.

The California Air Resources Board has monitored carbon tetrachloride at a number of locations, and found a mean value of 0.078 ppb (California Air Resources Board Toxic Air Contaminant Identification List Summary for Carbon Tetrachloride). The 0.08 ppb annual mean observed at Grand Junction – Powell is at the same level.

TETRACHLOROETHYLENE

Tetrachloroethylene, also known as perchloroethylene, is a chlorinated hydrocarbon with the formula C_2Cl_4. It exists in the atmosphere as a gas. It has a "chloroform-like" odor (NIOSH Pocket Guide to Chemical Hazards, Tetrachloroethylene). The primary uses of tetrachloroethylene are as a dry cleaning solvent, metal cleaning solvent, or for chemical production. Tetrachloroethylene is used in paints, inks, aerosols, glues, polishes, silicones and rubber products (CARB Fact Sheet on Tetrachloroethylene and OPPT Chemical Fact Sheet on Tetrachloroethylene).

Most emissions of tetrachloroethylene come from degreasing, dry cleaning, or chemical production facilities. There are microorganisms that can produce tetrachloroethylene (ATSDR Toxicological Profile For Tetrachloroethyelene).

As is true for many of the chlorinated hydrocarbons, breathing large concentrations of tetrachloroethylene has central nervous system effects including lightheadedness, coma, convulsions, double vision, intoxication, and death. It also can cause vomiting. In animal studies, it had effects on the liver and kidney. It also is an irritant to eyes, lungs, and skin. However, many of these health effects were observed in occupational settings, where exposure is much higher than in outdoor air. Some animal studies suggest that tetrachloroethylene exposure may lead to leukemia (NIOSH Registry of Toxic Effects of Chemical Substances Information for Tetrachloroethylene). Tetrachloroethylene has been associated with liver and kidney cancer in animals.

The ATSDR has established a Minimal Risk Level (MRL) based on nervous system effects in humans. It is important to note that EPA is currently re-evaluating the toxic potential of tetrachloroethylene, including its carcinogenicity, and therefore no relevant information is available in IRIS. In the interim, EPA recommends the use of CalEPA toxicity values as provisional values. The CalEPA cancer toxicity value is derived by considering data on liver tumors in male and female mice and mononuclear cell leukemia in male and female rats. EPA is currently working to revise the toxicity assessment for tetrachloroethylene.

The California Air Resources Board has monitored tetrachloroethylene at a number of locations within their state, and found a mean value of 0.019 ppb during 1996 (California Air Resources Board Toxic Air Contaminant Identification List Summary for Tetrachloroethylene). The annual mean at Grand Junction - Powell was 0.05 ppb. These levels are greater than the network-wide mean value for California. However, this compound was detected less than half the time.

1,3,5-TRIMETHYBENZENE AND 1,2,4-TRIMETHYLBENZENE

1,3,5-trimethylbenzene and 1,2,4-trimethylbenzene are isomers of the hydrocarbon formula C_9H_{12}. In pure form they are colorless liquids. They are used in chemical manufacturing of medicines, detergents, dyes, paints and inks. Trimethylbenzenes are a large component of distilled petroleum. They are also used as gasoline additives.

The largest sources of trimethylbenzenes in ambient air are likely to be automobiles, gasoline service stations, refineries, and chemical plants. In ambient air, trimethylbenzenes have a half-life of less than a day (EPA OPPT Chemical Summary For 1,2,4-Trimethylbenzene).

Health effects of trimethylbenzenes are similar to those of benzene. It damages the blood-clotting capacity of the body. Like the other volatile organic compounds, breathing large amounts can cause lightheadedness, headache, vomiting, convulsions, coma and death. It also irritates the skin and eyes, exerting a drying effect. Long-term exposure can lead to cough, reduced lung capacity, and bronchitis. However, these health effects are usually seen in workplaces, where levels are thousands of times higher than those in outdoor air. It is not known whether these compounds are carcinogenic. Some animal experiments suggest that they may cause bone formation problems for a developing fetus (EPA OPPT Chemical Summary For 1,2,4-Trimethylbenzene).

The Environmental Protection Agency cites national data indicating that average atmospheric concentrations of 1,2,4-trimethylbenzene are 0.58 ppb in rural areas, and 1.20 ppb in cities (EPA OPPT Chemical Summary For 1,2,4-Trimethylbenzene). The Grand Junction - Powell site had a mean value of 0.09 ppb. As the EPA citation is for 1988, it is likely that concentrations have gone down in recent years.

METALS

Arsenic and manganese are discussed below. Levels of lead observed in Grand Junction were below the Colorado state standard of 1.5 ug/m3 for a monthly average.

ARSENIC

Arsenic is a metal-like element that occurs naturally in the earth's crust. Its chemical symbol is As. It exists in the atmosphere as particulate matter, in compounds formed from combination with other atoms such as oxygen, chlorine, and sulfur (ATSDR Public Health Statement for Arsenic). In the past, arsenic was used as a pesticide for orchard crops. Today, the chief use is in chromated copper arsenate (CCA) used to "pressure-treat" wood, to preserve it from decay in marine or in-ground usage. It is also used in metal alloy, glass-making, and electrical semi-conductors.

