National Air Toxics Trends Study Grand Junction, Colorado

January through December 2011

Colorado Department
of Public Health
and Environment

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I.   EXECUTIVE SUMMARY

The Grand Junction air toxics monitors were originally established as a part of the 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, 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 2011 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 companion documents. The report, "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. The document, "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. This report discusses the chemical formula, sources and uses of each compound. The companion report 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, or 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 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	PM$_{10}$ Metals	TSP Metals	PAHs
Acrolein	Formaldehyde	Nickel	Hexavalent Chromium	Naphthalene
Tetrachloroethylene	Acetaldehyde	Arsenic		Benzo(a)pyrene
Benzene		Cadmium		
Carbon Tetrachloride		Manganese		
Chloroform		Beryllium		
Trichloroethylene		Lead		
1,3-Butadiene				
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), 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 2011 through December 2011. It is separated into sections covering the various compounds of interest. Sections 3, 4, 5, 6, and 9 discuss the compounds monitored as a part of this study. Sections 7, 8 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 site and Pitkin site) are in close proximity to one another. The Powell site is located on top of the Powell Building (approximately three stories in heights) 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 654-1/4 Pitkin Avenue. The hexavalent chromium and particulate samplers are located on the Powell Building, and the carbon monoxide analyzer, air toxics samplers, 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. Documentation regarding these sites, including maps, photographs, and aerial views, is available in the companion report, "Documentation for Grand Junction Urban Air Toxics Trends Monitoring Locations – Site Maps and Photographs." The sites are located on the southern end of the city 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. Twelve compounds were measured for this study. A listing of these compounds, as well as a summary of the collected data, is shown in Table 2 and Table 3. Of the twelve carbonyl compounds analyzed for, two are included on the mandatory monitoring list of 19 core HAPs. They are bolded in Table 2 and Table 3.

Table 2. Carbonyl Sample Summary – 2011

Compound	CAS Number	# of ND's	% ND
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%**
Hexaldehyde	66-25-1	0	0%
Propionaldehyde	123-38-6	0	0%
Valeraldehyde	110-62-3	0	0%
Tolualdehydes	NA	9	15%
2,5-Dimethylbenzaldehyde	5779-94-2	60	100%
Isovaleraldehyde	590-86-3	60	100%

ND = Not Detected

Table 3.   Carbonyl Average Concentration Comparison 2004-11

Analyte	Annual Averages (µg/m³)							
	2004	2005	2006	2007	2008	2009	2010	2011
2,5-Dimethylbenzaldehyde	*0.08*	*0.06*	*0.02*	*0.03*	*0.03*	*0.00*	*0.01*	*0.01*
Acetaldehyde	**10.53**	**5.39**	**4.25**	**5.03**	**4.48**	**2.89**	**1.95**	**2.43**
Acetone	18.39	11.08	9.69	12.45	12.35	5.57	5.13	4.92
Benzaldehyde	1.11	0.95	1.45	1.41	1.30	0.34	0.31	0.41
Butyraldehyde	0.91	1.18	1.00	1.06	0.92	0.35	0.34	0.39
Crotonaldehyde	0.67	0.62	0.50	0.57	0.55	0.22	0.20	0.16
Formaldehyde	**3.45**	**3.83**	**4.94**	**4.94**	**5.04**	**4.01**	**2.74**	**2.74**
Hexaldehyde	0.56	0.43	0.46	0.43	0.52	0.12	0.13	0.10
Isovaleraldehyde	*0.04*	*0.07*	*0.15*	*0.08*	*0.08*	*0.01*	*0.01*	*0.00*
Propionaldehyde	0.39	0.75	0.74	0.73	0.91	0.39	0.35	0.35
Tolualdehydes	0.61	0.63	1.11	0.98	0.77	0.18	0.19	0.19
Valeraldehyde	0.18	0.71	0.59	0.06	0.52	0.15	0.11	0.08

Bold = MQO Core Analyte

   Carbonyl compounds were sampled on an every-sixth-day basis for the year, for a total of 61 samples attempted. There was one missed sample. The data recovery rate of 98% exceeds the EPA goal for over 85% sample recovery.

   The annual mean concentrations for each carbonyl compound, from 2004 through 2011, 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. The isovaleraldehyde detection percentage of 0% is a decrease from the 3% detection rate in 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, 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. This compound has not been detected since 2006. During the pilot phase of this study in 2001-2002, 2,5-dimethylbenzaldehyde was detected 34 percent of the time. In 2005, the detection rate dropped to 4.8 percent, and it has not been found at detectable levels since that time.

Graphs

The summary data for carbonyl compounds measured during 2011 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 2011 were similar to those in 2010. In comparison, the national average concentrations for those compounds were 2.00, 2.57, and 2.86 micrograms per meter cubed, respectively.[4] The national average was calculated using data from the National Monitoring Programs (NMP), run by the EPA. The NMP includes the Photochemical Assessment Monitoring Stations (PAMS) network, Community-Scale Air Toxics Ambient Monitoring (CSATAM) Program, and the NATTS network. The formaldehyde and acetaldehyde values in Grand Junction were similar to the national averages, while the acetone average was larger.
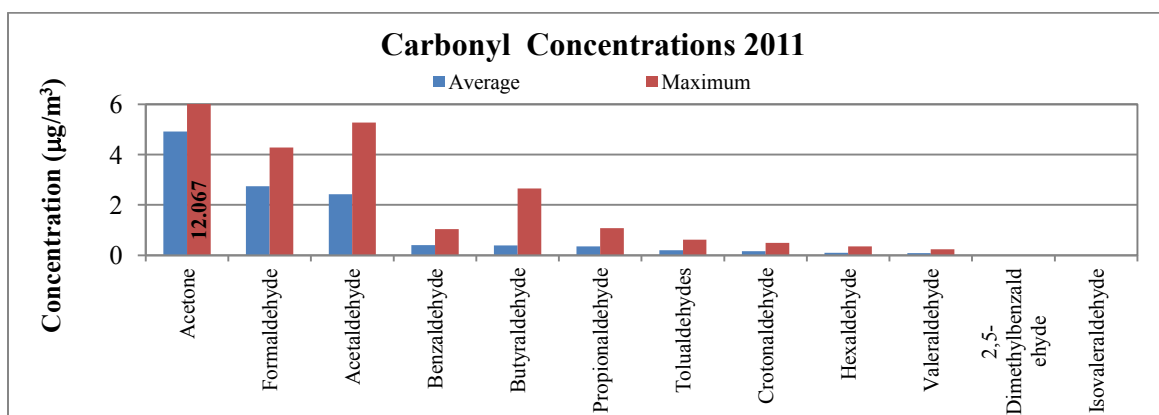
Figure 1. Annual Mean and Maximum Carbonyl Concentrations for 2011
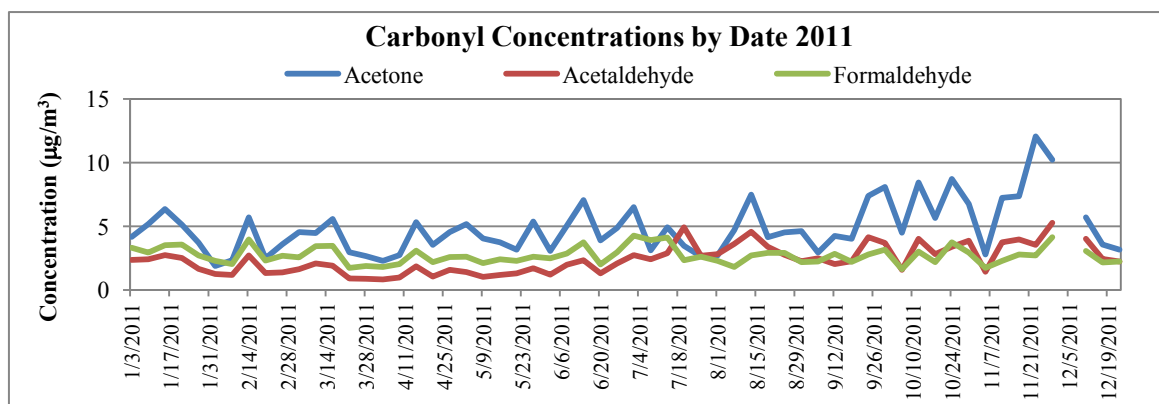
Figure 2. Carbonyl Sample Day Comparisons for 2011

[4] "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 shows the concentrations for select carbonyl compounds during the year. The compounds did not show much seasonal variation. This was also the case in 2010 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 peaks during the summer.

Figure 3 is a graph of the weekday versus weekend average carbonyl concentrations in 2011. 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 MDLs for the entire year, since they were non-detectable in all samples. Crotonaldehyde, and hexaldehyde, have weekend averages that are slightly higher than their weekday counterparts. Crotonaldehyde is emitted from the combustion of gasoline, as well as wood and tobacco burning.[5] 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.[6] It is also found naturally in many fruits, vegetables, meats, shellfish, and certain species of trees and plants.[7]
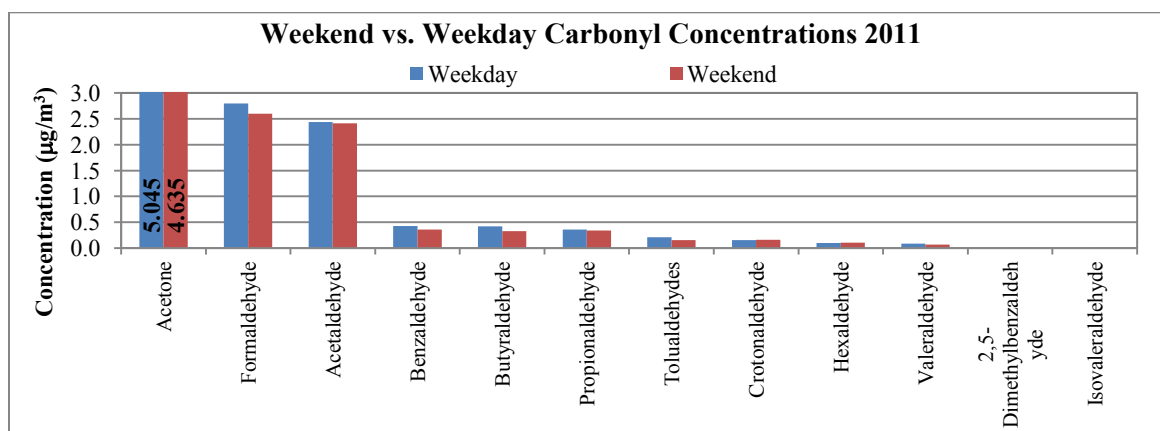
Figure 3. Weekday vs. Weekend Carbonyl Concentrations - 2011
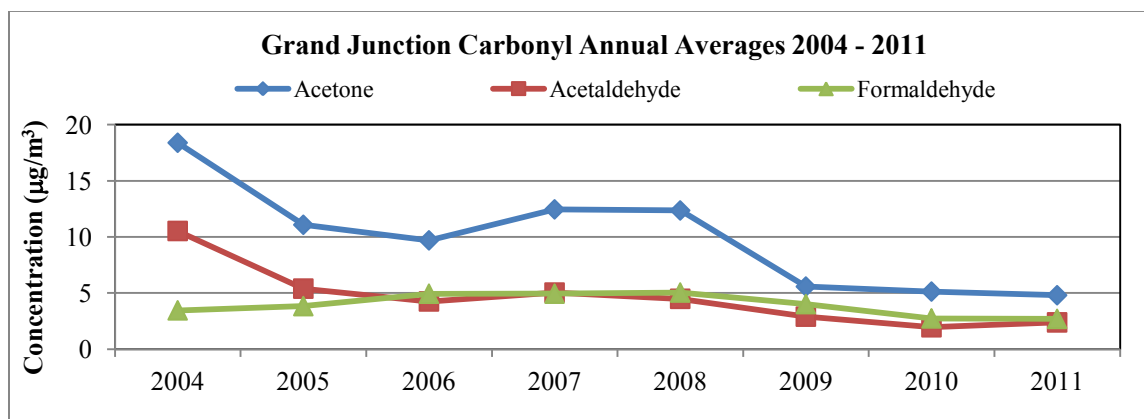
Figure 4. Carbonyl Annual Averages 2004 – 2011

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[5] Agency for Toxic Substances and Disease Registry. "Tox Facts for Crotonaldehyde." April 2002. http://www.atsdr.cdc.gov/toxfaqs/tf.asp?id=948&tid=197

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

[7] *Ibid.*

Grand Junction Carbonyl Annual Averages 2004 - 2011
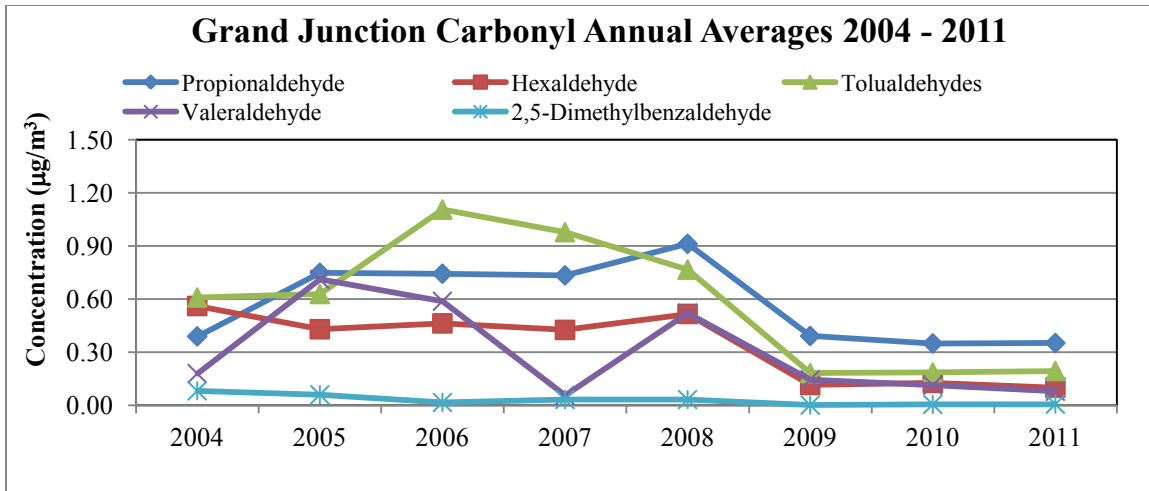
Figure 5. Carbonyl Annual Averages 2004 – 2011, ctd.

Grand Junction Carbonyl Annual Averages 2004 - 2011
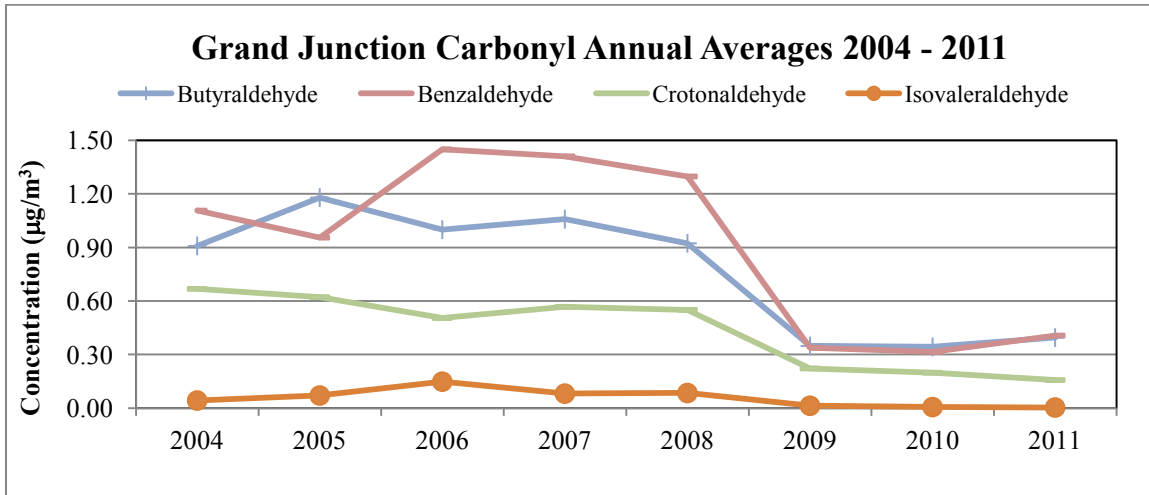
Figure 6. Carbonyl Annual Averages 2004 – 2011, ctd.

Figure 4 through Figure 6 are graphs of the annual average carbonyl concentrations at the Grand Junction site, for 2004 through 2011. 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 the two year average from 2010 through 2011. The formaldehyde average increased slightly from the first three-year average to the second, but then decreases again with the 2010-2011 average. Averages for the other two compounds continue to drop. The annual average concentration value for acetone in 2011 is less than half the value of the last 3 year average. The concentrations for acetaldehyde and formaldehyde in 2011 were both lower than the last 3-year average calculated for 2007 through 2009. The percentage differences between the 2004 through 2006, and 2007 through 2009 3-year averages for acetone, acetaldehyde, and formaldehyde are -22%, -38% and 14%, respectively.

[11]
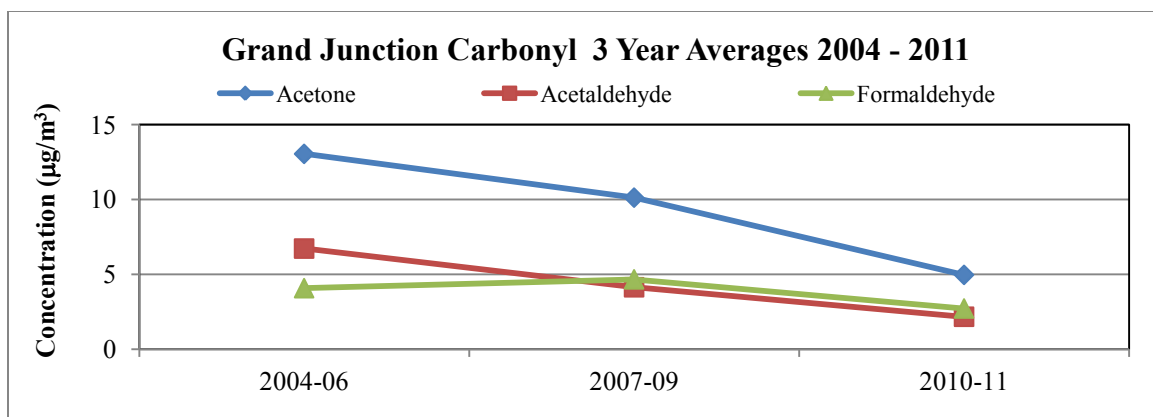
Figure 7. Carbonyl 3-Year Averages 2004 – 2011

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 2011 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. These are the same VOCs collected by all of the sites participating in the national air toxics study. VOCs were sampled on an every-sixth-day basis, for a total of 61 possible days. One sample was not collected, giving 60 samples on the year (98.4% sample recovery).

