Understanding Air Toxics and Carbonyl Pollutant Sources in Boulder County, Colorado

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1 INTRODUCTION

In 2006, the Boulder County Public Health Department (BCPH) and the University of Colorado at Boulder (CU) received a grant from the United States Environmental Protection Agency (EPA), Office of Air Quality Planning and Standards (OAQPS) to conduct a Community Based Air Toxics Study. The desired outcome of Boulder's Community Based Air Toxics Monitoring grant was to investigate the spatial and temporal characteristics of air toxics across Boulder County, which sits at the foothills of the Rocky Mountains. This was accomplished by monitoring for air toxics at multiple locations for a period of one year.

The sampling portions of this study began in March 2007 and extended through February 2008. The study monitored air toxics concentrations at five different sites located within Boulder County. The sampling sites included an urban area heavily influenced by vehicle traffic, three suburban areas that are influenced by multiple air pollution sources, and a remote background location that sits far from local pollution sources.

1.1 PURPOSE

The purpose of the Boulder County Community Scale Air Toxics Study (Boulder Study) was to collect data concerning air toxics concentrations in Boulder County. This project focused on collecting both temporally and spatially resolved data for selected air toxics in Boulder. The air toxics monitoring data was used to evaluate a community scale air dispersion model, as well as for comparisons with the most recent National Air Toxics Assessment (NATA) results for Denver and Boulder. Base samples of volatile organic compounds (VOCs) and carbonyls were collected for 24 hour periods (midnight to midnight) on a one-in-six day sampling frequency at five monitoring sites. Ozone was collected continuously at four locations, as the fifth South Boulder site was collocated with a Colorado Department of Public Health and the Environment (CDPHE) ozone site. In addition to the base sampling of VOCs and carbonyls using conventional monitoring techniques, additional data were collected using the same methods but with improved time resolution; specifically, eight 3-hour average samples for the same time periods as the base 24 hour average sampling. Meteorological data including wind speed, wind direction, ambient temperature, and barometric pressure were also continuously collected at each location.

1.2 BACKGROUND

Boulder County sits at the confluence of the high alpine wilderness of the Rocky Mountains, the urbanized Denver Metropolitan area, and the agricultural and intensive oil and gas activities in neighboring counties. This urban/rural interface creates a complex air quality environment characterized by shifting upslope and downslope air flow conditions that can intensify air toxics in relatively pristine environments. This is evidenced by the regional ozone concentrations which often peak in the foothills, not in the metro area or east of Denver.

Previous studies indicate that secondary pollutants such as acetaldehyde and formaldehyde are significant air toxics risk drivers and are also indicative of ozone formation along the Colorado Front Range (Riggs et al. 1996). The 1996 and 1999 National Air Toxics Assessment (NATA) estimates attempt to account for secondary production of these two compounds, although EPA acknowledges that their approach is subject to considerable uncertainty.

1.3 OBJECTIVES

Boulder County Public Health (BCPH) and its partners monitored VOC, carbonyls, and ozone at five locations to aid in air toxics model evaluation and air toxics source apportionment. This study was to evaluate the City and County of Denver's regional air toxics model. Timely carbonyl and tracer gas measurements enabled the county to better assess the impacts from primary and secondary air toxics pollutant sources in the urban-mountain interface.

Specifically, the study met the following objectives:

1) Delineate concentrations of local scale air toxics, including ozone. Build upon previous studies that have identified levels of acetaldehyde and formaldehyde well in excess of those found in more densely urbanized neighboring areas and National Air Toxics Assessment (NATA) predictions. Add more spatial resolution to the existing ozone monitoring effort undertaken by the Colorado Department of Public Health and the Environment. Use monitoring and modeling to assess the impact of secondary pollutants and understand the spatial and temporal variations of air toxics at the urban/mountain interface.
2) Evaluate and improve air quality exposure models. Use the spatial and temporal air toxics monitoring data to evaluate the NATA results for Boulder County and an established community-scale air dispersion model.
3) Support assessments of health effects. Provide timely data to address community concerns and to support and evaluate two extensive health consultations conducted in collaboration with the Agency for Toxic Substances and Disease Registry in northwest Boulder County.
4) Develop a baseline for longer-term monitoring. Create a monitoring and modeling capability, in partnership with the University of Colorado and the City and County of Denver, which can be built upon in subsequent years.
5) Guide air quality management strategies in Boulder County.

1.4 ROLES, RESPONSIBILITIES, AND PARTNERS

1.4.1 EPA Region 8 Office

EPA Regional Offices have been developed to address environmental issues related to the states within their jurisdiction and to administer and oversee regulatory and congressionally mandated programs. The major quality assurance responsibilities of EPA's Region 8 Office, in regards to the Ambient Air Quality Program, are the coordination of quality assurance matters at the Regional levels with the State and local agencies. This is accomplished by the designation of EPA Regional Project Officers who are responsible for the technical aspects of the program including:

- Reviewing Quality Assurance Project Plans (QAPP) by Regional QA Officers who are delegated the authority by the Regional Administrator to review and approve QAPPs for the Agency;
- Supporting the air toxics audit evaluation program;
- Evaluating quality system performance, through technical systems audits and network reviews whose frequency is addressed in the Code of Federal Regulations and Section 20;
- Acting as a liaison by making available the technical and quality assurance information developed by EPA Headquarters and the Region to the State and local agencies, and making EPA Headquarters aware of the unmet quality assurance needs of the State and local agencies.

The EPA Region 8 Office in Denver, Colorado provided direct oversight to the project through review of the quality assurance project plan, the conduct of system audits, and acting as a communication link with OAQPS. For this project, the Region 8 Project Officer was Marisa McPhilliamy and the Air Toxics Monitoring Coordinators were Kenneth Distler and Michael Copeland.

1.4.2 Boulder County Public Health (BCPH)

Boulder County Public Health (BCPH) received a grant for this project from the EPA Region 8 Office in Denver, Colorado. BCPH coordinated the grant, including contracting out sampling and laboratory analysis work to the University of Colorado at Boulder (CU), purchasing the necessary equipment, conducting portions of the data collection and interacting with the public through the website and community education programs.

BCPH assisted with the installation of the air monitoring stations and the development of standard operating procedures to assure data quality. BCPH contributed to, reviewed and integrated the final version of the Quality Assurance Project Plan. BCPH provided day-to-day oversight of the project. BCPH provided an air-monitoring technician who assisted with sample collection and laboratory support. BCPH and CU provided training and written procedures for the technician. Pam Milmoe of BCPH served as one of the two project managers, as well as the Quality Assurance Officer for BCPH.

1.4.3 University of Colorado at Boulder (CU)

The University of Colorado at Boulder was responsible for the direct, day-to-day operations of the air monitoring project. Professor Michael Hannigan (CU) was primarily responsible for oversight of CU's role in the project, and served as the CU Quality Assurance Officer. This included set-up and operation of the atmospheric sampling equipment for the project, coordinating sample collection, and analysis of the samples at the University of Colorado at Boulder. Detlev Helmig of the Institute of Arctic and Alpine Research (INSTAAR at CU) was primarily responsible for the operation of the laboratory that analyzed the samples collected in the project and the associated quality assurance activities. Professor Jana Milford (CU) was primarily responsible for the data analysis and source apportionment activities in the CU portion of the project.

1.4.4 Colorado Department of Public Health and Environment, Air Pollution Control Division (APCD)

Although it did not have direct involvement in day-to-day project operations, the APCD was interested in the results of this air monitoring project. The APCD has previously conducted short- and long-term air toxics monitoring in Denver and is interested in comparisons with previous years' data. APCD also volunteered time to upload all air monitoring data, including quality assurance data to the AQS. The data were formatted by CU. Units reported to AQS for all parameters measured were in ppbV (parts per billion by volume). In addition, APCD provided four ozone monitors and two shelters to house the sampling equipment.

1.4.5 Denver Department of Environmental Health

As part of this study, Denver Department of Environmental Health (DDEH) agreed to update their air toxics modeling assessment for the entire Denver metropolitan area, including most of Boulder County. The methods used in their assessment are summarized in Chapter 3. Results of their modeling assessment are provided in Chapter 6.

1.5 LIST OF POLLUTANTS

The selection of air toxics compounds to be monitored was mainly determined from information gleaned from previous air toxics monitoring in the metro Denver region. The target compounds included: formaldehyde, acetaldehyde, acrolein, benzene, toluene, and the xylenes. The target compounds are also directed towards chemical species that can provide assistance in determining the origin of the air toxics. Table 1.0 lists the target VOCs quantified in the Boulder Study with their EPA Air Quality System (AQS) parameter code.

Table 1.0: Target Volatile Organic Compounds Quantified in the Boulder Study

Target Volatile Organic Compounds	
VOC	**AQS Parameter Code**
n-hexane	43231
2,2-dimethylbutane	43244
n-butane	43212
trans-2-butene	43216
cis-2-butene	43217
1,2-butadiene	43223
benzene	45201
1-pentene	43224
n-heptane	43232
3-methylheptane	43253
2,3-dimethylpentane	43291
2-methyl-1-butene	43225
Toluene	45202
n-octane	43233
n-pentane	43220
cis-2-pentene	43227
2,3,4-trimethylpentane	43252
ethylbenzene	45203
m,p-xylene	45109
n-nonane	43235
styrene	45220
o-xylene	45204
2-methyl-2-butene	43228
3-methylpentane	43230
trans-2-hexene	43289
cis-2-hexene	43290
2-methyl-1-pentene	43246

Table 1.1 lists the carbonyl compounds quantified in the Boulder along with their respective AQS parameter code.

Table 1.1: Target Carbonyl Compounds Quantified in the Boulder Study

Target Carbonyl Compounds	
Carbonyl Compounds	**AQS Code**
formaldehyde	43502
acetaldehyde	43503
acetone	43551
propionaldehyde	43504
acrolein	43505
crotonaldehyde	43528
butyr/isobutyraldehyde	43329
benzaldehyde	45501

In addition, the project team operated continuous monitors for ozone at four of the sites. Monitoring was designed to meet the requirements in 40 CFR Part 58, Appendix A and EPA Monitoring Quality Assurance Manual requirements.

1.6 PREVIOUS STUDIES

Previous studies measuring ambient carbonyls and/or VOCs have been made since 1987 in the Denver Metro Area including Boulder County. Until 2004, it appears that no long-term carbonyl monitoring efforts had been made. Several shorter-term studies of carbonyls and VOCs have been made in the Denver Metro Area and were used for comparative purposes. In many cases the sample times and durations varied, which makes direct comparison difficult. Regardless, the overall results of these studies are presented in this section.

From December 1987 through mid-April 1998, Larry Anderson of the University of Colorado at Denver collected formaldehyde and acetaldehyde samples in downtown Denver in response to the implementation of a mandated oxygenated fuel program along Colorado's Front Range. According to the CDPHE, the concentrations of aldehydes in motor vehicle exhaust gases increased when ethanol or MTBE additives were used. Therefore, Anderson studied Denver's ambient air by observing formaldehyde-to-acetaldehyde ratios, aldehydes-to-carbon monoxide ratios, and the diurnal variations of formaldehyde and acetaldehyde before, during, and after the oxygenated fuels program. 24-hour and 4-hour averages were collected in this study, with six 4-hour samples being collected from 16:00 until 16:00. Anderson observed 4-hour average formaldehyde concentrations ranging from 1 to 18 ppbV and 24-hour averages ranging from 2.6 to 10 ppbV. For acetaldehyde, 4-hour average concentrations ranged from 0.5 to 10 ppbV and 24-hour average concentrations ranged from 1.7 to 3.5 ppbV (Anderson et al., 1998). Table 1.2 displays these values.

Table 1.2: 1987-1988 Denver study of average carbonyl concentration ranges for 4-hr and 24-hr samples to understand the effects of an oxygenated fuel program

Denver 1987-1988 Average Carbonyl Concentration Ranges (in ppbV)		
	4hr	**24hr**
formaldehyde	1.0 – 18.0	2.6 – 10.0
acetaldehyde	0.5 – 10.0	1.7 – 3.5

In 1996, Riggs et al. monitored carbonyls at three locations in Boulder and one location in Denver as part of a study that looked into the correlations of carbonyls with carbon monoxide (CO). Two of the 1996 Boulder sampling locations were near 2007 Boulder Air Toxics Study sites, as the 1996 Boulder Marine Street location (Marine) was near the 2007 Boulder site and the 1996 CU Mountain Research Station location (C1) was near the 2007 Niwot Ridge site. Six 4-hour winter samples were collected 24 hours per day, seven days per week from the Denver Auraria, Marine, and the Boulder 28th Street locations in 1996 from February 7 to March 8. Six discrete 4-hour samples were collected every other day from the 28th Street location during the same sampling period. Winter carbonyl data from the Denver Auraria location had been collected from November through February over a nine-year time period beginning in 1987. Six samples of 4-hour carbonyl data were collected at Marine, Auraria, and C1 during the 1996 summer period, July 11 through September 1 (Riggs et al., 1996). Table 1.3 shows the average carbonyl concentration ranges from the 1996 study.

Table 1.3: 1996 Denver/Boulder Study of winter time and summer time carbonyls to analyze correlations with CO

Denver/Boulder 1996 4-hr Average Carbonyl Concentration Ranges (in ppbV)						
	Winter 1996			**Summer 1996**		
	Auraria	**Marine**	**28th**	**Auraria**	**Marine**	**C1**
formaldehyde	0.33-13.5	0.4-7.4	0.3-6.2	1.51-9.84	0.84-7.23	0.13-17.32
acetaldehyde	0.33-6.8	0.1-18.7	0.3-17.3	0.41-5.75	0.66-21.74	0.95-53.12
acetone	0.27-6.8	0.1-44.6	0.1-36.3	0.02-5.72	0.08-39.20	0.06-66.93

In both 1996 and 1999, the EPA performed National-Scale Air Toxics Assessments (NATA) across the country in an effort to comprehensively evaluate the risk of cancer and other serious health effects from breathing air toxics. Monitoring data, atmospheric dispersion models, and population statistics are collectively used to generate results for a NATA. Additional HAPs were included in the 1999 assessment when compared to the 1996 assessment, although formaldehyde, acetaldehyde, and benzene were included in both. Modeled county median results from the Denver Metro Area show similar values for these compounds (EPA NATA, 1999). Table 1.4 provides the modeled results of three select compounds from the two assessments. The NATA results were reported in mass concentration units.

Table 1.4: EPA NATA results from 1996 and 1999 evaluations of air toxics in the Denver Metro Area

NATA Estimated County Median Concentration Ranges for Denver Metro Area (in μg/m^3)		
	1996	**1999**
formaldehyde	0.61-6.91	0.94-6.94
acetaldehyde	0.52-4.57	0.91-4.26
benzene	1.14-4.76	0.71-4.93

In 2004, the DDEH received a grant from EPA Region 8 to conduct long-term air toxics monitoring in Denver. The goal was to utilize existing local data to spatially and temporally allocate cumulative county-level emissions of air toxics across the Denver region.

DDEH was interested in assessing a dispersion model's ability to adequately predict air toxics exposures throughout Denver. Results for the 1996 baseline emissions year showed model-to-monitor ratios mostly within a factor of two, though air toxics data were sparse in the urban core.

Subsequent work by DDEH involved updating the emissions for 2002 and performing neighborhood scale modeling at an even higher resolution in a smaller geographic area of north Denver. The cumulative regional assessment was also updated with the 2002 NATA emissions inventories.

Therefore, DDEH conducted a study from June 2005 through May 2006 sampling carbonyls, VOCs, and black carbon. VOCs and carbonyls were sampled every six days from midnight to midnight, following EPA Compendium Methods TO-17 and TO-11A respectively. Improved time resolution samples were also collected, as six 4-hour samples were collected from midnight to midnight (Thomas et al., 2005). Table 1.5 shows the median 24-hour average concentrations of select air toxics.

Table 1.5: DDEH Air Toxics study results for 24-hr carbonyl and VOC samples

DDEH 2005-2006 Air Toxics Study: 24-hr Median Concentrations **(in ppbV)**				
	Auraria	**Swansea**	**Palmer**	**Vanderbilt**
formaldehyde	3.86	7.79	5.28	2.43
acetaldehyde	11.38	11.90	10.12	3.06
acrolein	0.07	0.07	0.07	0.07
benzene	0.89	1.06	0.70	0.54
toluene	2.42	3.33	1.51	2.11

The Auraria Campus is affected by several major thoroughfares including Interstate-25, Speer Boulevard and Colfax Avenue. The Swansea Elementary School site is subject to heavy industrial and commercial facilities, as well as Interstates 70 and 25, the major east-west and north-south thoroughfares through Denver, respectively. Palmer Elementary School is a suburban site one-third of a mile east of a hospital complex. There are few commercial businesses or major thoroughfares within a half-mile radius. Vanderbilt Park is downwind from numerous light commercial businesses as well as a coal burning power plant and is near the major thoroughfares of Interstate 25 and Santa Fe Drive. Vanderbilt Park was expected to have moderate to heavy traffic impacts.

In 2006, CDPHE set up a network of six sampling locations around the state of Colorado that monitored VOCs and carbonyls. The locations consisted of Welby, Denver-Camp, Fort Lupton, Grand Junction, Platteville, and Rocky Flats. The duration of monitoring periods varied from site to site, but all included samples taken during the summer months of 2006. For example, three samples were taken at the Rocky Flats site during June and July of 2006, while sixty samples were taken at the Grand Junction site from January to December 2006. Samples were taken either every three or six days, depending on the site. Samples taken at the Welby, Denver-Camp, Fort Lupton, Grand Junction, and Platteville sites were collected from 06:00 to 09:00, while samples collected the Rocky Flats site were collected from 13:00 to 16:00 (CDPHE, 2006). Table 1.6 shows the median 3-hour concentrations from the months of June and July 2006.

Table 1.6: Summer 2006 results from a CDPHE study of the Denver Metro Area

CDPHE June and July 2006 3-hr Median Concentrations **(in ppbV)**						
	Welby	**Denver-Camp**	**Fort Lupton**	**Grand Junction**	**Platteville**	**Rocky Flats**
formaldehyde	2.94	5.12	2.77	4.56	1.18	4.65
acetaldehyde	6.99	9.04	2.62	1.55	3.36	5.42
acetone	5.94	7.75	4.81	1.71	5.35	7.42
benzene	1.41	0.75	0.65	0.07	2.03	0.09
toluene	1.40	1.37	1.24	0.10	1.70	0.14

1.7 STUDY BOUNDARIES

This study attempts to assess the variation in concentrations within Boulder County; therefore, the study boundaries are at the neighborhood scale. Region 8 and the project team agreed that the optimum design for this study, given resource limitations, was to sample at five locations on a one-in-six day basis. It was anticipated that five monitoring sites would be sufficient to confirm whether concentrations of HAPs are uniform throughout Boulder, or have local variations. In addition, ground level ozone was monitored at each location to provide further information on seasonal and temporal variations within Boulder County. Higher time resolved samples were collected for one year at each location, with the exception of the Niwot Ridge site where only five months of higher time resolved samples were collected with approval of EPA Region 8.

1.7.1 Monitoring Locations

The Boulder County Community-Scale Air Toxics Assessment sites were located as follows:

1) *Niwot Ridge*. (AQS Site # 08-013-7004) A remote mountain location to assess both the upwind air and the potential back flush of the urban corridor. The Niwot Ridge Mountain Research Station is about 3 miles from the closest road, the Peak-to-Peak Highway.
2) *City of Boulder*. (AQS Site # 08-013-7001) A location in close proximity to the sites previously used in the Anderson study mentioned above, and near two of the busiest traffic intersections in the state.
3) *City of Longmont*. (AQS Site # 08-013-7002) An agricultural area and adjacent to oil and gas exploration to the north to assess the agricultural burning and oil and gas.
4) *City of Lyons*. (AQS Site # 08-013-7003) A small rural location in the mountain foothills to validate a recent health consultation and assess oil and gas activities to the north.
5) *South Boulder Creek State Ozone Monitor*. (AQS Site # 08-013-7005) A rural location along the South Boulder Creek and collocated with a state ozone monitoring station to capture air flows occurring along water drainages and provide insights into transport.

1.7.2 Temporal Boundaries

The temporal boundaries of the study are defined by the need to calculate, at a minimum, annual average concentrations. Thus, the monitoring period for the Boulder Community Scale Air Toxics Study is one year in duration.

The project collected 24-hour average samples once every sixth day at each of five sampling sites, for a one-year period. The one-in-six frequency is a standard air pollution sampling practice, designed to ensure that samples are taken to represent every day of the week. (That is, one week the samples are taken on Wednesday, the next sample day is a Tuesday; the third sample date is a Monday, etc). The one-year period covered all four seasons to capture the expected variation in meteorological conditions for the sites. In addition to this spatially distributed sampling, improved time resolution sampling was also done. This includes collection of eight 3-hour average samples for VOCs and carbonyls at each of the five sites (i.e., the core site). This sampling also occurred on a one-in-six day schedule.

1.8 MODELING AND SOURCE APPORTIONMENT APPROACH

Monitoring data collected during the Boulder County Air Toxics Study were inputs to modeling programs that evaluated fate and transport of air toxic compounds. Dispersion models predict ambient concentrations based on information collected by the user and supplied in the model input file. DDEH's established air dispersion model was run for a select period based on meteorological characteristics and county-level emission factors within the Denver Metropolitan Area.

Ozone Isopleth Plotting Research (OZIPR), a trajectory-type air quality simulation model, was used to relate ozone concentrations to levels of organic and nitrogen oxide (NOx) emissions. OZIPR was also used to evaluate model selected carbonyl compounds that were monitored during the study.

Principal Components Analysis (PCA) is a multivariate technique that was applied to arrays of measured pollution variables for the purpose of identifying potential sources, as well as each variable's mutual relationship. PCA was run on 24-hour VOC and carbonyl samples measured at each of the five sampling locations.

In addition to PCA, pairwise correlations were used to assist in identifying common sources of air pollutants. Pairwise correlations were run on 24-hour VOC and carbonyls, as well as 1-hour ozone values.

1.9 DESIRED PROJECT OUTCOME

The design of the monitoring network for this project is intended to address the question of intra-county variability in air toxics concentrations. In addition to validating DDEH's community scale dispersion model, statistical analyses of the results collected in Boulder County provided useful information about the spatial variability of the air toxics within the county. Collection of additional data with higher time resolution allowed us to determine how much variability occurs in the air toxics concentrations as a function of time of day. In addition, this replicate sampling provides additional data that allowed us to better understand the precision of the data. The added data for the ground level ozone provided additional information that was used to generate a better understanding of the contribution of different sources of air toxics.

The main goal of this study was to make quantitative determinations of hazardous air pollutant concentrations across Boulder County. In addition, this project created an opportunity to gain considerable information on the precision of VOC and carbonyl measurement techniques.

2 MONITORING METHODS

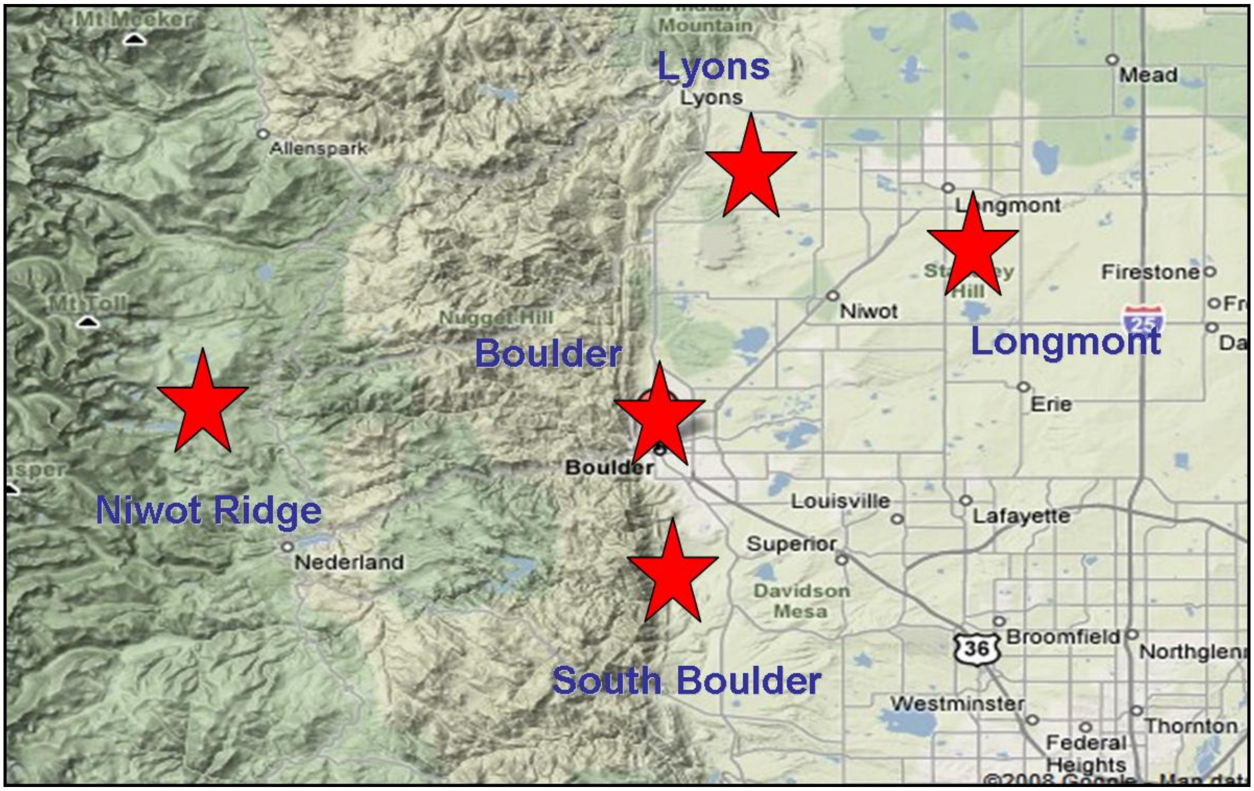
2.1 MONITORING LOCATIONS

The Boulder Study selected five locations, based on EPA guidelines, for air toxics monitoring. EPA has indicated a number of goals that should be met in siting air toxics monitoring locations. In order to leverage resources, existing monitoring stations should be utilized when appropriate. Often, these will be locations that already collect data for a number of criteria air pollutants such as particulate matter, ozone, and carbon monoxide. The stations should normally be located in community areas that are frequented by the public. Furthermore, stations should not be near individual, large air pollution sources. The reason for this requirement is to ensure that the measured levels are not dominated by one localized industry source, but represent typical exposures for significant proportions of the population.