Emission sources of arsenic include smelters, coal-fired power plants, wood-burning, metals operations, mining operations, and incinerators. Arsenic occurs naturally in many soils, so wind-blown dusts from exposed land can contain it. Mine tailings piles generally contain enriched levels of arsenic, resulting in emissions of arsenic in the particulate emissions that occur under windy conditions. Soils contaminated by smelter fall-out can also be a source of emissions during high winds. Burning wood treated with CCA also leads to arsenic emissions.

Arsenic's toxicity has led to its use as a poison. Orally ingesting large amounts can be fatal. The effects of inhalation are similar to the oral effects. Arsenic disturbs the gastro-intestinal system, leading to abdominal pain, vomiting, and diarrhea. It affects the central nervous system, leading to nerve damage in the legs and arms. It can damage the liver and kidney. Arsenic also has effects on the skin, causing dark patches (hyperpigmentation), and skin cancer. Arsenic also irritates the eyes, lungs, and skin. These effects have been observed in situations of occupational exposure that are significantly higher than concentrations seen in outdoor air. Exposure can lead to effects in the blood, such as anemia.

EPA has not established a Reference Concentration for arsenic. The Cal EPA has established a chronic reference level based on the developmental effects in mice; and other target organs included the cardiovascular system and nervous system. Arsenic exposure is known to cause lung cancer. EPA classifies arsenic in Group A, the known human carcinogens, based on an increased lung cancer mortality in multiple human populations exposed primarily through inhalation.

The Agency for Toxic Substances and Disease Registry (ATSDR) states that remote areas have concentrations of 0.001 to 0.003 µg/m3 arsenic in air, while urban locations range from 0.020 to 0.100 µg/m3 (ATSDR Toxicological Profile on Arsenic). The mean level of 0.0003 ug/m3 at Grand Junction – Powell site falls below the cited rural range. It is likely that national levels of arsenic have decreased in recent years.

MANGANESE

Manganese is a metal that occurs naturally in the earth's crust. Its chemical symbol is Mn. It exists in the atmosphere as particulate matter, in compounds formed from combination with other atoms. Manganese is used as an additive in metal processing and steel production. It is also used in ceramics, matches, glass, dyes, batteries, and as a pigment in paints (California Air Resources Board Fact Sheet on Manganese). It is also employed in wood preservatives. Organic forms of manganese are used as pesticides and for disease prevention in crops such as fruits, vegetables, and cotton.

Emission sources of manganese include petroleum refineries, steel producers, cement producers, coal-fired power plants, wood-burning, metals operations, mining operations, and incinerators. Manganese occurs naturally in some soils, so wind-blown dusts from exposed land can contain it. Soils contaminated by smelter fall-out can also be a source of emissions during high winds.

Manganese is considered an essential micronutrient in the human body. The body tends to regulate manganese concentrations, so oral exposure to small amounts naturally present in food is rarely a problem. Exposure of manganese by inhalation can lead to health effects. Manganese health effects on the respiratory system include lung irritation, chemical pneumonia, cough, and bronchitis. Manganese may damage the central nervous system. The disease known as "manganism", which results from manganese poisoning, includes psychological and nervous system damage. Individuals with manganism have a mask-like face, depression, uncontrollable laughter, and lethargy. The central nervous system effects include trouble with tremors, balance and walking that is similar to that of Parkinson's disease. Central nervous system damage can occur at exposure levels below those that lead to manganism. Examples are decreases in visual reaction time, hand steadiness, and eye-hand coordination. Manganese also affects the gastro-intestinal tract and the kidneys. However, it should be noted that these health effects have been observed in workers with long-term exposure to manganese fumes and dusts in industrial settings. These exposures were at levels hundreds or thousands of times higher than manganese levels in outdoor air.

EPA classifies manganese as Group D, unclassifiable as to carcinogenic potential. This is because there is little evidence to link it to cancer health effects. EPA has established a Reference Concentration for manganese based on an impairment of neurobehavioral function in humans in occupational exposure studies.

The California Air Resources Board monitored manganese in 1996. They report a network-wide average of 0.0212 µg/m3 total manganese (CARB Fact Sheet on Manganese). The 0.0130 annual mean measured at Grand Junction is below the California average.

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Manganese. Dated 2002. Web Address: **http://www.cdc.gov/niosh/ipcsneng/neng0232.html**

National Institute for Occupational Safety and Health. (NIOSH) Pocket Guide to Chemical Hazards.

Arsenic. Web Address: **http://www.cdc.gov/niosh/npg/npgd0038.html**
Manganese Compounds and fume (as Mn). Web Address: **http://www.cdc.gov/niosh/npg/npgd0379.html**

National Institute for Occupational Safety and Health. (NIOSH) Registry of Toxic Effects of Chemical Substances (RTECS).