Table 4.   VOC List with 2011 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%
Acetonitrile	75-05-8	0	0%

Compound	CAS Number*	# of ND's	% ND
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%
Ethylbenzene	100-41-4	0	0%
m,p-Xylene	100-01-6	0	0%
Methyl Ethyl Ketone	78-93-3	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%
Toluene	108-88-3	0	0%
Trichlorofluoromethane	75-69-4	0	0%
Trichlorotrifluoroethane	76-13-1	0	0%
Dichlorotetrafluoroethane	76-14-2	1	2%
1,1,1-Trichloroethane	71-55-6	3	5%
Methyl Isobutyl Ketone	108-10-1	4	7%
1,3-Butadiene	**106-99-0**	**7**	**12%**
Tetrachloroethylene	**127-18-4**	**7**	**12%**
Chloroform	**67-66-3**	**18**	**30%**
Bromomethane	74-83-9	25	42%
p-Dichlorobenzene	106-46-7	28	47%
Trichloroethylene	**79-01-6**	**40**	**67%**
Acrylonitrile	107-13-1	43	72%
1,2-Dichloroethane	107-06-2	44	73%
Dibromochloromethane	124-48-1	51	85%
o-Dichlorobenzene	95-50-1	51	85%
Hexachloro-1,3-butadiene	87-68-3	52	87%
m-Dichlorobenzene	541-73-1	54	90%
Vinyl chloride	**75-01-4**	**54**	**90%**
1,1,2,2-Tetrachloroethane	79-34-5	55	92%
Bromoform	75-25-2	55	92%
Chloroethane	75-00-3	55	92%
1,1-Dichloroethene	75-35-4	57	95%
1,2,4-Trichlorobenzene	120-82-1	57	95%
1,2-Dibromoethane	106-93-4	57	95%
Methyl Methacrylate	80-62-6	57	95%
1,1,2-Trichloroethane	79-00-5	59	98%
cis-1,3-Dichloropropene	10061-01-5	59	98%

Compound	CAS Number*	# of ND's	% ND
Ethyl tert-Butyl Ether	637-92-3	59	98%
Methyl tert-Butyl Ether	1634-04-4	59	98%
trans-1,2-Dichloroethylene	156-60-5	59	98%
1,1-Dichloroethane	75-34-3	60	100%
1,2-Dichloropropane	78-87-5	60	100%
Bromochloromethane	74-97-5	60	100%
Bromodichloromethane	75-27-4	60	100%
Chlorobenzene	108-90-7	60	100%
Chloromethylbenzene	100-44-7	60	100%
Chloroprene	126-99-8	60	100%
cis-1,2-Dichloroethylene	156-59-4	60	100%
Ethyl Acrylate	140-88-5	60	100%
tert-Amyl Methyl Ether	994-05-8	60	100%
trans-1,3-Dichloropropene	10061-02-6	60	100%

*CAS Number refers to the Chemical Abstract System Number. This is an alternate way of referencing organic chemicals, which can have multiple names.
ND = Not Detected
Bold = MQO Core Analyte

In 2011, as in 2010, there were 24 compounds detected in at least 90% of the samples taken. However, two compounds on the 2010 list were detected less than 90% of the time in 2011, and were removed from the list. In addition, there were two other compounds that went from detection rates of less than 90% in 2010, to rates greater than 90% in 2011. The two compounds that dropped off the list are 1,3-butadiene, and tetrachloroethylene. The detection rate for both compounds in 2011 was 88%. Both of those compounds are on the core list of 19 HAPs. The two compounds that made the 2011 list are 1,1,1-trichloroethane, and methyl isobutyl ketone. Table 5 is an alphabetical listing of the 24 compounds most frequently detected in 2011. Bolded compounds are on the list of 19 core HAPs.

Table 5.   VOCs Detected in Greater Than 90% of 2011 Samples

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

Bold = MQO Core Analyte

There were 11 compounds that were not detected at all during 2011, which is down from the 16 non-detects in 2010. There were 20 compounds that were detected in five percent, or less, of the samples in 2011. This

is a decrease from 2010, where 26 compounds were detected in five percent, or less, of the samples. This list of 20 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 maximum and mean concentrations for each of the 60 VOCs measured during the study. It should be noted that the annual means and maximums 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, with their respective MDLs for 2011, as well as their respective molecular weights. Bolded values indicate the compound is one of the 19 core HAPs. Italicized values indicate a detection rate of less than 90% for the year.

Table 6. VOC Data Summary 2011

Analyte	Molecular Weight (g/mol)	Average (µg/m³)	Maximum (µg/m³)	Avg. MDL (µg/m³)
1,1,1-Trichloroethane	133.41	0.065	0.115	0.120
1,1,2,2-Tetrachloroethane	*167.85*	*0.082*	*0.103*	*0.165*
1,1,2-Trichloroethane	*133.41*	*0.068*	*0.068*	*0.136*
1,1-Dichloroethane	*98.96*	*0.016*	*0.016*	*0.032*
1,1-Dichloroethene	*96.94*	*0.019*	*0.040*	*0.036*
1,2,4-Trichlorobenzene	*181.45*	*0.130*	*0.134*	*0.267*
1,2,4-Trimethylbenzene	120.20	0.699	8.702	0.138
1,2-Dibromoethane	*187.87*	*0.069*	*0.069*	*0.138*
1,2-Dichloroethane	*98.96*	*0.040*	*0.125*	*0.036*
1,2-Dichloropropane	*112.99*	*0.053*	*0.053*	*0.106*
1,3,5-Trimethylbenzene	120.20	0.234	1.824	0.128
1,3-Butadiene	***54.09***	***0.135***	***0.507***	***0.015***
Acetonitrile	41.05	0.538	2.653	0.040
Acetylene	26.04	1.375	4.399	0.017
Acrolein	**56.07**	**0.735**	**1.564**	**0.115**
Acrylonitrile	*53.06*	*0.069*	*0.755*	*0.026*
Benzene	**78.12**	**1.333**	**10.544**	**0.093**
Bromochloromethane	*129.39*	*0.021*	*0.021*	*0.042*
Bromodichloromethane	*163.83*	*0.084*	*0.084*	*0.168*
Bromoform	*252.73*	*0.126*	*0.129*	*0.258*
Bromomethane	*94.94*	*0.043*	*0.221*	*0.035*
Carbon Disulfide	76.13	1.500	4.390	0.103
Carbon Tetrachloride	**153.82**	**0.536**	**0.906**	**0.151**
Chlorobenzene	*112.56*	*0.048*	*0.048*	*0.097*
Chloroethane	*64.52*	*0.016*	*0.084*	*0.024*
Chloroform	***119.38***	***0.087***	***0.210***	***0.044***
Chloromethane	50.49	1.268	1.708	0.025
Chloromethylbenzene	*126.58*	*0.101*	*0.101*	*0.202*
Chloroprene	*88.54*	*0.014*	*0.014*	*0.029*
cis-1,2-Dichloroethylene	*96.94*	*0.018*	*0.018*	*0.036*
cis-1,3-Dichloropropene	*110.97*	*0.050*	*0.050*	*0.100*

[15]

Analyte	Molecular Weight (g/mol)	Average ($\mu g/m^3$)	Maximum ($\mu g/m^3$)	Avg. MDL ($\mu g/m^3$)
Dibromochloromethane	*208.29*	*0.087*	*0.089*	*0.179*
Dichlorodifluoromethane	120.91	2.761	3.323	0.054
Dichloromethane	84.94	1.313	23.589	0.035
Dichlorotetrafluoroethane	170.92	0.133	0.196	0.063
Ethyl Acrylate	*100.12*	*0.041*	*0.041*	*0.082*
Ethyl tert-Butyl Ether	*102.18*	*0.017*	*0.021*	*0.033*
Ethylbenzene	106.17	0.619	2.453	0.074
Hexachloro-1,3-butadiene	*260.76*	*0.185*	*0.197*	*0.395*
m,p-Xylene	106.17	1.968	8.989	0.148
m-Dichlorobenzene	*147.01*	*0.097*	*0.102*	*0.204*
Methyl Ethyl Ketone	72.11	1.082	2.244	0.463
Methyl Isobutyl Ketone	100.16	0.156	0.606	0.090
Methyl Methacrylate	*100.12*	*0.049*	*0.225*	*0.090*
Methyl tert-Butyl Ether	*88.15*	*0.015*	*0.036*	*0.029*
n-Octane	114.23	0.373	1.121	0.070
o-Dichlorobenzene	*147.01*	*0.101*	*0.111*	*0.222*
o-Xylene	106.17	0.713	2.857	0.078
p-Dichlorobenzene	*147.01*	*0.089*	*0.156*	*0.210*
Propylene	42.08	0.861	2.186	0.067
Styrene	104.16	1.450	8.691	0.094
tert-Amyl Methyl Ether	*102.18*	*0.033*	*0.033*	*0.067*
Tetrachloroethylene	***165.83***	***0.263***	***1.112***	***0.122***
Toluene	92.15	4.006	39.574	0.060
trans-1,2-Dichloroethylene	*96.94*	*0.016*	*0.032*	*0.032*
trans-1,3-Dichloropropene	*110.97*	*0.057*	*0.057*	*0.113*
Trichloroethylene	***131.29***	***0.086***	***0.322***	***0.134***
Trichlorofluoromethane	137.37	1.518	1.820	0.056
Trichlorotrifluoroethane	187.38	0.752	0.935	0.084
Vinyl chloride	***62.50***	***0.011***	***0.026***	***0.020***

MDL = Minimum Detection Level

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

In general, the concentrations from 2011 compared well with the 2010 data. However, some compounds did show average concentrations that were significantly lower than their 2010 values. For instance, dichloromethane, acetonitrile, and styrene all showed much larger annual average concentrations in 2010 as opposed to 2011. In 2011, their respective annual average concentrations were 1.313, 0.538, and 1.450 $\mu g/m^3$. In 2010, they were 91.65, 20.33, and 2.572 $\mu g/m^3$. The large decrease in concentrations arises from significantly elevated concentrations of these compounds on four sample days in 2010. 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 24 compounds that were detected in greater than 90% of the samples in 2011, 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 15 micrograms per meter cubed to a full-scale value of 2.0 micrograms per meter cubed. The compounds with the five largest annual average concentrations are toluene, dichlorodifluoromethane, m,p-xylene, trichlorofluoromethane, and carbon disulfide. Their values are 4.01, 2.76, 1.97, 1.52, and 1.50 micrograms per meter cubed, respectively. In comparison, the NMP national averages for the same compounds were 2.21, 2.74, 1.06, 1.57, and 2.88 micrograms per cubic meter, respectively.[8]
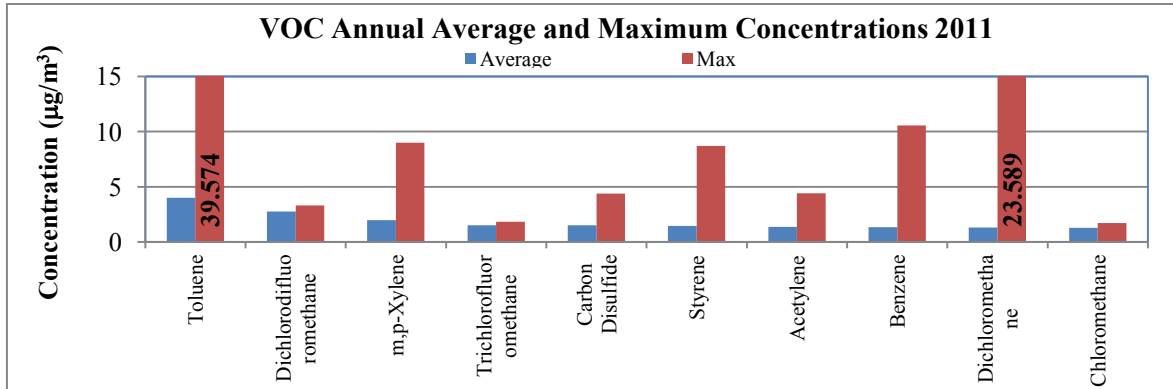
Figure 8. VOC Annual and Maximum Concentrations 2011
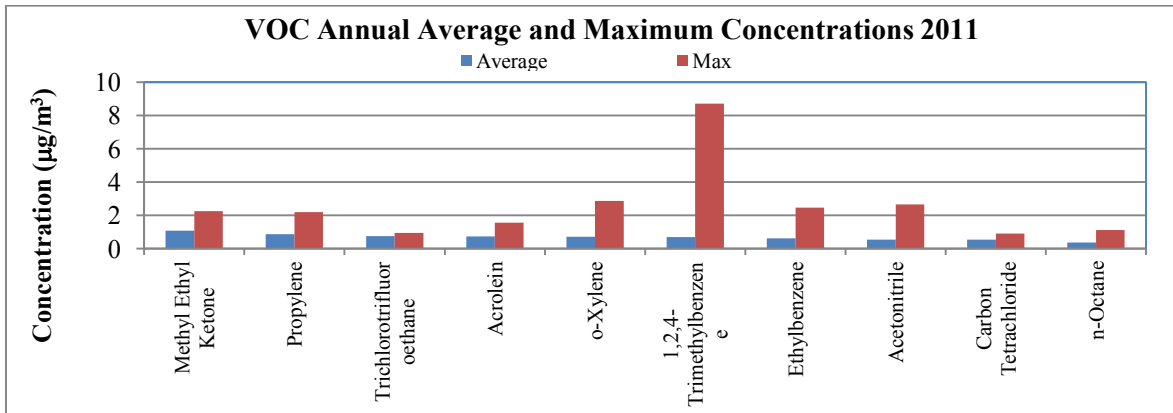
Figure 9. VOC Annual and Maximum Concentrations 2011, ctd.
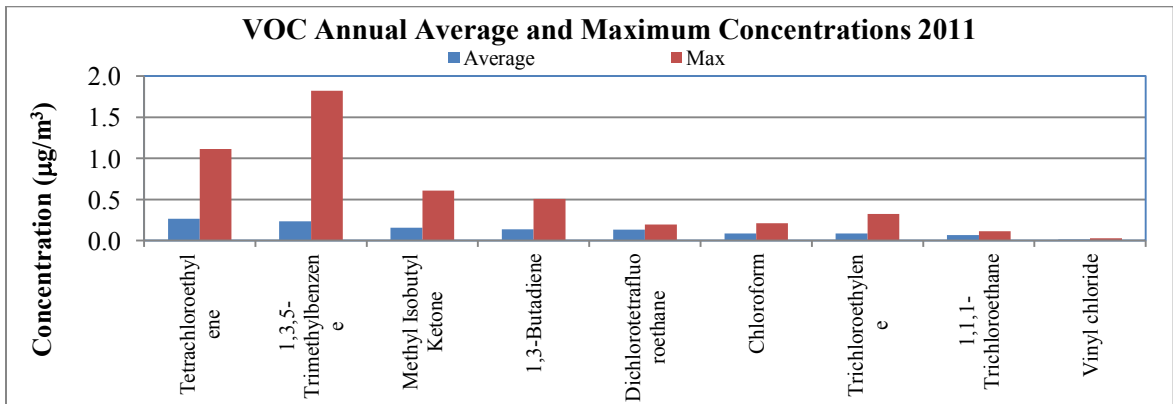
Figure 10. VOC Annual and Maximum Concentrations 2011, ctd.

[8] "2011 National Monitoring Programs Annual Report (UATMP, NATTS, CSATAM). US EPA. August 2013. http://www.epa.gov/ttnamti1/files/ambient/airtox/2011nmpreport.pdf.
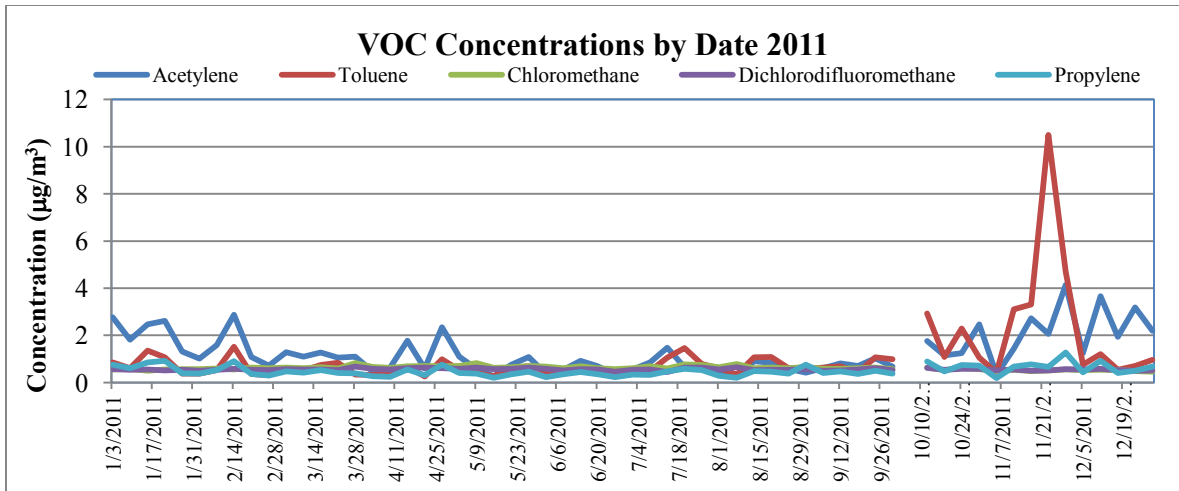
Figure 11. VOC Concentrations by Date 2011
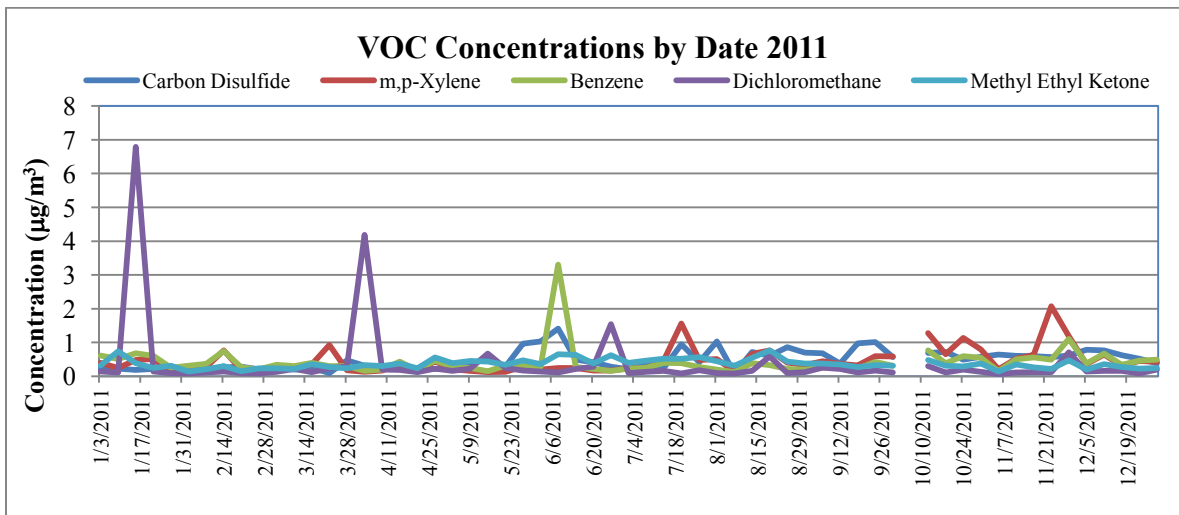
Figure 12. VOC Concentrations by Date 2011, ctd.
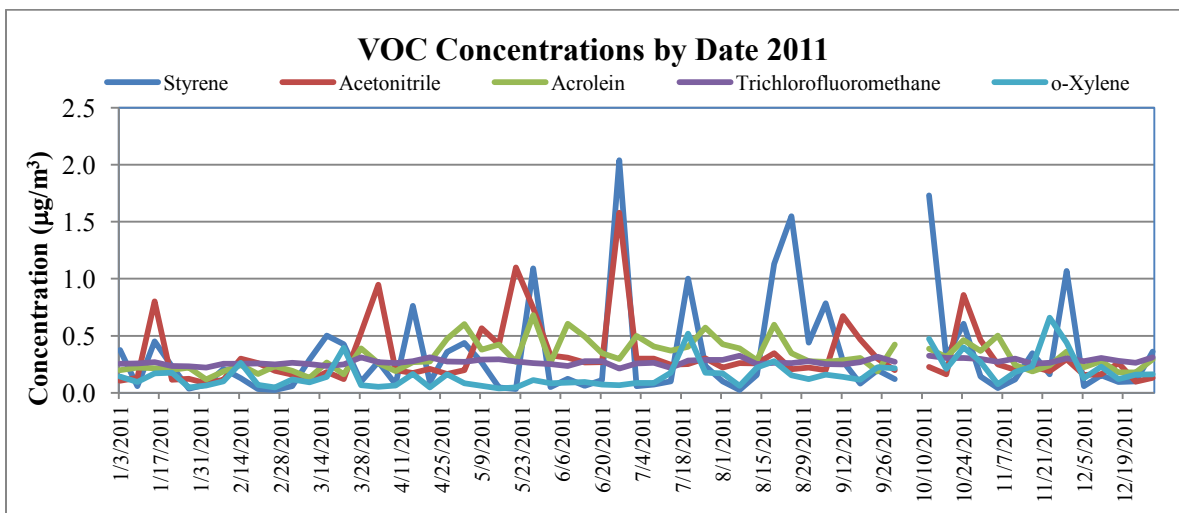
Figure 13. VOC Concentrations by Date 2011, ctd.
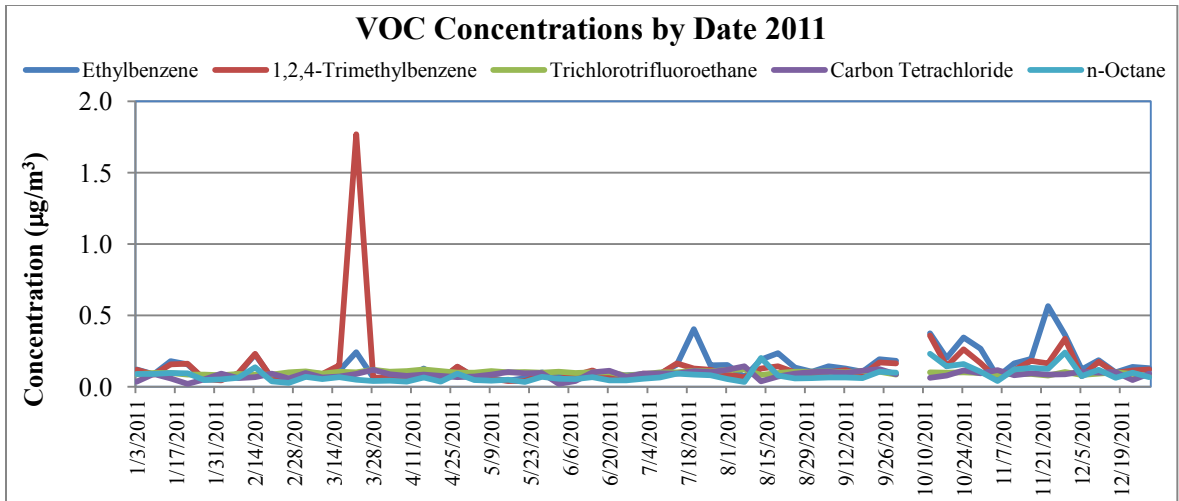
Figure 14. VOC Concentrations by Date 2011, ctd.
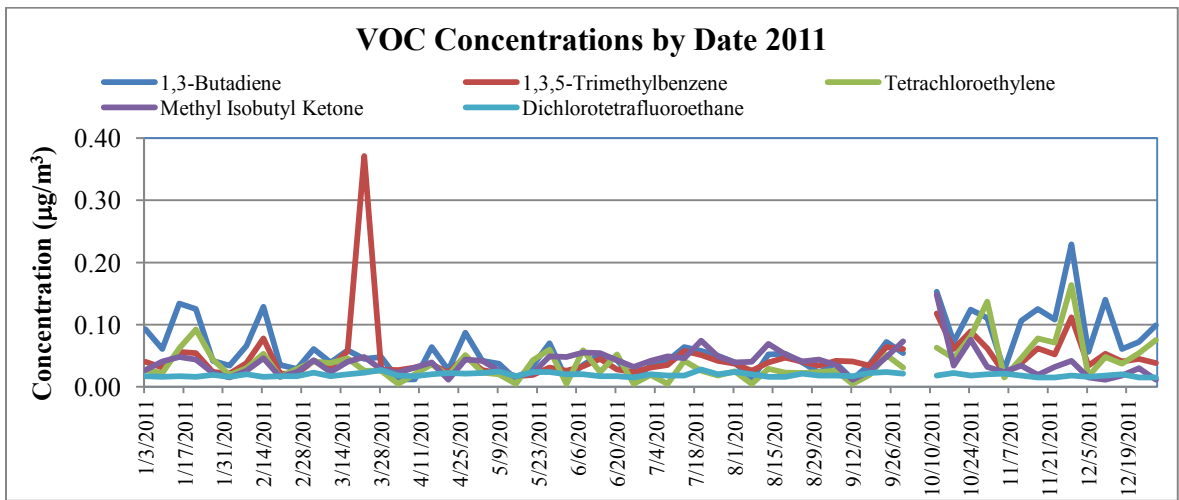
Figure 15. VOC Concentrations by Date 2011, ctd.
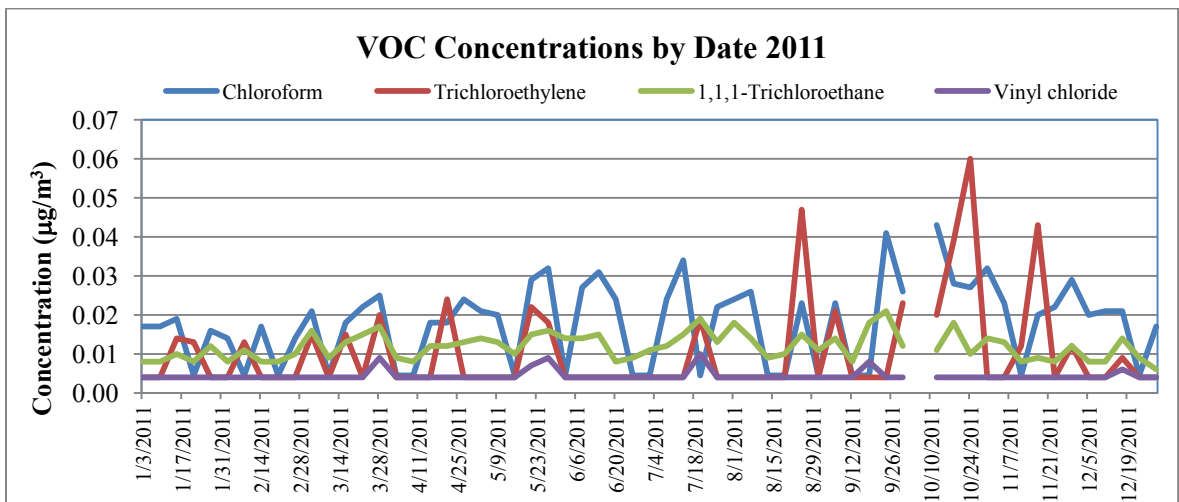
Figure 16. VOC Concentrations by Date 2011, ctd.