In order to address air toxics exposure at a neighborhood scale, as well as measuring air quality along a representative cross-section of the county, the Boulder Study selected five sites in the following locations. Figure 2.1 shows the five sampling locations of the Boulder Study.

1) *Niwot Ridge*. A remote mountain location to assess both the upwind air and the potential back flush of the urban corridor. The Niwot Ridge Research Station is about 3 miles from the closest road, the Peak-to-Peak Highway. (Northwest on map)
2) *City of Boulder*. A location in close proximity to the sites previously used in the Anderson study mentioned above, and near two of the busiest traffic intersections in the state. (Southeast of center on map)
3) *City of Longmont*. An agricultural area and adjacent to oil and gas exploration to the north to assess the effect of agricultural burning and oil and gas production. (Northeast on map)
4) *City of Lyons*. A small rural location in the mountain foothills to validate a recent health consultation and assess contributions from oil and gas activities to the north.
5) *South Boulder Creek State Ozone Monitor*. A rural location along the South Boulder Creek and collocated with a state ozone monitoring station to capture air flows occurring along water drainages and provide insights into transport.

Figure 2.1: Location of the Five Air Toxics Monitoring Sites in Boulder County



(Mapquest, 2007)

2.2 SAMPLING METHODS

Air quality data, which measured the concentrations of selected volatile organic compounds, carbonyl compounds, and ozone, were collected for a one-year study period. In the basic sampling portion of the project, VOC samples were collected in SUMMA canisters and analyzed by EPA Compendium Method TO-15. The carbonyl samples were collected on 2,4-dinitrophenyl hydrazine (DNPH) coated cartridges; these samples were analyzed by EPA Compendium Method TO-11A. Both VOC and carbonyl samples were collected on a one in six day sampling schedule at each of the five sampling sites used in this program. The sampling equipment used for the VOC sampling and the carbonyl sampling was designed and constructed at CU by INSTAAR. Appendix D of the QAPP describes these samplers, gives the standard operating procedures for TO-15 and TO-11A sampling, and provides examples of the forms used to record sampling activities.

Sampling trailers were used at the Longmont, Lyons, and South Boulder sampling locations during the sampling campaign. Figure 2.2 shows the sampling trailer located at the Lyons sampling site. The Niwot Ridge sampling site was located in a permanent tractor-trailer occupied by the National Oceanic and Atmospheric Administration (NOAA). The Boulder site was located in a garage bay at a fire station in Boulder. Photos of each sampling location are included in Appendix A.

Figure 2.2: Sampling Trailer at the Lyons Site

Each shelter was equipped to accommodate the rotating sampling equipment capable of providing higher time resolution air quality data. A computer-operated sampling system was installed in each shelter that was set up to continuously log instrumentation parameters, as well as both indoor and outdoor environmental parameters. This PC-based system was fully automated using Labview software and data acquisition programs. VOC auto-samplers, carbonyl auto-samplers, and ultraviolet absorption ozone analyzers were all controlled through the PC. The heated inlet line, consisting of ¼-inch Silcosteel, can be seen in Figure 2.2, housed the VOC and carbonyl inlet.

CU transformed the logged data and analytical data into the EPA AQS format. The AQS is a nationwide computer database for regulatory monitoring done in the United States. William Kotasek with CDPHE performed the AQS data entry/upload services for the project.

2.3 FIELD ACTIVITIES

The initial field activities consisted of installation of the air monitoring equipment. INSTAAR installed all sampling equipment for VOCs, carbonyls, and ozone at the applicable sampling sites.

The main field activity consisted of the air sampling performed by INSTAAR, with assistance of CU. The sampling schedule is shown in Table 2.1. INSTAAR also conducted all sampling equipment maintenance and quality assurance activities, as described in the standard operating procedures. See the Boulder QAPP, which is included in Appendix B, for sampling equipment Standard Operating Procedures (SOPs).

Table 2.1: Boulder Study monitoring schedule March 2007 through February 2008 *(sample days highlighted in grey)*

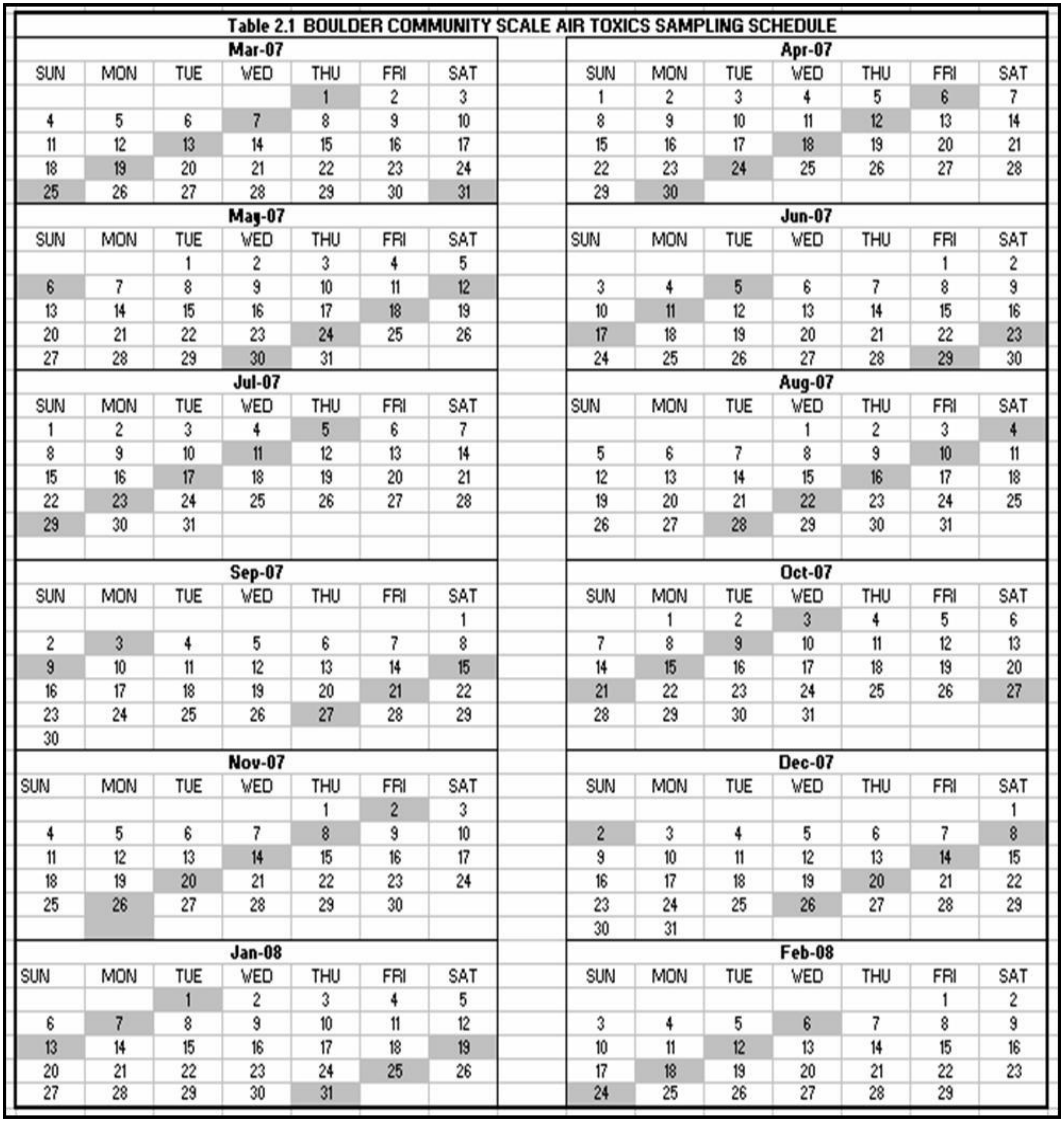


Table 2.1 BOULDER COMMUNITY SCALE AIR TOXICS SAMPLING SCHEDULE

Mar-07

SUN	MON	TUE	WED	THU	FRI	SAT
				1	2	3
4	5	6	**7**	8	9	10
11	12	**13**	14	15	16	17
18	**19**	20	21	22	23	24
25	26	27	28	29	30	**31**

Apr-07

SUN	MON	TUE	WED	THU	FRI	SAT
1	2	3	4	5	**6**	7
8	9	10	11	**12**	13	14
15	16	17	**18**	19	20	21
22	23	**24**	25	26	27	28
29	**30**					

May-07

SUN	MON	TUE	WED	THU	FRI	SAT
		1	2	3	4	5
6	7	8	9	10	11	**12**
13	14	15	16	17	**18**	19
20	21	22	23	**24**	25	26
27	28	29	**30**	31		

Jun-07

SUN	MON	TUE	WED	THU	FRI	SAT
					1	2
3	4	**5**	6	7	8	9
10	**11**	12	13	14	15	16
17	18	19	20	21	22	**23**
24	25	26	27	28	**29**	30

Jul-07

SUN	MON	TUE	WED	THU	FRI	SAT
1	2	3	4	**5**	6	7
8	9	10	**11**	12	13	14
15	16	**17**	18	19	20	21
22	**23**	24	25	26	27	28
29	30	31				

Aug-07

SUN	MON	TUE	WED	THU	FRI	SAT
			1	2	3	**4**
5	6	7	8	9	**10**	11
12	13	14	15	**16**	17	18
19	20	21	**22**	23	24	25
26	27	**28**	29	30	31	

Sep-07

SUN	MON	TUE	WED	THU	FRI	SAT
						1
2	**3**	4	5	6	7	8
9	10	11	12	13	14	**15**
16	17	18	19	20	**21**	22
23	24	25	26	**27**	28	29
30						

Oct-07

SUN	MON	TUE	WED	THU	FRI	SAT
	1	2	**3**	4	5	6
7	8	**9**	10	11	12	13
14	**15**	16	17	18	19	20
21	22	23	24	25	26	**27**
28	29	30	31			

Nov-07

SUN	MON	TUE	WED	THU	FRI	SAT
				1	**2**	3
4	5	6	7	**8**	9	10
11	12	13	**14**	15	16	17
18	19	**20**	21	22	23	24
25	**26**	27	28	29	30	

Dec-07

SUN	MON	TUE	WED	THU	FRI	SAT
						1
2	3	4	5	6	7	**8**
9	10	11	12	13	**14**	15
16	17	18	19	**20**	21	22
23	24	25	**26**	27	28	29
30	31					

Jan-08

SUN	MON	TUE	WED	THU	FRI	SAT
		1	2	3	4	5
6	**7**	8	9	10	11	12
13	14	15	16	17	18	**19**
20	21	22	23	24	**25**	26
27	28	29	30	**31**		

Feb-08

SUN	MON	TUE	WED	THU	FRI	SAT
					1	2
3	4	5	**6**	7	8	9
10	11	**12**	13	14	15	16
17	**18**	19	20	21	22	23
24	25	26	27	28	29	

2.4 ANALYTICAL ACTIVITIES

The laboratories at INSTAAR were the only laboratories that analyzed samples from this project. Specifically, INSTAAR's analytical involvement for Method TO-

15 was in the analysis of canisters, cleaning the canisters, and preparation and return of evacuated canisters for the VOC sampling. For carbonyls, the INSTAAR laboratories were responsible for the purchase of commercially prepared 2,4-dinitrophenylhydrazine (DNPH) cartridges for sampling of carbonyls in air, as well as the analysis of the cartridges using method TO-11A.

Analytical efforts adhered to all procedures set forth in the QAPP relevant to sample collection and analysis. This included strict adherence to the applicable sampling method, timely purchase and use of applicable calibration and/or reference standards, collection of duplicate and/or collocated samples, and all instrument and sampler troubleshooting and oversight. Laboratory SOPs can be found in the Boulder QAPP.

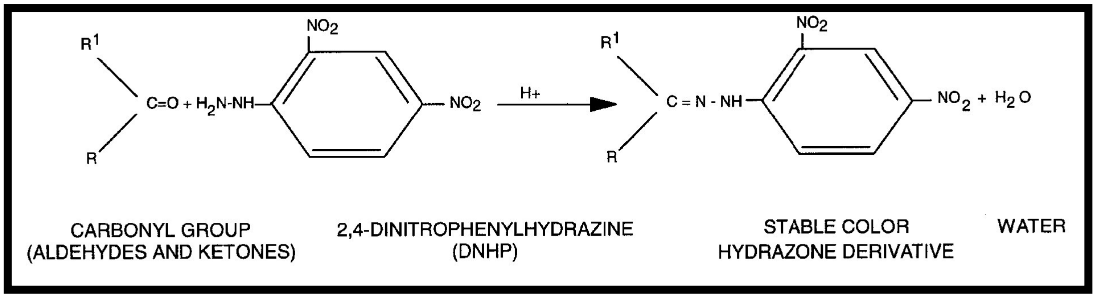
2.4.1 Carbonyls

Following EPA Method TO-11A, aldehydes/ketones in the ambient air were collected during the 24 hour (midnight to midnight) sampling period on a one in six day basis, at the five sampling locations, and in eight three-hour average samples collected once every month. Ozone in the sample air can cause both positive and negative artifacts in the sampling of carbonyls by derivatization on DNPH (Helmig et al.,1997). Consequently, ozone was removed by selectively reacting ozone in a denuder. The recommendation of Compendium Method TO-11A was followed by using a potassium-iodide ozone scrubber for this purpose. The technical design was met according to recommendations given in TO-11A, where 1 meter-long ¼-inch outside diameter copper tubing was coated by purging and subsequent drying with an aqueous solution of dissolved potassium iodide. Denuders were tested prior to field use in the lab by pulling ambient air through the denuder and measuring the remaining ozone with an ozone monitor. Only denuders that remove ozone below 2 ppbV were utilized for field sampling. Denuders were heated and temperature-controlled to 65°C. It has been shown that under these conditions ozone is removed effectively in the air stream for up to 100,000 ppbV-hours. Denuders were replaced with newly prepared denuders and again tested after their removal in the lab after one month of use, which were well below the 100,000 ppbV-hours capacity.

Membrane particle filters with 5.0µm pore size were ozone-conditioned and used at the inlet of the carbonyl/VOC sampling line. The sampling line consisted of ¼-in Silcosteel and was heated to a constant 65°C. The sampling line was continuously purged outside of sampling times to prevent any contamination from stagnant air.

Carbonyl samples were sampled at a mass-flow controlled rate around 650 mL/min, which yielded an effective sample volume of 100 L for the 3-hour samples and 1000 L for the 24-hour averaged samples. The carbonyls quantified in this project are listed above in Table 2.1. Leak checks were performed on each autosampler before and after the collection of a sample. If a cartridge did not pass a leak check, the leak was repaired and a new cartridge was used.

Samples were collected on Supelco DNPH silica cartridges. Organic carbonyl compounds react with DNPH-coated silica gel cartridges in the presence of a strong acid to form a stable derivative according to the following reaction:



(EPA Method TO-11A, January 1999)

where R and R^1 are an organic alkyl or aromatic group (ketones) or either substituent is a hydrogen atom (aldehydes). After the sample was collected on the DNPH cartridge and at the time of a site visit, the cartridges were removed from the temperature-controlled autosampler, capped, placed in either a clean Pyrex culture tube or a glass Mason jar with a screw cap, and stored in a cooler packed with ice. Cartridges were immediately placed in a dedicated refrigerator upon return to the laboratory and stored free of direct light at 4°C until further analysis.

Following cartridge extraction, samples were analyzed on a High Performance Liquid Chromatograph (HPLC) equipped with a reverse-phase C-18 column and ultraviolet diode-array detector for separation and analysis of the hydrazone derivative.

During field sampling activities, carbonyl field blanks and duplicates were collected during each sampling period to evaluate cleanliness and reproducibility.

2.4.2 VOCs

Volatile organic compounds were monitored according to the EPA Method TO-15. Air samples were collected at each of the five selected monitoring sites using the whole air sampling approach with subsequent sample analysis in INSTAAR's Atmospheric Research Laboratory. Besides detection by mass spectrometry (MS), as defined by TO-15, a second flame ionization detector (FID) with post-column flow splitting was utilized. While MS identification is of importance for the unequivocal identification of analytes, FID detection yields improved accuracy and more stable detector response for quantification. Six-liter volume silico-passivated SUMMA canisters were equipped with flow-controlled, passive sampling devices, which were set to a flow rate around 3 mL min^{-1} to yield collection of a approximately 4300 mL air sample over a 24-hour sampling period. A second set of same-volume SUMMA canisters were equipped with 24 mL min^{-1} flow (approximate) controllers, and were used for collection of the same volume air samples over 3 hours sampling time for the diurnal cycle measurements that were made once a month at each site.

A sodium-thiosulfate-impregnated glass fiber filter was inserted in the flow path upstream of the canisters for removal of ozone. Studies by a number of researchers (Helmig 1997) have shown that it is important to selectively remove ozone in the sampling stream as ozone may react and alter the sample composition during pre-concentration onto adsorbent tubes as well as by post-collection reaction in sample canisters. Many different scrubbing techniques have been investigated (Helmig 1997 and Pollmann et al., 2005). It has also been shown that certain methods, such as scrubbing of ozone with potassium iodide (KI) can cause other, secondary interferences (Helmig and Greenberg, 1995). Sodium-thiosulfate-impregnated glass fiber filters have been used by our group and others over many years and have been shown to effectively remove ozone without changing the sample composition in VOC sampling. Filters were prepared in house. These filters have been shown to quantitatively remove ozone in greater than 1.0m3 of ambient air. These filters were replaced monthly and tested for ozone removal before and after field use. Initially, filters were to be replaced after every sampling period. However, testing the filters after field utilization demonstrated significant ozone removal well after one month of field placement. Filters were tested for their ozone removal efficiency by pulling ozone-laden air with a known ozone concentration through a laboratory-use only ozone monitor.

Once returned to the lab, sample volumes of 500 mL were drawn at 50 mL/min constant flow from each SUMMA canister with a custom-made sample extraction-focusing inlet system. Samples were dried by flowing through a peltier-cooled (-20°C) water trap. VOCs were then concentrated on a Peltier-cooled (-30°C) micro-adsorbent trap. Analytes were then injected onto a DB-1 capillary column for temperature-programmed gas-chromatography separation with dual detection FID and MS analysis. Quantified VOCs are listed in Table 1.0.

2.4.3 Ozone

An ultraviolet (UV) absorption ozone analyzer was utilized at each location to monitor ambient ground-level ozone concentrations. BCPH/CU installed and maintained every ozone analyzer. BCPH and CDPHE maintained and managed the analyzer at the South Boulder site. Ozone data were recorded following 40 CFR 50 Appendix D and EPA-600/4-79 methods.

Prior to field placement, each analyzer was calibrated against a transfer standard using five calibration points between 0 and 400 ppbV and two zero points. If an analyzer did not meet the criteria specified in the 40 CFR 58 Appendix D, it was not used during the study.

For the outdoor ozone inlet, a 40mm diameter, 5um-pore size membrane filter was placed in a filter holder, positioned vertically, and connected to ¼-inch Teflon tubing. Gravimetric analysis was performed on each membrane filter by determining pre and post weight. All filters were ozone-conditioned by pulling a flowrate of 1 L/min of generated ozone at a concentration in air of at least 200 ppbV for 24 hours. Filters were removed and replaced monthly. As indicated above, in a separate smaller study, removed membrane filters were checked for ozone scrubbing capacity using generated ozone at a known concentration. For ozone monitoring in areas near the non-attainment threshold, ozone scrubbing capacity from the inlet could have a significant impact.

The length of the ¼-inch Teflon tubing that was run from the outdoor inlet to the analyzer inlet varied from 15 to 25 ft. All Teflon tubing used for ozone sampling was ozone-conditioned prior to field placement using the same process as the membrane filters.

Analyzer diagnostics were recorded continuously and checked weekly. If diagnostic values did not meet the specified operational criteria, the instrument was immediately serviced. Sampling flowrates varied from site to site and fell between 0.35 to 0.9 L/min.

Following 40 CFR Part 58, zero/precision/spans were performed on each ozone analyzer once every two weeks using a transfer standard ozone photometer to verify that the performance of site analyzers remained within ±2% of the photometer. During the course of the study, all ozone analyzers passed all two-point zero/precision/span checks. It should be noted that zero/precision/spans at the Niwot Ridge site occurred only during the ozone season due to the logistical difficulty of getting the transfer standard photometer to the high alpine site. Zero checks only were performed during this time, all of which passed the criteria. Ken Distler of EPA Region 8 approved this decision.

In addition to bimonthly zero/precision/span checks, each ozone analyzer was checked quarterly against the transfer standard calibration photometer. Using six points (zero and five points between zero and 80% of full scale), a calibration curve equation was constructed by means of a least squares linear regression. Ambient ozone concentrations were evaluated using the linear regression equation. Additional ozone sampling details can be found in the Ozone Sampling and Analysis SOP that INSTAAR generated, which is included in the Boulder QAPP.

2.5 INSTRUMENT CALIBRATION AND FREQUENCY

2.5.1 Instruments Requiring Calibration

Sampling instruments and analyzers requiring calibration were: the active samplers used for carbonyl sampling; the ozone analyzers; and the VOC sampling with subsequent gas chromatography analysis. The CU laboratory was responsible for calibration of all field instrumentation.

Laboratory instruments needing calibration were the HPLC used for the carbonyl analyses; and the automated gas chromatograph–flame ionization/mass spectrometry detection system used for the VOC analyses. The CU laboratory was responsible for calibration of this laboratory instrumentation.

2.5.2 Calibration Methods and Frequency

The active samplers used for the carbonyl sampling were required to have the flow calibrated. Flow calibrations were performed using a BIOS Dry-Cal instrument. The calibration of the BIOS Flow calibrator was checked quarterly against a primary volumetric bubble flow calibrator that has been designated by the CU laboratory as the primary standard for all flow measurements. In addition to continuously logging the mass-flow controlled flow rate, volumetric flow rate checks in the field were performed weekly using the BIOS Dry-Cal.

The passive VOC sampling system did not require calibration. Flow was passively routed into the SUMMA canister, at a slow rate that was set by a mechanical mass-flow controller. As canister contents are analyzed directly in parts per billion of air, it was not necessary to know an accurate total flow rate during the sample period, as long as it was constant over time. The constant sampling rates of the mechanical mass flow controllers were checked quarterly. Mass flow controllers were serviced or replaced if more than a 10% deviation of flow was observed over the target 24-hour sampling period. This test also entailed checking the absolute flow rates to assure that they were low enough that a slight vacuum (five to eight inches of mercury) was present at the end of the 24-hour sample period to ensure that the full period was sampled.

The continuous GC system was calibrated at least once per month using a dynamic dilution system to generate a dynamic range of concentrations of a mixture of VOCs from a primary, high concentration, multi-component VOC standard. Blank and single point calibration samples were run at least once every week. If there was evidence of significant change in the zero and/or span data, the system was scheduled for maintenance and recalibration as soon as possible.

The continuous analyzers for ozone are calibrated on a quarterly basis unless there are changes that suggest maintenance might be required sooner. Every month there were at least two zero/precision/span checks for the ozone analyzers. If the control charts for the zero and span data indicated a potential problem, the analyzer was scheduled for maintenance and calibration as soon as possible.

2.6 CALIBRATION STANDARDS, MATERIALS, AND APPARATUS

The calibration procedures for VOCs, carbonyls, and ozone are described in detail in the Boulder QAPP.

2.7 DATA ASSESSMENT TECHNIQUES

The data assessment techniques used to ensure quality data are included in the SOPs for monitoring of that air pollutant in the Boulder QAPP. In addition, EPA Region 8 conducted a systems audit of the Boulder Study. This review followed a uniform checklist that EPA Headquarters has developed for all air monitoring studies in the United States. Region 8 approved the sampler siting, sampling schedule, the air monitoring plan, and QAPP. The Region 8 Air Toxics Monitoring Coordinator present during the audit was Kenneth Distler.