Arsenic, dated October 2002. Web Address: **http://www.cdc.gov/niosh/rtecs/cg802c8.html**
Manganese, dated October 2002. Web Address: **http://www.cdc.gov/niosh/rtecs/008d8678.html**

New Jersey Department of Health and Senior Services. "Hazardous Substance Fact Sheets" for Various Substances. Web Address: **http://www.state.nj.us/health/eoh/rtkweb/rtkhsfs.htm**

Arsenic, dated June 1998.
Manganese, dated September 1999.

Occupational Safety and Health Administration. (OSHA) "OSHA Comments from the January 19, 1989 Final Rule on Air Contaminants Project". (Rule remanded by court and not currently in force).

Manganese Fume. Web Address: **http://www.cdc.gov/niosh/pel88/7439-96.html**

Appendix B: Documentation for Grand Junction Urban Air Toxics Trends Monitoring Locations

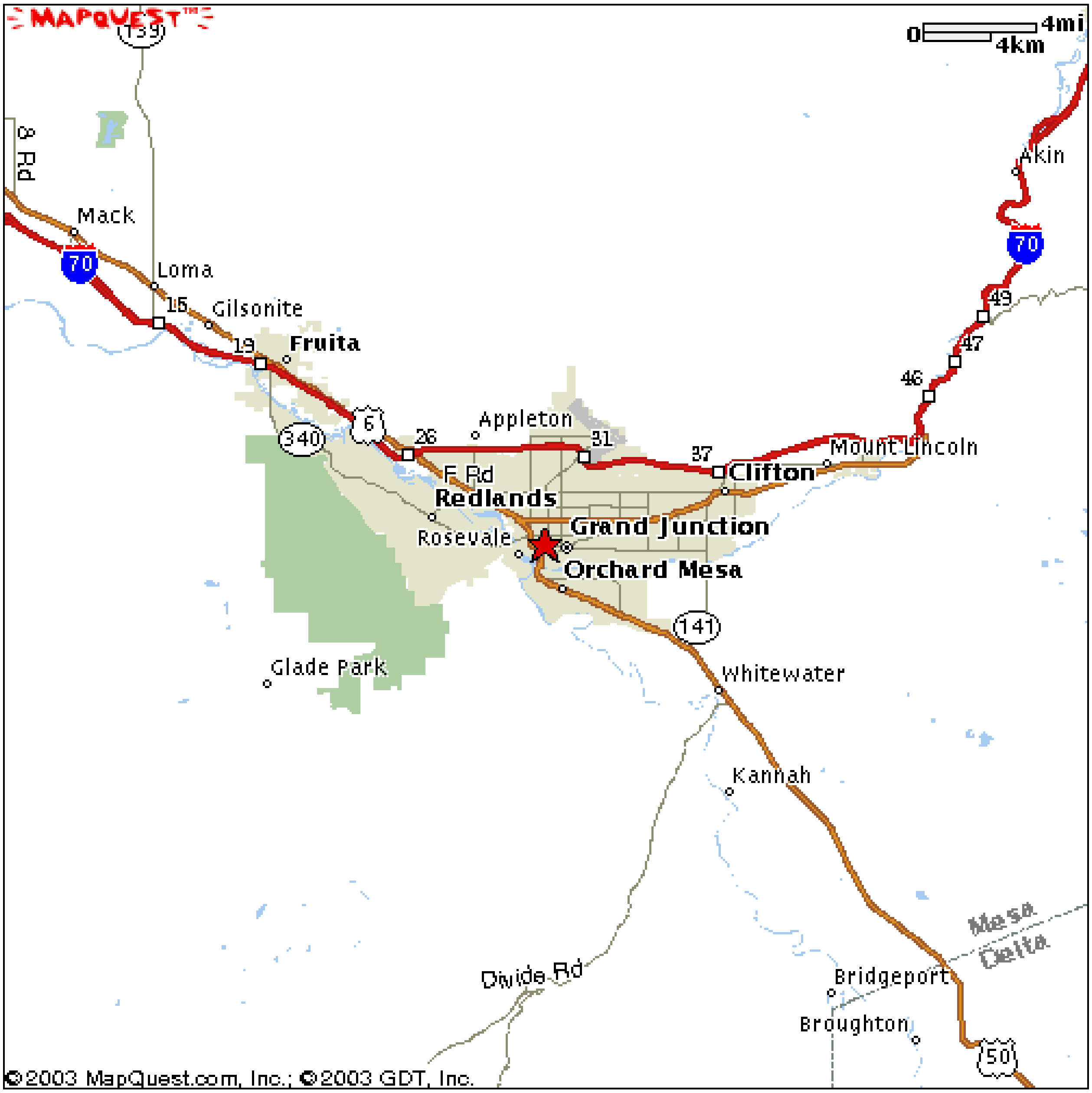
REGIONAL MAP (5 - 30 miles)