[19]

Figure 11 through Figure 16 show the concentrations of the 24 most detected VOCs 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 11 . VOC concentrations are typically higher in the summer due to the higher temperatures, and longer availability of ultraviolet rays for the photolytic process.

Figure 17 through Figure 23 graphically illustrate the weekday versus weekend VOC concentrations in 2011for 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. 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.
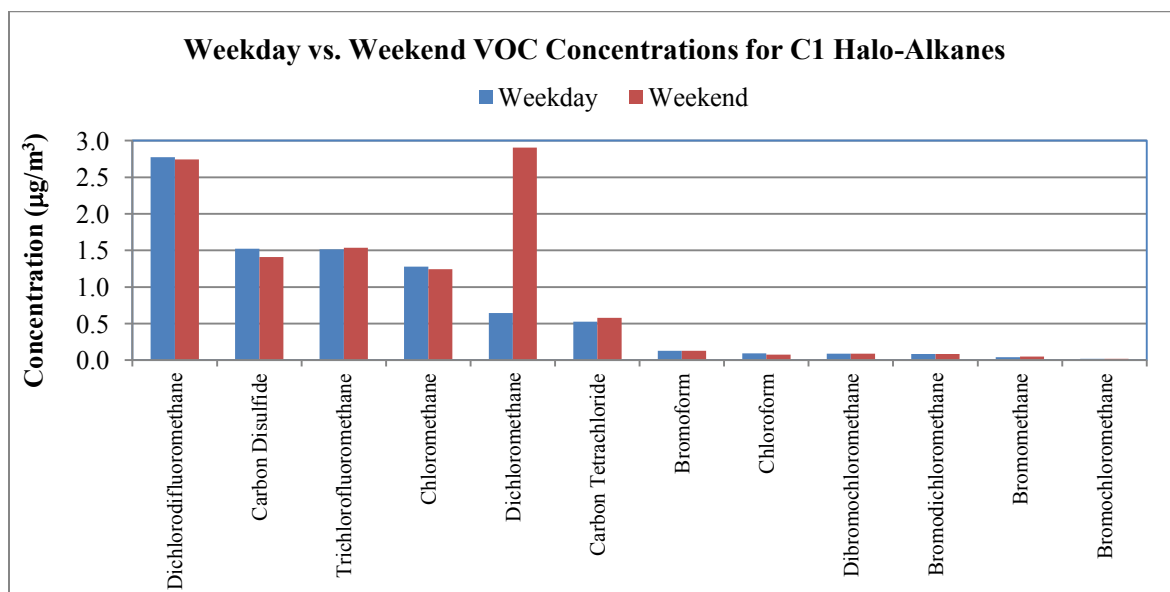
Figure 17.   **VOC Weekday vs. Weekend Comparison for C1 Alkanes**
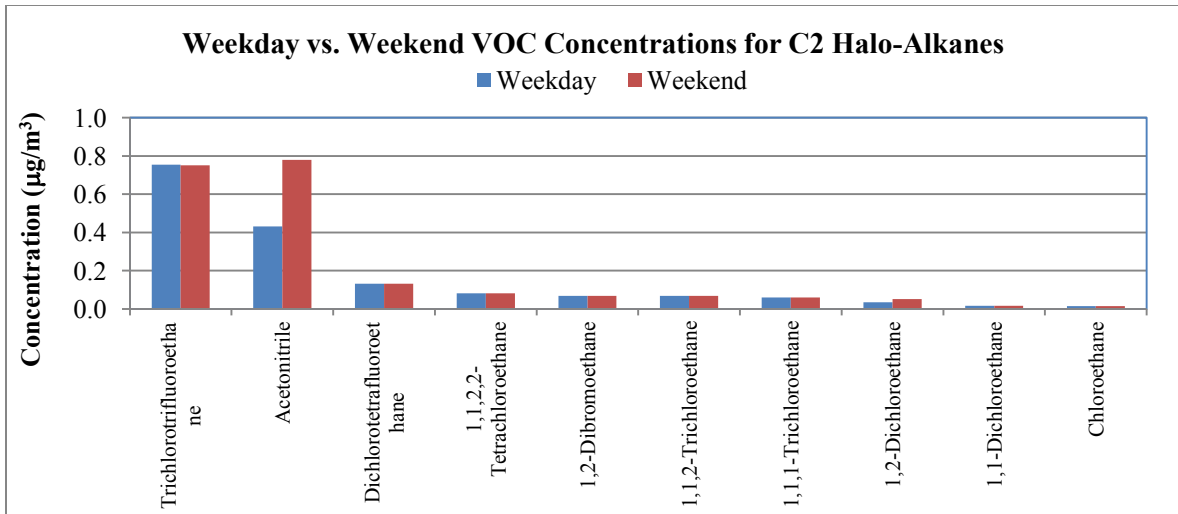
Figure 18. VOC Weekend vs. Weekday Concentrations for C2 Alkanes
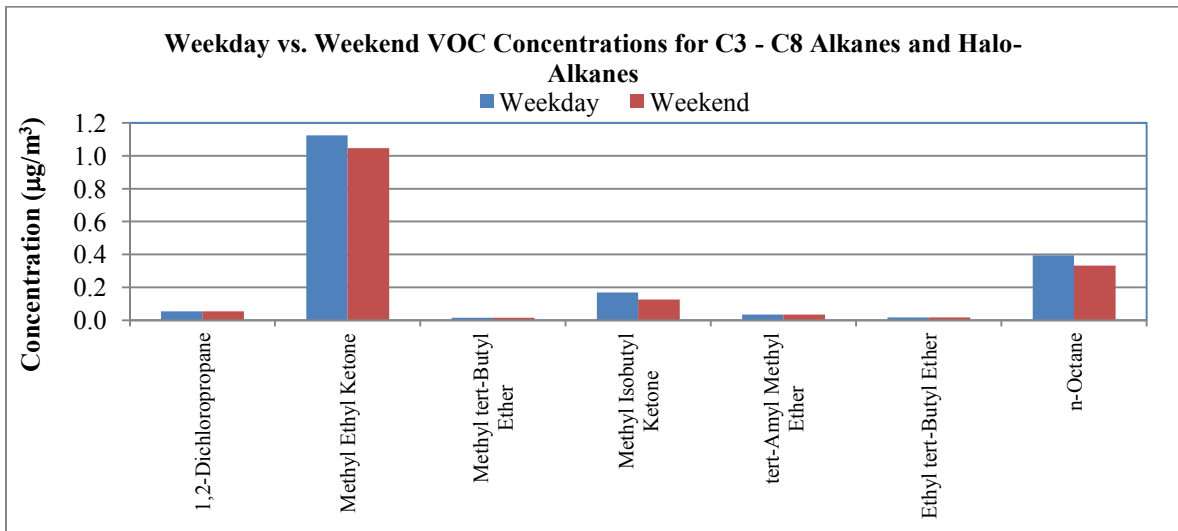
Figure 19. VOC Weekend vs. Weekday Concentrations for C3 – C8 Alkanes
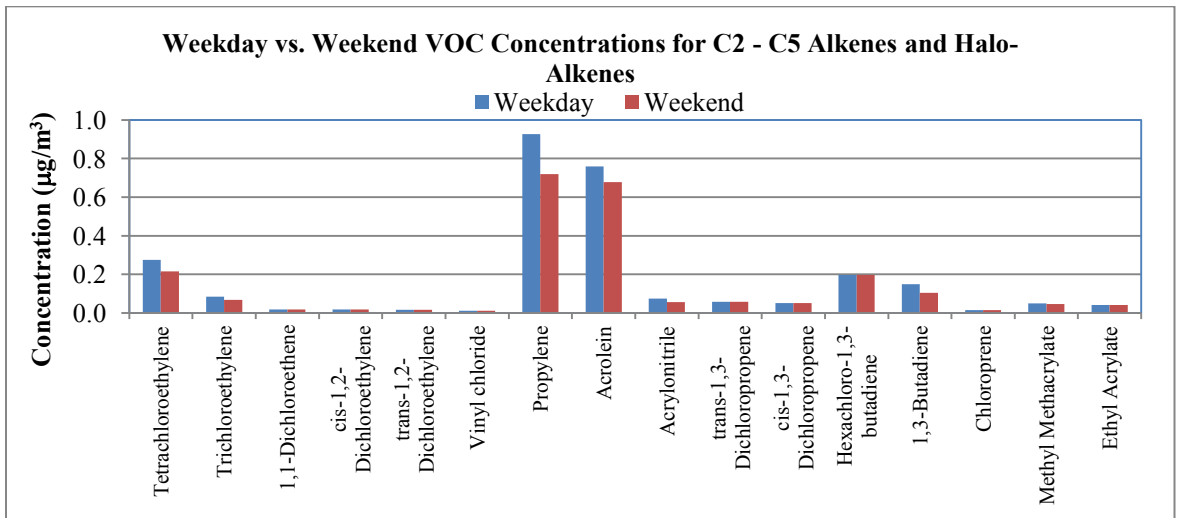
Figure 20. VOC Weekend vs. Weekday Concentrations for C2-C5 Alkenes

[21]
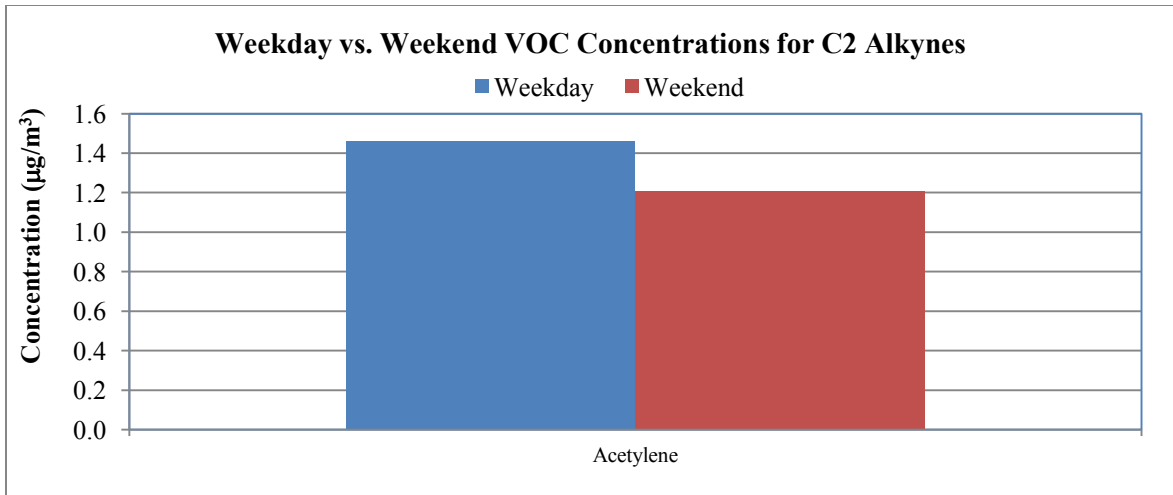
Figure 21.   **VOC Weekend vs. Weekday Concentrations for Alkynes**
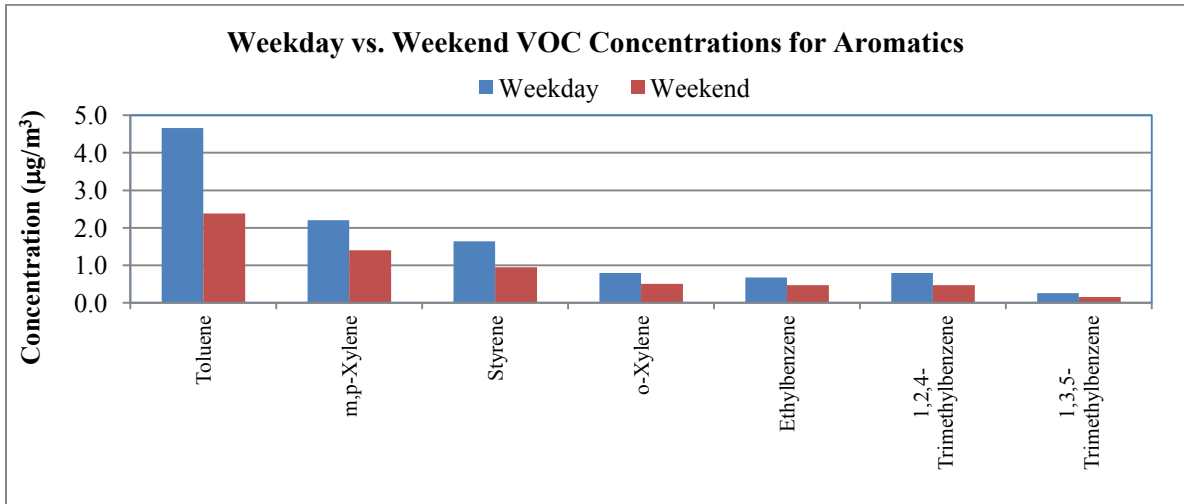
Figure 22.   **VOC Weekend vs. Weekday Concentrations for Aromatics**
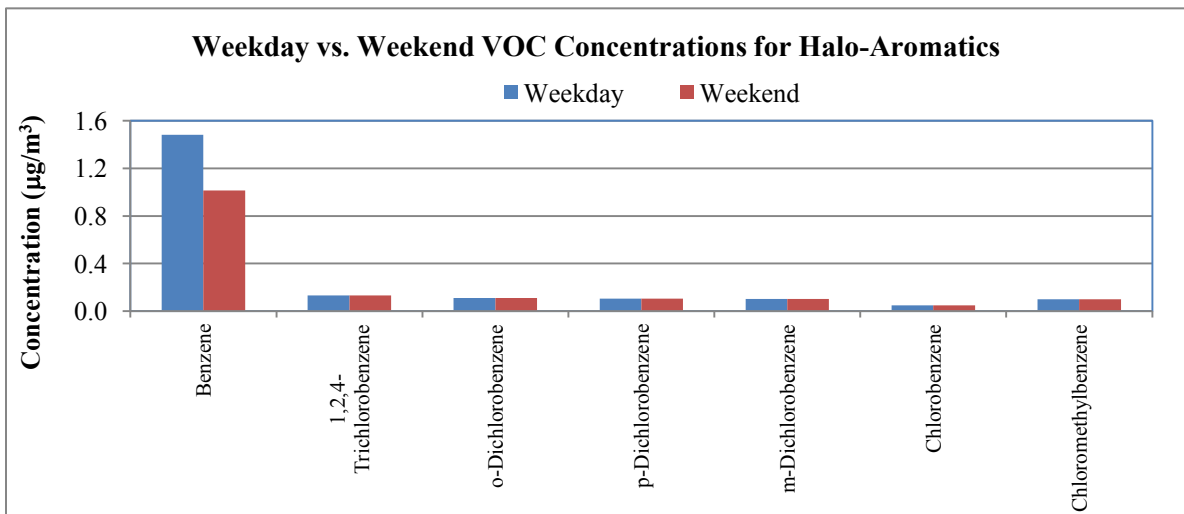
Figure 23.   **VOC Weekend vs. Weekday Concentrations for Aromatics, ctd.**
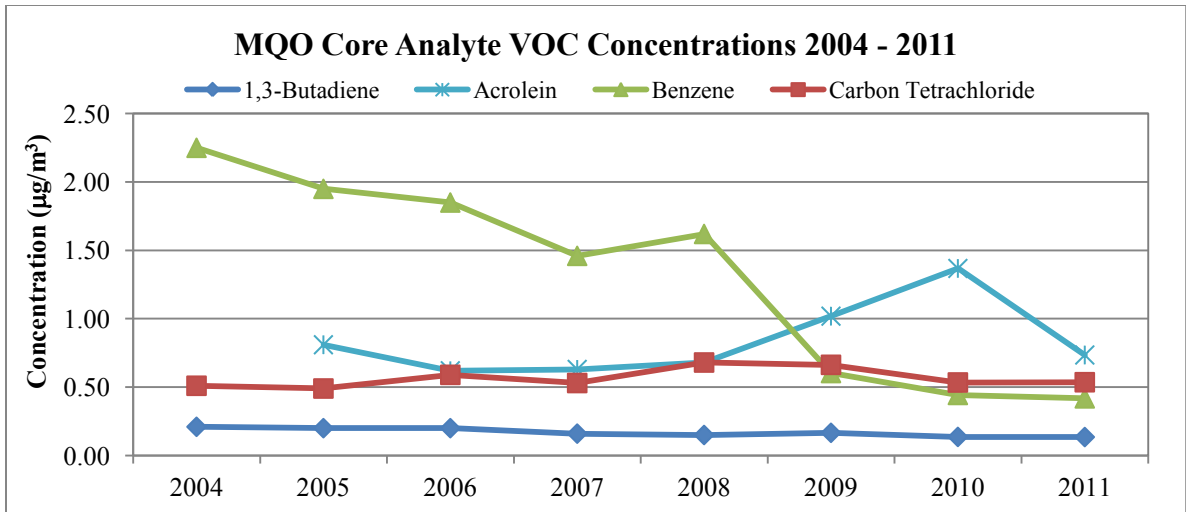
Figure 24.   MQO Core Analyte VOC Concentrations 2004 – 2011
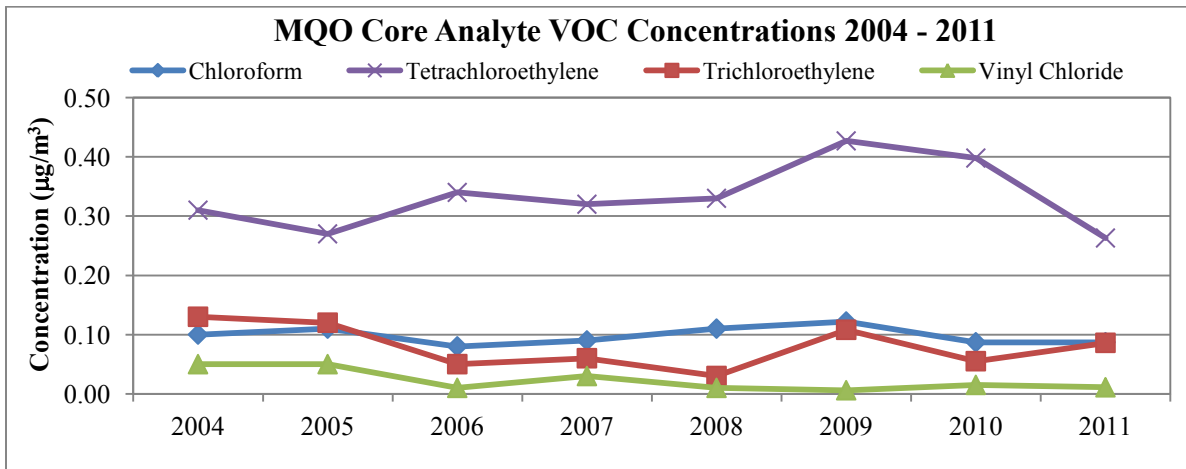
Figure 25.   MQO Core Analyte VOC Concentrations 2004 – 2011, ctd.