3 MODELING METHODOLOGY

3.1 OZONE AND SECONDARY CARBONYLS (Contributed by Molly Brodin, University of Colorado at Boulder)

OZIPR is a trajectory-based air quality simulation model developed by the U.S. Environmental Protection Agency (EPA). It is available as a free download from http://www.epa.gov/scram001/dispersion_alt.htm#ozipr, as are the "User's Guide for Executing OZIPR" and "A Simplified Approach for Estimating Secondary Production of Hazardous Air Pollutants (HAPs) Using the OZIPR Model" documents referenced at the end of this section.

OZIPR utilizes a simple one-dimensional box model to simulate complex chemical and physical processes. The physical representation of the model is as a well-mixed column of air reaching from the ground to the top of the mixed-layer. The air column is initialized with background surface concentrations of the species of interest; the additional amount of each of the species emitted from local sources during each hour is added as the modeling run progresses. The model air column expands upward as the inversion boundary of the mixed layer rises throughout the day, incorporating air that was above the column and contains background aloft concentrations of the chemical species of interest. The column cannot expand horizontally. Chemical mechanisms act upon the constituents within the air column, simulating the chemical processes occurring in the environment. With no diffusion from the box, mass can only be removed from the system through deposition (Gery and Crouse, 1990).

The OZIPR model was run to model formation of ozone and other secondary air toxics for the period of May – Aug 2007. There were 19 days modeled during this time period. These days were the designated sampling days according to the EPA 6-day monitoring schedule, and were the days for which VOC and carbonyl data were collected. (The final sampling day of August, the 28th, was not modeled because meteorological data were not available.) The time period modeled was the 12-hour period from 0600 to 1800 MDT for each day; these hours were selected to correspond with the period of greatest photochemistry for each day as well as the 3-hour sampling schedule of the air toxics monitoring. Because OZIPR will not run if the modeled time period begins before sunrise, for the late summer, starting with July 29, the modeled time period was shifted to 0700 to 1900. The modeled region was an area of 1056 km^2, bounded approximately by Boulder County limits to the north, south, and east, and by the edge of the foothills to the west (Figure 3.1). This region encompasses the more "urbanized" portion of Boulder County. Each day was modeled using two different assumptions of Boulder County conditions. The first case, "Boulder," assumes that only those emission sources located within the modeled region are significant. The second case, "Metro," assumes that the air in Boulder County originates in an equivalent sized box surrounding Denver (Figure 3.2), and is carried, undiluted, by prevailing winds to Boulder County.

3.1.1 Chemical Mechanism

The chemical mechanism used in OZIPR for this modeling work was the "cal97.mec" file available with the OZIPR download from the EPA. This mechanism is based on the SAPRC97 mechanism developed by W. P. L. Carter, available online at http://pah.cert.ucr.edu/~carter/saprc97.htm. The SAPRC97 mechanism is slightly modified in cal97.mec to include five additional reactions explicitly describing the formation of acrolein from 1,3-butadiene and the destruction of acrolein. The file was further modified in this study to include acetone (ACET) in the VOC compound listing. The complete mechanism file used in the BCPH model can be found in Appendix C-1.

The associated zenith angle file, "zen.cal" was used from the EPA files as well. This file provides the reaction rate factors by solar zenith angle for photolysis reactions. Latitude (40.0), longitude (105.16), date, time zone (MDT), and model time period (0600 – 1800) are included in the input file. OZIPR uses these parameters to determine the zenith angle and corresponding reaction rate factor for each hour. The zenith angle file can be found in Appendix C-2. This file contains "L1" values, which are absolute reaction rate factors versus 10 zenith angles (0, 10, 20, 30, 40, 50, 60, 70, 78, and 86 degrees), as well as relative reaction rate values (R values) for each photochemical reaction used in the chemical mechanism, which are multiplied by the L1 values. All days were modeled using this unmodified zenith angle file. Seven of the modeled days had significant cloud cover (defined as broken clouds or overcast for more than half the modeled hours of the day). For these days, the reaction rate factors were modified to reflect reduction in solar radiation due to cloud cover; the calculations leading to this reduction was explained below in the discussion of meteorological data.

3.1.2 Meteorological Data

Hourly temperature and dewpoint data were obtained for each modeled day from the National Climactic Data Center (NCDC) online database at http://www.ncdc.noaa.gov/oa/ncdc.html. Jefferson County Airport was selected as the station most representative of Boulder County for which hourly data were available. For those days without adequate data recorded at Jefferson County Airport (defined as missing more than 4 of the modeled hours or having 2 or more hours missing at the beginning or end of the modeled time period), Denver International Airport data was used as the next best substitute. Hourly relative humidity values were calculated from the dewpoint for use in the model based on the Clausius Clapeyron equation.

Table 3.1: Minimum and maximum mixing height depths and maximum temperatures for each modeled day

Date	Min Mixing Depth (m)	Max Mixing Depth (m)	Max Temp (deg C)
5/6	260	1987	55
5/12	250	3255	82
5/18	250	3213	79
5/24	250	2413	63
5/30	308	2079	64
6/5	250	2019	84
6/11	250	3974	91
6/17	250	4695	95
6/23	250	3496	92
6/29	250	2560	86
7/5	250	2867	88
7/11	250	1506	82
7/17	250	3432	97
7/23	250	3079	93
7/29	250	1088	86
8/4	250	2161	88
8/10	250	2695	93
8/16	250	2207	88
8/22	250	1386	82

The daily ambient pressure was defined as the pressure recorded at 6am at the Boulder Fire Station site. Hourly mixing layer depths for each modeled day were obtained using the National Oceanic and Atmospheric Administration (NOAA) HYSPLIT model and archived meteorological data, available online at http://www.arl.noaa.gov/ready/hysplit4.html. The HYSPLIT-WEB internet-based version of the model was used. The input parameters, to match Jefferson County Airport, were latitude = 39.92, longitude = -105.12, starting height = 1724 m above sea level. Maximum and minimum mixing height depths and maximum temperatures for each day are shown in Table 3.1.

The NCDC also provides hourly cloud cover information. There are four classes of cloud cover reported, shown in Table 3.2. The average cloud cover for the reported class was used to calculate the reduction in solar radiation according to the equation developed by Kasten and Czeplak (Kasten and Czeplak, 1980),

$$K = K_0\,(1 + aN^b)$$

Where K_0 is the cloudless solar radiation and K is the radiation modified for cloud cover. The parameters a and b are empirical coefficients which relate to how much the solar radiation is affected by the clouds, and varies by location depending on the type of clouds typically found there. Because Kasten and Czeplak's work was done in Hamburg, Germany, a coastal location, another study by Muneer and Gul (2000) was used to obtain the parameters a and b. Their study looked at five cities in the United Kingdom, from which Finningley was selected as the most interior, providing values of a = -0.71 and b = 3.7. The L1 values in the zenith angle file are reduced according to the Kasten and Czeplak equation for second run for each of the cloudy days. Because L1 values are fixed parameters, not hourly values, it was not possible to adjust for hourly variations in cloud cover. Instead, a daily average was taken for those days with significant cloud cover, and the L1 values in the zenith angle file were adjusted for this average cover prior to the model run.

Table 3.2: NCDC Cloud Cover Classes

Class	Cloud cover range	Average cloud cover
CLR	< 1/8	0
SCT	1/8 – 4/8	5/16
BKN	5/8 – 7/8	6/8
OVC	> 7/8	1

3.1.3 VOC Reactivities

The SAPRC97 mechanism lumps VOC compounds into classes of similar reactivity for use in the chemical reaction calculations; 15 classes were defined in this study (ACET, ALK4, ALK7, ETHE, PRPE, TBUT, TOLU, XYLE, TMBZ, RCHO, BDIE, HCHO, ALD2, ACRO, NRHC). The "reactivity" listing in OZIPR describes the fraction of VOCs attributed to each class; it is used to properly allocate hourly VOC inventories. Fractions are listed for local emissions, transported surface-layer air, and air above the boundary layer that is incorporated during its daily rise.

To estimate local emission reactivities, VOC data were used from sampling conducted by the Colorado Department of Public Health and Environment (CDPHE) in August-September 2003. The data set included average concentrations for morning (6 – 9 am) and afternoon (1 – 4 pm) time periods. The morning time period was assumed to be representative of "pure" emissions before much photoreaction has taken place and was used for determining emission reactivities. Data were available for the CAMP, Welby, NREL, Chatfield Reservoir, and Platteville monitoring sites. Data from the NREL site were assumed to best represent Boulder County, and therefore were used for the

"Boulder" case. CAMP was selected as the best representative of the "Metro" case.

The 78 reported compounds were allocated to their appropriate reactivity classes based upon the class assignments documented by Carter. In cases where it was unclear from Carter's work where a compound fit, the reaction rate constant was used to find the best match (such as in the case of Propyne, assigned to the ALK4 category). The concentrations of each compound were weighted using their OH reaction rate constants, with the equation:

$$C_{k,i}\,(\text{ppmC}) = C_i \times [1 - \exp(-koh_i \times \text{INTOH})] / [1 - \exp(-koh_k \times \text{INTOH})]$$

C_i in this equation is the measured concentration of compound i from the CDPHE VOC data, and $C_{k,i}$ is its concentration weighted for class k. koh_i is the reaction rate constant for the OH reaction of compound i at 298 K, obtained from Carter's documentation for the SAPRC99 mechanism at pah.cert.ucr.edu/ftp/pub/carter/pubs/s99appa.pdf. The class reaction rate constant, koh_k (also at 298 K) was obtained from the SAPRC97 mechanism file. INTOH was set at 50 ppt-min, a value used by Carter in his work. The only reactivity classes that were not summed in this way were the alkenes. They are assumed to react completely, and their unweighted concentrations are summed instead. A few of the compounds for which data were available did not have reactions listed in the s99appa.pdf document. Koh values for m,o,p-ethyltoluene were filled in from Seinfeld and Pandis (2006) and that for 2,5-dimethyl benzaldehyde from Tse et al. (1997). No documented koh could be found for m,p-diethylbenzene, so it was approximated as the same as the ethyltoluenes. 2,2,3-trimethyl pentane was approximated as 2,2,4-trimethyl pentane.

Approximately 30% of the measured VOCs in the CDPHE study were not identified. This total concentration was distributed among the open-ended classes (ALK4, ALK7, NRHC, RCHO, TBUT, TMBZ, TOLU) based on their relative percentages of identified compounds. The final class assignments, reactivity weights, and CAMP and NREL measured concentrations can be found in Appendix C-3.

Transported surface layer and aloft reactivity fractions were assumed to be equal for the air transport patterns of Boulder County. To obtain these background values, the CAMP and NREL weighted concentrations for each class were scaled according to the relative percentage of each class of VOC measured at Niwot Ridge in the BCPH study versus the lower elevation sites in Boulder County (South Boulder, Boulder, Longmont, and Lyons). To avoid skewing the results due to concentrations below the detection limit at Niwot Ridge, only those compounds for which there were measureable concentrations were used to represent each class. The 6-9 am samples were averaged for May – August 2007 for Niwot Ridge and for the other 4 sites together. A scaling factor was then calculated for each class, which was multiplied by each class concentration for CAMP and NREL. An example calculation is:

$$[(\text{n-butane} + \text{n-pentane})_{\text{Niwot Ridge Average}} / (\text{n-butane} + \text{n-pentane})_{\text{Lower Elevation Average}}] \times \text{NREL ALK4} = \text{Aloft ALK4}$$

The new scaled concentrations were then summed to get total emissions, and the fractions present of each class calculated again for aloft and transported air. BDIE, ETHE, and PRPE classes had no measured (or detected) concentrations in the BCPH study. Their scaling factors were assumed to be the same as TBUT. TMBZ also had no concentrations to use and was set to be the same as TOLU. The NRHC class was assumed to be merely diluted between Boulder and Niwot Ridge, so its scaling factor was the same as the dilution ratio of CO at Niwot Ridge versus the CAMP or Longmont monitors (this is the only class which had a different scaling factor for the two modeling cases).

3.1.4 NO_2 Fractions

The initial NO_2 fraction was set to the default value of 0.25. The model is not sensitive to this value, and this fraction is not expected to vary significantly with location, so this is a reasonable simplification. The emission fraction was obtained from NO_2 and NO emission inventory data provided by Greg Brinkman (these emission data was further discussed in the "emissions" section of this report). The average fraction throughout the 12-hour modeled period was taken for each of the two cases.

3.1.5 Transported Surface and Aloft Concentrations

The aloft NO_x concentration was obtained from data measured by NOAA at the Erie tower (40.050 N, 105.010 W) in the summer of 2007 (Provided by Steve Brown). The NO and NO_2 concentrations measured were summed to get NO_x, and then averaged over the 6 am hour for May – August of 2007. The NO_x average concentration at 250 m and higher was used for the aloft concentration. The transported surface layer concentration was set to zero because we are not separating out controllable and transported emissions in this model run. Consequently, the measured initial surface layer NOx concentration used for the initial concentration input includes transported and controllable emissions.

The aloft CO concentration was set to the average summertime value at Niwot Ridge. Information provided by Paul Novelli of NOAA stated that summertime CO concentrations are in the range of 80 – 100 ppb; the midpoint, 90 ppb, was used in the model. As described for NO_x, the CO transported surface layer concentration was set to 0.

The aloft VOC concentration was obtained through the VOC scaling process described in the “reactivity” section. The scaled VOC concentrations for each category were summed, and this value was used as the aloft concentration. Once again, the transported surface layer concentration was set to 0.

The transported surface and aloft concentrations of O_3 were assumed to be equal to those at Niwot Ridge C-1. The 6 am hourly average concentration measured at the site was averaged for May – August to obtain the background concentration. The transported surface and aloft concentrations are summarized in Table 3.3.

Table 3.3: Transported surface and aloft concentrations used in OZIPR modeling

	NREL	**CAMP**
O_3 Surface	0.043	0.043
O_3 Aloft	0.043	0.043
VOC Surface	0	0
VOC Aloft	0.028	0.073
NO_x Surface	0	0
NOx Aloft	0.002	0.002
CO Surface	0	0
CO Aloft	0.090	0.090

3.1.6 Deposition Rates

Deposition rates were set to typically accepted values for topography similar to that of Boulder County, provided by Dr. Laurens Ganzeveld of the Department of Environmental Sciences at Wageningen University and Research Centre, Wageningen, Netherlands. These values are shown in Table 3.4. Because OZIPR is not highly sensitive to deposition rates, it was not expected that these values would have a significant effect on the outcome of the model. However, sensitivity tests were run for two days (a relatively high ozone day and a moderate ozone day) to quantify the sensitivity. For each of the two days, each of the 6 compounds whose deposition rates were included in the model was varied individually to 1/2 and 2 times its expected value.

Table 3.4: Deposition velocities used in OZIPR modeling

Compound	Rate (cm/s)
NO_2	0.5
O_3	1
HNO_3	2
H_2O_2	2
PAN	0.5
HCHO	1

3.1.7 Emissions

CO, NO_x, and VOC emissions data were provided by Greg Brinkman. Emissions were processed using SMOKE v2.3 to speciate and allocate the emissions inventories spatially and temporally. The area and point source inventories are from the Western Regional Air Partnership (WRAP) inventories. For mobile sources, the Vehicle Miles Traveled (VMT)-based inventory is from the VISTAS Phase II Emissions and Modeling – 2002 Base F VMT Input; VMT was converted to emissions using emissions factors from EPA's MOBILE6 model. Biogenic emissions were processed using the BEIS3 model in SMOKE. Ultimately, hourly emissions values were obtained for each of the modeled areas, as an average over the period of June 15 to July 31, 2006. These hourly values were in moles, and were converted to units of ppmC by the ideal gas law, using the modeled area (1056 km^2) an initial boundary layer height of 250 m, an average pressure of 0.83 atm, and temperature of 298 K. The SMOKE model splits VOCs into classes according to the CB4 system. Consequently, the mole values had to be multipled by the number of carbons for each CB4 class to get ppmC. The ppmC concentrations for each hour were divided by the initial concentrations for CO, NO_x, and VOC to be input into the model as emission ratios.

3.1.8 Initial Concentrations

The initial VOC concentration (in ppbC) was taken from the CDPHE sampling data. The total concentration, including unidentified compounds, measured in the study for NREL and CAMP were used for the Boulder and Metro cases, respectively.

The initial NO_x concentration for the Boulder case was obtained from data measured by NOAA at the Erie tower in the summer of 2007, processed as described above. The NO_x average concentration at 20 m and lower was used for the initial surface layer concentration. The initial NO_x concentration for the Metro case was obtained by summing NO and NO_2 measurements and averaging the 6 am hourly values for May through August 2007 for the CDPHE CAMP monitor.

Initial CO concentrations were obtained from CDPHE monitor data for Longmont and CAMP monitors, for Boulder and Metro cases, respectively. The 6 am hourly values for June and July of 2007 were averaged for each location.

3.1.9 Final Input

A sample input file for a single day using each of the air-mass source cases is included in Appendix C-4. These files show all of the values generated by the methods described above. Only the meteorology was varied from day to day (with the exception of the deposition sensitivity and cloud cover test cases).

A summary of all model runs performed is provided in Table 3.5.

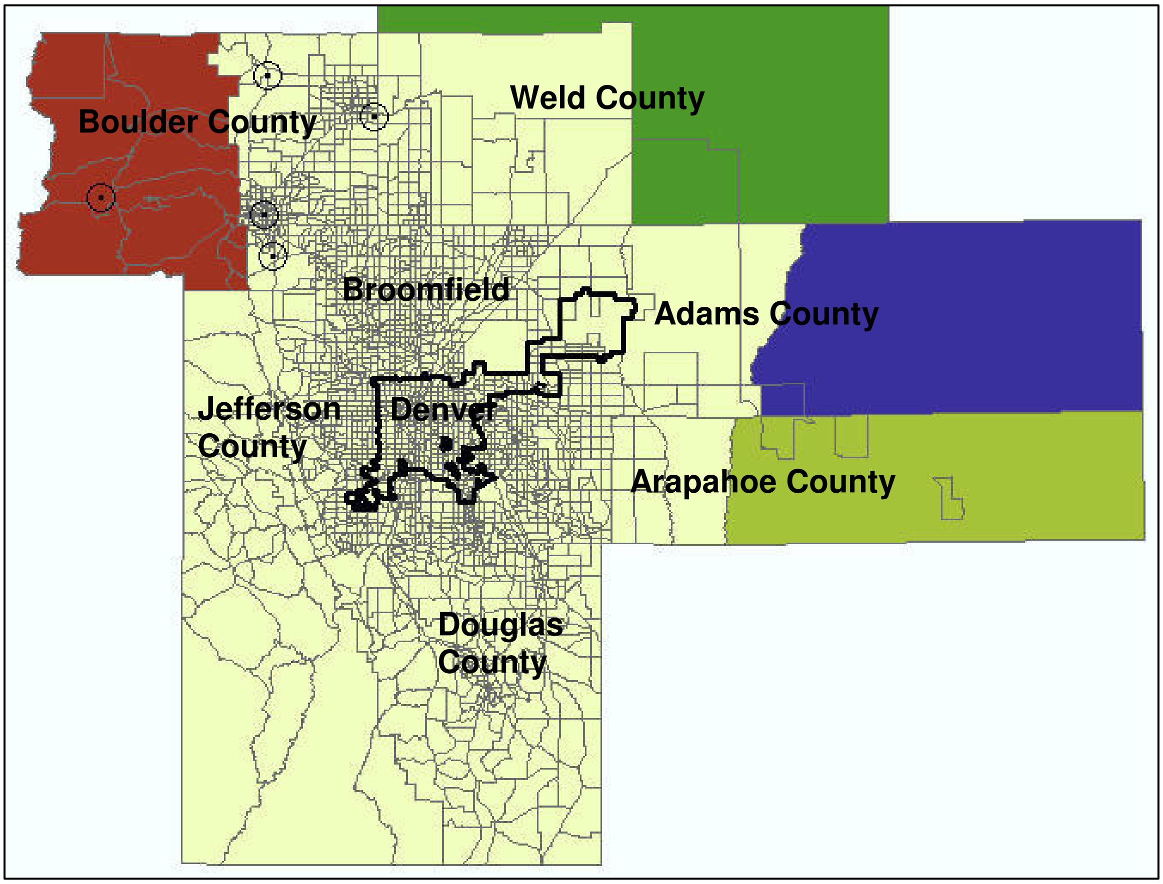
Table 3.5: Ozone modeling runs performed for this study ("Dep Sens" stands for deposition sensitivity, as explained above)

Date	Boulder	Boulder Cloud Adjust	Metro	Metro Cloud	NO2 Dep Sens	O3 Dep Sens	HNO3 Dep Sens	H2O2 Dep Sens	PAN Dep Sens	HCHO Dep Sens
5/6	1	1	1	1						
5/12	1		1							
5/18	1		1							
5/24	1	1	1	1	2	2	2	2	2	2
5/30	1	1	1	1						
6/5	1	1	1	1						
6/11	1		1							
6/17	1		1							
6/23	1		1							
6/29	1		1							
7/5	1		1		2	2	2	2	2	2
7/11	1		1							
7/17	1		1							
7/23	1		1							
7/29	1	1	1	1						
8/4	1	1	1	1						
8/10	1		1							
8/16	1		1							
8/22	1	1	1	1						
Total	19	7	19	7	4	4	4	4	4	4

3.2 *DISPERSION MODELING (Contributed by Gregg Thomas and Sabrina Williams, Denver Department of Environmental Health)*

As part of this study, Denver Environmental Health (DEH) agreed to update their air toxics modeling assessment for the entire Denver metropolitan area, including most of Boulder County. Specifically, the model domain included all but the Niwot Ridge monitoring location. Figure 3.1 shows the greater Denver-Boulder region. The yellow shaded portion is the model domain used in this study. The model domain comprises the historic non-attainment boundary.

Figure 3.1: The Denver Metropolitan region, the AERMOD model domain (yellow shaded area), and the Boulder air toxics monitoring locations (circles). Sub-county scale polygons delineate traffic analysis zone (TAZ) boundaries



The DDEH modeling assessment was conducted using the AERMOD dispersion model. The detailed methodology and results from the previous Denver air toxics assessments are documented elsewhere (Thomas, 2004; Thomas et al., 2007). A brief summary of the major elements of the updated assessment conducted as part of this study are contained in this report.

Denver has not previously validated their air toxics modeling assessment with data from counties other than Denver and Adams counties, since these were the only locations where air toxics data had historically been collected. In addition to evaluating area and mobile source inventories common to the rest of the metropolitan area, the Boulder dataset also provides an opportunity to explore air toxics emissions associated with oil and gas exploration, which is of high significance in the region.

There were four main components of the air toxics modeling assessment:

1) developing and/or compiling emissions inventories;
2) developing spatial and temporal surrogates to apportion county-level data to traffic analysis zone (TAZ) polygons;
3) setting up and running the AERMOD air dispersion model, and
4) processing the predicted concentrations in a Geographic Information System (GIS).

3.2.1 Emissions Inventories and Background Concentrations

Background concentrations used in the air toxics modeling assessment were as follows:

- Benzene background = 0.35 µg/m^3 or 0.11 ppbv
- Formaldehyde background = 0.25 µg/m^3 or 0.2 ppbv

In addition, secondary contributions of 0.14 ppbv for acetaldehyde and 0.39 ppbv for formaldehyde were added to the modeled primary contributions for these pollutants. Background concentrations for all other pollutants were set to zero, so modeled concentrations of these other pollutants reflect local emissions only.

The emissions inventory for this assessment was generated from several different sources:

- The USEPA National Emissions Inventory (NEI) for 2002 was used to generate area source and nonroad mobile source emissions (except diesel particulate matter) at the county level. The 2002 NEI was unadjusted for 2005, but it is assumed that emissions from those categories were similar to 2005.
- MOBILE6.2 was run by DDEH using local parameters for fleet registration, VMT, fuels, and inspection and maintenance (I/M 240) data. Instead of using the fleet average emission factor from MOBILE6.2, DDEH also applied additional criteria to differentiate between hot running and cold-start emissions, as well as average speeds on different road types. The result is that an emission factor for each road type was applied to cumulative VMT by road type in each county. This methodology is explained in Thomas et al., 2007.
- The Western Regional Air Partnership (WRAP) also developed county level criteria pollutant inventories for Colorado and other states for 2002 to support Regional Haze modeling across the western U.S. State-wide projected

inventories for 2008 were utilized to estimate 2005 emissions were estimated by interpolating between years. Only elemental carbon (EC) as PM_{10} from heavy duty onroad and nonroad diesel vehicles was used from the WRAP inventory. The EC data were not a focus of the Boulder air toxics study. WRAP mobile source emissions inventory data are available at http://www.wrapair.org/forums/ef/UMSI/index.html.

- Oil and gas exploration VOC emissions were obtained from Environ (2008) based on work to support 2006 CAMx ozone modeling for inclusion in Colorado's State Implementation Plan (SIP) revision. VOC data were speciated using mass speciation profiles developed in 2002 for the Denver-Julesburg basin (CDPHE, 2003).