AQS ID: **08-077-0017** Site Name: **Grand Junction – Powell Building**

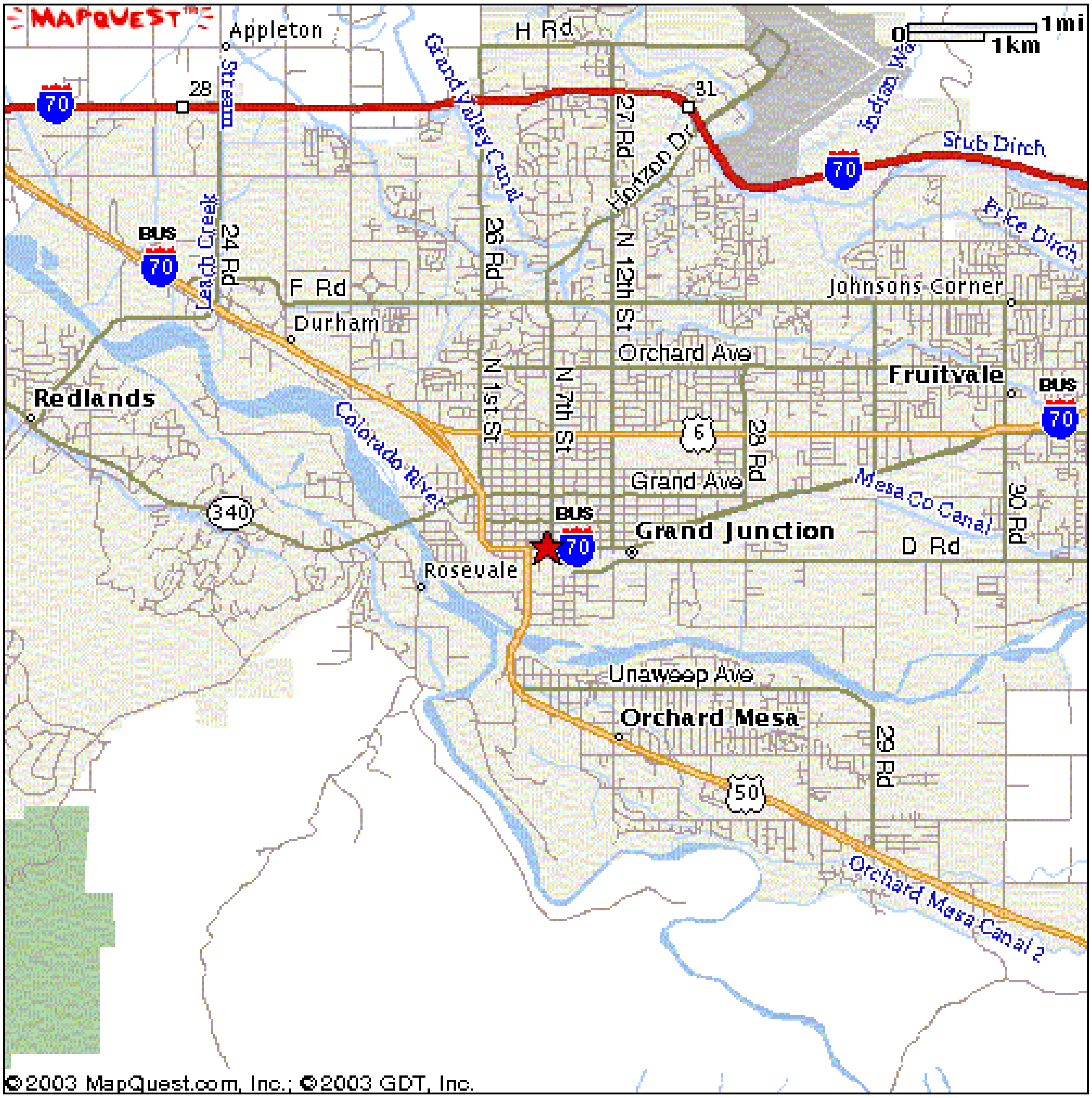
650 South Avenue, Grand Junction, CO 81501
GPS: Zone 12, 710962 E, 4326741 N, elev. 1396m
39° 03’ 51” N, 108° 33’ 42” W