   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 for benzene, 1,3-butadiene, trichloroethylene, and vinyl chloride appear to indicate a general downward trend in concentration values since 2004. A calculation of the 3-year average concentrations (2007 – 2009) for those compounds also shows that the overall concentration average is dropping compared to the previous 3 year average (2004 – 2006), with values of -39%, -22%, -34%, and -58%, respectively. The graphs of the remaining four compounds appear to indicate a trend of increasing concentrations since 2004. This is confirmed when comparing the successive three year averages for acrolein, carbon tetrachloride, chloroform, and tetrachloroethylene. They show increases of 9%, 18%, 11%, and 17%, respectively, when comparing the 2004 through 2006 averages to the 2007 through 2009 averages.

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.   PM$_{10}$ METALS

The metals data included in the initial version of this report, published January 6, 2014, 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 2011 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, two were missed or voided, leaving a total of 59 samples collected (96.7% sample recovery). On one of those voided sample dates, however, the collocated sampler was in operation, and that sample was not voided, so the values obtained using the collocated sampler were substituted for the voided sample's values, giving a final data recovery percentage of 98.4%. Table 7 shows the percentage of the samples in which each metal was detected. The bolded compounds are a part of the list of MQO Core Analytes. Arsenic, nickel, lead, and manganese were detected in 90% or more of the samples. Beryllium was never detected, while cadmium was detected in 25% of the samples.

Table 7.   Metals List with 2011 Detection Rates

Compound	CAS Number	# of ND's	% ND
Arsenic	**7440-38-2**	**0**	**0%**
Manganese	**7439-96-5**	**0**	**0%**
Nickel	7440-02-0	1	2%
Lead	7439-92-1	2	3%
Cadmium	7440-43-9	44	75%
Beryllium	7440-41-7	59	100%

Bold = MQO Core Analyte

Table 8 summarizes the annual mean concentrations for each of the metals measured during the study, from 2004 through 2011, and is organized from the highest 2011 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 limit in place of the non-detect samples. These compounds, and their results, are italicized in the table. Results show that manganese and lead were the compounds with the highest annual averages. The table indicates that nickel has the third highest annual average concentration in 2011. The other metals were present at lower concentrations. The manganese, lead, and nickel concentrations for 2011 were slightly higher than the values in 2010, while the arsenic concentration was approximately half the 2010 value.

Table 8.   Metals Data Summary 2011

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 ($\mu g/m^3$)
Manganese	0.0130	0.01199	0.01504	0.01523	0.01474	0.00870	0.00834	0.00882
Lead	0.0049	0.00401	0.00433	0.00426	0.00248	0.00209	0.00205	0.00279
Nickel	0.0006	0.00091	0.00119	0.00144	0.00143	0.00088	0.00180	0.00211
Arsenic	0.0003	0.00213	0.00288	0.00422	0.00243	0.00087	0.00132	0.00067
Cadmium	*0.0001*	*0.00035*	*0.00026*	*0.00024*	*0.00014*	*0.00023*	*0.00020*	*0.00021*
Beryllium	*0.0001*	*0.00091*	*0.00059*	*0.00069*	*0.00019*	*0.00013*	*0.00014*	*0.00014*

Bold = MQO Core Analyte, *Italics = less than 90% detection rate*

Graphs

The metal compounds measured during the study are graphed in

. This figure shows that manganese, lead, and nickel were the metals with the largest average concentrations, having values of 8.82, 2.79, and 2.11 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.[9] Figure 27 and Figure 28 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 2011 data. Manganese has the largest amount of variability in the concentration values recorded, with values ranging from just slightly over zero to near 0.025 micrograms per meter cubed.
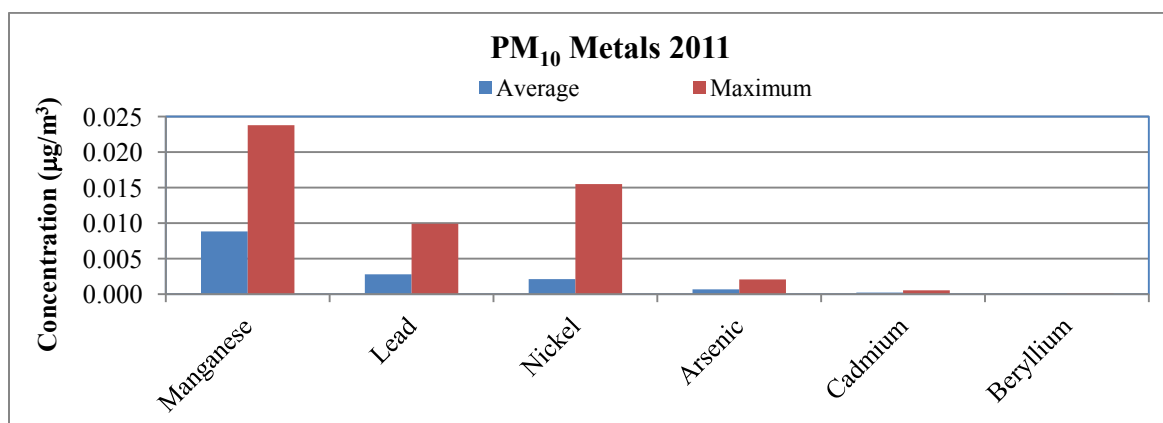
Figure 26.   PM$_{10}$ Metals Average and Maximum Concentrations 2011

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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.
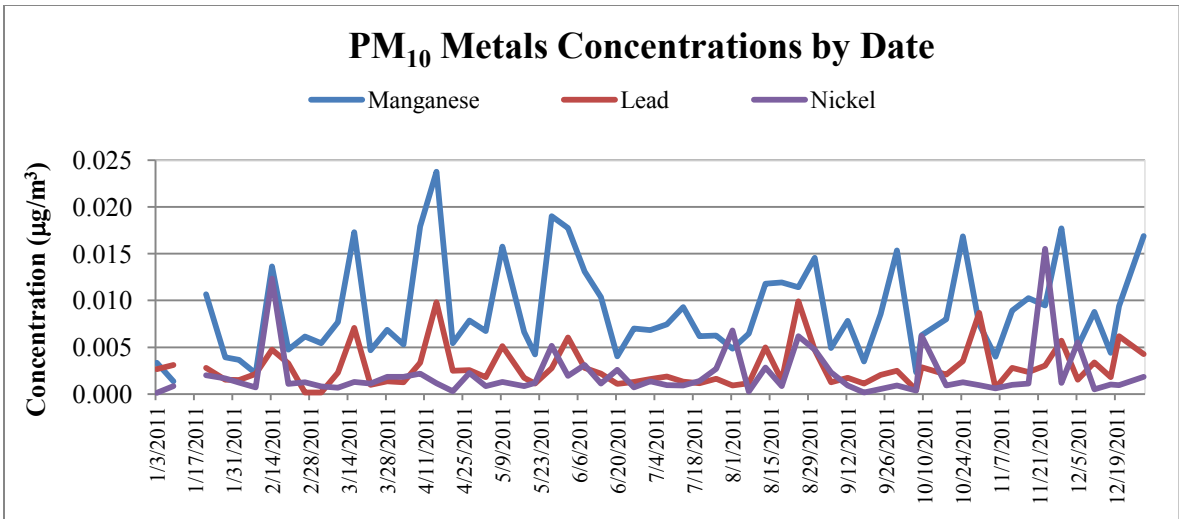
Figure 27. **PM$_{10}$ Metals Concentrations by Date 2011**
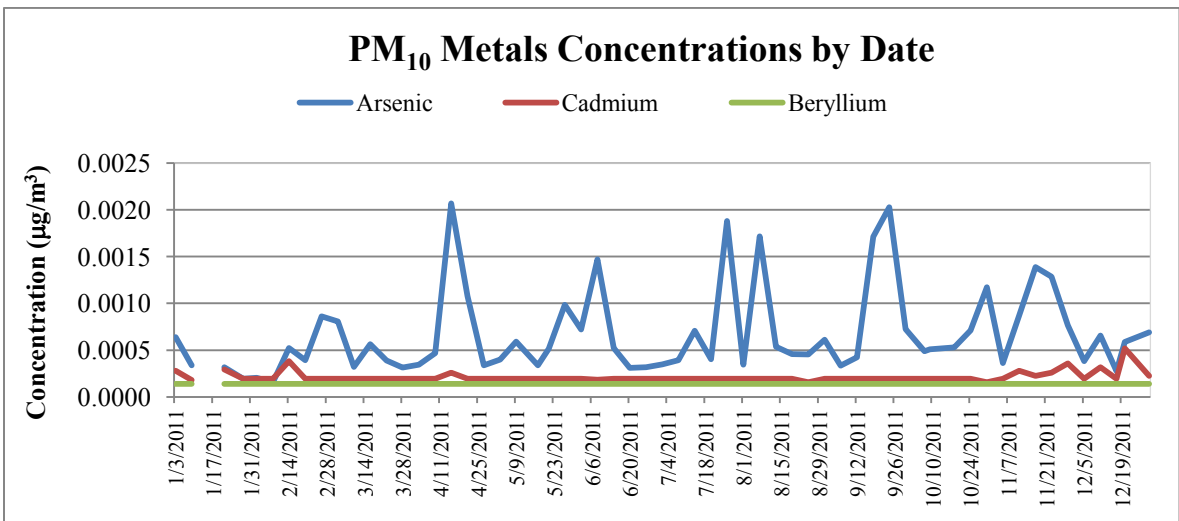
Figure 28. **PM$_{10}$ Metals Concentrations by Date 2011, ctd.**
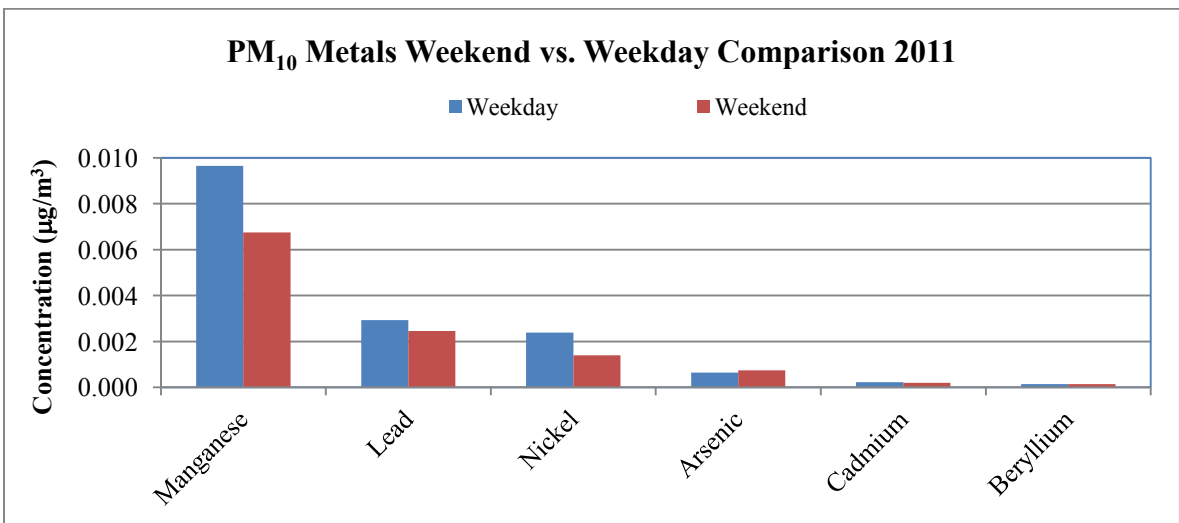
Figure 29. **PM$_{10}$ Metals Weekend versus Weekday Comparison 2011**
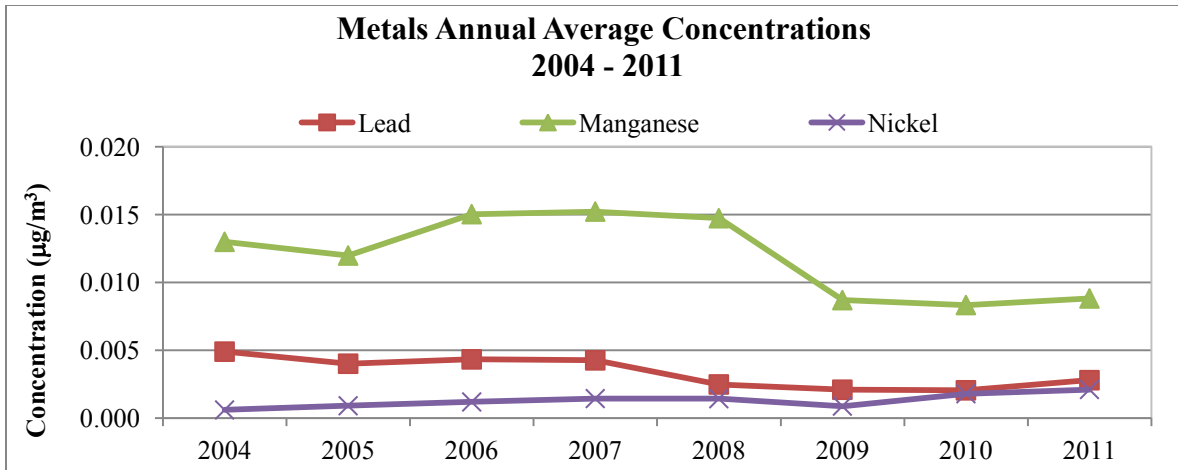
Figure 30.　　　　　PM$_{10}$ Metals Annual Average Concentrations 2004 – 2011
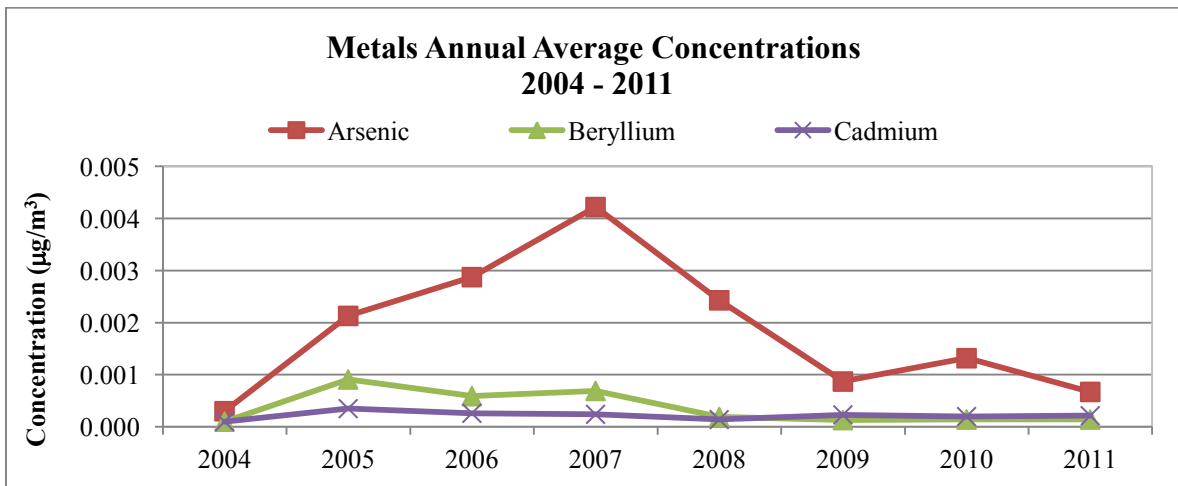
Figure 31.　　　　　PM$_{10}$ Metals Annual Average Concentrations, 2004 – 2011

Figure 29 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, except for arsenic. The 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 30 and Figure 31 are graphs of the annual average concentrations for each of the PM$_{10}$ metals from 2004 through 2011. The graphs show a general downward trend in the concentration values for all compounds, except nickel. A calculation of the 3-year averages from 2004 to 2006, and 2007 to 2009, shows a decrease in concentrations for all compounds except arsenic and nickel. 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. 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

[27]

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. Blank amounts are subtracted from the raw concentration data.