Emissions inventories were developed for benzene, toluene, ethylbenzene, total xylenes, diesel PM_{10} as elemental carbon (EC), n-hexane, n-butane, n-pentane, formaldehyde and acetaldehyde. These pollutants have been identified in historic monitoring campaigns in Colorado as compounds that are almost always detected. Butane and pentane in this inventory come strictly from oil and gas exploration. In reality, motor vehicle fuels contain the same compounds, but are not estimated in mobile source inventories due primarily to their low toxicity. They are of interest in this research because they are good oil and gas emission indicators.

The emissions inventories in this study are primarily for 2005. It is common practice for published emission inventories to lag by several years. Since we are using 2007-08 monitoring data to compare with predicted concentrations using 2005 emissions, caveats are necessary when attempting absolute comparisons of predicted-to-observed concentrations. Nevertheless, inventories between 2005 and 2007 are not expected to be different by more than ± 10 percent.

Note that Adams, Arapahoe, Boulder, and Weld counties are only partially within the modeling domain (see Figure 3.1). Onroad mobile source emissions were created using VMT data from the Denver Regional Council of Governments (DRCOG) travel demand model (TDM). The model domain essentially encompasses the area covered by the TDM network. For nonroad, area, and oil and gas VOC emissions, surrogate data was applied to apportion the county-wide emissions to the portion of the county within the modeling domain.

Table 3.6 lists the MOBILE6.2 derived onroad air toxics emissions by county within the modeling domain. Table 3.7 lists the vehicle miles traveled (VMT) for each county (or portion thereof) within the modeling domain in. Table 3.7 also lists fraction of total VMT within each county that is attributed to each road type. There is significant variation across counties in the type of VMT. Therefore, the approach to develop road type specific emission factors takes on added significance.

Table 3.8 lists the nonroad emissions for each county (or portion thereof) within the model domain. The 2002 NEI and the 2002 WRAP diesel PM_{10} are both included, however only the WRAP data was utilized in this assessment. The datasets compare relatively well, but with appreciably higher WRAP diesel PM_{10} emissions in Weld County. The difference may be due to greater diesel engine in use in the oil and gas exploration sector per the WRAP (i.e. drill rigs).

Table 3.6: 2005 MOBILE6.2 onroad mobile source emission inventory by county (tons per year)

Pollutant	Adams	Arapahoe	Boulder	Broomfield	Denver	Douglas	Jefferson	Weld	Total Emissions
Formaldehyde	65.9	69.0	37.7	10.0	88.3	47.9	83.2	16.9	**419**
Acetaldehyde	34.2	36.0	19.8	5.2	45.9	24.9	43.3	8.8	**218**
Benzene	169.0	180.0	99.0	25.6	227.5	122.9	215.1	43.5	**1083**
Toluene	413.5	442.6	243.7	62.5	557.4	300.6	527.3	106.5	**2654**
Ethylbenzene	63.9	68.5	37.7	9.7	86.2	46.4	81.5	16.4	**410**
Xylenes	232.8	249.1	137.2	35.2	313.8	169.2	296.8	60.0	**1494**
n-Hexane	67.6	73.7	40.4	10.2	91.6	48.9	86.6	17.3	**436**
Diesel PM10 EC[1]	68.1	77.1	49.0	11.0	100.2	50.6	100.2	16.9	**473**

[1] 2002 WRAP Heavy Duty Diesel PM10 Elemental Carbon, adjusted downward 10% taking into account fleet turnover since 2002. Per WRAP, 72% of onroad PM10 EC is from Heavy Duty diesels.

Table 3.7. 2005 DRCOG VMT by county within the modeling domain and fraction of total VMT in each county by road type

	Description	Adams[1]	Arapahoe[1]	Boulder[1]	Broomfield	Denver	Douglas	Jefferson	Weld[1]
--	Annual VMT	3.99E+09	3.96E+09	2.10E+09	6.02E+08	5.25E+09	2.89E+09	4.90E+09	1.00E+09
Road Type	**Values below are VMT fractions by road type in each county**								
1	Freeway	0.497	0.221	0.127	0.518	0.416	0.503	0.381	0.462
2,3	Arterials	0.274	0.549	0.511	0.230	0.339	0.271	0.369	0.259
4,5	Minor Art/Collector	0.161	0.134	0.257	0.167	0.174	0.131	0.154	0.171
6,8	Local/ramp	0.068	0.095	0.105	0.086	0.071	0.095	0.096	0.108

[1] Travel Demand Model derived VMT only covers a portion of the county (limited to the historic non-attainment area boundary)

Table 3.8. 2002 nonroad mobile source emission inventories by county (tons per year). For Diesel PM_{10}, the WRAP data was used in this assessment

	Adams	Arapahoe	Boulder	Broomfield	Denver	Douglas	Jefferson	Weld	Total Nonroad
Formaldehyde	39.0	58.9	31.3	4.3	81.1	31.6	42.1	30.9	**319**
Acetaldehyde	17.2	25.1	13.6	1.9	27.9	13.7	18.0	13.5	**131**
Benzene	42.2	98.7	49.7	6.0	91.6	47.7	81.2	32.7	**450**
Toluene	95.4	238.0	126.2	14.8	195.6	121.3	203.3	78.2	**1073**
Ethylbenzene	24.7	63.2	32.9	3.9	51.5	32.4	53.9	19.7	**282**
Xylenes	98.1	249.8	132.6	15.5	200.9	129.6	215.2	79.6	**1121**
Hexane	16.6	41.5	21.7	2.6	33.9	21.3	35.6	13.4	**187**
2002 NEI Diesel PM10	170.7	207.9	119.8	17.3	248.7	118.1	136.4	139.9	**1159**
2002 WRAP Diesel PM10 EC[1]	196.4	176.7	113.2	16.4	259.9	118.3	112.8	222.7	**1216**

[1] 2002 WRAP Nonroad Diesel PM10 Elemental Carbon. For nonroad inventory, WRAP estimates 95% of PM10 EC is from diesel vehicles.

Table 3.9 lists the area source emissions for each county (or portion thereof) within the model domain. This inventory is solely obtained from the 2002 NEI. Diesel PM_{10} emissions are not reported in the area source NEI. Table 3.10 lists 2006 emissions from oil and gas exploration as documented by Morris et al. (2008) to support photochemical ozone modeling for inclusion in the recent ozone SIP. Oil and gas emissions were removed from the area source inventory in Table 3.9 so as not to double count emissions included in Table 3.10.

Butane and pentane were included to represent emissions related to oil and gas exploration. While not classified as air toxics, these pollutants are ozone precursors and are of significant interest in the region because of the recent designation of ozone non-attainment for the 1997 8-hour ozone national ambient air quality standard (NAAQS). In this inventory, oil and gas exploration is the only source of these pollutants. In reality, these compounds are emitted ubiquitously throughout the area as they are also prevalent in gasoline. Even so, at some locations the contribution of emissions from oil and gas exploration is expected to outweigh that from the other sectors, as evidenced by short-term speciated non-methane organic carbon (SNMOC) observations conducted by the Colorado Department of Public Health and Environment (CDPHE) in 2003 and 2006.

Railroad emissions of diesel PM_{10} were treated separately from the 2002 NEI for nonroad sources and are listed in Table 3.11. Railroad emissions were spatially allocated using miles of track length as determined from GIS. Other nonroad emissions, which are more ubiquitous, were allocated widely across each county using a combination of VMT and population surrogates.

Table 3.9. 2002 area source emissions inventory by county (tons per year)

	Adams	Arapahoe	Boulder	Broomfield	Denver	Douglas	Jefferson	Weld	Total Area
Formaldehyde	0.8	1.1	0.6	0.0	1.3	0.4	1.2	0.4	**6**
Acetaldehyde	0.0	0.1	0.1	0.0	0.1	0.0	0.1	0.0	**0**
Benzene	17.5	21.1	17.3	0.6	27.5	10.5	29.6	17.8	**142**
Toluene	36.5	45.9	28.9	2.8	44.6	22.3	48.3	26.9	**256**
Ethylbenzene	7.1	6.0	3.4	1.5	5.2	2.9	5.8	3.0	**35**
Xylenes	40.4	37.3	20.7	1.4	38.5	18.4	41.9	16.0	**215**
Hexane	5.9	10.4	7.0	7.0	7.4	5.0	9.0	13.6	**65**
2002 NEI Diesel PM	--	--	--	--	--	--	--	--	**--**

Table 3.10. 2006 oil and gas exploration emissions inventory by county (tons per year)

	Adams	Arapahoe	Boulder	Broomfield	Denver	Douglas	Jefferson	Weld	Total Oil and Gas
Formaldehyde				Not able to estimate					--
Acetaldehyde				Not able to estimate					--
Benzene	2.4	0.1	0.9	0.2	0.2	0.0	0.0	103.0	**107**
Toluene	2.7	0.1	1.0	0.3	0.2	0.0	0.0	115.9	**120**
Ethylbenzene	0.1	0.0	0.0	0.0	0.0	0.0	0.0	5.2	**5**
Xylenes	0.6	0.0	0.2	0.1	0.0	0.0	0.0	27.0	**28**
Hexane	12.6	0.6	4.8	1.3	0.8	0.0	0.0	535.8	**556**
Diesel PM				Not able to estimate					--
n-Butane[1]	134.5	6.5	51.6	13.5	8.8	0.0	0.0	5733.1	**5948**
Pentane[1]	47.3	2.3	18.1	4.7	3.1	0.0	0.0	2014.6	**2090**

[1] n-Butane and pentane are exclusive to the oil and gas inventory. The NEI and MOBILE6.2 do not estimate such emissions.

Table 3.11. 2002 railroad diesel PM_{10} emissions inventory by county (tons per year)

	Adams	Arapahoe	Boulder	Broomfield	Denver	Douglas	Jefferson	Weld	Total Railroad
Formaldehyde	Included in Nonroad Inventory								--
Acetaldehyde	Included in Nonroad Inventory								--
Benzene	Included in Nonroad Inventory								--
Toluene	Included in Nonroad Inventory								--
Ethylbenzene	Included in Nonroad Inventory								--
Xylenes	Included in Nonroad Inventory								--
Hexane	Included in Nonroad Inventory								**0**
Diesel PM	22.9	10.0	8.1	1.8	6.3	11.4	7.8	31.0	**99**
n-Butane	Not able to estimate								**0**
Pentane	Not able to estimate								**0**

3.2.2 Spatial and Temporal Allocation of County Level Emissions

Onroad mobile source emissions developed using the MOBILE6.2 emissions model were spatially allocated using the DRCOG TDM data. Traffic analysis zone (TAZ) polygons were used to describe the sub-county distribution of emissions (see Figure 3.1). There are 2660 TAZs in the DRCOG domain, but only 2629 TAZs are covered by the TDM. TAZ boundaries are fully contained within each county (i.e. there is no overlap across counties).

Spatial surrogates for onroad mobile sources were calculated as follows:

1. Using GIS, the TAZ network was clipped using polygon boundaries;
2. VMT were then assigned to each TAZ and summed by road type;
3. Total VMT by road type within each county (or portion thereof) was calculated, and
4. Each TAZ was then assigned a fraction of county level VMT by road type.

Table 3.7 lists the total VMT for each county and the fraction of VMT for each road type within the county (steps 1-3 above). Heavy duty vehicle VMT (or commercial VMT in the TDM data) within each TAZ was tracked separately from light duty VMT. This surrogate was only used to allocate diesel PM_{10} emissions. HD VMT generally ranges from 3-5 percent of the total VMT, but on certain road links can exceed 10 percent.

Temporal emissions profiles for onroad mobile sources were generated using a 1999 analysis of hourly traffic counts at nine sites across Metropolitan Denver (see Figure 3.2). This diurnal profile looks similar to that seen in other cities. Updates for later years were not performed, but it is assumed the diurnal distribution has not changed appreciably. Temporal profiles by season, day of week, and hour were developed.

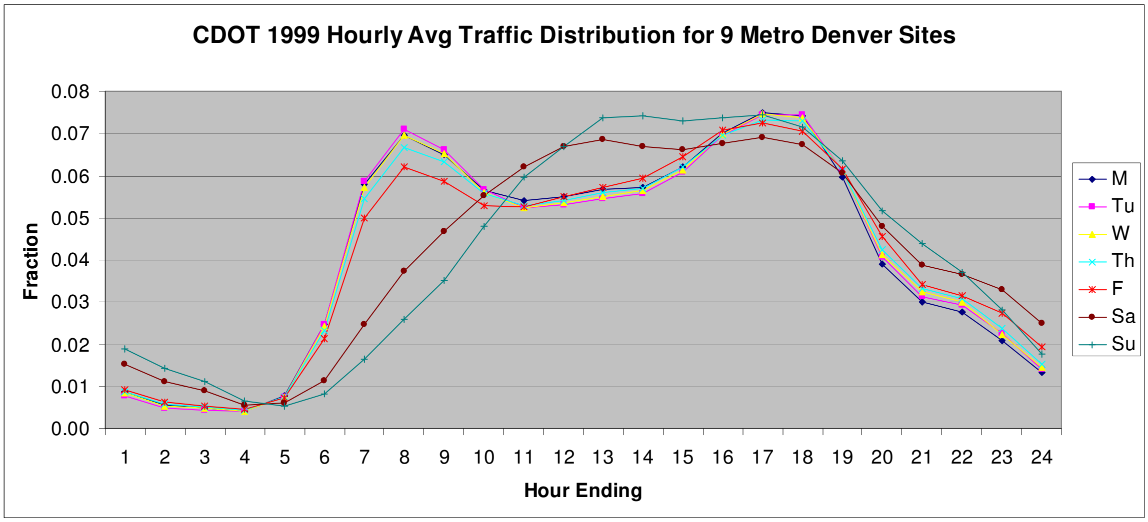


Figure 3.2: 1999 average hourly traffic fractions by day of week at nine Metro Denver sites

Nonroad mobile source emissions were spatially allocated using a combination of population, VMT, and inverse population surrogates. For emissions sources such as landscape equipment emissions, population was determined to be the most useful surrogate. For agricultural emissions, an inverse population density surrogate was considered best. For construction related emissions, a combination surrogate was used to differentiate between highway related construction (related more to VMT) and agricultural or new residential construction (inverse population density). More detail regarding this methodology can be found in Thomas (2004).

Nonroad emissions (from the 2002 NEI) were provided at the county level. However, only portions of four counties were captured in the model domain (based on the DRCOG TDM coverage). Therefore, adjustments had to be made to capture the approximate emissions in the model domain. For Adams, Arapahoe, and Boulder counties, 85-90 percent of the 2002 NEI county emissions were retained for this assessment. However, Weld County had only 40 percent of the nonroad mobile emissions retained, due to a much smaller fraction of the county being located within the model domain.

2002 NEI nonroad emissions were not adjusted for 2005 based mainly on a lack of county level data to support such a change. The Western Regional Air Partnership (WRAP) coordinates regional haze modeling for states in the western U.S. WRAP developed county-level emissions inventories for 2002, with state-wide projections to 2008, 2013 and 2018. Interpolating between 2002 and 2008 state-wide data, 2005 nonroad VOC emissions were forecast to decrease by six percent from 2002 and PM_{10} emissions by four percent. Nonroad mobile source temporal profiles are documented in Thomas (2004).

Area source emissions (from the 2002 NEI) were spatially allocated using population or inverse population density surrogates. To determine how to weight each surrogate, emission categories were tracked separately and summed to provide county level emission rates and the appropriate surrogate was then applied. Certain categories such as wood burning, architectural surface coatings, and household products were allocated using the population surrogate. Others like commercial/institutional/industrial heating and agricultural pesticide application were allocated using inverse population density. Temporal emissions profiles for area sources are described in Thomas (2004).

Oil and gas emissions were spatially allocated to each TAZ using the number of active wells divided by the total number of wells in each county. 2006 GIS data from the Colorado Oil and Gas Conservation Commission web site were used to calculate this surrogate. There was not sufficient data to determine temporal emissions profiles for oil and gas sources. Therefore, diurnal emissions were assumed to be constant.

Railroad diesel PM_{10} emissions were spatially allocated by calculating the miles of track length in each TAZ and dividing that by the county total. In this manner, TAZs with no rail length received zero railroad emissions. There was not sufficient data to determine temporal emissions profiles for railroad sources. Therefore, diurnal emissions were assumed to be constant.

Finally, emissions from all source categories were summed. Since TAZs were defined in AERMOD as polygon area sources, emission rates were divided by the area of each TAZ to express the emissions in terms of flux (grams per second per square meter). Weights from each emissions category were then used to weight temporal emissions profiles accordingly.

3.2.3 The AERMOD Dispersion Model

Previous air toxics modeling assessments conducted by Denver used the Industrial Source Complex Short Term model (ISCST3). Since December 2006, AERMOD is the EPA preferred model. AERMOD version 070206 was used for this assessment, and incorporates the additional functions for urban air toxics that were previously only available in the ISC model. A full list of EPA preferred and recommended air dispersion models can be found on the EPA web site at http://www.epa.gov/scram001/dispersion_prefrec.htm).

The main inputs to the AERMOD model include emissions, meteorology, receptor, and terrain data. More detailed data such as temporal emissions profiles and physicochemical properties of individual air toxics were also included.

Emissions sources (i.e. TAZs) were defined as polygon area sources. There are 2629 TAZs in the entire model domain. To keep model run times feasible, model runs were set up for each county. The emissions source term was described as a flux (grams per second per square meter). Weighted temporal emissions profiles were developed for each pollutant as described in Thomas (2004). Temporal profiles used in AERMOD were by season, day of week (M-F, Sat, Sun), and hour of day.

The TAZ centroids were used as receptors in AERMOD. When modeling pollutants at the county level, receptors from neighboring counties in the vicinity of the county boundary were included. Past experience with ISC3 and AERMOD indicate that the predicted impact from area sources beyond a mile away is negligible.

A 5-year meteorological dataset was used for this assessment. 2002-2006 surface meteorological data from Denver International Airport and upper air data from the nearby site of the former Stapleton Airport were used. Although there are slight diurnal differences in meteorological conditions between Denver and Boulder, annual average concentrations based on meteorology alone are not expected to differ significantly. The dataset was processed in AERMET by a professional vendor using DEH specific inputs.

Terrain data was processed in the AERMAP calculated from 1:24,000 (7.5 min) Digital Elevation Models (DEMs).

Within AERMOD, the TOXICS option was utilized to employ the Sampled Chronological Input Model (SCIM) option. This option samples meteorological data every 25 hours. Without the SCIM option, urban air toxics applications with thousands of sources and receptors would take weeks or months to run. For example, using the SCIM option for Denver County (with 500 area sources and 600 receptors) AERMOD runs for gaseous pollutants take approximately 24 hours. Without the SCIM option, it would take 3 weeks to run an individual pollutant for Denver County alone. Boulder County runs would take 1 week per pollutant. The SCIM option is only recommended for five year meteorological datasets. In this way, each hour of the day is sampled 1750 times in AERMOD, which should capture most of the variation in meteorology across seasons and years.

An example AERMOD input file is available upon request from DDEH.

4 DATA QUALITY ASSURANCE/QUALITY CONTROL

4.1 MEASUREMENT QUALITY OBJECTIVES

EPA Compendium Methods TO-15 and TO-11A were selected as the primary methods for analyzing VOC and carbonyl samples in this study. 40 CFR Part 51 was the primary method for analyzing ozone. The QAPP outlined several data assessment techniques that were utilized to evaluate the effectiveness and reliability of these methods for this study.

4.1.1 Completeness

Completeness is the percentage of valid data reported compared to the total number of samples that are scheduled to be collected during the sampling period (in this case one year). For this project, different completeness targets were developed for different methods and for different times. Completeness is determined using the following equation:

$$Completeness = \left[\frac{D_x - D_c}{D_c} \right] \times 100$$

With regard to discrete measurements, D_x is the number of samples for each species that valid results are obtained and D_c is the number of samples that were scheduled to be collected and analyzed during the year. Completeness for continuous methods is the percentage of valid hours of data obtained from the total hours of scheduled sampling, over a given time period. Minimum sample completeness for all TO-11A, and TO-15 samples must be ≥85%. Minimum sample completeness for ozone must be ≥ 90%.

To gain a better understanding for the reasons samples were lost, additional completeness definitions were used and are as follows:

- *Analytical Completeness*
  Analytical completeness, as defined in this project, was determined by dividing the number of valid samples by the number of attempted samples. Reasons for sample loss include: power outages, analytical instrumentation failure, and sampling instrumentation failure.

- *Sampling Completeness*
  Sampling completeness, as defined in this project, was determined by dividing the number of sample attempts by the number of sampling periods. The reason for sample loss was due to an insufficient amount of automated carbonyl samplers. This issue was corrected by May 2, 2007.

- *Total Completeness*
  Total completeness, as defined in this project, was determined by dividing the number of valid samples by the number of sampling periods. This value includes both analytical and sampling completeness percentages.

Table 4.1 displays the completeness percentages for benzene, which had the **lowest** completeness percentage of all VOCs. The 80% completeness did not meet the ≥ 85% completeness set forth in the QAPP. As described earlier, benzene contamination in borrowed SUMMA canisters reduced overall completeness for that compound. All other VOC compounds had overall completeness values greater than 85%, which satisfy the requirements of ≥ 85% completeness in the QAPP.

Table 4.1: Benzene completeness percentages across all sites for 3-hour and 24-hour samples

Benzene Completeness for 3-hr and 24-hr Samples										
	Boulder		**Longmont**		**Lyons**		**Niwot Ridge**		**South Boulder**	
	3 hr	**24 hr**	**3 hr**	**24 hr**	**3 hr**	**24 hr**	**3 hr**	**24 hr**	**3 hr**	**24 hr**
Analytical	82	84	80	84	85	82	69	80	74	80
Sampling	100	100	100	100	100	100	100	100	100	100
Total	82	84	80	84	85	82	69	80	74	80
*Overall Analytical Completeness: **80%***										
*Overall Sampling Completeness: **100%***										
*Total Completeness: **80%***										

Table 4.2 displays the completeness percentages for formaldehyde. All other carbonyls shared the **same** completeness percentages as formaldehyde. A shortage of carbonyl autosamplers from March 1, 2007 until May 6, 2007 reduced overall completeness. All eight quantified carbonyls exceeded the ≥ 85% goal of completeness specified in the QAPP.

Table 4.2: Formaldehyde completeness percentages across all sites for 3-hour and 24-hour samples

Formaldehyde Completeness for 3-hr and 24-hr Samples										
	Boulder		**Longmont**		**Lyons**		**Niwot Ridge**		**South Boulder**	
	3 hr	**24 hr**	**3 hr**	**24 hr**	**3 hr**	**24 hr**	**3 hr**	**24 hr**	**3 hr**	**24 hr**
Analytical	88	95	100	95	100	97	100	91	100	97
Sampling	100	93	100	97	100	95	100	93	100	93
Total	88	89	100	92	100	92	100	85	100	90
*Overall Analytical Completeness: **96%***										
*Overall Sampling Completeness: **97%***										
*Total Completeness: **94%***										

Table 4.3 displays the ozone coverage statistics for each site. Reasons for ozone data loss include power losses, zero/precision/span activities, and calibration activities. It should be noted that the CDPHE operated the South Boulder site and validated the ozone data collected at the site.

Table 4.3: Monthly data coverage for 1-hour ozone averages

	Boulder											
Month	**Mar 07**	**Apr 07**	**May 07**	**Jun 07**	**Jul 07**	**Aug 07**	**Sep 07**	**Oct 07**	**Nov 07**	**Dec 07**	**Jan 08**	**Feb 08**
% Coverage	87	100	95	98	97	99	99	81	100	85	100	99
	Longmont											
Month	**Mar 07**	**Apr 07**	**May 07**	**Jun 07**	**Jul 07**	**Aug 07**	**Sep 07**	**Oct 07**	**Nov 07**	**Dec 07**	**Jan 08**	**Feb 08**
% Coverage	87	99	81	88	100	99	85	100	100	100	100	99
	Lyons											
Month	**Mar 07**	**Apr 07**	**May 07**	**Jun 07**	**Jul 07**	**Aug 07**	**Sep 07**	**Oct 07**	**Nov 07**	**Dec 07**	**Jan 08**	**Feb 08**
% Coverage	99	99	100	99	99	100	99	100	100	100	100	99
	Niwot Ridge											
Month	**Mar 07**	**Apr 07**	**May 07**	**Jun 07**	**Jul 07**	**Aug 07**	**Sep 07**	**Oct 07**	**Nov 07**	**Dec 07**	**Jan 08**	**Feb 08**
% Coverage	100	90	78	53	99	99	99	99	99	100	99	100
	South Boulder*											
Month	**Mar 07**	**Apr 07**	**May 07**	**Jun 07**	**Jul 07**	**Aug 07**	**Sep 07**	**Oct 07**	**Nov 07**	**Dec 07**	**Jan 08**	**Feb 08**
% Coverage	99	98	97	96	98	97	98	97	84	86	90	93

***The CDPHE was responsible for monitoring and validating ozone data at the South Boulder sampling site.**

Overall coverage for the BCPH/CU sites, which include Boulder, Longmont, Lyons, and Niwot Ridge, was 95% from March 2007 through February 2008. The BCPH QAPP specified ≥ 90% as a completeness goal, which was exceeded by approximately 5%.