AQS ID: **08-077-0018** Site Name: **Grand Junction – Pitkin Shelter**

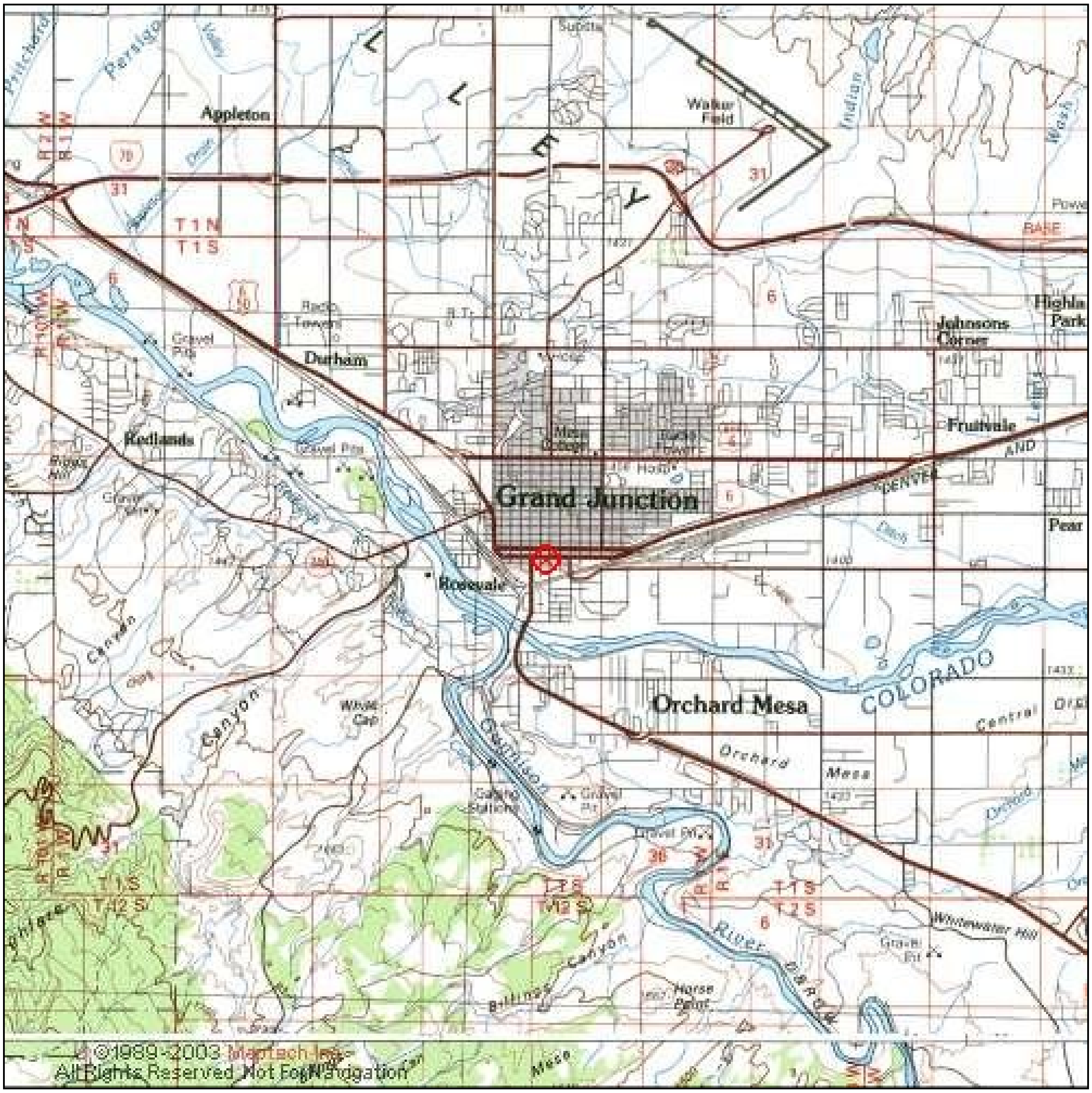
645 ¼ Pitkin Avenue, Grand Junction, CO 81501
GPS: Zone 12, 710962 E, 4326741 N, elev. 1396m
39° 03’ 51” N, 108° 33’ 42” W



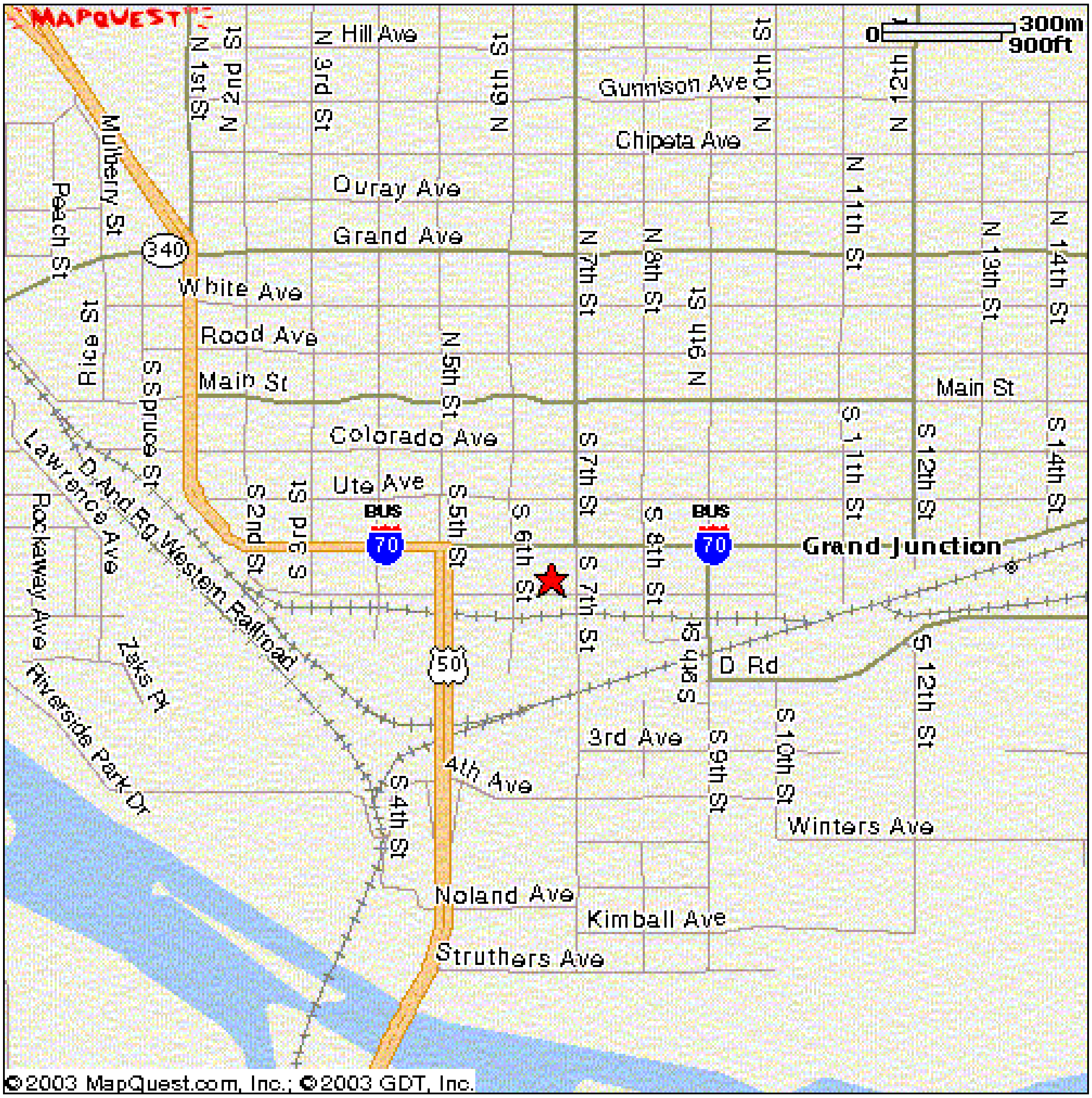
REGIONAL MAP (5 - 30 miles)