Precision of Sample Results

   Twelve duplicate precision samples were run in 2011. The agreement between samples was generally good, with a twenty percent or less difference between the concentration values for some of the compounds that were detected in both the primary and duplicate samples (lead, manganese, and cadmium). For nickel and arsenic, however, the average percent difference was at 241%, and 53% on the year, respectively. This could be due to possible problems with the extraction process in the lab.

VI.   HEXAVALENT CHROMIUM

Summary Statistics

   Hexavalent chromium data collected at the Grand Junction – Powell station in 2011 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 59 being analyzed (96.7% sample recovery). Table 9 shows that hexavalent chromium was detected in greater than 70 percent of the samples taken in 2011. Table 10 shows the average hexavalent chromium concentrations recorded from 2005 through 2011. 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 2011 are greater than those from 2010. Until then, the average and maximum values seen in 2009 were lower than those seen in 2008 (0.0208 and 0.6850 ng/m^3, respectively), and 2007 (0.0155 and 0.0928 ng/m^3, respectively).

Table 9.   Hexavalent Chromium Sample Summary 2009-11

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

Table 10. Hexavalent Chromium Average and Maximum Concentrations 2009-11

	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)
Analyte							
Hexavalent Chromium	0.023	0.03	0.0155	0.0208	0.0082	0.0125	0.0160

Graphs

Figure 32 shows the annual average and maximum hexavalent chromium concentrations for 2009, 2010 and 2011. Figure 33 shows hexavalent chromium concentrations during the 2011 calendar year. All but two 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.[10] The maximum concentrations in 2009, 2010, and 2011 occurred on September 28, 2009, June 1, 2010, and December 29, 2011.
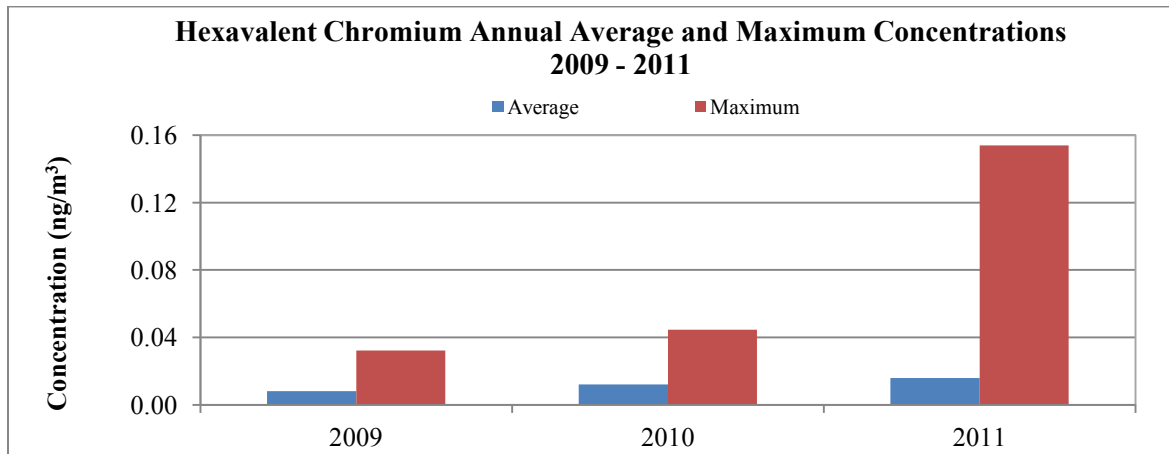
Figure 32.   **Hexavalent Chromium Annual Average and Maximum 2009-11**
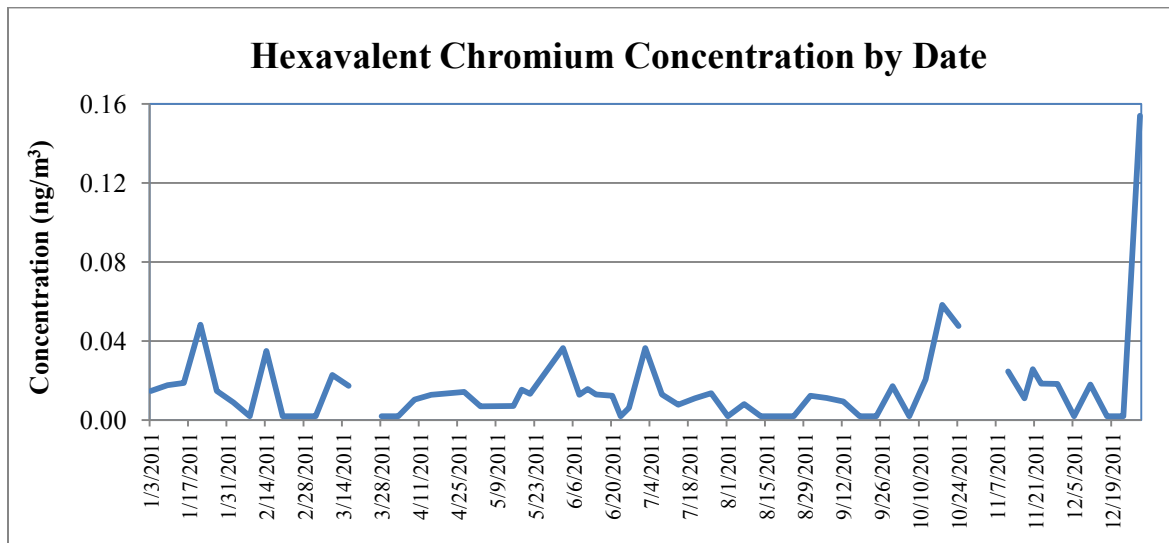
Figure 33.   **Hexavalent Chromium Concentrations by Date 2011**

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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.
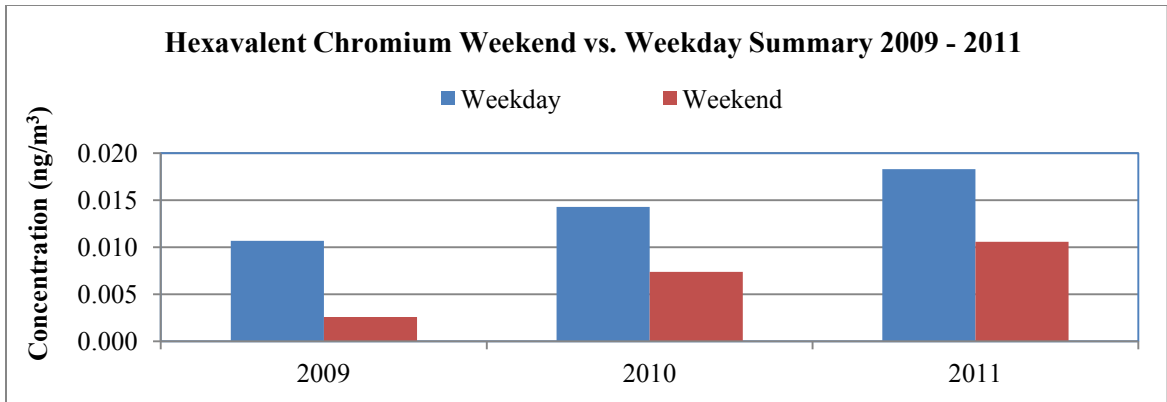
Figure 34.   **Hexavalent Chromium Weekend vs. Weekday Summary**
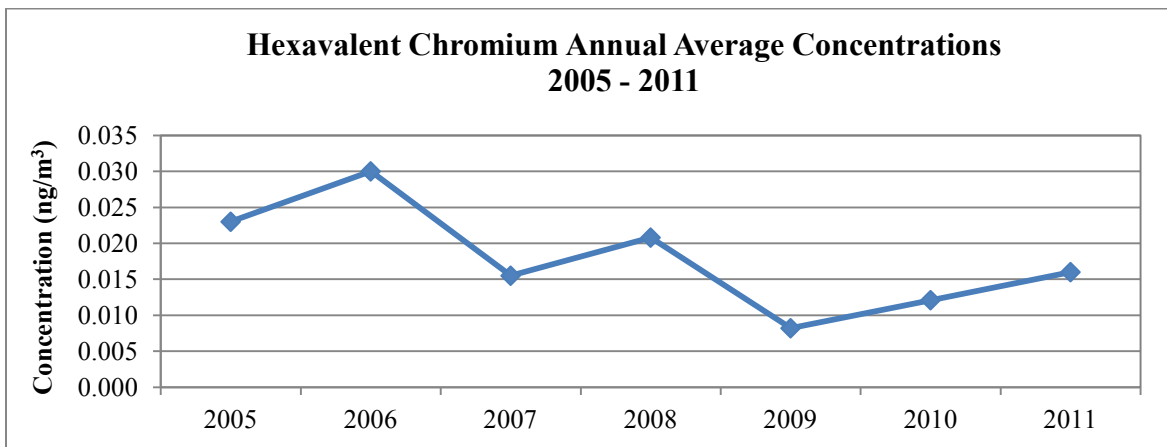
Figure 35.   **Hexavalent Chromium Annual Average Concentrations 2005 – 2011**

Figure 34 is a summary of the weekday versus weekend hexavalent chromium concentrations for 2009 through 2011. 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 35 is a graph of the annual average hexavalent chromium concentrations from 2005 through 2011. 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 0.023 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

Four 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 gives an idea of the precision of the analytical method. In general, the duplicate samples showed good agreement, varying from a minimum percent difference of -11% to a maximum of 13%.

VII. 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. This sampler serves 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 2011, the percentage of PM$_{10}$ data recovery was 89.1 percent, with 129 samples attempted, and 115 collected on the primary sampler. For 6 of the 14 missed/voided samples, the collocated sampler was in operation, and those values replaced the missing values for the primary sampler. This brings the data recovery rate to 93.8%.

Table 11. PM$_{10}$ Average Concentrations 2004 – 2011

Analyte	2004 Average (µg/m³)	2005 Average (µg/m³)	2006 Average (µg/m³)	2007 Average (µg/m³)	2008 Average (µg/m³)	2009 Average (µg/m³)	2010 Average (µg/m³)	2011 Average (µg/m³)
PM$_{10}$ (every 3rd day)	29	25.6	30.1	29.6	28.7	24.5	22.9	18.4
PM$_{10}$ (every 6th day)	----	----	----	----	----	25.4	19.1	18.4

Table 11 lists the average concentrations observed at the Grand Junction site from 2004 through 2011. The table lists average concentrations for the entire every third day sampling period, as well as the subset of concentrations obtained from the same sampler on the same days that the air toxics analyzers were in operation (every sixth day), from 2009 through 2011. 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 2011 was 41 micrograms per meter cubed.

Graphs

Figure 36 is a graph of the PM$_{10}$ concentration data recorded every sixth sampling day. The graph does not indicate any type of seasonal variability in the concentrations of the coarse particulate matter. The concentration range for PM$_{10}$, on an every sixth day sampling period, is from just over five micrograms per meter cubed, to just under 40 micrograms per meter cubed in 2011.

Grand Junction Trends 2011 --- PM$_{10}$
*** Air Toxics sampling days ***
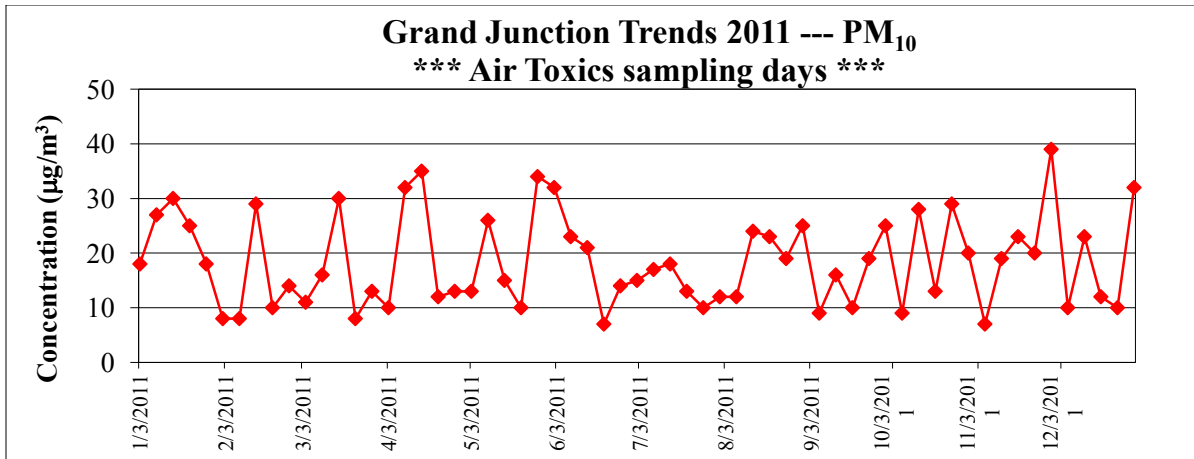
Figure 36.   PM$_{10}$ Concentrations by Date (every 6th Day)

Grand Junction PM$_{10}$ Weekday vs. Weekend Concentrations 2009-2011
Every 6th Day Schedule
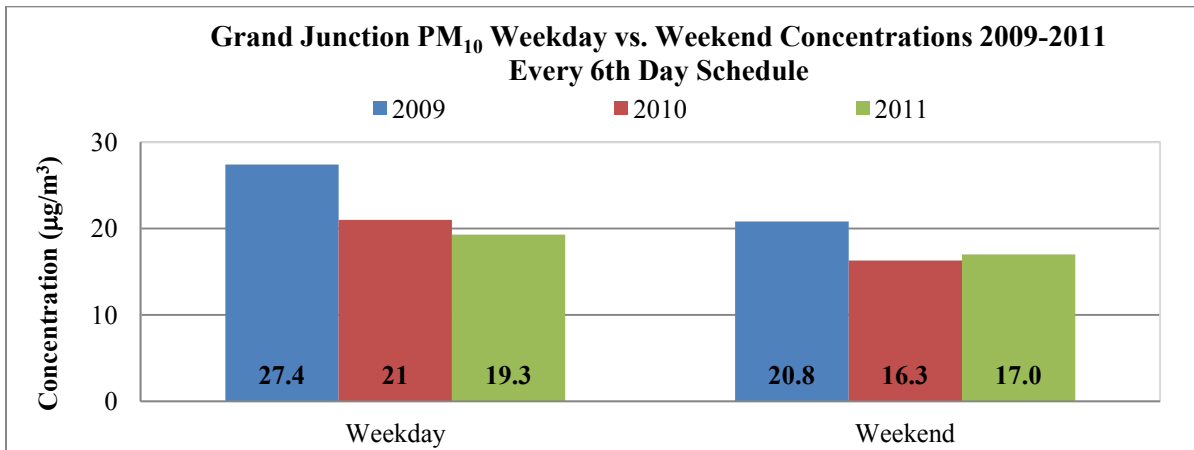
Figure 37.   PM$_{10}$ Weekend vs. Weekday Comparison 2009-11, every 6th day

Figure 37 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 38 is a graph of the annual average PM$_{10}$ concentrations from 2004 through 2011.

PM$_{10}$ Annual Average Concentrations 2004-2011
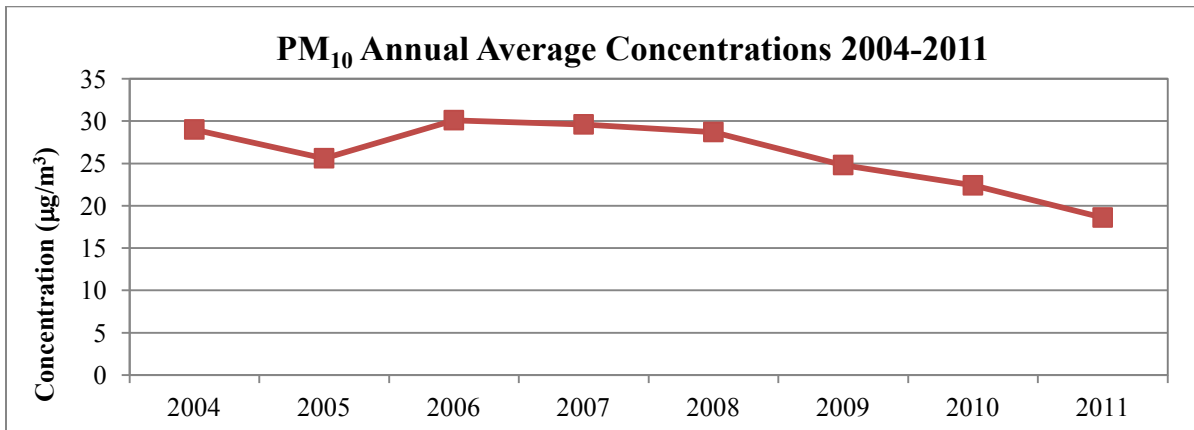
Figure 38.   PM$_{10}$ Annual Average Concentrations 2004 – 2011

[32]

Quality Assurance/Quality Control

Field Blanks

There were no field blanks taken for PM_{10}.

Precision of Sample Results

Collocated samples were run approximately 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.

VIII. $PM_{2.5}$

Sample Statistics Summary

The Colorado Department of Public Health and Environment operates a sampler 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: 2011 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 data only, and does not include any speciated results. In 2011, the percentage of $PM_{2.5}$ data recovery was 93.8 percent, with 129 samples attempted, and 121 collected.