4.1.2 Minimum Detection Limits

The minimum detection limit (MDL) is defined as a statistically determined value above which the reported concentration can be differentiated, at a specific probability, from a zero concentration. Analytical procedures and sampling equipment impose specific constraints on the determination of detection limits.

Following 40CFR Part 136, Appendix B, the MDLs were determined for carbonyls and VOCs. Analytical procedures and sampling equipment impose specific constraints on the determination of detection limits. For ozone, MDLs were determined by challenging the instruments with purified zero air. However, for techniques like the DNPH based sampling techniques, the MDLs are determined by blanks. For all cartridge sampling techniques, both field blanks and laboratory blanks were collected. Field blanks are defined as sample cartridges that travel to the field site with the devices that were utilized in sample collection. The device was installed in the sampling equipment just like a device that was to be sampled. The only difference is that no air is actively drawn through the sampling device. This blank may also be called a passive blank, since it is capable of passively collecting small quantities of the compounds of interest. When the samples are removed after the sample run, the field blank is also removed and processed in the same manner as all other samples. It is returned to the laboratory in the same manner as the sample devices. The storage and handling of the samples and field blanks are identical. Laboratory (lab) blanks are devices that are processed in exactly in the same manner as all other sampling devices. It is just stored in the laboratory as all sampling devices are stored after sampling and prior to analysis. The lab and field blanks undergo exactly the same analysis procedures as are used for the samples from the field. The following sections illustrate how MDLs are quantified for the various types of sampling. The MDLs were determined using the following equation:

$$MDL = t_{(n-1,1-a=0.99)} \times \sigma$$

where σ is the standard deviation of the replicate zero analyses, *t* is the student's *t* value appropriate to a 99% confidence level with n-1 degrees of freedom.

4.1.3 Continuous Measurements

The configuration of the continuous gas monitors (in particular the ability to introduce standards at the sample inlet) allows for the determination of the MDL for each continuous analyte. The MDL includes all sampling and analytical procedures and therefore represents a detection limit that can be applied to ambient concentrations. The MDL concentration is determined in zero air and therefore does not address matrix interferences.

The MDL for each continuous gas monitor was determined through statistical evaluation of the zero check using the equation given above in this section.

4.1.4 Discrete Measurements

Many of the measurements made in air quality studies require that samples be collected and then returned to the laboratory for analysis. Standards for the determination of detection limits for these laboratory instruments are prepared in the laboratory and therefore are not subject to the same procedures and equipment as the ambient samples. This detection limit is referred to as the instrument detection limit (IDL). The IDL is indicative of the ability of the instrument to differentiate, at a specific probability, between zero and a specific concentration. The IDL standard does not experience the same handling procedures; extraction or desorption from sampling devices prior to HPLC or GC analysis. Therefore the IDL does not provide information relating to the actual detection limit in an ambient sample.

For carbonyl analyses, field blanks were collected each week and were extracted and analyzed. Blank values were subtracted. We determined the areas of the blanks for each of the target compounds.

4.1.4.1 Carbonyls

Table 4.4 shows the average MDL for both 3-hour and 24-hour carbonyl samples. The MDL was different for the two sampling durations due to the total volume of ambient air collected during sampling.

Table 4.4: Average MDLs for 3-hour and 24-hour carbonyl samples collected in the Boulder Study

Average MDLs for 3-hour and 24-hour Carbonyl Samples		
Analyte	**3-hr MDL (in ppbV)**	**24-hr MDL (in ppbV)**
formaldehyde	0.744	0.063
acetaldehyde	0.470	0.040
acrolein	0.135	0.011
acetone	0.759	0.065
propionaldehyde	0.076	0.006
crotonaldehyde	0.179	0.015
butyraldehyde	0.096	0.008
benzaldehyde	0.139	0.012

The MDLs were calculated according to CFR40 Part136B, using the MDL equation mentioned above. The MDLs for formaldehyde, acetaldehyde, and acetone, which were found in all field blanks, were calculated by taking the standard deviation of peak areas for each compound and multiplying them by the Student's t value corresponding to the number of field blanks. For the other carbonyls that were not regularly found in field blanks, the standard deviation of the peak areas from replicate HPLC runs was multiplied by the Student's t value corresponding to the number of replicates. The minimum number of replicates used for each MDL determination was eight.

4.1.4.2 VOCs

Table 4.5 shows the average MDL for the VOC samples. The detection limit for the 24 and 3-hour samples was the same due to the analytical method used.

Table 4.5: Average MDL for both 3-hr and 24-hour VOC samples

Average MDLs for VOCs			
Analyte	**MDL (in ppbV)**	**Analyte**	**MDL (in ppbV)**
n-hexane	0.028	**n-pentane**	0.033
2,2-dimethylbutane	0.028	**cis-2-pentene**	0.034
n-butane	0.042	**2,3,4-trimethylpentane**	0.021
trans-2-butene	0.043	**ethylbenzene**	0.021
cis-2-butene	0.043	**m,p-xylene**	0.021
1,2-butadiene	0.044	**n-nonane**	0.019
benzene	See below	**Styrene**	0.021
1-pentene	0.034	**o-xylene**	0.021
n-heptane	0.024	**2-methyl-2-butene**	0.034
3-methylheptane	0.021	**3-methylpentane**	0.028
2,3-dimethylpentane	0.024	**trans-2-hexene**	0.028
2-methyl-1-butene	0.034	**cis-2-hexene**	0.028
toluene	0.024	**2-methyl-1-pentene**	0.028
n-octane	0.021		

Due to benzene contamination issues with SUMMA canisters, separate benzene MDLs have been for individual canisters and to account for the addition of canister heating during the cleaning processes, which was added part-way through the sampling campaign.

4.1.5 Precision

Precision is a measure of the deviation from the average response and is calculated as:

$$\sigma = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(\bar{x} - x_i)^2}$$

where $\bar{x}$ is the mean of the set of measurements and the x_i is the i-th individual measurement in the set of n measurements performed. The precision was expressed in terms of $\bar{x} \pm 1.96\sigma$. The band represents the 95% confidence band about the mean.

Precision of measurement were calculated by determining the standard deviation for a set of parallel, side-by-side measurements.

Precision for the GC/FID and GC/MS system was determined using multiple analyses of a calibration mixture used throughout the study. These calibration measurements were made through out the entire study. These data were used as described above to determine the standard deviation in the set of measurements.

4.1.6 Representativeness

Generally, representativeness expresses how closely a sample reflects the characteristics of the surrounding environment. This is usually quantified in terms of monitoring scale. It is beyond the scope of this report to discuss monitoring scale in detail; however, monitoring scale must be understood for the project. In this project, we are primarily interested in hazardous air pollutants. The scale for hazardous air pollutants is the neighborhood scale, which is defined as representing an area in the order of 0.5 to 4.0 kilometers. A goal of the project was to better understand hazardous air pollutant exposures throughout Boulder County, which is represented by an urban scale of the order of 4 to 25 kilometers. We employed five different monitoring sites in this project that were chosen to represent different neighborhoods and environments, as demonstrated by the community scale modeling. For more details on the locations and site layout, please refer to Appendix C of the QAPP.

4.1.7 Comparability

Comparability reflects the extent to which measurements of the same observable agree among different methods or at different locations. This is a major focus of this project and was carefully evaluated as a part of this project. We looked not only at method comparability, but also at temporal and spatial aspects of comparability.

4.2 DUPLICATE/COLLOCATED SAMPLING

For the TO-15, and TO-11A methods, duplicate or collocated samples were collected at a frequency of at least 10% of the total samples. The acceptance criteria specified in the QAPP is <15% Relative Percent Difference (RPD) for analytes found at concentrations greater than 5 times the MDL.

Absolute Relative Percent Difference (RPD) expresses average concentration differences relative to the average concentrations detected during replicate analyses. The RPD is calculated as follows:

$$RPD = \left[\frac{|X_1 - X_2|}{\overline{X}} \right] x100\,\%$$

where,

X_1 is the ambient air concentration of a given compound measured in one sample;

X_2 is the concentration of the same compound measured during replicate analysis;

and $\overline{X}$ is the arithmetic mean of X_1 and X_2.

Duplicate 24-hour VOC samples were taken during each sampling period. Duplicate 24-hour carbonyl samples, on the other hand, were taken only when an extra carbonyl sampler was available. One 24-hour VOC and carbonyl duplicate sample was taken during each sampling period.

4.2.1 Carbonyls

Table 4.6 shows the average absolute relative percent difference of duplicate carbonyl samples collected. Many of the samples collected contained compounds, such as acrolein and crotonaldehyde, which were near or below detection limits. Therefore, large percent differences were determined for these non-abundant compounds. Overall, the average percent difference amongst all quantified carbonyls was 21.6%.

Table 4.6: Average Absolute Percent Difference of Duplicate Carbonyl Samples

Analyte	# of samples	Average Absolute RPD
formaldehyde	12	6.3
acetaldehyde	12	6.9
acrolein	12	25.7
acetone	12	5.5
propionaldehyde	12	35.9
crotonaldehyde	12	43.2
butyraldehyde	12	14.6
benzaldehyde	12	34.9
	Overall Average RPD	***21.6%***

Bias is a measure of systematic or persistent distortion of a measurement process which causes errors in one direction. Table 4.7 shows the relative measurement bias for the 24-hour duplicate carbonyl measurements.

Table 4.7: Relative measurement bias for 24-hour carbonyls

Analyte	Bias
formaldehyde	0.05
acetaldehyde	0.05
acrolein	0.40
acetone	0.04
propionaldehyde	0.16
crotonaldehyde	0.57
butyraldehyde	0.11
benzaldehyde	0.33

Formaldehyde, acetaldehyde, and acetone were the most abundant carbonyls measured in the Boulder Study. Each of these compounds have low measurement biases, which indicates minimal sampling errors. Crotonaldehyde and acrolein have much higher biases, but were seldom detected.

4.2.2 VOCs

Table 4.8 shows the absolute average relative percent difference of duplicate VOC samples collected. Many of the samples collected contained compounds, such as cis-2-butene and crotonaldehyde, which were near or below detection limits. Therefore, large percent differences were determined for these non-abundant compounds. The percent difference value for benzene was large and can be attributed to contaminated SUMMA canisters. Overall, the average relative percent difference for all quantified VOCs was 26%.

Table 4.8: Average Absolute Relative Percent Difference of Duplicate VOC Samples

Analyte	# of samples	Average Absolute RPD
n-butane	35	12
trans-2-butene	10	36
cis-2-butene	5	14
1_2-butadiene	0	4
1-pentene	7	29
2-methyl-1-butene	7	19
n-pentane	33	21
cis-2-pentene	3	12
2-methyl-2-butene	6	19
2_2-dimethylbutane	0	7
3-methylpentane	27	33
2-methyl-1-pentene	5	39
hexane	33	24
trans-2-hexene	0	11
cis-2-hexene	1	11
benzene	35	79
23-dimethylpentane	5	21
heptane	31	22
2_3_4-trimethylpentane	2	37
toluene	34	23
3-methylheptane	9	11
octane	24	28
ethylbenzene	29	49
m&p-xylene	34	36
styrene	9	20
o-xylene	23	51
nonane	23	36
	Overall Median	***26***

Table 4.9 shows the measurement bias for the eleven of the more abundant 24-hour duplicate VOC measurements. N-butane was the most abundant VOC measured and had the lowest relative bias value.

Table 4.9: Relative measurement bias for 24-hour VOCs

Analyte	Bias
n-butane	0.16
n-pentane	0.31
hexane	0.32
heptane	0.31
toluene	0.29
octane	0.41
ethylbenzene	0.63
m&p-xylene	0.44
styrene	0.32
o-xylene	0.67
nonane	0.50

4.2.3 National Air Toxics Trend Stations (NATTS) Proficiency Test (PT) Standards and National Performance Audit Program (NPAP)

A NATTS PT is a type of assessment in which a sample, the composition (spiked) of which is unknown to the analyst, is provided to test whether the analyst/laboratory can produce analytical results within the specified acceptance criteria. BCPH/CU participated in NATTS PT for EPA Compendium Methods TO-15 and TO-11A for carbonyls and VOCs, respectively. Alion Science and Technology (Alion), an EPA-contracted laboratory, provided the spiked samples. For the Method TO-15 NATTS PT, INSTAAR sent one cleaned SUMMA canister to Alion. Alion spiked the canister with known concentrations of select VOCs and returned it to INSTAAR for analysis. INSTAAR also sent two 2,4-DNPH cartridges, one PT sample and one blank, to Alion. Alion spiked the PT cartridge and returned the trip blank to INSTAAR for HPLC analysis. The acceptance criteria of the NATTS PT are 75-125 % of the RPD from the known concentration to the analyzed concentration. INSTAAR passed both NATTS PTs for all compounds, with the exception of ethylbenzene. Table 4.10 displays the PT results, as received from Alion. A spreadsheet of NATTS results for all quantified compounds is included in Appendix D.

Table 4.10: NATTS PT results for carbonyl and VOC analytical performance

NATTS PT Results for Methods TO-11A and TO-15				
Analyte	**BCPH Result (ppbV)**	**Alion Result (ppbV)**	**Absolute RPD**	**Pass**
formaldehyde	1.63	2.00	18.5	Yes
acetaldehyde	2.13	2.50	14.8	Yes
n-butane	2.54	2.56	0.8	Yes
n-pentane	2.17	2.39	9.6	Yes
3-methylpentane	2.79	3.04	8.6	Yes
hexane	2.29	2.41	5.1	Yes
heptane	2.24	2.38	6.1	Yes
toluene	2.27	2.48	8.8	Yes
octane	2.05	2.45	17.8	Yes
ethylbenzene	1.96	2.61	28.4	No
m&p-xylene	3.75	4.59	20.1	Yes
o-xylene	1.88	2.30	20.1	Yes

It should be noted that NATTS PT carbonyl results reported by CU were generated using imprecisely diluted calibration standards. At the time of the NATTS PT for carbonyls, appropriate labware used to dilute calibration standards was not available and introduced additional human error. Appropriate labware was obtained following receipt of NATTS PT results and was used to generate calibration standards that were applied to all final carbonyl data. Applying the calibration standards that were used to generate final carbonyl data improved the carbonyl NATTS PT results for formaldehyde and acetaldehyde by 10%.

5 MONITORING RESULTS

5.1 CARBONYLS (TO-11A)

Final 24 and 3-hour carbonyl data for the five Boulder Study sites are included in Appendix E.

5.1.1 24-Hour Samples

5.1.1.1 Detection Frequency

Table 5.1 shows the number of valid samples collected at each site during the monitoring program and the detection frequency for each compound. Detection rates varied among analytes from 100% to less than 50%; moreover, compounds that are difficult to monitor such as crotonaldehyde were seldom detected, i.e., in 15% or less of samples.

Table 5.1: 24-hour TO-11A sample counts and detection rates

	Boulder		**Longmont**		**Lyons**		**Niwot Ridge**		**S. Boulder**	
	# of samples	**% Detect**	**# of samples**	**% Detect**	**# of samples**	**% Detect**	**# of samples**	**% Detect**	**# of samples**	**% Detect**
formaldehyde	54	100	56	100	56	100	52	100	55	100
acetaldehyde	54	100	56	100	56	100	52	100	55	100
acrolein	54	94	56	89	56	84	52	37	55	80
acetone	54	100	56	100	56	100	52	100	55	100
propionaldehyde	54	100	56	98	56	100	52	73	55	98
crotonaldehyde	54	15	56	11	56	14	52	10	55	9
butyraldehyde	54	100	56	100	56	96	52	98	55	100
benzaldehyde	54	52	56	45	56	13	52	13	55	40

The most frequently detected carbonyl compounds were formaldehyde, acetone and acetaldehyde, respectively, which were detected in 100% of samples at all sites. Crotonaldehyde was the least detected of the eight quantified carbonyl compounds at all locations. The Boulder site showed the greatest overall carbonyl concentrations while the Niwot Ridge site showed the lowest.

5.1.1.2 Data Summary

The summary statistics for the 24 hour TO-11A samples are shown below in Table 5.2.

Table 5.2: 24 hour TO-11A summary statistics (ppbV)

	Boulder				**Longmont**			
	Max	**Min**	**Mean**	**Median**	**Max**	**Min**	**Mean**	**Median**
formaldehyde	4.75	0.86	2.26	2.14	4.51	0.50	1.80	1.42
acetaldehyde	1.88	0.42	0.97	0.91	2.67	0.24	0.90	0.76
acrolein	0.10	0.00	0.05	0.05	0.10	0.00	0.04	0.04
acetone	5.03	0.48	2.14	2.12	2.70	0.36	1.29	1.23
propionaldehyde	0.27	0.03	0.12	0.12	0.44	0.00	0.14	0.13
crotonaldehyde	0.14	0.00	0.01	0.00	0.11	0.00	0.01	0.00
butyraldehyde	0.58	0.02	0.23	0.20	0.54	0.01	0.20	0.17
benzaldehyde	0.19	0.00	0.03	0.02	0.21	0.00	0.03	0.00
	Lyons				**Niwot Ridge**			
	Max	**Min**	**Mean**	**Median**	**Max**	**Min**	**Mean**	**Median**
formaldehyde	5.92	0.44	1.60	1.18	5.72	0.24	1.05	0.94
acetaldehyde	2.82	0.16	0.62	0.47	1.75	0.07	0.38	0.34
acrolein	0.12	0.00	0.03	0.02	0.07	0.00	0.01	0.00
acetone	2.50	0.34	1.19	1.08	3.16	0.25	1.22	1.05
propionaldehyde	0.44	0.01	0.09	0.07	0.20	0.00	0.04	0.03
crotonaldehyde	0.08	0.00	0.01	0.00	0.08	0.00	0.00	0.00
butyraldehyde	0.36	0.00	0.14	0.13	0.28	0.00	0.09	0.08
benzaldehyde	0.11	0.00	0.01	0.00	0.12	0.00	0.01	0.00
	South Boulder							
	Max	**Min**	**Mean**	**Median**				
formaldehyde	3.76	0.34	1.62	1.27				
acetaldehyde	1.73	0.15	0.64	0.56				
acrolein	0.07	0.00	0.03	0.02				
acetone	2.61	0.33	1.24	1.15				
propionaldehyde	0.22	0.00	0.09	0.08				
crotonaldehyde	0.10	0.00	0.01	0.00				
butyraldehyde	0.36	0.01	0.14	0.13				
benzaldehyde	0.16	0.00	0.02	0.00				

Figure 5.1 displays the Boulder location having the highest values of formaldehyde, acetaldehyde, and acetone. The Longmont site had the second highest formaldehyde concentrations, as well as the highest acetaldehyde and acetone readings. The Niwot Ridge site had the lowest readings of formaldehyde, acetaldehyde, and acetone, followed by Lyons and South Boulder respectively. Formaldehyde, acetone, and acetaldehyde were the most abundant carbonyls at all five sites, in that respective order.

Figure 5.1: 24-Hour median concentrations of the three most prevalent carbonyl compounds at the five monitoring locations.

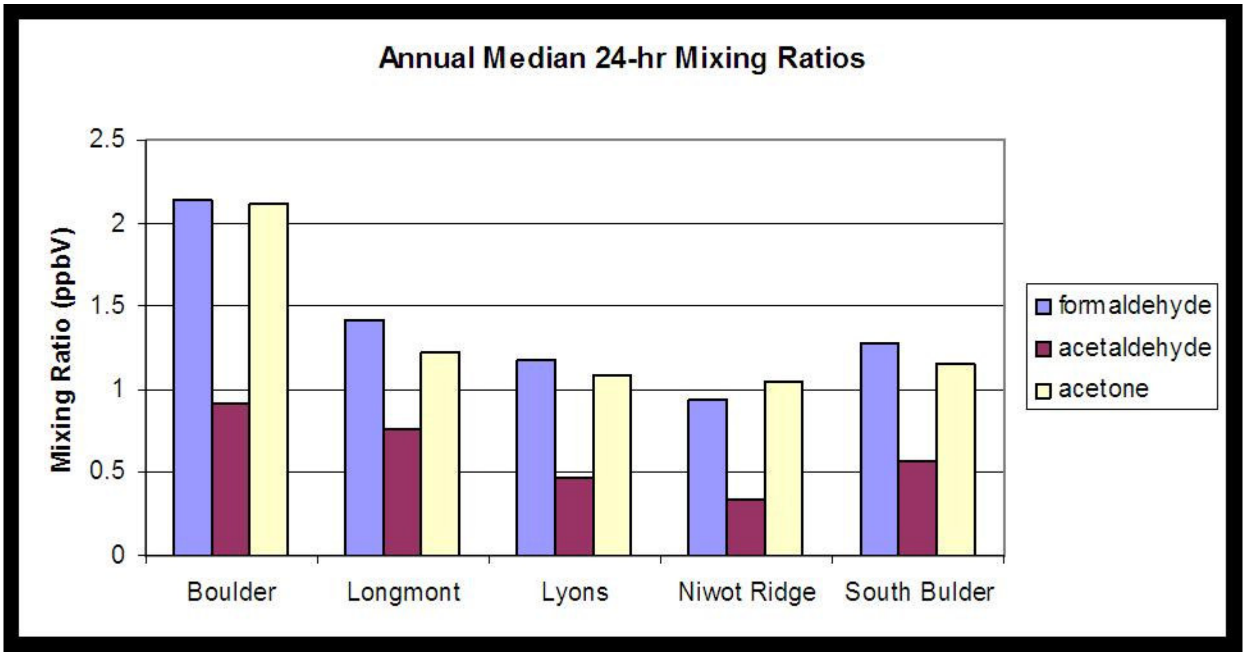
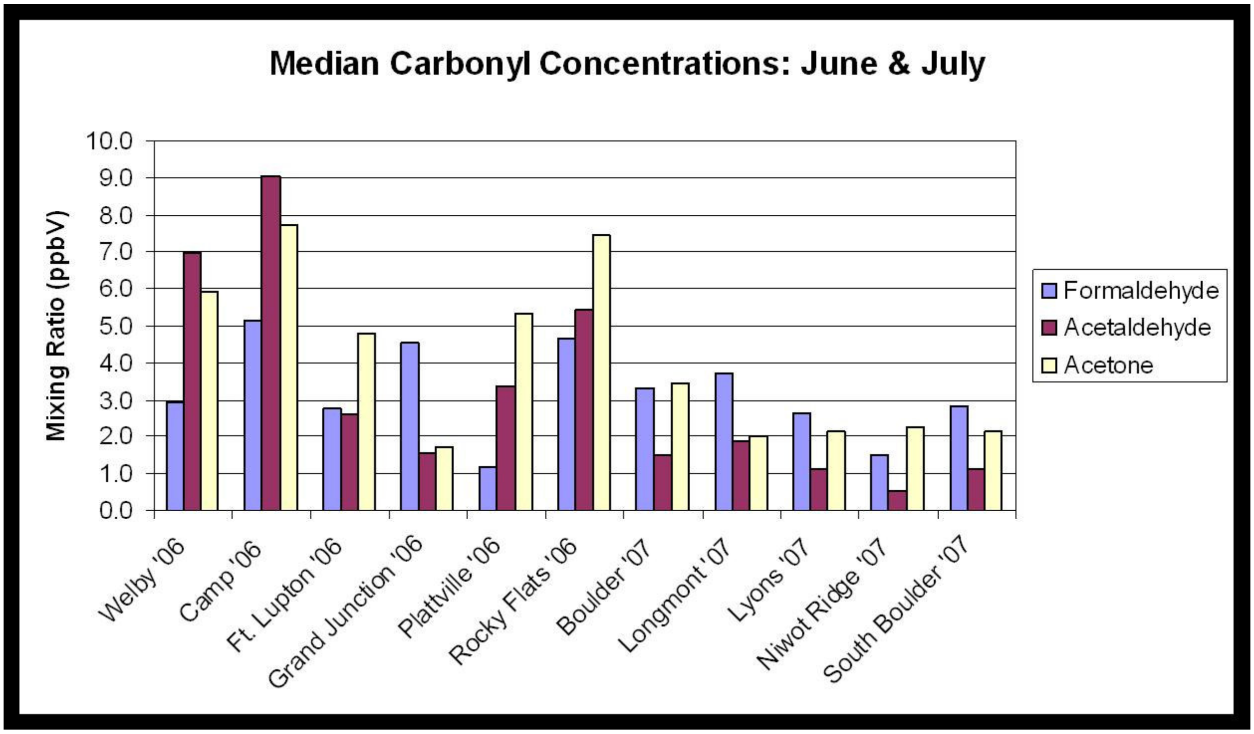


Figure 5.2 shows the median concentrations from this study compared to concentrations measured in 2006 by CDPHE. Samples collected by the CDPHE are median 3-hour samples taken from 06:00 to 09:00, with the exception of the Rocky Flats site where samples were taken from 13:00 until 16:00. The BCPH/CU values in Figure 5.2 are median 24-hour concentrations. The Boulder Study generally observed lower concentrations, when compared to the 2006 values. It is important to note that the number of samples collected during 2006 vary from site to site and are as few as three samples at certain sites.