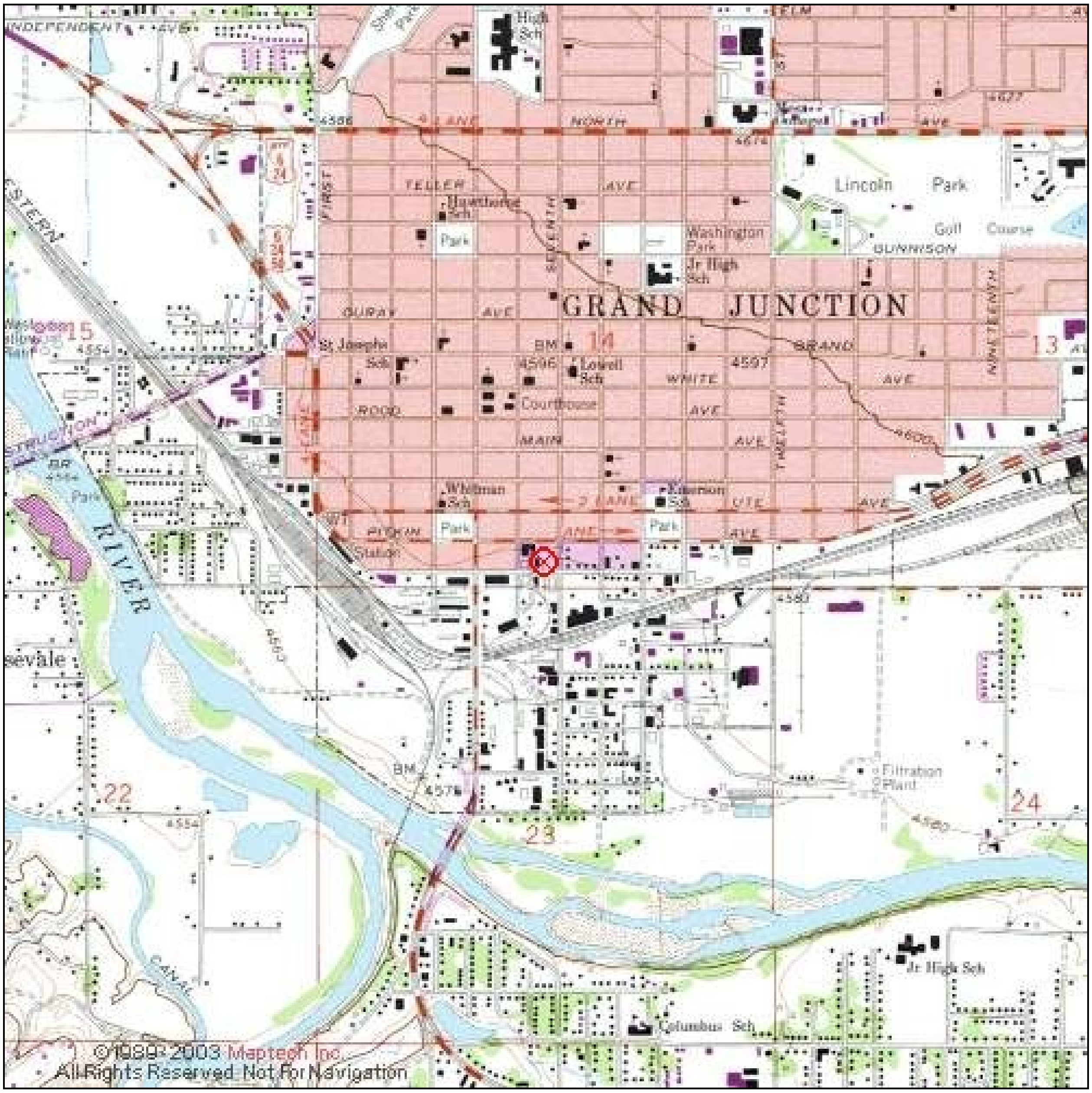
REGIONAL MAP (5 - 30 miles)