Table 12. $PM_{2.5}$ Average Concentrations 2005-2011

Analyte	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 ($\mu g/m^3$)
$PM_{2.5}$ (every 3rd day)	8.36	9.70	9.49	9.11	9.80	9.00	7.08
$PM_{2.5}$ (every 6th day)	----	----	----	----	10.49	8.41	6.79

Table 12 lists the annual average $PM_{2.5}$ concentrations at the Grand Junction sites for 2005 through 2011. $PM_{2.5}$ emissions are generated by agriculture, and the combustion of automobile fuels, coal, wood, etc. The table lists concentrations for the entire every third day sampling period, for 2005 through 2011, as well as concentrations obtained on the same days that the air toxics analyzers were in operation (every sixth day), for 2009, 2010, and 2011. The "every sixth day" values presented in Table 12 are a subset of the "every third day" sample set, and represent data collected in tandem with the air toxics analyzers. The averages are very similar for the third and sixth day sampling in 2011, and are less than half of the annual standard level of 15 micrograms per meter cubed. The maxima for the third and sixth day sampling are the same, at 23.9 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 every sixth day sampling is shown in Figure 39. It shows 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 agriculture, and household wood burning.
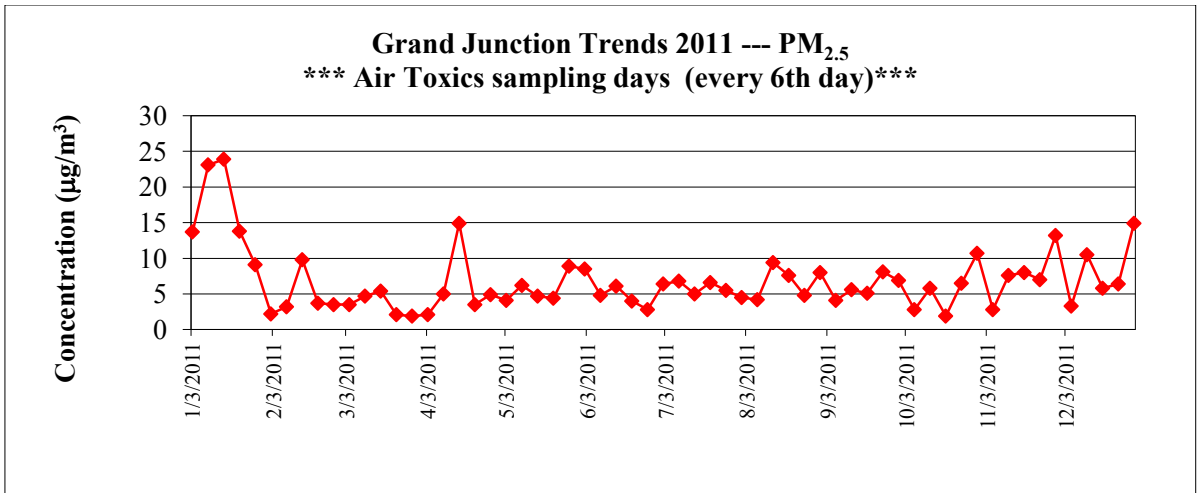
Figure 39.   PM$_{2.5}$ Concentration by Date, Every 6th Day Sampling 2011
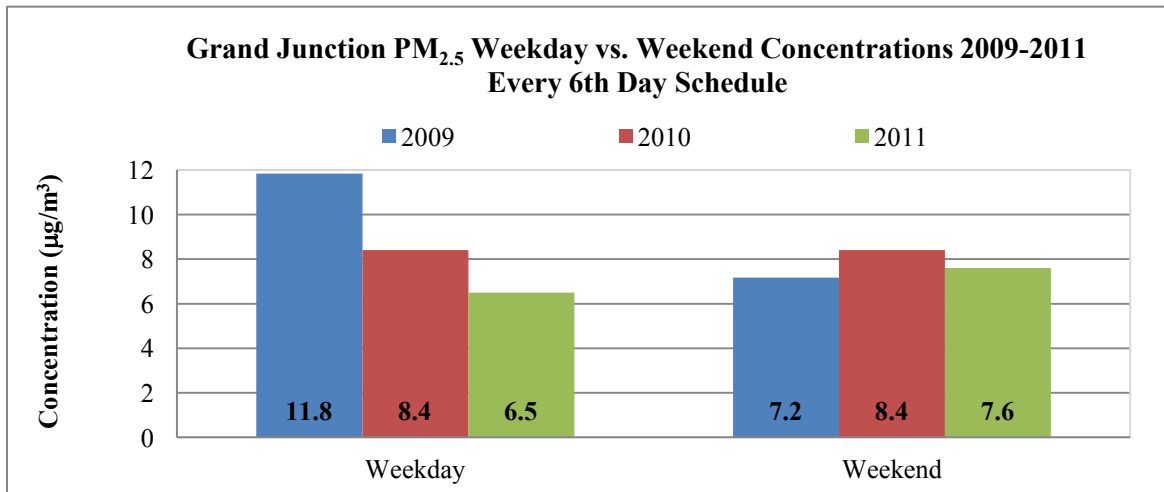
**Figure 40.**   PM$_{2.5}$ Weekend vs. Weekday Comparison 2009-11, every 6th day

Figure 40 shows how the weekend versus weekday average concentrations compare for 2009-2011, for the every 6th day sampling schedule. For the six-day sampling periods in 2009, weekday averages were larger than the weekend averages.   The weekday averages have decreased since 2009. The weekend averages have been variable since 2009. Figure 41 shows the annual average concentrations for PM$_{2.5}$ for 2005 through 2011. The overall average trend seems to be decreasing since 2009.
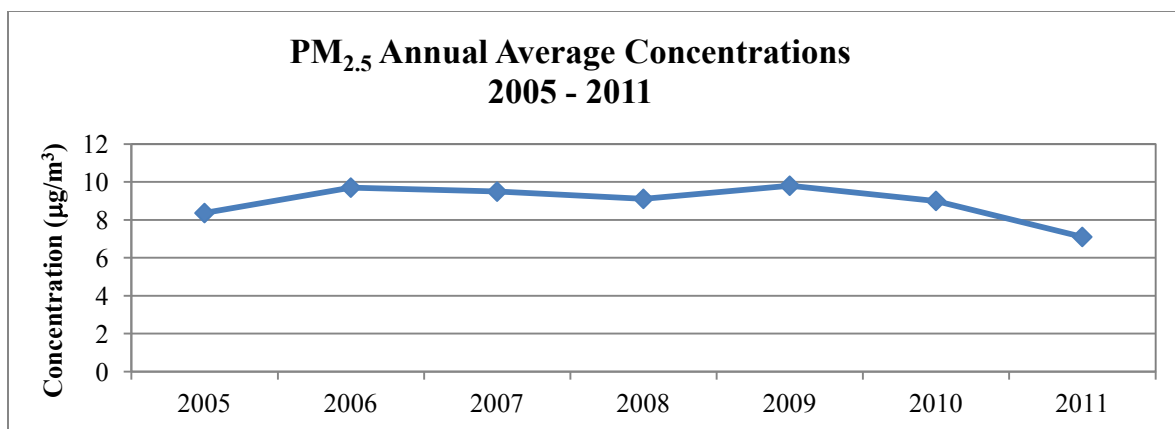
Figure 41.   **PM$_{2.5}$ Annual Average Concentrations 2005 – 2011**

Quality Assurance/Quality Control

Field Blanks

There were no field blanks taken for PM$_{2.5}$.

Precision of Sample Results

No collocated samples were run for PM$_{2.5}$.

IX.   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 61 were collected for analysis (100% 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 13 and Table 14. Bolded values indicate that compound is one of the MQO Core Analytes. Italicized values indicate a detection rate of less than 90% for the year. Fifteen 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. Eleven compounds were detected in every sample taken. These are: 9-fluorenone, acenaphthene, anthracene, Benzo(b)fluoranthene, chrysene, fluoranthene, fluorene, naphthalene, phenanthrene, pyrene, and retene.

[35]

Table 13. PAH Sample Summary Data 2011

Compound	CAS Number	# of ND's	% ND
9-Fluorenone	486-25-9	0	0%
Acenaphthene	83-32-9	0	0%
Anthracene	120-12-7	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%
Retene	483-65-8	0	0%
Benzo (e) pyrene	192-97-2	1	2%
Benzo (g,h,i) perylene	191-24-2	1	2%
Indeno(1,2,3-cd)pyrene	193-39-5	3	5%
Benzo (a) anthracene	56-55-3	5	8%
Coronene	191-07-1	8	13%
Benzo (a) pyrene	**50-32-8**	**17**	**28%**
Acenaphthylene	208-96-8	20	33%
Benzo (k) fluoranthene	207-08-9	21	34%
Cyclopenta[cd]pyrene	27208-37-3	36	59%
Perylene	198-55-0	39	64%
Dibenz (a,h) anthracene	53-70-3	45	74%

ND = Not Detected
Bold = MQO Core Analyte

   Table 14 summarizes the annual mean concentrations for each PAH measured during the study, from 2008 through 2011. 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 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. Compounds italicized in the table below indicate a detection rate of less than 90%. Naphthalene had the largest annual average of the PAH compounds with a value of 158.09 nanograms per meter cubed in 2011. This is over ten times greater than the next closest average concentration, which is phenanthrene, with 14.02 nanograms per meter cubed. Naphthalene is found in tobacco smoke, mothballs, coal tar production, and from the combustion of coal and oil.

Table 14. PAH Annual Average Values 2008 - 2011

Analyte	2008 Average (ng/m^3)	2009 Average (ng/m^3)	2010 Average (ng/m^3)	2011 Average (ng/m^3)
9-Fluorenone	*1.53*	2.67	2.34	2.13
Acenaphthene	8.41	11.34	7.30	10.54
Acenaphthylene	*2.12*	*3.68*	*2.50*	*2.22*

Analyte	2008 Average (ng/m^3)	2009 Average (ng/m^3)	2010 Average (ng/m^3)	2011 Average (ng/m^3)
Anthracene	*0.63*	1.65	0.89	0.77
Benzo (a) anthracene	*0.20*	*0.39*	*0.25*	0.26
Benzo (a) pyrene	***0.18***	***0.33***	***0.20***	***0.22***
Benzo (b) fluoranthene	0.36	0.72	0.50	0.48
Benzo (e) pyrene	*0.19*	*0.39*	*0.24*	0.23
Benzo (g,h,i) perylene	*0.26*	0.43	0.28	0.25
Benzo (k) fluoranthene	*0.10*	*0.21*	*0.14*	*0.14*
Chrysene	0.35	0.68	0.49	0.48
Coronene	*0.15*	*0.23*	*0.13*	*0.11*
Cyclopenta[cd]pyrene	*0.16*	*0.19*	*0.10*	*0.13*
Dibenz (a,h) anthracene	*0.06*	*0.06*	*0.03*	*0.05*
Fluoranthene	2.52	3.79	3.30	3.35
Fluorene	5.15	9.20	6.44	7.67
Indeno(1,2,3-cd)pyrene	*0.21*	*0.37*	*0.24*	0.23
Naphthalene	**111.88**	**189.13**	**147.04**	**158.09**
Perylene	*0.07*	*0.08*	*0.09*	*0.07*
Phenanthrene	11.98	17.91	13.92	14.02
Pyrene	1.81	2.87	2.28	2.19
Retene	0.67	1.37	1.04	0.85

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 42 through Figure 45. Naphthalene is the most variable, with concentrations ranging from 10.4 to 390 nanograms per meter cubed. Naphthalene had the largest annual average concentration, followed by phenanthrene, and acenaphthene, with values of 158.09, 14.02, and 10.54 nanograms per meter cubed. In comparison, the NMP national averages for these compounds in 2011 were 81.7, 9.92, and 4.64 nanograms per meter cubed, respectively.[11] 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.[12] 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.[6]

[11] "2011 National Monitoring Programs Annual Report (UATMP, NATTS, CSATAM). US EPA. August 2013. http://www.epa.gov/ttnamti1/files/ambient/airtox/2011nmpreport.pdf.

[12] "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

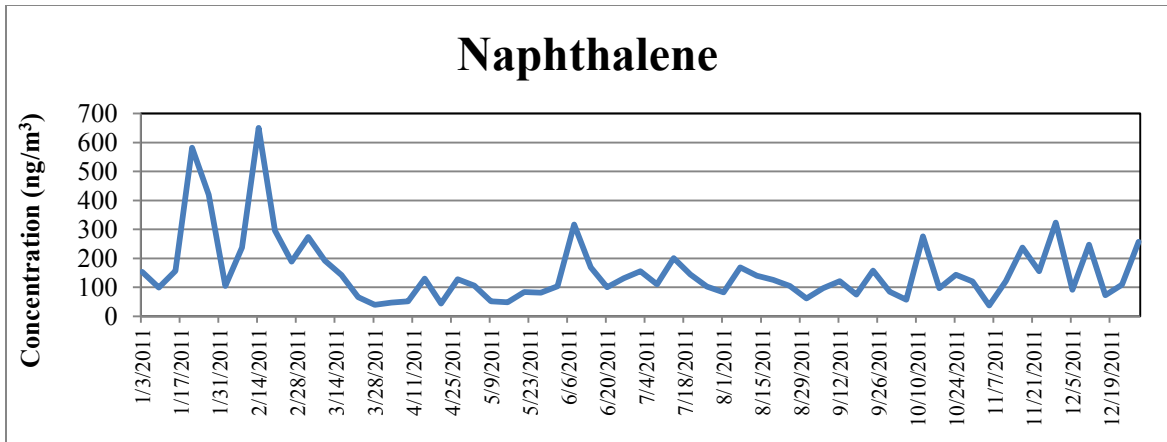**Figure 42.**   Naphthalene Concentration by Date 2011
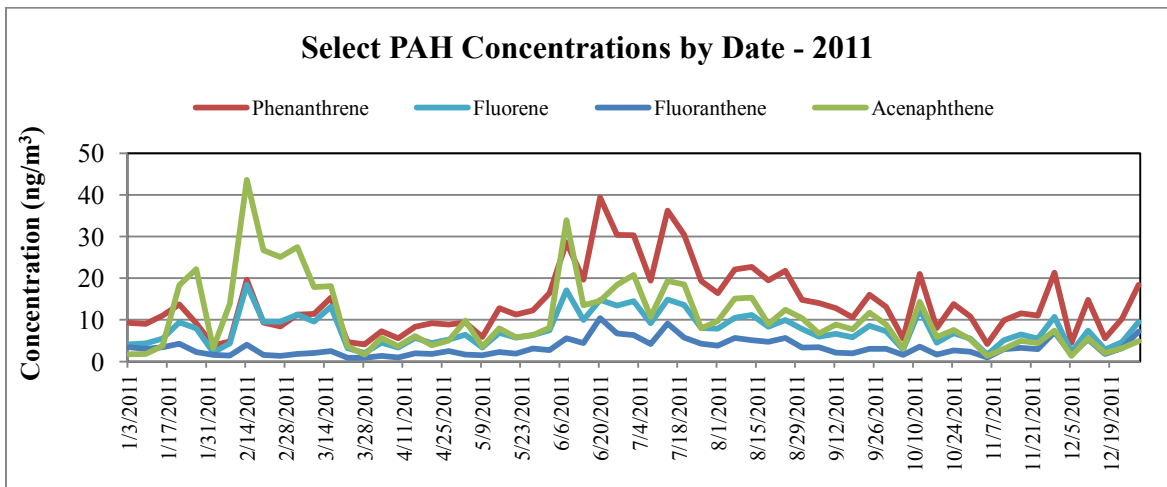

Figure 43.   Select PAH Concentrations by Date 2011
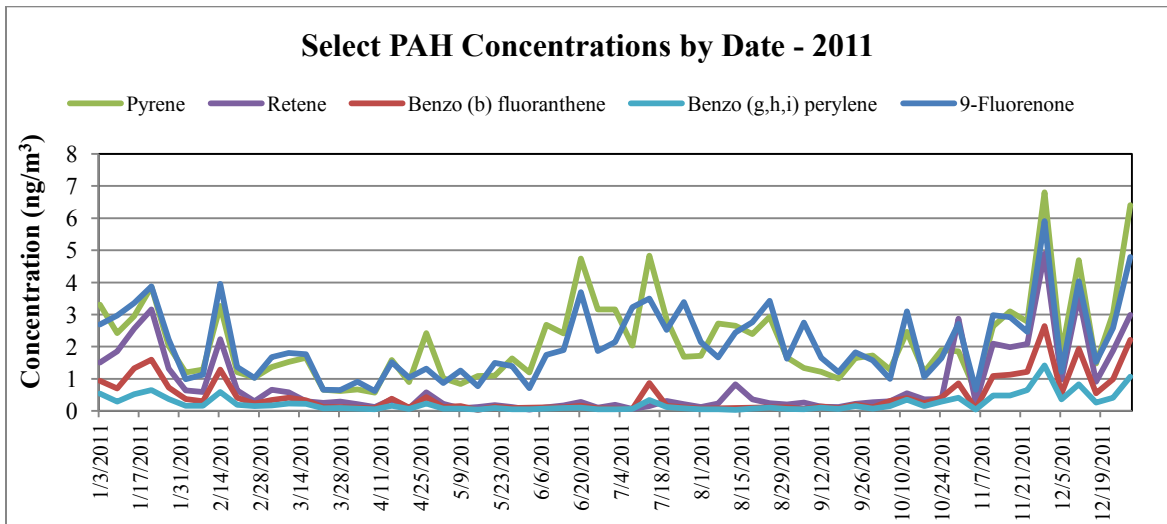

Figure 44.   Select PAH Concentrations by Date 2011, ctd.
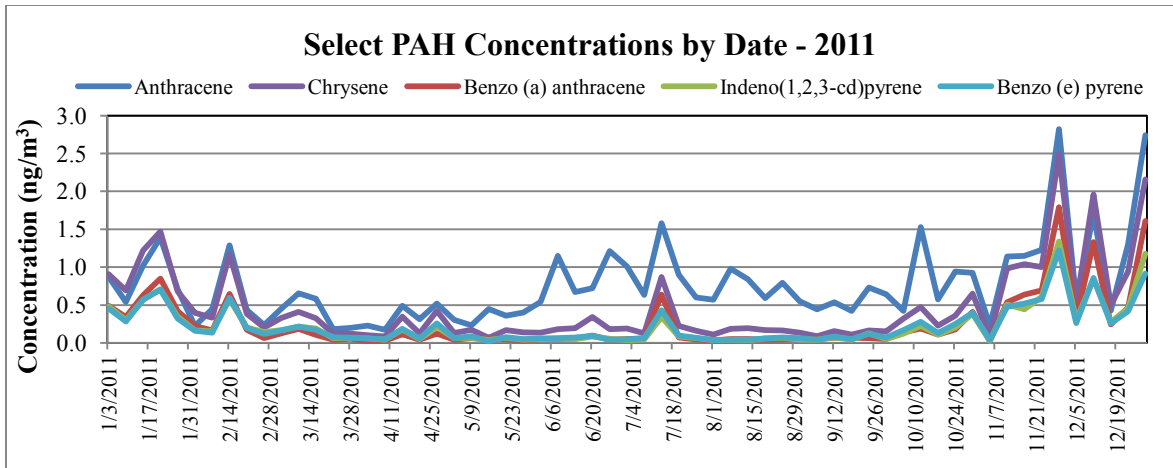
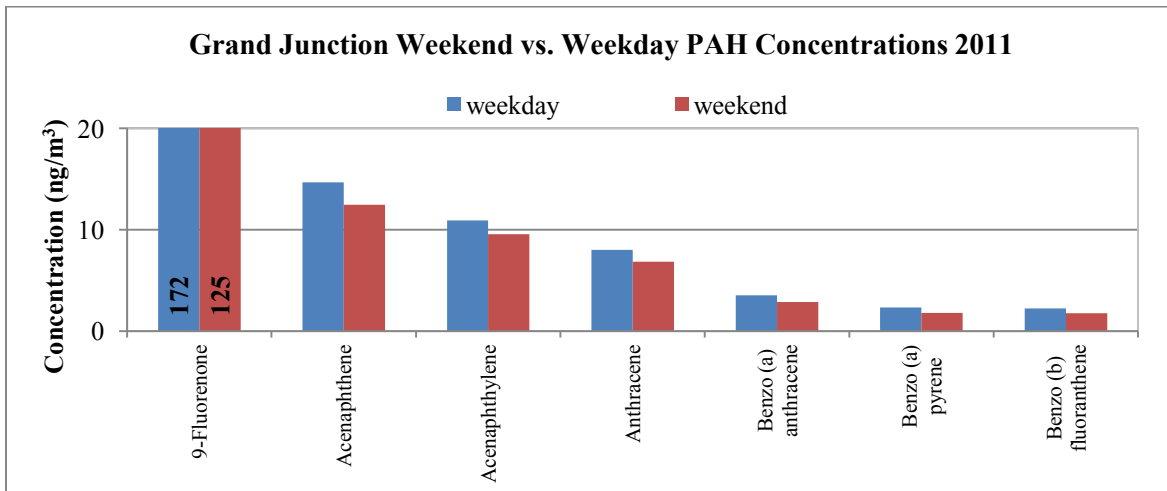**Figure 45.**   Select PAH Concentrations by Date 2011, ctd.

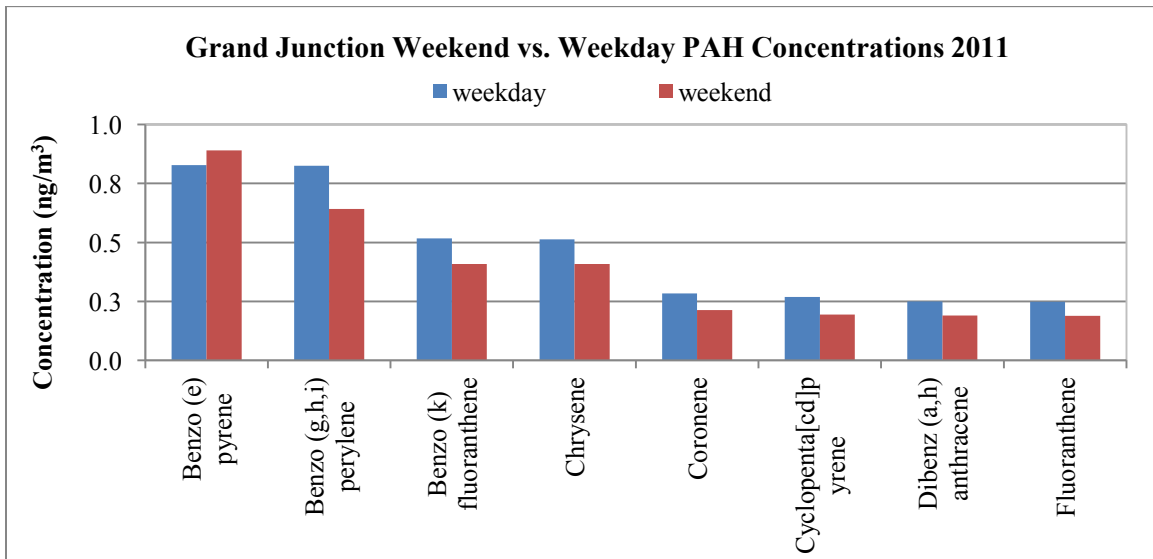**Figure 46.**   PAH Weekend vs. Weekday Concentrations 2011

Figure 47.   PAH Weekend vs. Weekday Concentrations 2009-11, ctd.