Figure 5.2: 24-hour median carbonyl concentrations from 2006 CDPHE Study and 2007-2008 Boulder Study



5.1.1.3 *Correlation Coefficients*

A correlation matrix of the 24-hour concentrations of the eight carbonyls was calculated for each site. The correlation matrix of 24-hour carbonyls for the Boulder site is shown in Table 5.3. Correlation matrices of 24-hour carbonyls at the five Boulder Study sites can be found in Appendix F. The bold values indicate that the calculated correlation coefficients are greater than 0.65, indicating fairly strong correlation.

Table 5.3: Boulder 24-hour carbonyls correlation coefficient matrix

	formaldehyde	acetaldehyde	acrolein	acetone	propionaldehyde	crotonaldehyde	butyraldehyde	benzaldehyde
formaldehyde	**1**							
acetaldehyde	**0.91**	**1**						
acrolein	0.10	0.30	**1**					
acetone	**0.73**	**0.78**	0.08	**1**				
propionaldehyde	**0.86**	**0.89**	0.22	**0.78**	**1**			
crotonaldehyde	0.23	0.23	0.05	0.12	0.25	**1**		
butyraldehyde	**0.67**	**0.67**	0.24	**0.82**	**0.74**	0.13	**1**	
benzaldehyde	0.08	0.08	0.18	0.13	0.12	0.05	0.02	**1**

Table 5.3 shows that the concentrations of formaldehyde, acetaldehyde, acetone, propionaldehyde, and butyraldehyde are relatively well correlated. It should be noted that acrolein, crotonaldehyde, and butyraldehyde were seldom detected, which may explain their relatively low correlation with the other carbonyls.

5.1.2 3-hour Samples

5.1.2.1 Detection Frequency

Table 5.4 shows the number of valid samples collected at each site during the monitoring program and the detection frequency for each compound. As expected, the detection rates of the 3-hour samples were lower when compared to the 24-hour samples due to the higher MDLs of the 3-hour samples. Again, the three most prevalent carbonyl compounds were formaldehyde, acetone, and acetaldehyde.

Table 5.4: TO-11A 4-hour sample counts and detection rates

	Boulder		Longmont		Lyons		Niwot Ridge		S. Boulder	
	# of samples	**% Detect**	**# of samples**	**% Detect**	**# of samples**	**% Detect**	**# of samples**	**% Detect**	**# of samples**	**% Detect**
formaldehyde	91	98	104	88	104	67	64	50	112	70
acetaldehyde	91	86	104	79	104	37	64	27	112	48
acrolein	91	8	104	2	104	0	64	0	112	1
acetone	91	91	104	78	104	47	64	66	112	60
propionaldehyde	91	29	104	54	104	20	64	22	112	16
crotonaldehyde	91	0	104	1	104	2	64	0	112	1
butyraldehyde	91	71	104	75	104	49	64	50	112	71
benzaldehyde	91	1	104	5	104	3	64	3	112	3

5.1.2.2 Data Summary

The summary statistics for the 3-hour TO-11A samples are shown below in Table 5.5. The Longmont and Boulder sites had the greatest overall concentrations of 3-hour carbonyl samples, while the Niwot Ridge recorded the lowest concentrations.

Table 5.5: 3-hour TO-11A summary statistics

	Boulder				**Longmont**			
	Max	**Min**	**Mean**	**Median**	**Max**	**Min**	**Mean**	**Median**
formaldehyde	5.67	0.48	2.37	2.18	9.43	0.16	1.81	1.39
acetaldehyde	3.08	0.14	1.04	0.95	2.97	0.18	0.92	0.74
acrolein	0.29	0.00	0.03	0.00	0.25	0.00	0.02	0.00
acetone	18.56	0.00	2.23	1.57	5.14	0.29	1.54	1.29
propionaldehyde	0.60	0.00	0.06	0.00	0.92	0.00	0.01	0.00
crotonaldehyde	0.09	0.00	0.00	0.00	0.40	0.00	0.01	0.00
butyraldehyde	2.20	0.00	0.27	0.24	0.94	0.00	0.24	0.23
benzaldehyde	3.72	0.00	0.04	0.00	0.37	0.00	0.02	0.00
	Lyons				**Niwot Ridge**			
	Max	**Min**	**Mean**	**Median**	**Max**	**Min**	**Mean**	**Median**
formaldehyde	4.67	0.00	1.41	0.98	3.73	0.04	0.90	0.71
acetaldehyde	1.78	0.00	0.51	0.37	1.62	0.00	0.34	0.18
acrolein	0.05	0.00	0.00	0.00	0.05	0.00	0.00	0.00
acetone	3.53	0.05	1.13	0.74	5.20	0.09	1.40	1.23
propionaldehyde	0.35	0.00	0.04	0.00	0.34	0.00	0.04	0.00
crotonaldehyde	0.65	0.00	0.01	0.00	0.06	0.00	0.00	0.00
butyraldehyde	2.00	0.00	0.17	0.09	0.69	0.00	0.13	0.10
benzaldehyde	0.39	0.00	0.01	0.00	0.90	0.00	0.02	0.00
	South Boulder							
	Max	**Min**	**Mean**	**Median**				
formaldehyde	3.94	0.08	1.40	1.18				
acetaldehyde	2.24	0.00	0.55	0.47				
acrolein	1.10	0.00	0.01	0.00				
acetone	4.36	0.00	1.30	0.85				
propionaldehyde	0.60	0.00	0.04	0.00				
crotonaldehyde	0.23	0.00	0.00	0.00				
butyraldehyde	1.36	0.00	0.21	0.01				
benzaldehyde	0.44	0.00	0.01	0.00				

Figure 5.6: 3-hour TO-11A median concentrations (ppbV) of the three most prevalent carbonyl compounds at the five sampling locations

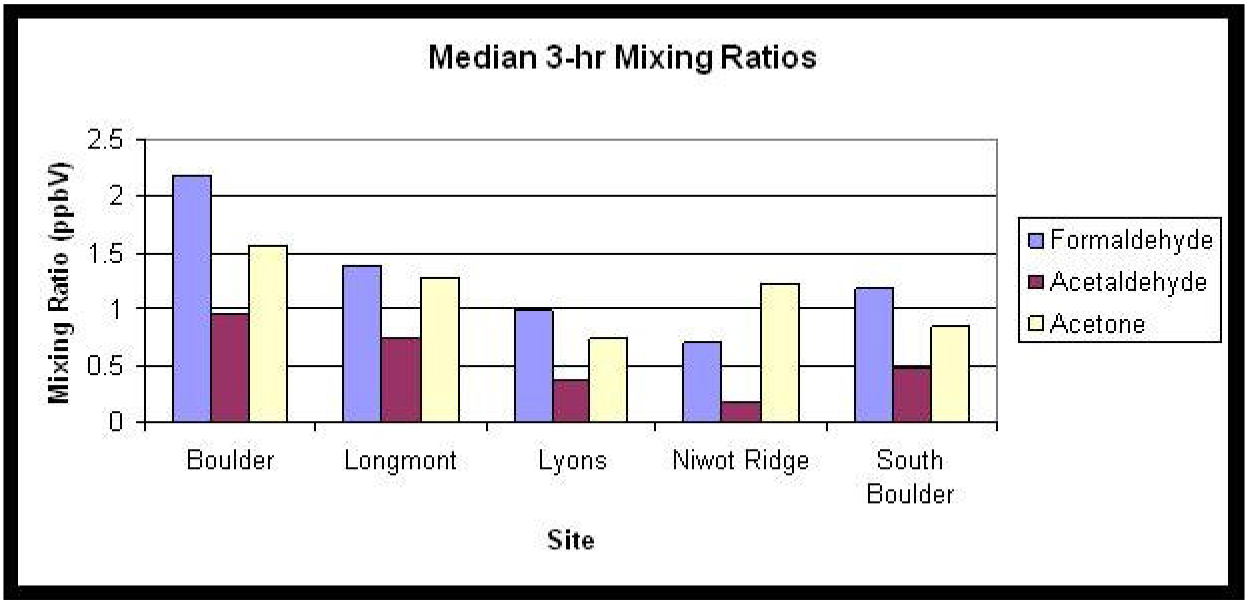


Figure 5.6 shows that the 3-hour median concentrations were highest at the Boulder site for formaldehyde, acetaldehyde and acetone. This agrees with the 24-hour data, which also showed that the Boulder location had the highest concentrations of carbonyls. Overall, the greatest concentrations of carbonyls occurred during the daylight hours.

Figure 5.3: Typical 3-hr composite plot of formaldehyde, acetaldehyde, and acetone. This specific plot represents the consecutive samples taken at Longmont on July 17, 2007

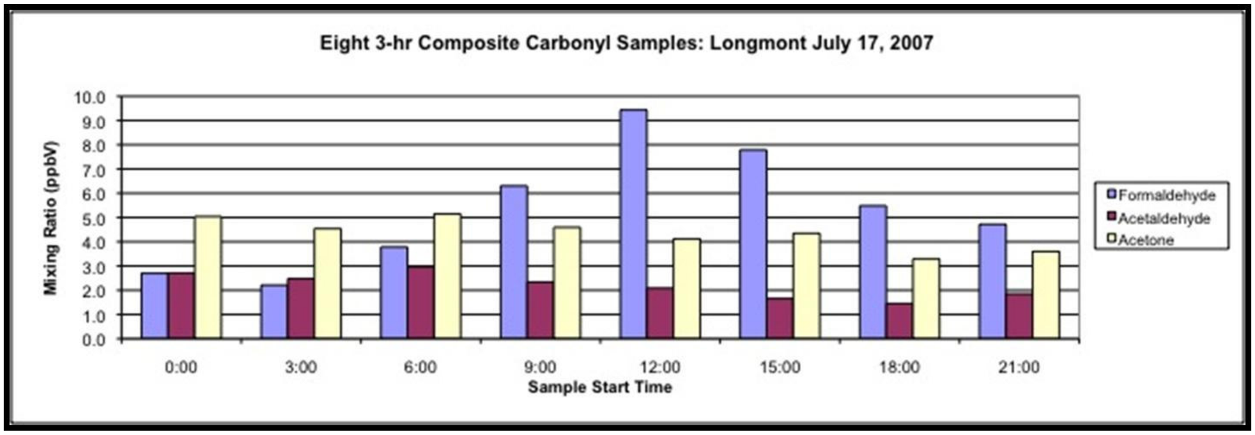


Figure 5.3 shows the typical shape of the eight consecutive samples taken during a 24-hour sampling period. Greater formaldehyde concentrations of formaldehyde, across all

sites, were noticed during the daytime hours. Unlike formaldehyde, acetone concentrations remained fairly consistent throughout the course of the day.

5.1.2.3 Correlation Coefficients

A correlation matrix was calculated for each site for each of the eight quantified carbonyls sampled in a 3-hour duration. The correlation matrix for the Boulder site is shown in Table 5.7 and the four remaining matrices can be found in Appendix F. The bold values indicate that the calculated correlation coefficients are greater than 0.65, indicating fairly strong correlation.

Table 5.7: 3-hour TO-11A correlation coefficient matrix for the Boulder site

	Formaldehyde	**Acetaldehyde**	**Acrolein**	**Acetone**	**Propionaldehyde**	**Crotonaldehyde**	**Butyraldehyde**	**Benzaldehyde**
formaldehyde	**1**							
acetaldehyde	**0.84**	**1**						
acrolein	0.15	0.33	**1**					
acetone	0.61	0.50	0.33	**1**				
propionaldehyde	0.12	0.23	0.05	-0.04	**1**			
crotonaldehyde	0.13	0.19	-0.06	0.12	-0.01	**1**		
butyraldehyde	0.56	0.45	-0.05	**0.82**	0.00	0.12	**1**	
benzaldehyde	0.10	0.08	0.04	0.03	0.03	-0.01	-0.02	**1**

For the Boulder site, the 3-hour concentrations correlations compounds did not show as strong of a correlation as the 24-hour carbonyl samples. This could be due to a number of issues, but detection limitations due to the shorter sampling duration are believed to have a considerable effect. Formaldehyde/acetaldehyde and acetone/butyraldehyde showed relatively strong correlations for the 3-hour samples.

5.1.2.4 Comparison of 24-hour and 3-hour Carbonyl Data

To compare the 24-hour to the eight 3-hr carbonyl samples, the mixing ratios of the eight 3-hour samples were summed and then divided by eight to yield a 24-hr average. Relative percent differences (RPDs) were then calculated, which displayed the relationship between the two sampling methods.

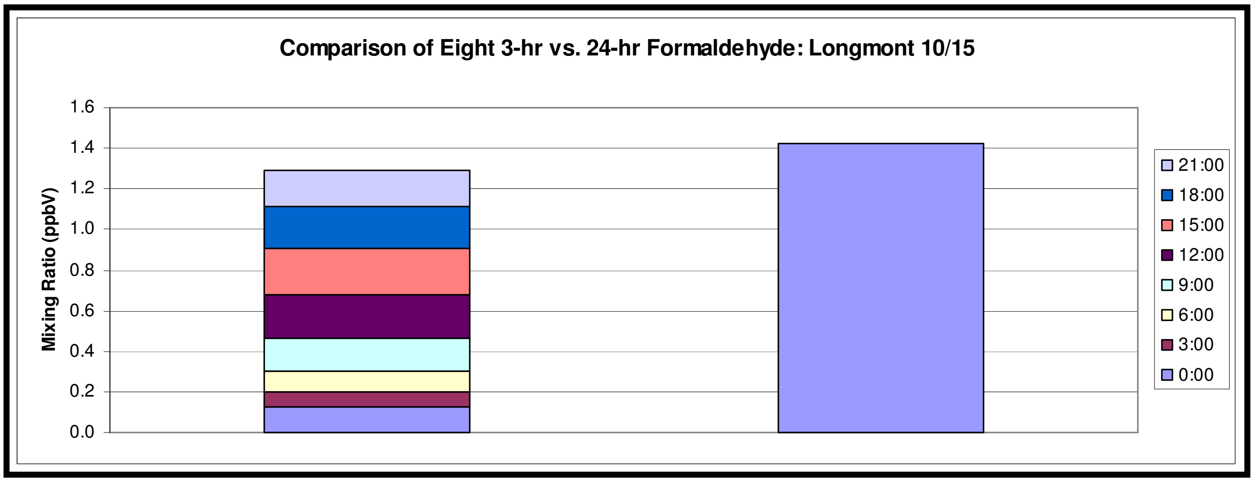
Table 5.8 displays the relative percent difference for formaldehyde, acetaldehyde, and acetone between the eight 3-hour carbonyl samples and the 24-hour sample taken during the same period. Sample periods where eight valid 3-hour samples or one valid 24-hour sample were unavailable were not included in this analysis. Overall, the comparisons of the 3-hour and 24-hour samples were less than 21% absolute RPD.

Table 5.8: Average absolute RPD of the average of five 3-hr carbonyl samples when compared to the 24-hr carbonyl sample taken during the same period

Average Absolute RPD of Eight 3-hr Samples vs. 24-hr Samples		
	n	**Absolute RPD (%)**
formaldehyde	40	10.2
acetaldehyde	40	20.2
acetone	40	19.3

Figure 5.4 shows a representative bar graph of 3-hr and 24-hr formaldehyde samples. Each 3-hour sample was divided by eight, as each sample represents one-eighth of the 24-hour average. All carbonyl samples were blank-subtracted.

Figure 5.4: Comparison of eight 3-hour versus 24-hour values of formaldehyde taken during the same time period at Longmont on October 15, 2007



5.2 VOCs (TO-15)

All 24 and 3-hour VOC data from the five Boulder Study sites is included in Appendix E.

5.2.1 24-hour Samples

5.2.1.1 Detection Frequency

Table 5.9 shows the number of valid VOC samples collected at each site during the monitoring program and the detection frequency for each compound. Detection rates varied among analytes from 100% for n-butane at all sites to 25% for octane at Niwot Ridge.

Table 5.9: 24-hour TO-15 sample counts and detection rates

	Boulder		**Longmont**		**Lyons**		**Niwot Ridge**		**S. Boulder**	
	# of samples	**% Detect**	**# of samples**	**% Detect**	**# of samples**	**% Detect**	**# of samples**	**% Detect**	**# of samples**	**% Detect**
n-butane	54	100	60	100	57	100	56	100	57	100
n-pentane	54	100	60	100	57	100	56	96	57	98
hexane	54	100	60	100	57	98	56	88	57	98
toluene	54	98	60	100	57	100	56	100	57	96
octane	54	98	60	95	57	79	56	25	57	49
ethylbenzene	54	100	60	98	57	96	56	66	57	89
m&p-xylene	54	98	60	100	57	100	56	80	57	96
o-xylene	54	98	60	93	57	67	56	29	57	75
nonane	54	96	60	92	57	65	56	36	57	37

5.2.1.2 Data Summary

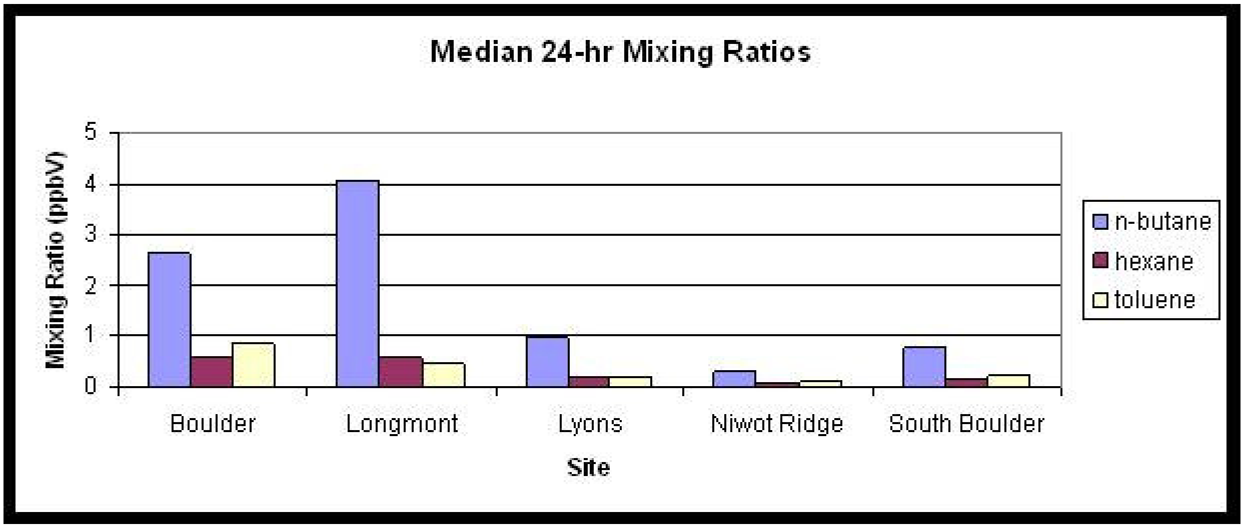
Table 5.20 shows the 24-hour TO-15 summary statistics for nine of the 27 quantified VOCs at each sampling location. Complete data summary tables including all 27 quantified VOCs are included in Appendix E. n-butane was the most abundant VOC across all five sites, with the greatest concentrations occurring at the Longmont site.

Table 5.20: 24-hour TO-15 summary statistics (ppbV)

	Boulder				**Longmont**			
	Max	**Min**	**Mean**	**Median**	**Max**	**Min**	**Mean**	**Median**
n-butane	13.42	0.38	3.21	2.60	21.54	0.26	4.85	4.06
n-pentane	8.81	0.14	1.35	1.11	6.72	0.11	1.76	1.56
hexane	4.37	0.07	0.70	0.57	2.06	0.05	0.64	0.59
toluene	9.51	0.00	1.46	1.15	1.42	0.06	0.47	0.47
octane	0.42	0.00	0.07	0.06	0.16	0.00	0.06	0.06
ethylbenzene	1.26	0.00	0.21	0.17	0.21	0.00	0.08	0.08
m&p-xylene	4.12	0.00	0.65	0.57	0.49	0.05	0.20	0.19
o-xylene	1.33	0.00	0.20	0.17	0.15	0.00	0.06	0.06
nonane	0.22	0.00	0.05	0.04	0.08	0.00	0.03	0.03
	Lyons				**Niwot Ridge**			
	Max	**Min**	**Mean**	**Median**	**Max**	**Min**	**Mean**	**Median**
n-butane	6.00	0.21	1.34	0.96	2.30	0.08	0.47	0.33
n-pentane	1.90	0.06	0.48	0.41	0.75	0.00	0.17	0.11
hexane	0.66	0.00	0.21	0.20	0.98	0.00	0.12	0.07
toluene	0.44	0.05	0.19	0.18	0.55	0.03	0.13	0.11
octane	0.09	0.00	0.03	0.03	0.09	0.00	0.01	0.00
ethylbenzene	0.69	0.00	0.06	0.04	0.26	0.00	0.04	0.03
m&p-xylene	0.89	0.02	0.11	0.08	0.51	0.00	0.10	0.06
o-xylene	0.35	0.00	0.03	0.03	0.18	0.00	0.02	0.00
nonane	0.08	0.00	0.02	0.02	0.16	0.00	0.02	0.00
	South Boulder							
	Max	**Min**	**Mean**	**Median**				
n-butane	6.90	0.17	1.25	0.77				
n-pentane	2.07	0.00	0.44	0.31				
hexane	0.96	0.00	0.20	0.17				
toluene	2.23	0.00	0.25	0.22				
octane	0.18	0.00	0.02	0.00				
ethylbenzene	0.42	0.00	0.06	0.04				
m&p-xylene	1.37	0.00	0.14	0.10				
o-xylene	0.42	0.00	0.04	0.03				
nonane	0.26	0.00	0.02	0.00				

Figure 5.5 shows the median concentrations of n-butane, hexane, and toluene that were observed at the five sites. The Longmont site recorded the highest values for n-butane, followed by the Boulder site. The Niwot Ridge site had the overall lowest concentrations for the VOCs measured, which was expected due to its background location.

Figure 5.5: 24-hour TO-15 mean concentrations at the monitoring locations



5.2.1.3 Correlation Coefficients

Correlation coefficients were calculated for analytes detected in the 24-hour TO-15 samples. The correlation matrix for the Boulder location is shown in Table 5.11.

Table 5.11: 24-hour TO-15 correlation coefficient matrix at Boulder

	n-butane	**n-pentane**	**hexane**	**toluene**	**octane**	**ethylbenzene**	**m&p-xylene**	**o-xylene**	**nonane**
n-butane	**1**								
n-pentane	**0.71**	**1**							
hexane	0.61	**0.98**	**1**						
toluene	0.52	**0.84**	**0.86**	**1**					
octane	0.61	**0.95**	**0.97**	**0.83**	**1**				
ethylbenzene	0.48	**0.89**	**0.93**	**0.83**	**0.93**	**1**			
m&p-xylene	0.51	**0.90**	**0.94**	**0.83**	**0.95**	**0.99**	**1**		
o-xylene	0.48	**0.91**	**0.95**	**0.85**	**0.96**	**0.98**	**0.99**	**1**	
nonane	0.45	**0.79**	**0.83**	**0.70**	**0.87**	**0.88**	**0.90**	**0.89**	**1**

Table 5.11 shows that all analytes are positively correlated to each other. However, the strength of the correlations varied by both site and analyte. Complete correlation matrices with all 27 quantified VOCs are included in Appendix F.

5.2.2 3-Hour Samples

5.2.2.1 Detection Frequency

Table 5.12 shows the number of valid 3-hour samples collected at each site and the detection frequency for each compound. Detection rates varied among analytes from 100% for n-butane and toluene at all sites to 39% for o-xylene at Niwot Ridge. As with the 24-hour data, n-butane and n-pentane were the most prevalent VOCs and were detected in a majority of samples at the five monitoring sites.