SITE MAP (1/4 - 1 mile)

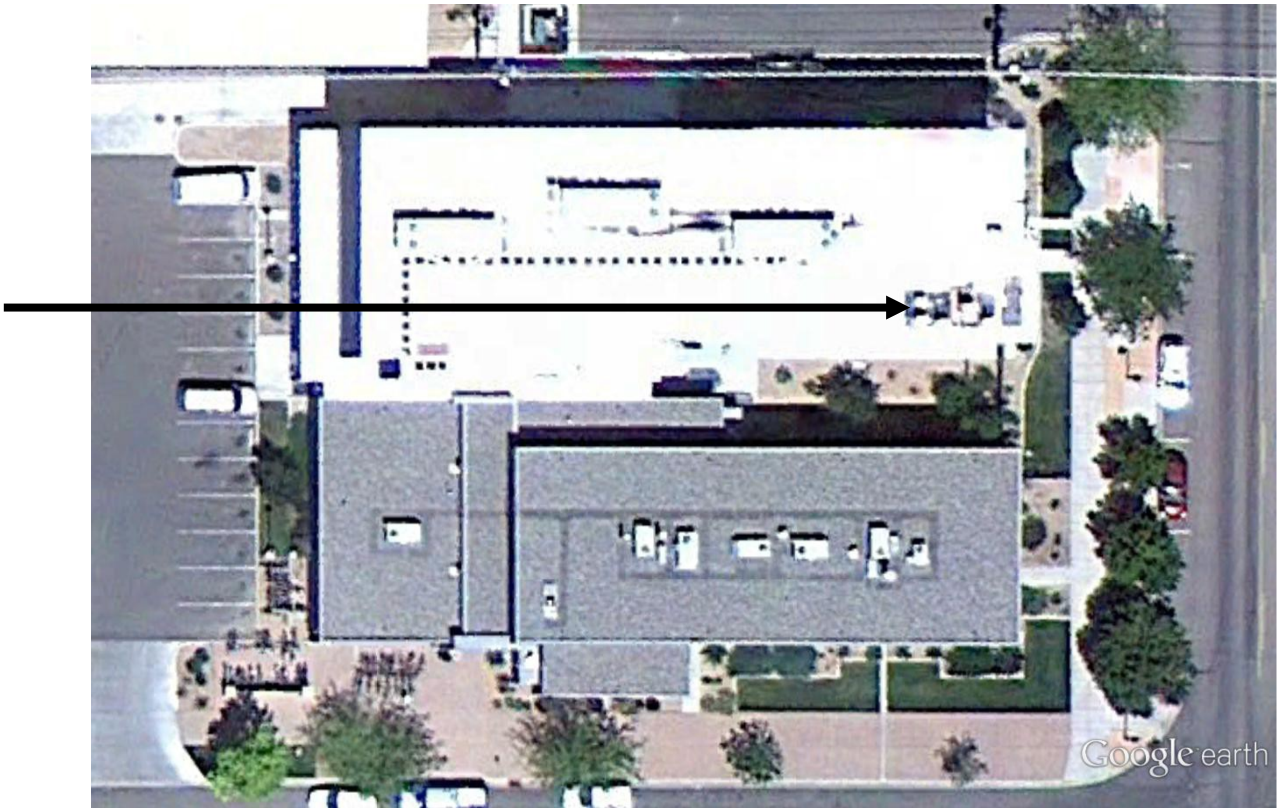


SITE MAP (1/4 - 1 mile)



SITE MAP (1/4 - 1 mile)