[39]

Figure 46 and Figure 47 are graphs of the weekend and weekday concentrations for all the PAH compounds detected in greater than 90% of the samples, for 2011. The weekday averages were larger than the weekend values for all compounds, except benzo(e)pyrene.   This compound had larger weekend values than weekday values. The values for naphthalene are off the chart with a weekday average of 172 nanograms per meter cubed, and a weekend average of 125 nanograms per meter cubed. Figure 48 through Figure 50 are graphs of the annual average concentrations for the fifteen compounds detected in greater than 90% of the samples taken in 2011. The graphs show that from 2008 to 2009 there was an increase in all the annual averages for those compounds, and from 2009 to 2011 there was a decrease, followed by a slight increase. Six of the fifteen compounds followed this trend, while the other nine compounds showed a decrease from 2010 to 2011.
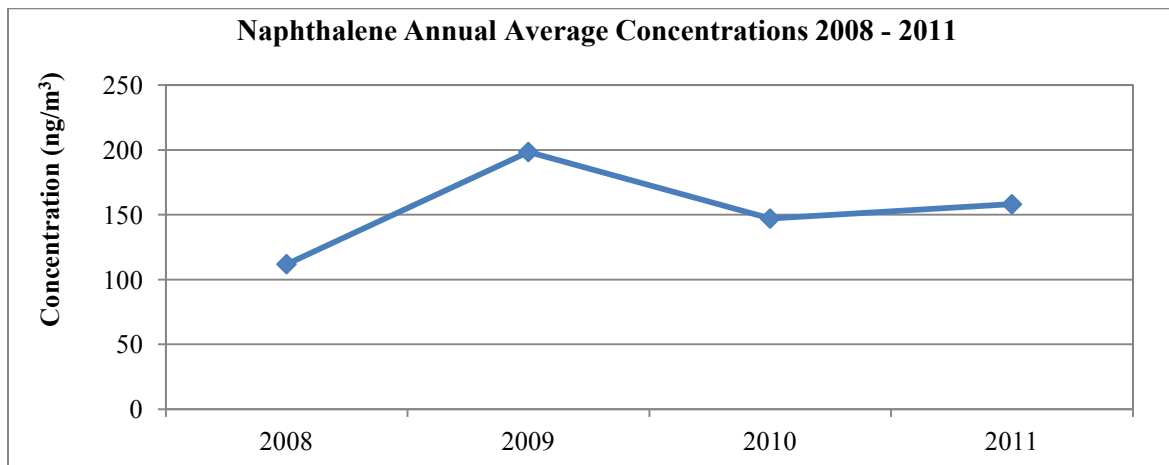

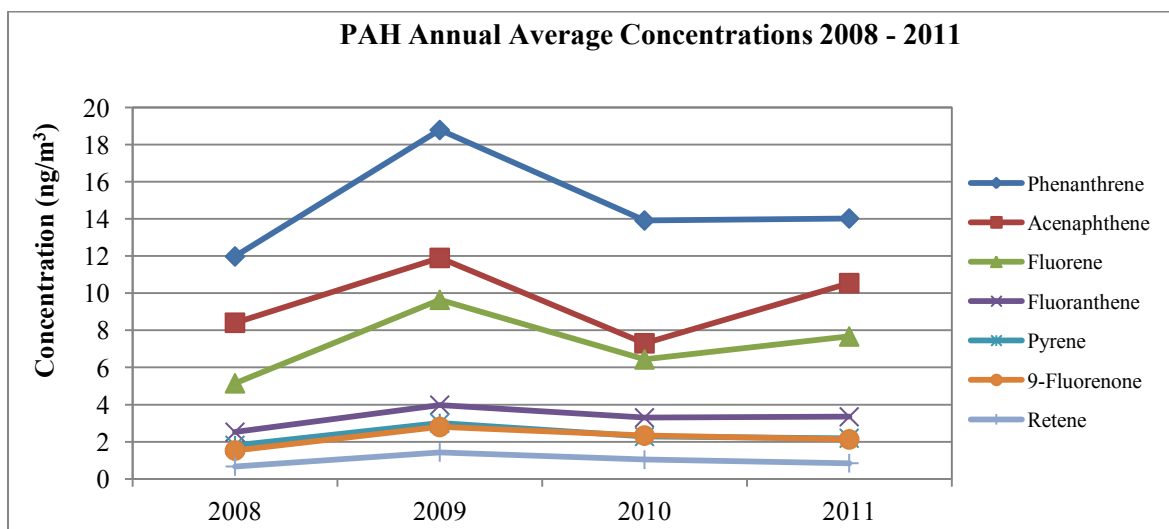**Figure 48.**   **Naphthalene Annual Average Concentrations 2008 – 2011**

Figure 49.   **Select PAH Annual Average Concentrations 2008 – 2011**
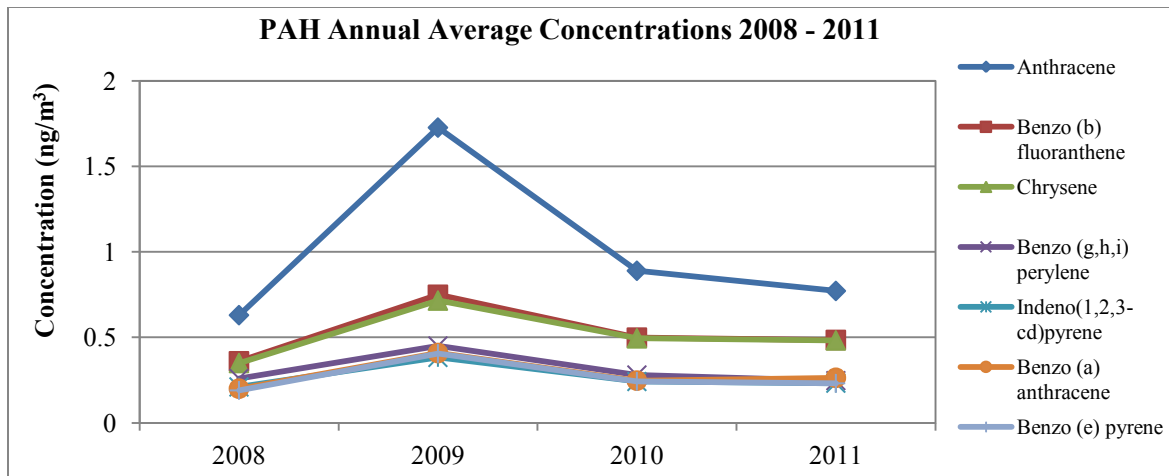
Figure 50.   **Select PAH Annual Average Concentrations 2008 – 2011, ctd.**

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 2011, 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 2011. 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.

X.   METEOROLOGY

A meteorological tower at the Pitkin shelter site measures wind speed, wind direction, relative humidity, and temperature. The 2011 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 two percent of the time. For example, just below 9% of the winds are from the west-northwest. 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. It should be noted here that the legend lists the wind speeds in units of meters per second, and not miles per hour (mph). All wind speeds were converted from mph to m/s.

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.
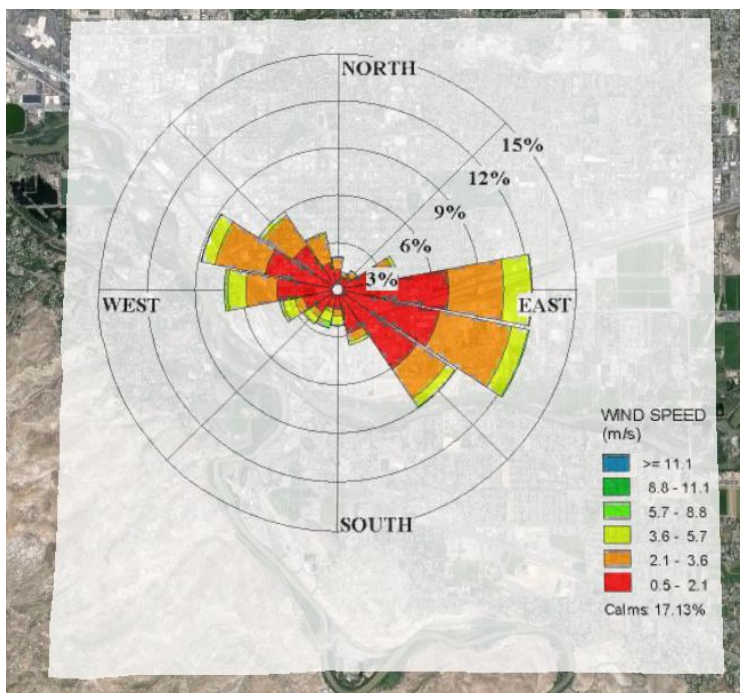
Figure 51.   Wind Rose for Grand Junction 2011

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 photooxidation reactions .[13] 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 particular interest to researchers are two different classes of particulates: course (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 15.

Table 15. Correlation Coefficient Values for Carbonyls-Particulates

Correlations	r - PM_{10}	r-$PM_{2.5}$
Acetone	0.752	0.322
Acetaldehyde	0.591	0.252
Formaldehyde	0.832	0.667

[13] 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

Correlations	r - PM_{10}	r-$PM_{2.5}$
Butyraldehyde	0.755	0.201
Benzaldehyde	0.879	0.380
Crotonaldehyde	0.822	0.307
Propionaldehyde	0.651	0.312
Hexaldehyde	0.857	0.332
Tolualdehydes	0.858	0.431
Valeraldehyde	0.384	0.092

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. Benzaldehyde still shows the strongest correlation with an "r" value of 0.879, which is down from 0.939 in 2010. The "big three" carbonyls, formaldehyde, 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 0.667. A graph of the three carbonyls with the highest "r" value for the PM_{10} correlation is shown in Figure 52.

The final graph presented in this section is a snapshot of the chemical make-up of the carbonyls group from 2004 through 2011. Figure 53 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.
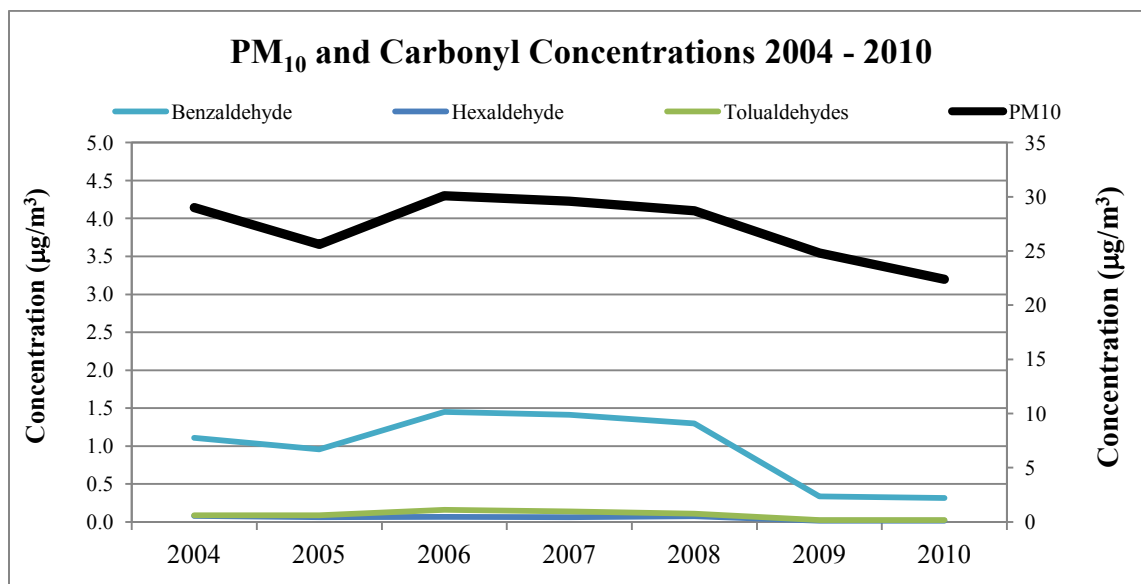

Figure 52.   **PM_{10} – Carbonyl Concentration Comparison**

Carbonyl Composition 2004 - 2011

Legend (top to bottom):
- Isovaleraldehyde
- 2,5-Dimethylbenzaldehyde
- Valeraldehyde
- Tolualdehydes
- Hexaldehyde
- Propionaldehyde
- Crotonaldehyde
- Benzaldehyde
- Butyraldehyde
- Formaldehyde
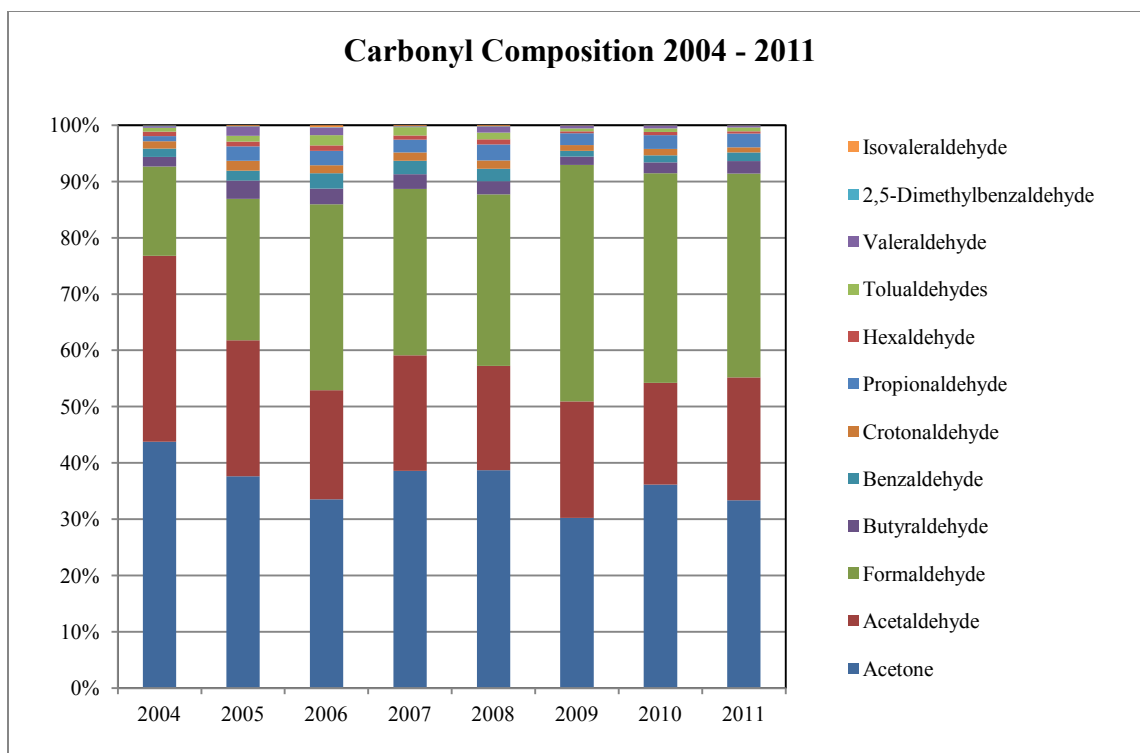- Acetaldehyde
- Acetone

Figure 53.   **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. 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.

   Table 16 is a listing of the correlation coefficients (r) for each of the 24 VOC compounds data sets, with both $PM_{2.5}$ and PM_{10} data sets. For the VOC - PM_{10} correlation, only benzene correlated fairly well with the course particulate concentrations, with a correlation coefficient value of 0.804. Carbon disulfide showed the best correlation with the fine particulate matter, having a correlation coefficient value of 0.861. The Figure 54 is a graph of the benzene and PM_{10} concentrations.

Table 16.   **VOC – Particulate Correlation Coefficient Values**

Analyte	r-PM_{10}	r-$PM_{2.5}$
1,2,4-Trimethylbenzene	0.268	-0.308
1,3,5-Trimethylbenzene	0.205	-0.397
1,3-Butadiene	0.619	0.422
Acetonitrile	-0.207	-0.268
Acetylene	0.456	0.503
Acrolein	-0.501	-0.038
Benzene	0.804	0.292

| Analyte	r-PM$_{10}$	r-PM$_{2.5}$
Carbon Disulfide	0.667	0.861
Carbon Tetrachloride	0.179	0.572
Chloromethane	-0.162	0.298
Dichlorodifluoromethane	-0.085	0.271
Dichloromethane	-0.372	-0.185
Dichlorotetrafluoroethane	-0.429	-0.171
Ethylbenzene	0.165	-0.224
m,p-Xylene	0.190	-0.188
Methyl Ethyl Ketone	0.189	0.053
n-Octane	-0.753	-0.848
o-Xylene	0.178	-0.197
Propylene	0.494	0.155
Styrene	-0.387	-0.573
Tetrachloroethylene	0.063	0.681
Toluene	0.183	-0.132
Trichlorofluoromethane	0.163	0.263
Trichlorotrifluoroethane	0.081	0.397
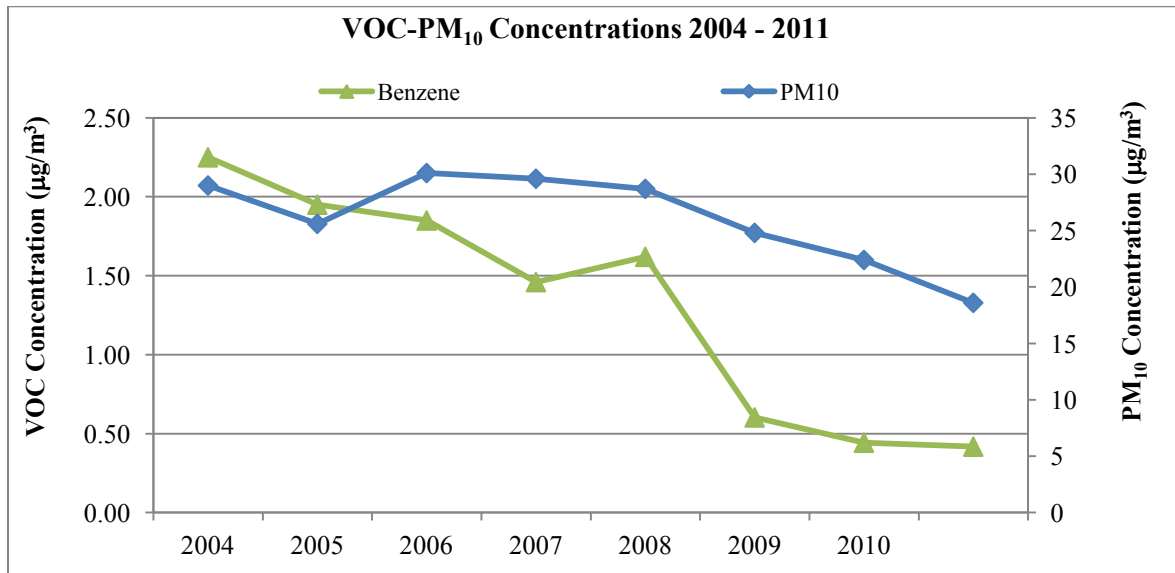
Figure 54. **VOC – PM$_{10}$ Concentration Comparison**