Table 5.12: 3-hour TO-15 sample counts and detection rates

	Boulder		**Longmont**		**Lyons**		**Niwot Ridge**		**South Boulder**	
	# of samples	**% Detect**	**# of samples**	**% Detect**	**# of samples**	**% Detect**	**# of samples**	**% Detect**	**# of samples**	**% Detect**
n-butane	93	100	94	100	95	100	56	100	96	100
n-pentane	93	100	94	100	95	100	56	89	96	100
hexane	93	98	94	99	95	99	56	77	96	96
toluene	93	100	94	100	95	100	56	91	96	100
octane	93	97	94	88	95	63	56	39	96	53
ethylbenzene	93	100	94	100	95	85	56	73	96	82
m&p-xylene	93	100	94	100	95	99	56	89	96	96
o-xylene	93	100	94	97	95	61	56	39	96	64
nonane	93	98	94	83	95	52	56	54	96	43

5.2.2.2 Data Summary

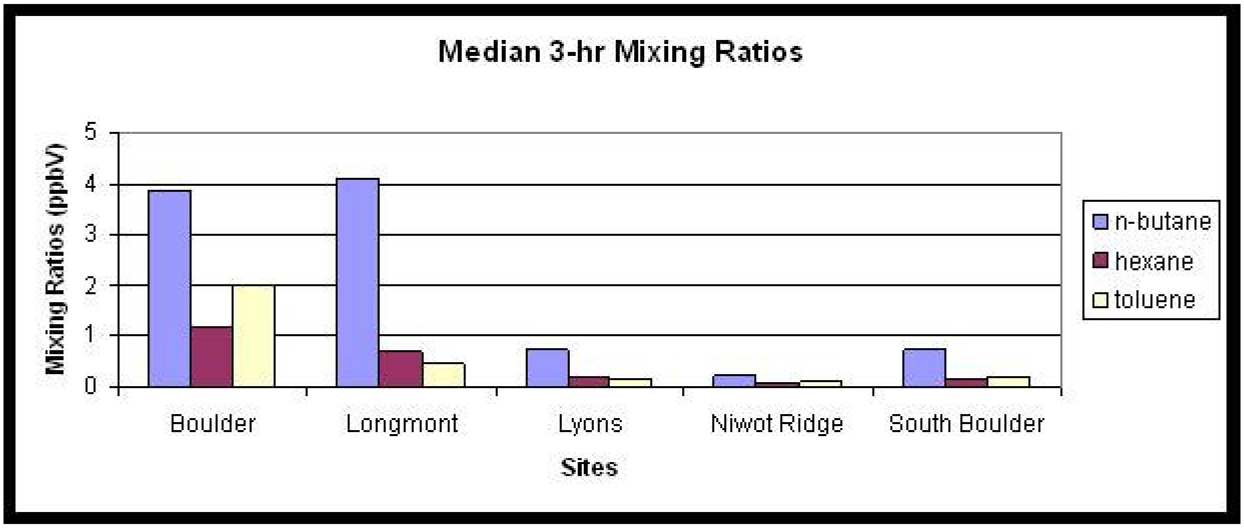
The 3-hour TO-15 summary statistics are shown in Table 5.13. Large maximum values were observed at the Boulder site. The Niwot Ridge site showed the lowest overall 3-hr VOC means.

Table 5.13: 3-hour TO-15 summary statist

	Boulder				Longmont			
	Max	**Min**	**Mean**	**Median**	**Max**	**Min**	**Mean**	**Median**
n-butane	74.49	0.67	6.41	3.87	33.76	0.44	5.77	4.10
n-pentane	50.73	0.31	3.33	1.97	10.99	0.21	2.08	1.75
hexane	28.84	0.00	2.45	1.17	4.01	0.00	0.85	0.71
toluene	49.06	0.48	3.81	1.98	1.76	0.13	0.56	0.47
octane	2.89	0.00	0.18	0.09	0.24	0.00	0.07	0.06
ethylbenzene	5.81	0.07	0.50	0.28	0.33	0.03	0.10	0.08
m&p-xylene	23.88	0.21	1.70	0.99	0.75	0.04	0.24	0.20
o-xylene	7.68	0.07	0.54	0.30	0.30	0.00	0.07	0.06
nonane	1.46	0.00	0.11	0.07	0.25	0.00	0.04	0.04
	Lyons				**Niwot Ridge**			
	Max	**Min**	**Mean**	**Median**	**Max**	**Min**	**Mean**	**Median**
n-butane	4.77	0.08	1.17	0.73	1.32	0.07	0.35	0.25
n-pentane	1.57	0.06	0.44	0.33	1.71	0.00	0.16	0.11
hexane	2.79	0.00	0.26	0.21	7.78	0.00	0.23	0.08
toluene	0.54	0.05	0.17	0.15	3.03	0.00	0.19	0.11
octane	0.17	0.00	0.02	0.02	0.19	0.00	0.01	0.00
ethylbenzene	0.26	0.00	0.05	0.04	0.27	0.00	0.04	0.03
m&p-xylene	0.56	0.02	0.09	0.07	0.70	0.00	0.08	0.06
o-xylene	0.18	0.00	0.02	0.02	0.14	0.00	0.02	0.00
nonane	0.10	0.00	0.02	0.02	0.07	0.00	0.02	0.02
	South Boulder							
	Max	**Min**	**Mean**	**Median**				
n-butane	9.90	0.06	1.32	0.76				
n-pentane	3.35	0.04	0.47	0.35				
hexane	1.22	0.00	0.21	0.17				
toluene	0.86	0.05	0.24	0.20				
octane	0.09	0.00	0.02	0.02				
ethylbenzene	0.28	0.00	0.05	0.04				
m&p-xylene	0.46	0.00	0.12	0.08				
o-xylene	0.11	0.00	0.03	0.03				
nonane	0.07	0.00	0.02	0.00				

Figure 5.6 compares 3-hour medians of certain compounds detected in VOC samples at all sites. This graph shows that the Boulder and Longmont sites had the greatest concentrations of n-butane, hexane, and toluene of the five locations.

Figure 5.6: 3-hour TO-15 mean concentrations



5.2.2.3 Correlation Coefficients

The correlation matrix for the 3-hour TO-15 samples at the Boulder site is shown below in Table 5.14.

Table 5.14: 3-hour TO-15 Boulder correlation coefficient matrix

	n-butane	**n-pentane**	**hexane**	**toluene**	**octane**	**ethylbenzene**	**m&p-xylene**	**o-xylene**	**nonane**
n-butane	**1**								
n-pentane	**0.92**	**1**							
hexane	0.55	**0.65**	**1**						
toluene	**0.86**	**0.95**	0.62	**1**					
octane	**0.87**	**0.98**	0.63	**0.95**	**1**				
ethylbenzene	**0.85**	**0.97**	0.64	**0.98**	**0.97**	**1**			
m&p-xylene	**0.87**	**0.98**	0.64	**0.98**	**0.98**	**1**	**1**		
o-xylene	**0.86**	**0.98**	**0.65**	**0.98**	**0.99**	**1**	**1**	**1**	
nonane	**0.82**	**0.95**	0.63	**0.93**	**0.97**	**0.96**	**0.96**	**0.97**	**1**

5.2.2.4 Comparison of 24-hour and 3-hour VOC Data

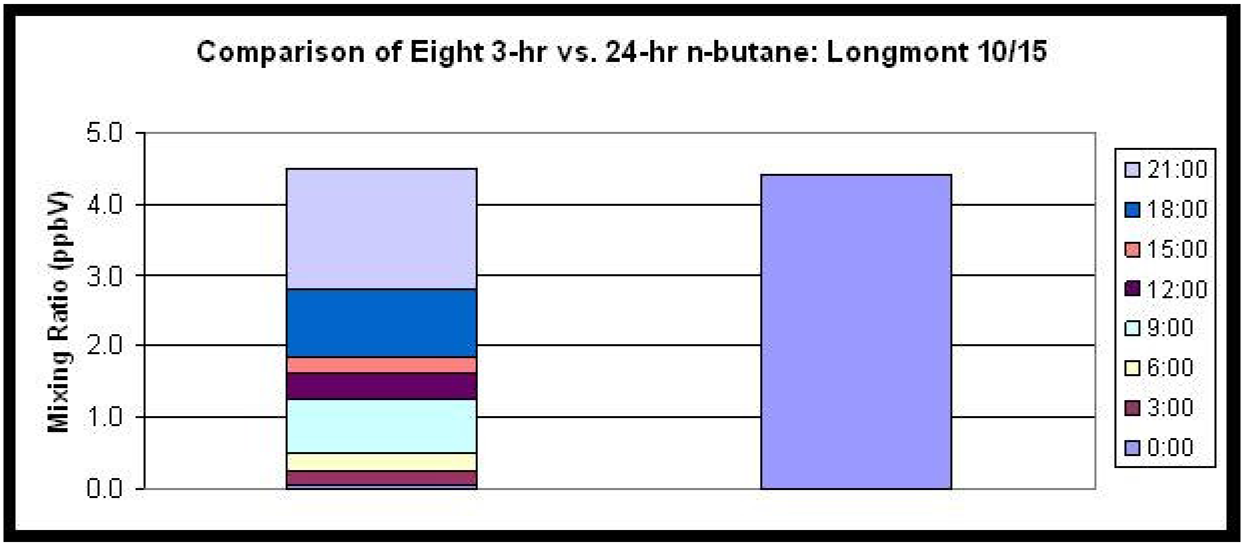
Table 5.15 displays the relative percent difference for each VOC compound for the eight 3-hour versus the 24-hour analysis. Sample periods where eight valid 3-hour samples or one valid 24-hour sample were unavailable were not included in this analysis. This table includes all data from all sites. Overall, the comparisons of the 3-hour and 24-hour samples were fairly good. In most cases, the absolute RPD was about 30%. Numerous VOCs were not included in this analysis due to their limited detection.

Table 5.15: Average RPD of the average of eight 3-hr VOC samples compared to the 24-hr VOC sample taken during the same period

Average Absolute RPD of Eight 3-hr Samples vs. 24-hr Samples		
	n	Absolute RPD (%)
n-butane	39	12.0
n-pentane	39	23.2
3-methylpentane	39	48.2
hexane	39	32.5
heptane	39	36.8
toluene	39	30.3
octane	39	66.2
ethylbenzene	39	49.3
m&p-xylene	39	37.4
o-xylene	39	78.6
nonane	39	75.8

Figure 5.7 shows a representative bar graph of 3-hr and 24-hr n-butane samples. Each 3-hour sample was divided by eight, as each represents one-eighth of the 24-hour average.

Figure 5.7: Comparison of eight 3-hour versus 24-hour values of n-butane taken during the same time period at Longmont on October 15, 2007



5.3 *OZONE*

5.3.1 1-hr Ozone Data

Monthly ozone data coverage is shown in Table 5.16. Overall, monthly data coverage was greater than 80%, with the exception of May and June 2007 at the Niwot Ridge site. The major reasons for loss of coverage include site power losses and zero/precision/span calibration activities.

Table 5.16: Monthly data coverage for 1-hour ozone averages

	Boulder											
Month	**Mar 07**	**Apr 07**	**May 07**	**Jun 07**	**Jul 07**	**Aug 07**	**Sep 07**	**Oct 07**	**Nov 07**	**Dec 07**	**Jan 08**	**Feb 08**
% Coverage	87	100	95	98	97	99	99	81	100	85	100	99
	Longmont											
Month	**Mar 07**	**Apr 07**	**May 07**	**Jun 07**	**Jul 07**	**Aug 07**	**Sep 07**	**Oct 07**	**Nov 07**	**Dec 07**	**Jan 08**	**Feb 08**
% Coverage	87	99	81	88	100	99	85	100	100	100	100	99
	Lyons											
Month	**Mar 07**	**Apr 07**	**May 07**	**Jun 07**	**Jul 07**	**Aug 07**	**Sep 07**	**Oct 07**	**Nov 07**	**Dec 07**	**Jan 08**	**Feb 08**
% Coverage	99	99	100	99	99	100	99	100	100	100	100	99
	Niwot Ridge											
Month	**Mar 07**	**Apr 07**	**May 07**	**Jun 07**	**Jul 07**	**Aug 07**	**Sep 07**	**Oct 07**	**Nov 07**	**Dec 07**	**Jan 08**	**Feb 08**
% Coverage	100	90	78	53	99	99	99	99	99	100	99	100
	South Boulder*											
Month	**Mar 07**	**Apr 07**	**May 07**	**Jun 07**	**Jul 07**	**Aug 07**	**Sep 07**	**Oct 07**	**Nov 07**	**Dec 07**	**Jan 08**	**Feb 08**
% Coverage	99	98	97	96	98	97	98	97	84	86	90	93

***The CDPHE was responsible for monitoring and finalizing ozone data at the South Boulder sampling site.**

5.3.1.1 Data Summary

The summary statistics for the 1-hour ozone values are shown below in Table 5.17. Negative ozone values are a result of offset corrections, which were adjusted monthly for each analyzer. Elevated ozone levels were noticed at all sites during the ozone season extending from May until August, with the exception of the Niwot Ridge site. Relatively stable ozone concentrations were observed at the Niwot Ridge site throughout the study, regardless of season. The Longmont site experienced ozone concentrations that would reach zero ppbV during the nighttime hours. The Boulder site also experienced low ozone concentrations into the morning hours.

Table 5.17: 1-hour ozone summary statistics (ppbV)

	Boulder											
	Mar 07	**Apr 07**	**May 07**	**Jun 07**	**Jul 07**	**Aug 07**	**Sep 07**	**Oct 07**	**Nov 07**	**Dec 07**	**Jan 08**	**Feb 08**
Max	64.7	58.6	63.5	71.2	82.8	84.9	64.2	57.0	54.4	43.3	52.5	58.7
Min	-0.3	0.5	3.5	2.9	1.6	-0.7	-1.5	2.7	1.2	0.3	0.9	2.6
Mean	21.7	26.9	33.5	34.3	33.2	31.9	23.5	22.9	16.8	15.9	21.9	25.0
Median	21.1	25.3	33.5	34.3	31.8	32.8	23.1	21.3	15.1	13.2	20.2	24.3
	Longmont											
	Mar 07	**Apr 07**	**May 07**	**Jun 07**	**Jul 07**	**Aug 07**	**Sep 07**	**Oct 07**	**Nov 07**	**Dec 07**	**Jan 08**	**Feb 08**
Max	67.0	66.3	68.4	91.7	103.6	90.5	77.1	69.2	49.7	47.1	57.8	57.1
Min	-1.3	-1.5	1.8	3.6	1.0	0.3	1.5	-0.1	0.1	0.3	0.2	0.2
Mean	24.5	31.4	33.6	36.8	39.4	35.7	28.9	23.8	16.6	17.8	19.4	25.5
Median	26.5	30.9	33.5	35.9	39.3	35.1	26.4	24.9	15.2	15.3	18.8	27.6
	Lyons											
	Mar 07	**Apr 07**	**May 07**	**Jun 07**	**Jul 07**	**Aug 07**	**Sep 07**	**Oct 07**	**Nov 07**	**Dec 07**	**Jan 08**	**Feb 08**
Max	68.6	70.8	67.6	85.0	97.3	95.9	77.6	65.0	59.0	48.7	60.4	59.4
Min	10.6	1.5	11.2	14.5	8.8	12.3	8.0	2.6	1.7	1.3	2.7	4.7
Mean	35.2	38.2	42.4	44.6	47.4	45.9	39.1	33.8	31.0	31.2	33.6	36.9
Median	36.0	37.4	42.4	43.6	46.1	45.8	39.4	34.5	31.3	32.7	34.4	38.2
	Niwot Ridge											
	Mar 07	**Apr 07**	**May 07**	**Jun 07**	**Jul 07**	**Aug 07**	**Sep 07**	**Oct 07**	**Nov 07**	**Dec 07**	**Jan 08**	**Feb 08**
Max	73.3	73.1	72.0	83.4	91.1	80.6	71.3	59.2	63.4	70.4	61.2	63.7
Min	30.5	19.9	13.1	19.5	7.7	6.7	14.5	10.8	20.6	11.9	32.4	26.1
Mean	48.9	51.2	50.2	48.6	47.6	47.4	43.3	40.5	42.1	41.1	45.3	49.7
Median	49.4	53.9	52.8	50.5	49.7	49.4	45.0	41.4	43.0	42.9	45.1	50.1
	South Boulder*											
	Mar 07	**Apr 07**	**May 07**	**Jun 07**	**Jul 07**	**Aug 07**	**Sep 07**	**Oct 07**	**Nov 07**	**Dec 07**	**Jan 08**	**Feb 08**
Max	78.0	70.8	67.6	85.0	97.3	95.9	77.6	65.0	59.0	48.7	60.4	59.4
Min	2.0	1.5	11.2	14.5	8.8	12.3	8.0	2.6	1.7	1.3	2.7	4.7
Mean	36.1	38.2	42.4	44.6	47.4	45.9	39.1	33.8	31.0	31.2	33.6	36.9
Median	38.0	37.0	42.0	42.0	46.0	44.0	37.0	32.0	31.5	36.0	38.5	37.0

*** The CDPHE was responsible for monitoring and finalizing ozone data at the South Boulder sampling site.**

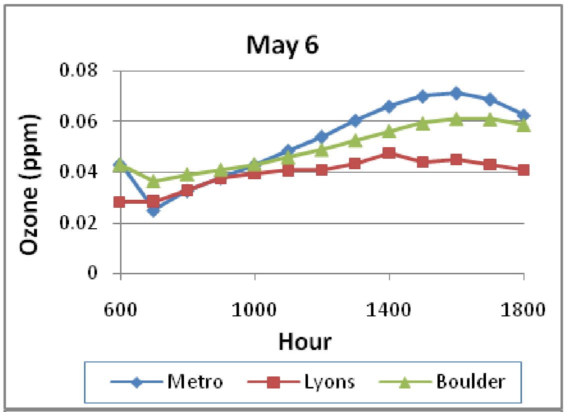
6 MODELING RESULTS

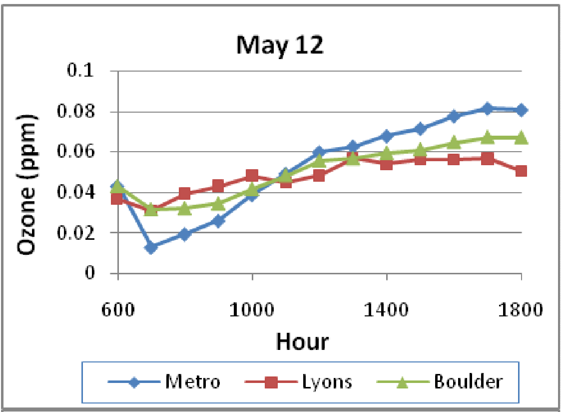
6.1 OZIPR Modeling Results for Ozone and Secondary Carbonyls

6.1.1 Boulder and Metro Base Case Ozone Results

The OZIPR model was used to model ozone over the eastern half Boulder County for 19 days of the summer of 2007. The model was run using two different sets of parameters for background concentrations and emissions of relevant species: the Boulder case assumed the emissions that originate in the modeled region of Boulder County are the ones that are present to contribute to ozone formation, while the Metro case assumes emissions from the area surrounding Denver are carried to Boulder County, where they can then contribute to ozone formation.

The model results were compared to the measured ozone concentrations at the Lyons site in northern Boulder County. The Lyons ozone monitor is situated in a semi-rural location not too near to any significant pollution sources, and therefore can be considered to be representative of an average Boulder County ozone concentration. The modeled results for the Boulder and Metro cases as well as measured ozone concentrations at Lyons are pictured below in Figure 6.1. A summary of performance statistics can also be found below in Table 6.1. Overall, the OZIPR model performed well at predicting measured concentrations at the Lyons monitoring site.


May 6
Ozone (ppm)
0.08
0.06
0.04
0.02
0
600
1000
1400
1800
Hour
Metro
Lyons
Boulder


May 12
Ozone (ppm)
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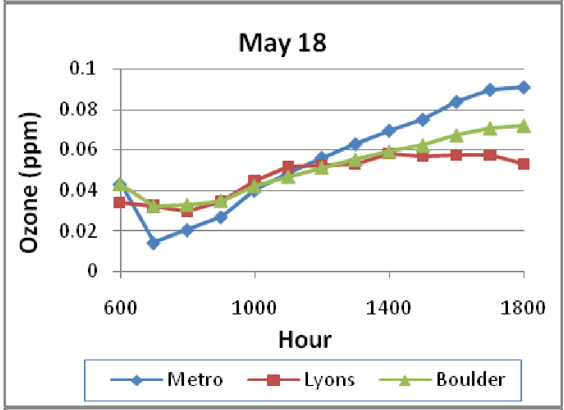
0.06
0.04
0.02
0
600
1000
1400
1800
Hour
Metro
Lyons
Boulder


May 18
Ozone (ppm)
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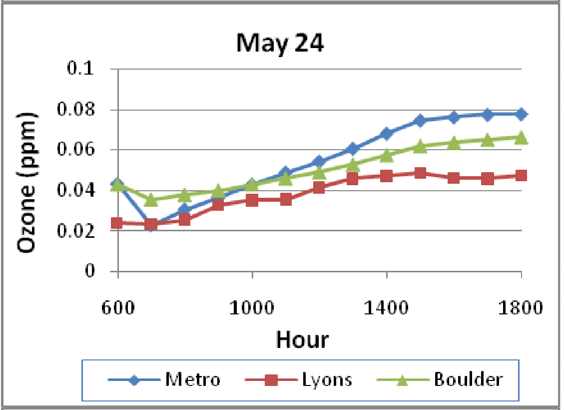
0.06
0.04
0.02
0
600
1000
1400
1800
Hour
Metro
Lyons
Boulder


May 24
Ozone (ppm)
0.1
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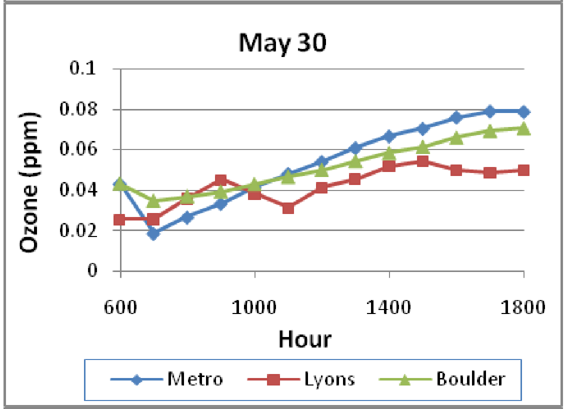
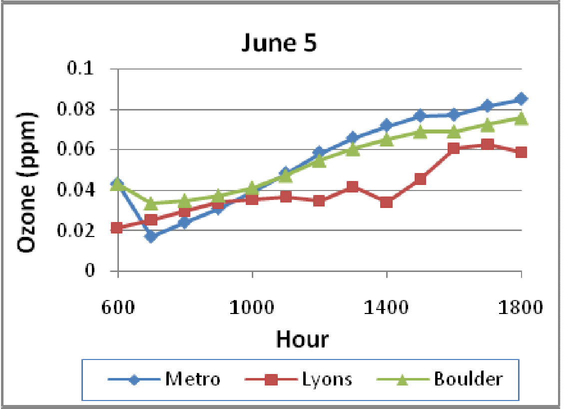
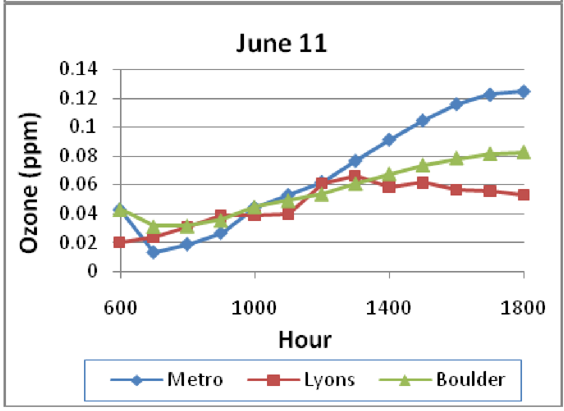
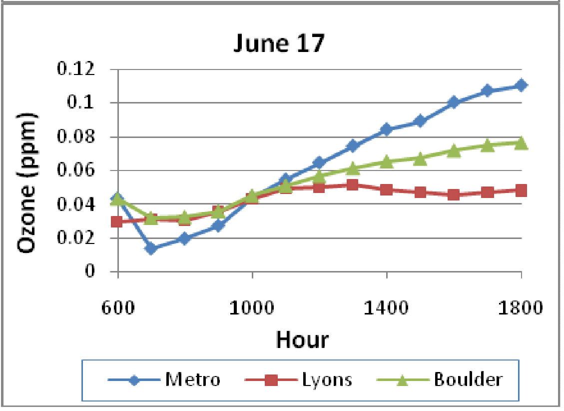
0.06
0.04
0.02
0
600
1000
1400
1800
Hour
Metro
Lyons
Boulder


May 30
Ozone (ppm)
0.1
0.08
0.06
0.04
0.02
0
600
1000
1400
1800
Hour
Metro
Lyons
Boulder


June 5
Ozone (ppm)
0.1
0.08
0.06
0.04
0.02
0
600
1000
1400
1800
Hour
Metro
Lyons
Boulder


June 11
Ozone (ppm)
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
600
1000
1400
1800
Hour
Metro
Lyons
Boulder