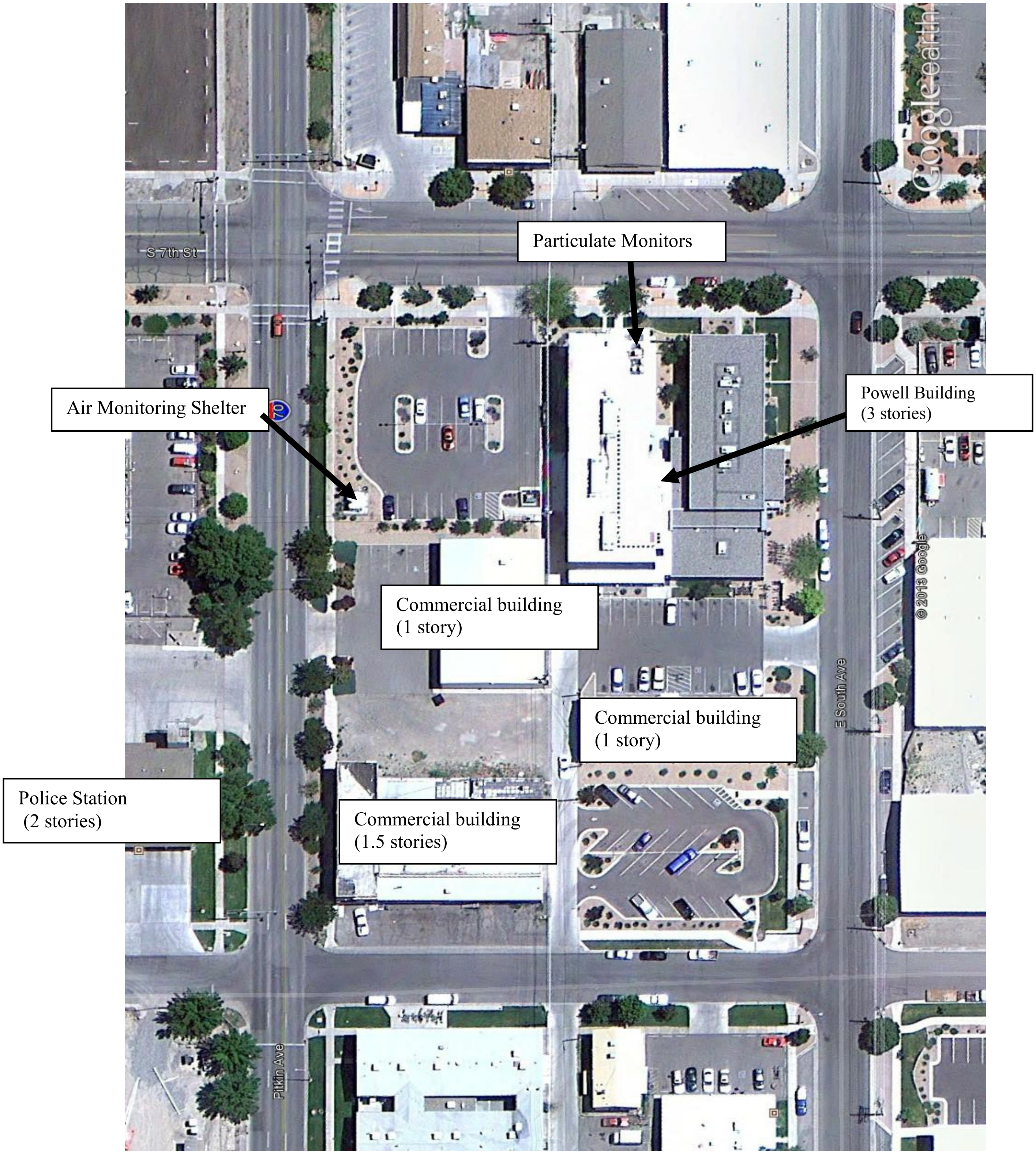
AIRS ID: **08-077-0017** Site Name: **Grand Junction – Powell Building**



SITE MAP (1/4 - 1 mile)

AIRS ID: **08-077-0018** Site Name: **Grand Junction – Pitkin (shelter)**

SITE MAP (1/4 - 1 mile)



AQS ID: **08-077-0017** Site Name: **Grand Junction – Powell Building**

Photo Date: 10/16/2013

Looking **NORTH**

Looking **NORTHEAST**

AQS ID: **08-077-0017** Site Name: **Grand Junction – Powell Building**

Photo Date: 10/16/2013

Looking **EAST**

Looking **SOUTHEAST**

AQS ID: **08-077-0017** Site Name: **Grand Junction – Powell Building**

Photo Date: 10/16/2013

Looking **SOUTH**

Looking **SOUTHWEST**

AQS ID: **08-077-0017** Site Name: **Grand Junction – Powell Building**

Photo Date: 10/16/2013

Looking **WEST**

Looking **NORTHWEST**

AQS ID: **08-077-0017** Site Name: **Grand Junction – Powell Building**

Photo Date: 10/16/2013

Site Photo: Particulate samplers (looking **SOUTH)**

AQS ID: **08-077-0018** Site Name: **Grand Junction – Pitkin Shelter**

Photo Date: 10/16/2013

Looking **NORTH**

Looking **NORTHEAST**

AQS ID: **08-077-0018** Site Name: **Grand Junction – Pitkin Shelter**

Photo Date: 10/16/2013

Looking **EAST**

Looking **SOUTHEAST**

AQS ID: **08-077-0018** Site Name: **Grand Junction – Pitkin Shelter**
Photo Date: 10/16/2013

Looking **SOUTH**

Looking **SOUTHWEST**

AQS ID: **08-077-0018** Site Name: **Grand Junction – Pitkin Shelter**

Photo Date: 10/16/2013

Looking **WEST**

Looking **NORTHWEST**

AQS ID: **08-077-0018** Site Name: **Grand Junction – Pitkin Shelter**

Photo Date: 10/16/2013

Site Photo: Shelter and inlets (looking **NORTHWEST**)