The VOC – PM$_{2.5}$ correlation also showed only one compound with a strong correlation. Carbon disulfide correlated well with the fine particulate matter concentrations, showing a positive r-value of 0.861. Figure 55 shows the concentration graphs for carbon disulfide, and PM$_{2.5}$ concentrations.
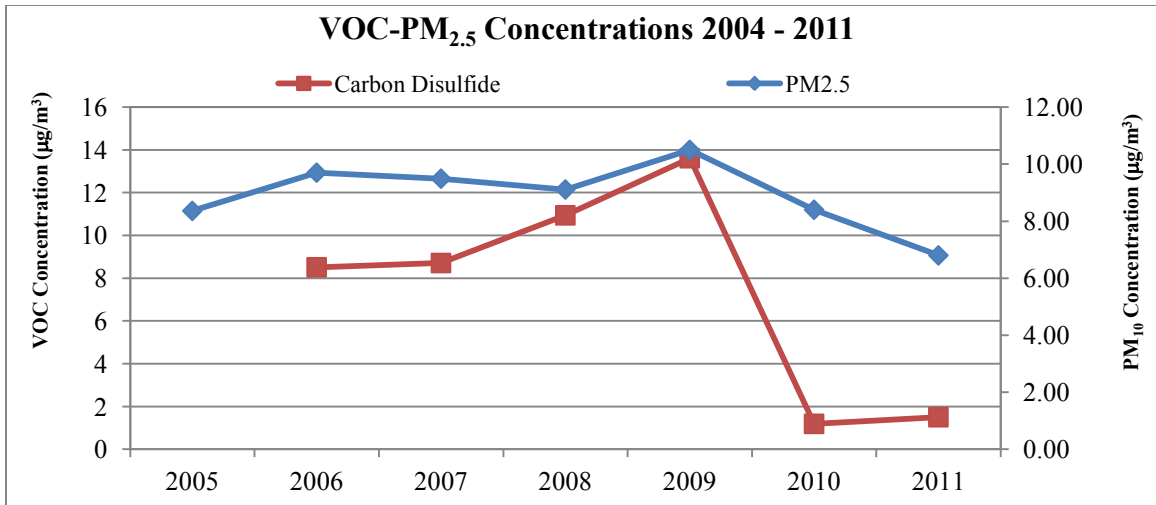
Figure 55.   **VOC – PM$_{2.5}$ Concentration Comparison**

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 56. Although the graphs only shows data from 2009 through 2011, the year to year variability is easily seen.
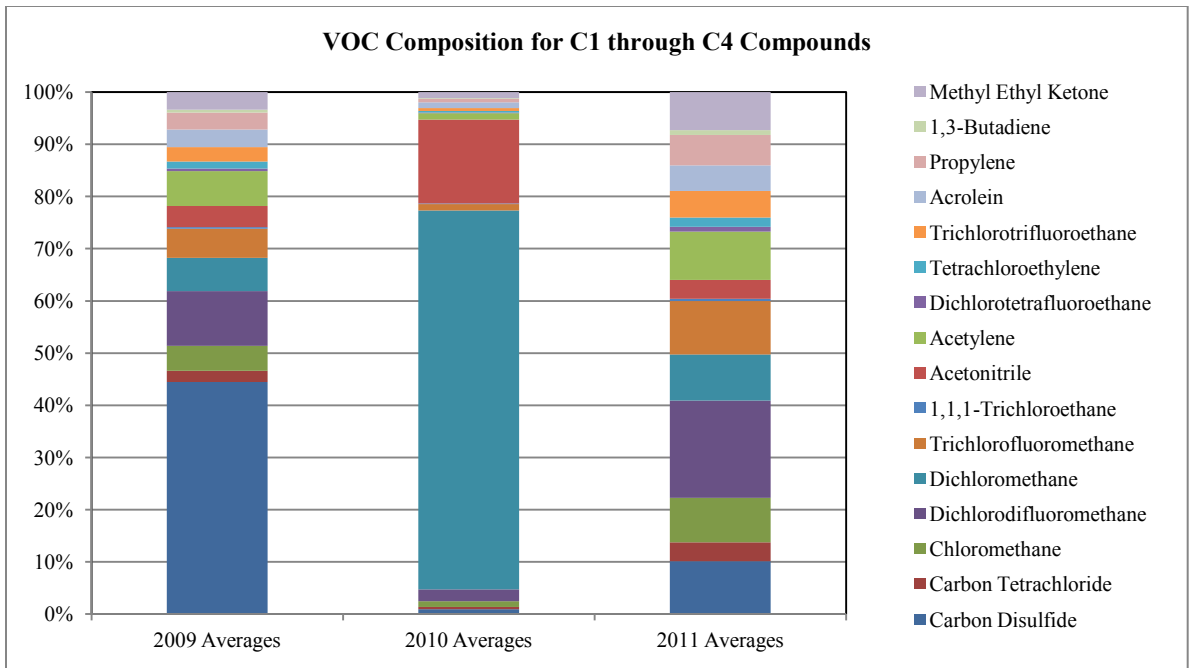

Figure 56.   **Total VOC Composition for C1 through C4 Compounds**

Figure 57 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 C8 compounds is from motor vehicle traffic, due to the consistent nature of the chemical makeup, and the site's nearness to a major road.
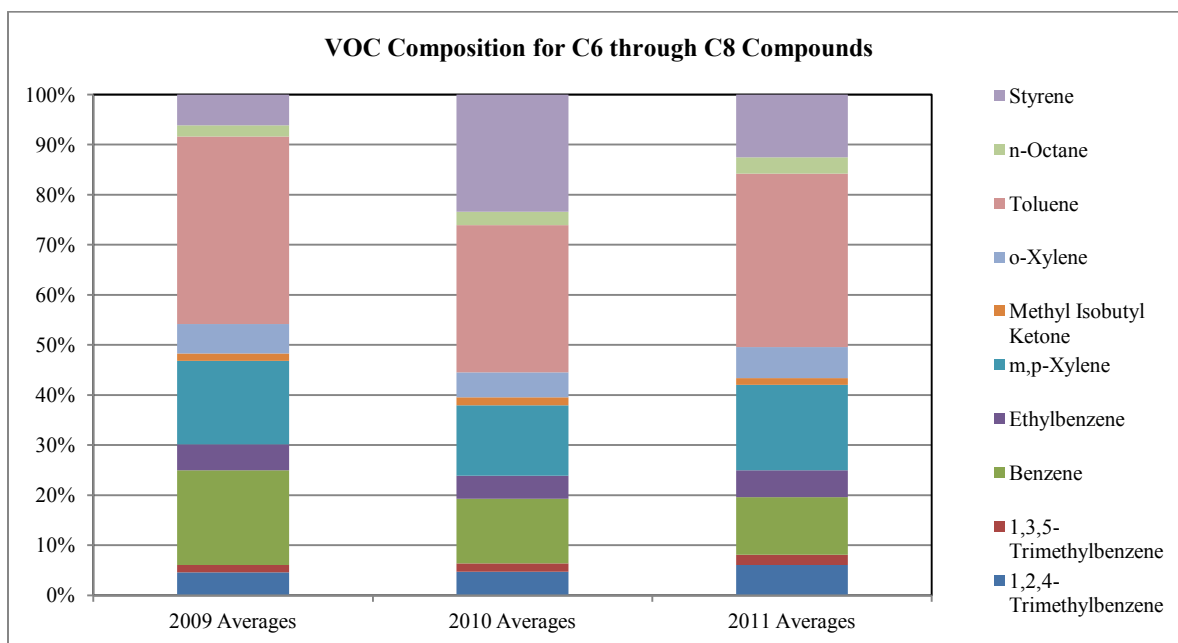
[46]

Figure 57. **Total VOC Composition for C6 through C8 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 17 lists the correlation coefficient values for each of the PAH compounds that were detected in greater than 90% of the samples taken in 2011. 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. All compounds showed positive correlations with the $PM_{2.5}$ concentrations, with the lowest value being 0.267 for anthracene. The strongest correlation between the PAH and $PM_{2.5}$ concentrations was seen with pyrene. A correlation coefficient of 0.823 was obtained for this compound. Overall, the PAHs appear to selectively 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. The compounds with the three largest correlation coefficient values are graphed in Figure 58.

Table 17. **PAH – Particulate Correlation Coefficient Values**

PAH correlations	r - PM_{10}	r - $PM_{2.5}$
9-Fluorenone	-0.383	0.346
Acenaphthene	-0.126	0.580
Anthracene	-0.200	0.267
Benzo (b) fluoranthene	-0.368	0.328
Benzo (e) pyrene	-0.447	0.295
Benzo (g,h,i) perylene	-0.172	0.555
Chrysene	-0.373	0.370
Fluoranthene	-0.107	0.611
Fluorene	0.041	0.713

[47]

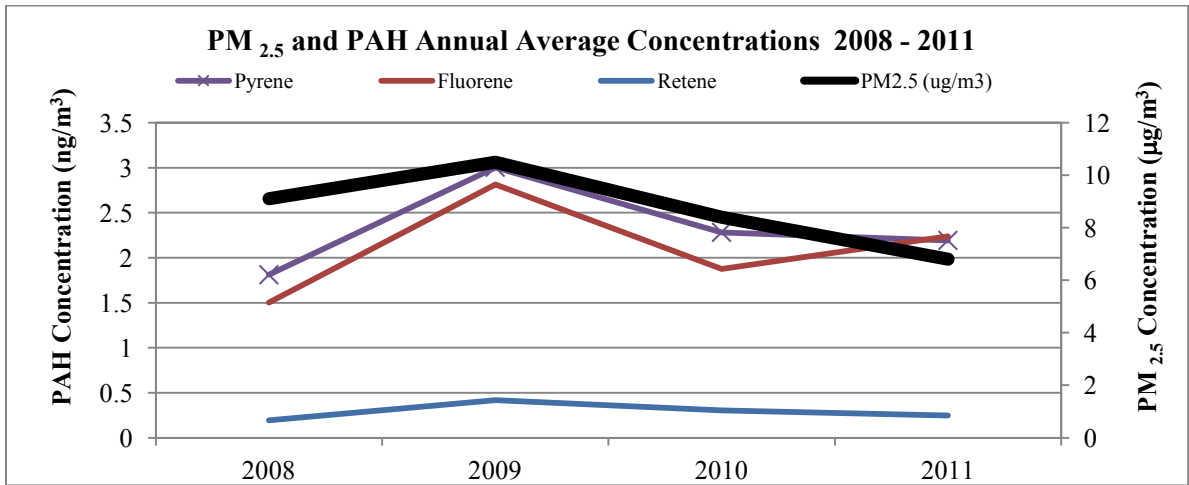| PAH correlations	r - PM$_{10}$	r - PM$_{2.5}$
Naphthalene	-0.164	0.558
Phenanthrene	-0.214	0.517
Pyrene	0.219	0.823
Retene	0.053	0.714

Figure 58.   **PAH – PM$_{2.5}$ Concentration Comparison**

Figure 59 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.
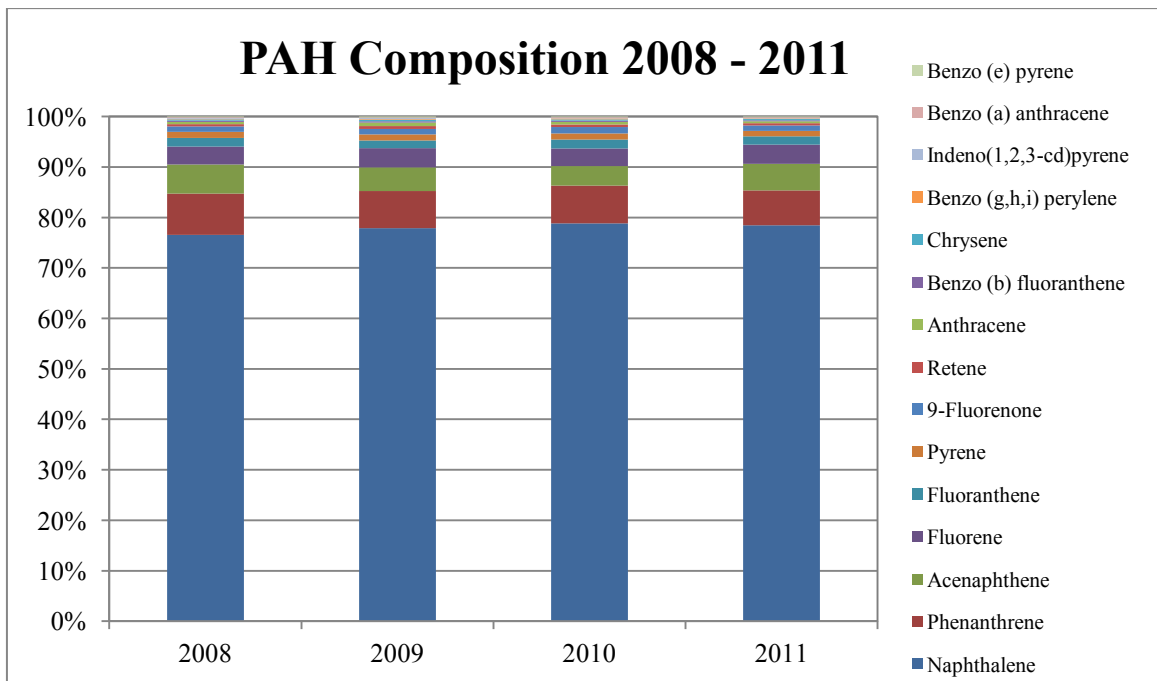

Figure 59.   **PAH Chemical Composition 2008 – 2011**

[48]

Metals Correlations and Sample Composition

The light metals in this group are analyzed 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 18. Manganese concentrations correlated well with the PM_{10} concentrations, having an r-value of 0.860. There were no significant correlations between any of the metals compounds and the $PM_{2.5}$ concentrations. This suggests that the metals may be coming from geologic crustal, rather than industrial, sources. A graph of the PM_{10} and manganese concentrations is seen in Figure 60.

Table 18.   Metals – Particulates Correlation Coefficients

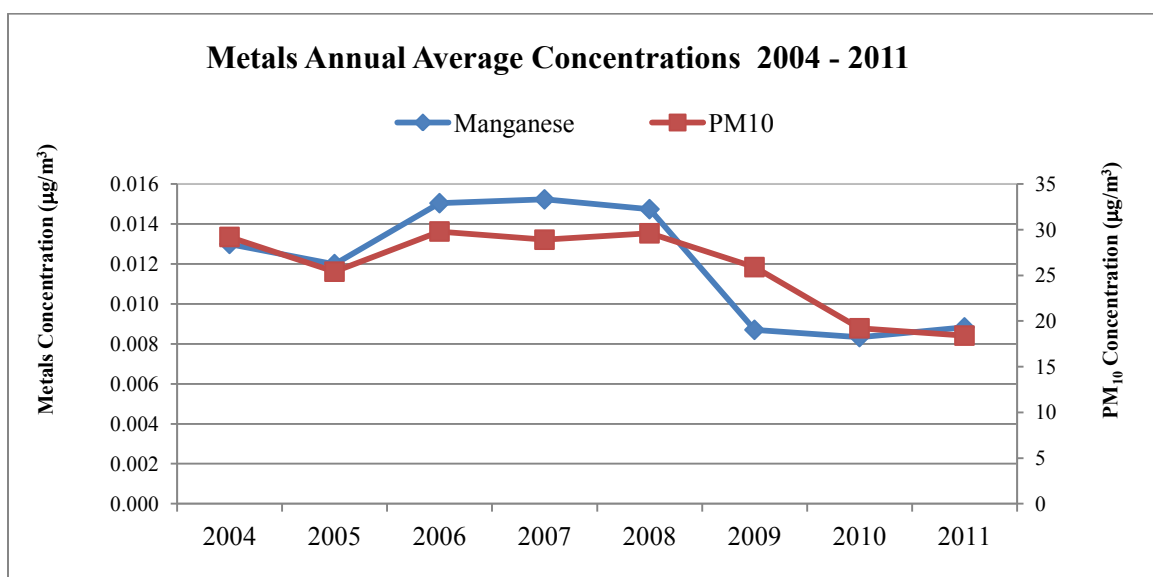| Analyte	r-PM_{10}	r-$PM_{2.5}$
Arsenic	0.479	-0.008
Lead	0.573	0.246
Manganese	0.860	0.303
Nickel	-0.677	-0.765

Figure 60.   Metals – PM_{10} Concentration Comparison

Figure 61 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.
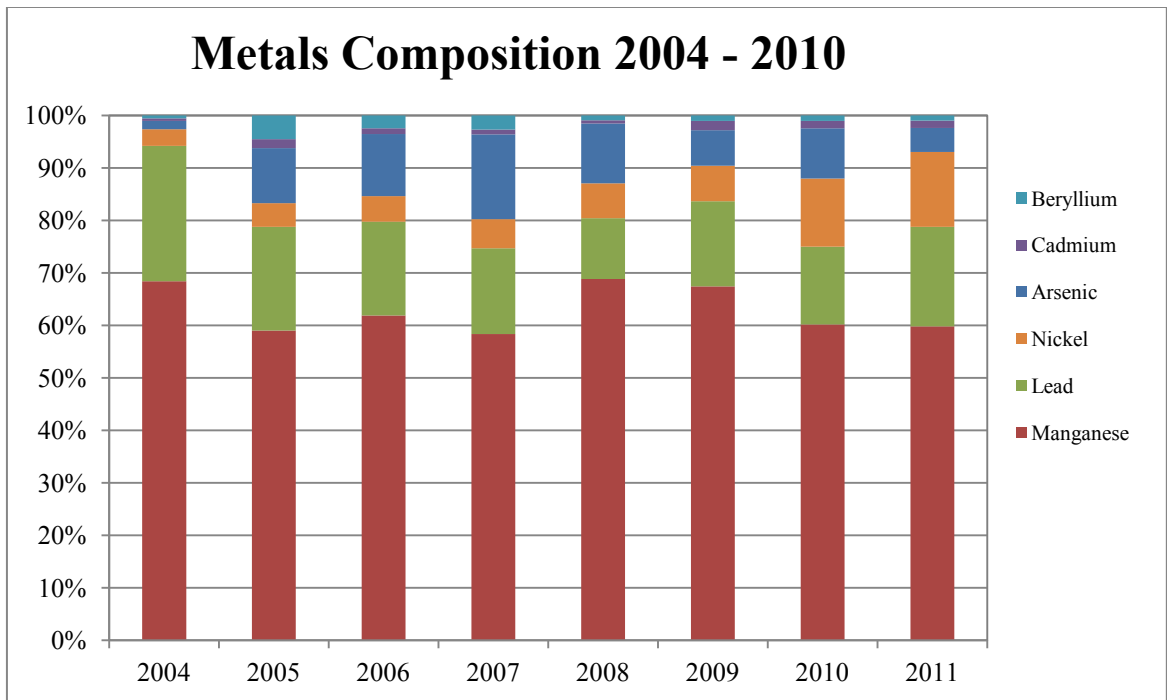
[49]

Figure 61. **Metals Chemical Composition 2004 – 2011**

XII. SUMMARY AND CONCLUSIONS

   The National Air Toxics Trends Study in Grand Junction for 2011 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 0.832 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 0.384. A comparison of the $PM_{2.5}$ concentrations with the carbonyls again showed that formaldehyde correlated the best, but had a low coefficient value of 0.667. Many of the carbonyls showed no correlation at all with the $PM_{2.5}$ values.

   Twenty-four volatile organic compounds are ubiquitous, having been detected in 90% of the air samples for 2011. Going back to 2009, there were 26 compounds detected in at least 90% of the samples. From 2009 to 2011, the makeup of the C1 to C4 group was highly variable, with large concentrations of carbon disulfide in 2009, but not in 2010 or 2011, as well as large concentrations of dichloromethane in 2010, but not in 2009 or 2011. The C6 through C8 group showed more consistency in the constituent concentrations from 2009 to 2011.

   For the metals, lead and manganese showed the highest average concentrations. Hexavalent chromium is an extremely small fraction of the chromium in air, comprising less than one percent of the total chromium concentration. The highest polycyclic aromatic hydrocarbons in air were naphthalene, acenaphthene, and phenanthrene, all of which correlated well with $PM_{2.5}$ values. All of the other PAH compounds also correlated somewhat with $PM_{2.5}$ values, with correlation coefficients ranging from 0.295 to 0.823.

   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 2012, 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. Calculation of the three year average concentrations to date has shown a decrease in the majority of the concentrations of the compounds of

interest. However, only two successive three year averages have been able to be calculated to this point, so it is difficult to draw any real conclusions about concentration trends until further data are collected. Enough data will have been collected by the end of 2012 to calculate a third three year average. At that time, more concrete conclusions may be able to be made.