June 17
Ozone (ppm)
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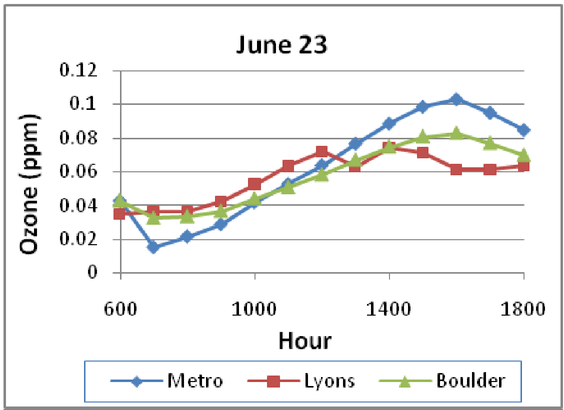
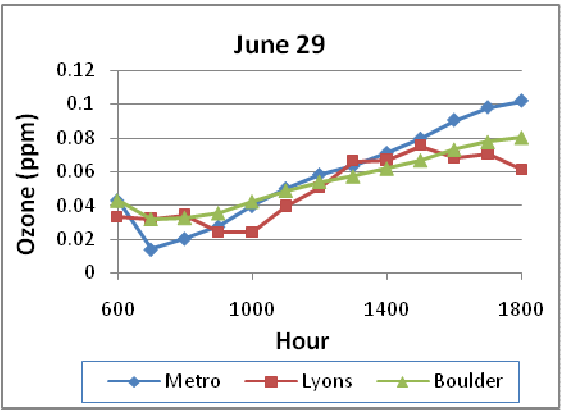
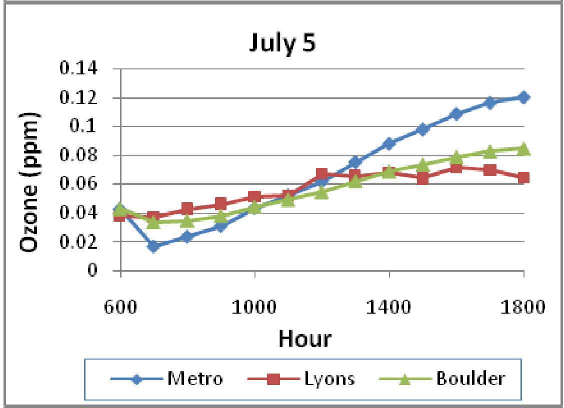
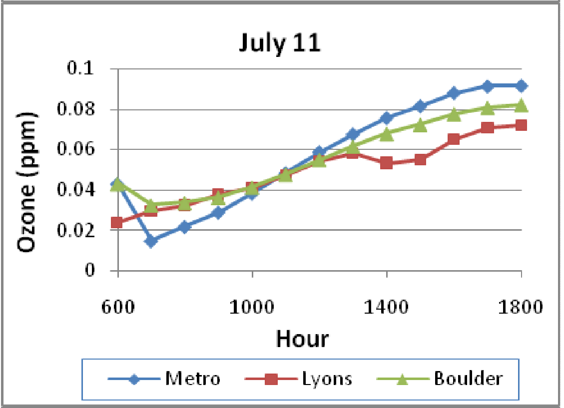
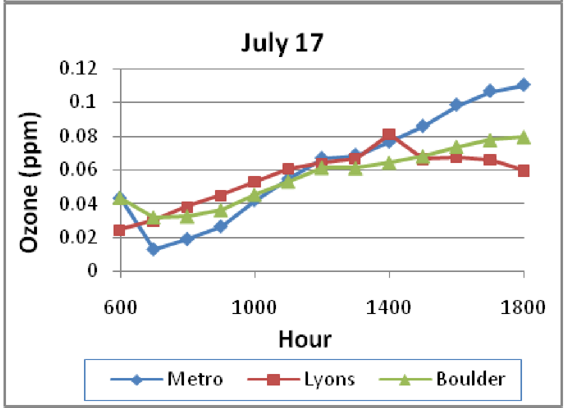
0.1
0.08
0.06
0.04
0.02
0
600
1000
1400
1800
Hour
Metro
Lyons
Boulder

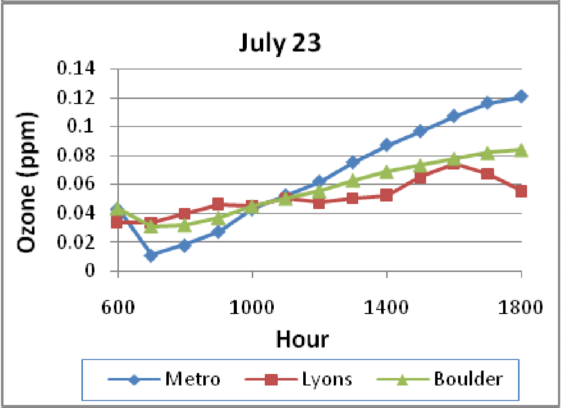

June 23
Ozone (ppm)
0.12
0.1
0.08
0.06
0.04
0.02
0
600
1000
1400
1800
Hour
Metro
Lyons
Boulder

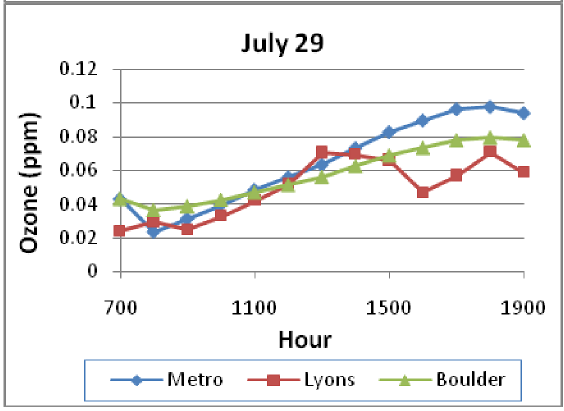

June 29
Ozone (ppm)
0.12
0.1
0.08
0.06
0.04
0.02
0
600
1000
1400
1800
Hour
Metro
Lyons
Boulder

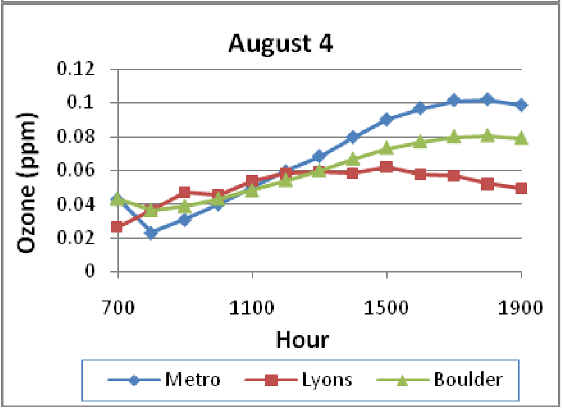

July 5
Ozone (ppm)
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
600
1000
1400
1800
Hour
Metro
Lyons
Boulder


July 11
Ozone (ppm)
0.1
0.08
0.06
0.04
0.02
0
600
1000
1400
1800
Hour
Metro
Lyons
Boulder


July 17
Ozone (ppm)
0.12
0.1
0.08
0.06
0.04
0.02
0
600
1000
1400
1800
Hour
Metro
Lyons
Boulder


July 23
Ozone (ppm)
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
600
1000
1400
1800
Hour
Metro
Lyons
Boulder


July 29
Ozone (ppm)
0.12
0.1
0.08
0.06
0.04
0.02
0
700
1100
1500
1900
Hour
Metro
Lyons
Boulder


August 4
Ozone (ppm)
0.12
0.1
0.08
0.06
0.04
0.02
0
700
1100
1500
1900
Hour
Metro
Lyons
Boulder

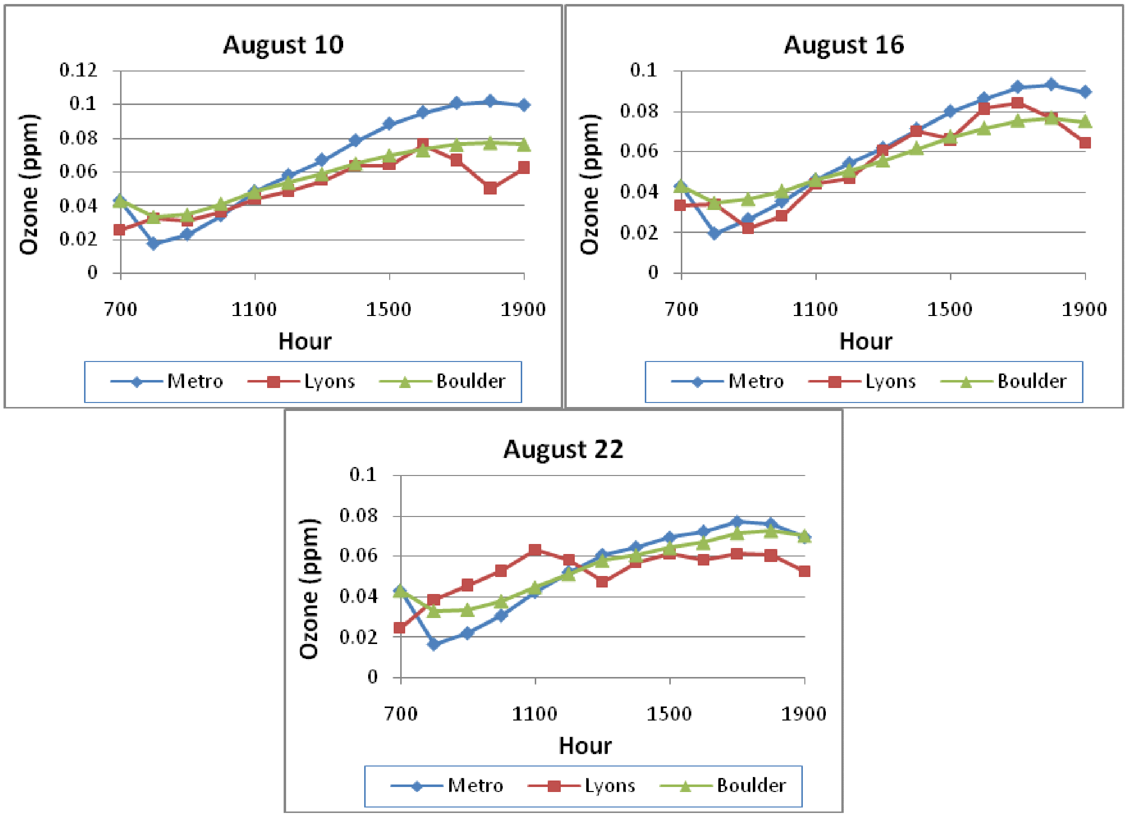


Figure 6.1: Comparison of OZIPR predictions and observed ozone concentrations at Lyons, CO

In general, the ozone predicted by the Boulder case seems the best representative of the measured ozone at Lyons. The model results for the Metro case tend to under-predict morning ozone concentrations, likely due to higher NO_x concentrations leading to increased titration of ozone before photochemical production has become significant. The Metro case also over-predicts afternoon concentrations, by as much as 70 ppb on June 11, when ozone concentration predicted by the Metro model rose to 125 ppb. This over-predicting trend is due to the significantly higher VOC and NO_x concentrations for the Metro case, which lead to much greater ozone production. The bias values in Table 6.1 reveal that the afternoon over-prediction by the Metro case is more significant than the morning under-prediction with positive biases consistently larger than those for the Boulder case. The Root Mean Square Error (RMSE) further reveals that the Boulder case is more representative of the measured results at Lyons with significantly smaller values than for the Metro case. August 16 is one possible exception to this trend, where the performance statistics for the Metro case were not much worse than for the Boulder case. This result suggests that on this day, winds may have been carrying air from the Denver area to Boulder County. Correlation coefficients for the two model cases are similar. This is an expected result as the OZIPR model prediction of ozone formation generally follows a similar shape of increase throughout the day with the same meteorological conditions.

Table 6.1: Model performance statics for ozone, comparing predictions with values observed at Lyons, CO

	Bias Metro (ppm)	Bias Boulder (ppm)	RMSE Metro (ppm)	RMSE Boulder (ppm)	Correl Coeff Metro	Correl Coeff Boulder
6-May	0.0131	0.0102	0.0168	0.0114	0.92	0.84
12-May	0.0053	0.0031	0.0175	0.0080	0.90	0.87
18-May	0.0079	0.0037	0.0186	0.0076	0.91	0.90
24-May	0.0162	0.0122	0.0195	0.0129	0.96	0.93
30-May	0.0112	0.0092	0.0178	0.0118	0.82	0.80
5-Jun	0.0149	0.0136	0.0207	0.0159	0.83	0.84
11-Jun	0.0225	0.0089	0.0375	0.0145	0.78	0.78
17-Jun	0.0218	0.0119	0.0350	0.0162	0.78	0.80
23-Jun	0.0064	0.0011	0.0216	0.0105	0.83	0.82
29-Jun	0.0085	0.0042	0.0179	0.0099	0.86	0.87
5-Jul	0.0112	0.0003	0.0279	0.0095	0.89	0.89
11-Jul	0.0074	0.0058	0.0158	0.0085	0.97	0.96
17-Jul	0.0055	-0.0016	0.0237	0.0098	0.79	0.81
23-Jul	0.0159	0.0058	0.0318	0.0120	0.87	0.86
29-Jul	0.0148	0.0078	0.0222	0.0137	0.77	0.74
4-Aug	0.0171	0.0086	0.0292	0.0157	0.64	0.60
10-Aug	0.0133	0.0046	0.0253	0.0111	0.77	0.77
16-Aug	0.0064	0.0011	0.0113	0.0079	0.94	0.94
22-Aug	-0.0003	0.0005	0.0166	0.0114	0.68	0.61

For several of the days (May 6, May 24, May 30, June 5, July 29, August 4, August 22) both the Boulder and Metro cases significantly over-predicted the measured ozone concentrations. These were days with significant cloud cover, which decreases the amount of photochemical radiation present to contribute to ozone formation. The OZIPR model is designed as a “worst case” prediction of ozone concentration, and always assumes full sun. Consequently, it is to be expected that on significantly cloudy days, the model will over estimate the rate of ozone photochemistry. A method to adjust for this cloud cover was tested, and the results are discussed later in this report.

The Boulder case generally traced the measured ozone concentration at Lyons quite well, especially before 2 pm, as evidenced by the low bias and RMSE values in Table 6.1. This result indicates that the OZIPR model with the parameters selected is able to represent ozone production in Boulder County with reasonable accuracy. In the late afternoon, there is frequently a drop in ozone, or in production rate, for the measured results at Lyons which does not appear in the modeled results, reflected in the consistently positive biases. This is most likely due to afternoon thunderclouds which decrease photochemical radiation, and possible thundershowers which can lead to wet scavenging of ozone. On those days with only clouds in the last few hours of the day, the average daily cloud cover was not enough to model it as a cloudy day, but it causes a significant effect during those cloudy hours. An ability to account for hourly cloud cover would result in a great improvement to the accuracy of the OZIPR model.

Although every effort was made to obtain the most accurate data possible for all the parameters entered into the model, all of these parameters result in sources of uncertainty. In addition to the cloud cover and dry deposition rate sensitivities discussed below, there are a few other parameters that may not have been perfectly representative of the conditions of Boulder County in the summer of 2007. The first is the meteorological data, obtained from either Jefferson County Airport or Denver International Airport. In general, temperatures are very similar across the region, within a few degrees. However, because of the topography of the region, there may have been days for which clouds were hovering around the foothills, decreasing the sunlight in Boulder County, which were not recorded at the meteorological stations used for this study. This is mostly only an issue in considering the cloud cover adjustment, however. Relying upon VOC measurements at the NREL monitoring site is another case where the alternate location may not be a perfect match with conditions in Boulder County. Although the NREL site in Golden is the most likely to be similar to Boulder County from the CDPHE monitoring site choices available, the VOC sources are certainly somewhat different. This affects both background VOC concentrations and reactivities for the model. Similarly, use of NO_x data from the Erie tower, just east of Boulder County, may not be perfectly representative of Boulder County background air. Fortunately, the OZIPR model is not highly sensitive to initial NO_x or VOC concentrations. There is also plenty of room for error in the calculation of VOC reactivities and the VOC scaling approach used to calculate background concentrations and reactivities at Niwot Ridge. Possible inaccuracies in these calculations include the assumption that 6 – 9 am averages are representative of pure emissions, the limited number of species available to represent each class, and the treatment of unidentified compounds. However, given the data available, the approach used provided the most reasonable values possible.

6.1.2 Deposition Sensitivity Test Results

Sensitivity tests were performed with respect to the deposition velocities of the six compounds for which deposition rates were specified: NO_2, O_3, HNO_3, H_2O_2, PAN, and HCHO. For the sensitivity analysis, the deposition rate of each compound was individually varied to ½ and 2 times the average value used in the base case. The sensitivity was tested for two days, July 5 and May 24; the maximum ozone predicted using the base deposition rates for these two days were 85 and 66 ppb, respectively. The Boulder case parameters were used for the deposition sensitivity tests.

The deposition rate of ozone itself was the only rate that had a significant effect on ozone concentrations predicted by the model. The variations of NO_2 and PAN caused less than 0.5% difference in the predicted ozone concentrations and H_2O_2 and HNO_3 deposition rate changes affected the ozone outcome by less than 0.1%. Ozone had a slightly more noticeable dependence on the deposition rate of HCHO, which caused a maximum of 1.3% change in ozone concentration.

Changing the ozone deposition rate had a greater effect on the ozone concentrations predicted on July 5 (Figure 6.2), which was the higher ozone day of the two days modeled.

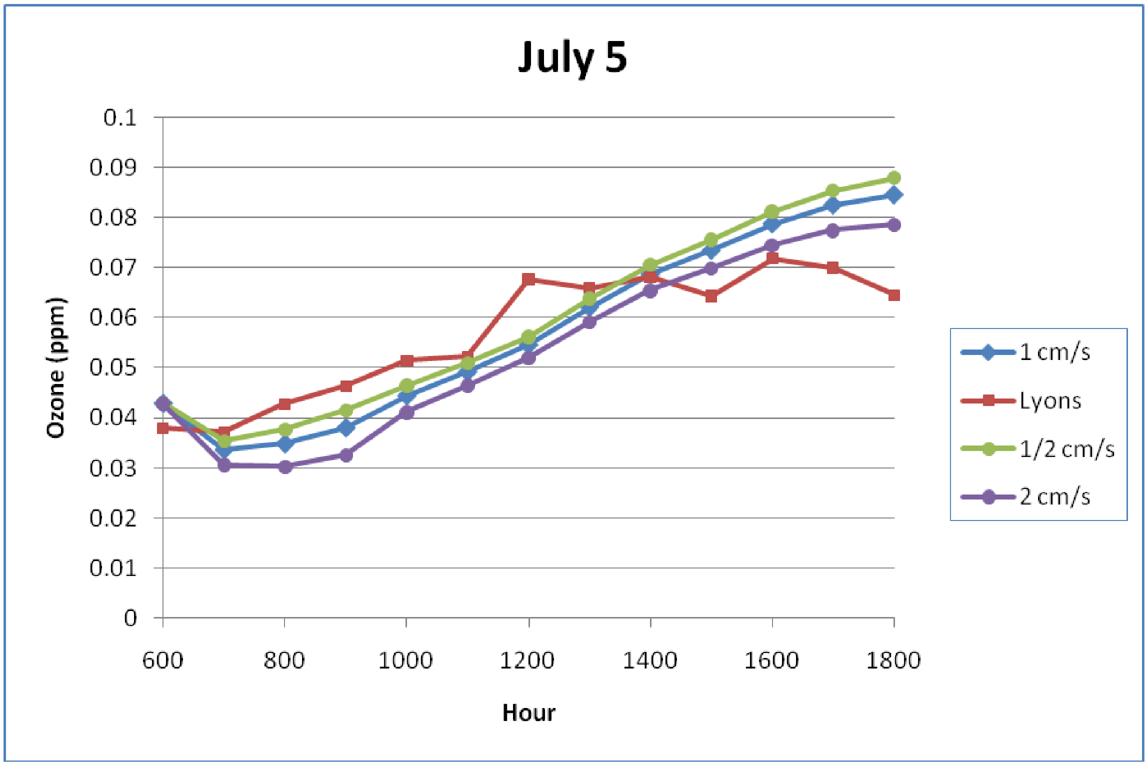


Figure 6.2: Sensitivity of predicted ozone concentrations on July 5 to changes in ozone deposition rates and comparison of to observed concentrations at Lyons, CO

The 9:00 hour had the largest change, an 8.7% (3.3 ppb) increase relative to the base case for the 0.5 cm/s deposition rate and a 14.4% (5.5 ppb) relative decrease for the 2 cm/s deposition rate.

On May 24 (Figure 6.3), the 9:00 hour again showed the greatest percentage changes in predicted ozone concentration, an increase of 5.2% (2.1 ppb) for the 0.5 cm/s deposition rate and a decrease of 9.2% (3.7 ppb) for the 2 cm/s deposition rate. Because May 24th was a cloudy day, even the 2 cm/s deposition rate overpredicted the measured ozone concentration.

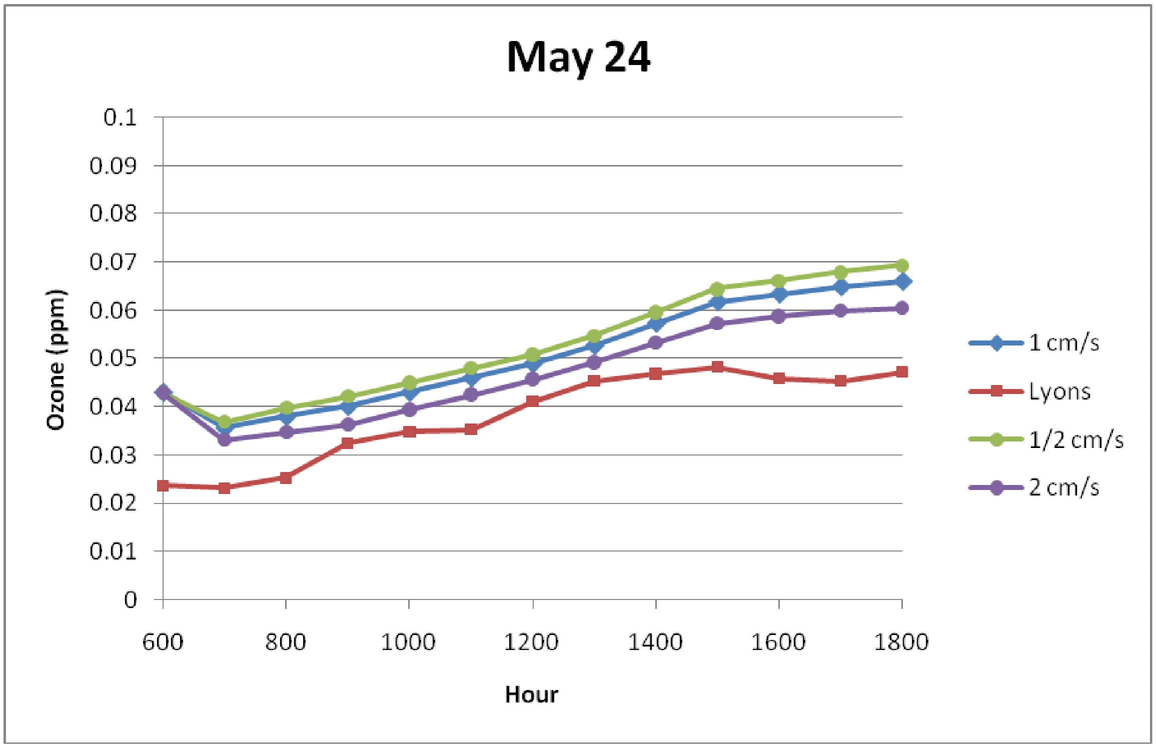


Figure 6.3: Sensitivity of predicted ozone concentrations on May 24 to changes in ozone deposition rates and comparison of to observed concentrations at Lyons, CO

July 5 was hot and dry, while May 24 was cooler with high humidity. The mixing layer depths were relatively similar on the two days, with July 5 having just 16% higher boundary layer rise. The more significant ozone depletion by dry deposition on July 5 may be due to the lower relative humidity on that morning, leading to decreased ozone formation. Humidity increases the rate of ozone formation reactions. In the early morning, before the zenith angle becomes large, the higher relative humidity on May 24 apparently outweighs its lower temperature, allowing for more rapid ozone formation than the morning of July 5.

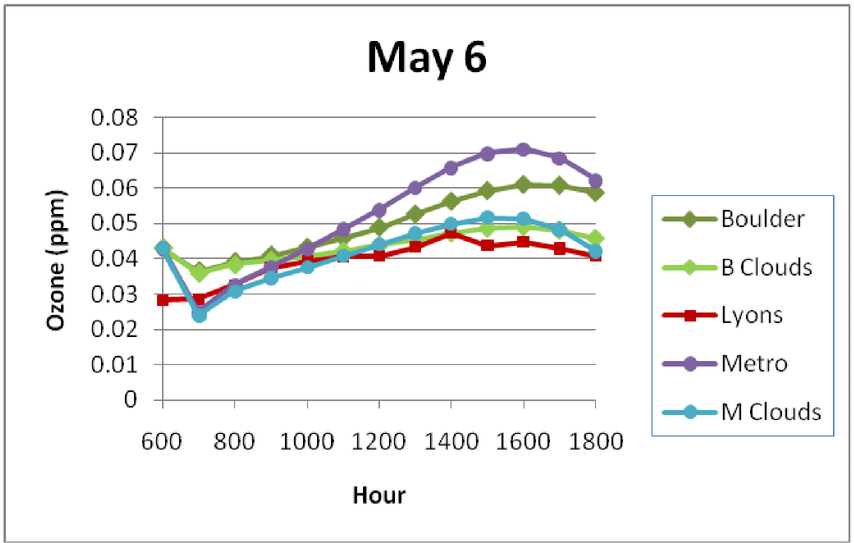
It is probable that dry deposition rates for all species decrease in Boulder County throughout the summer because drier soil conditions lead to decreased uptake through leaf stomata. Based on this deposition sensitivity test, ozone removal by dry deposition may be under-predicted in May and over-predicted in August by as much as 5 – 10% because of the average deposition values used in the model.

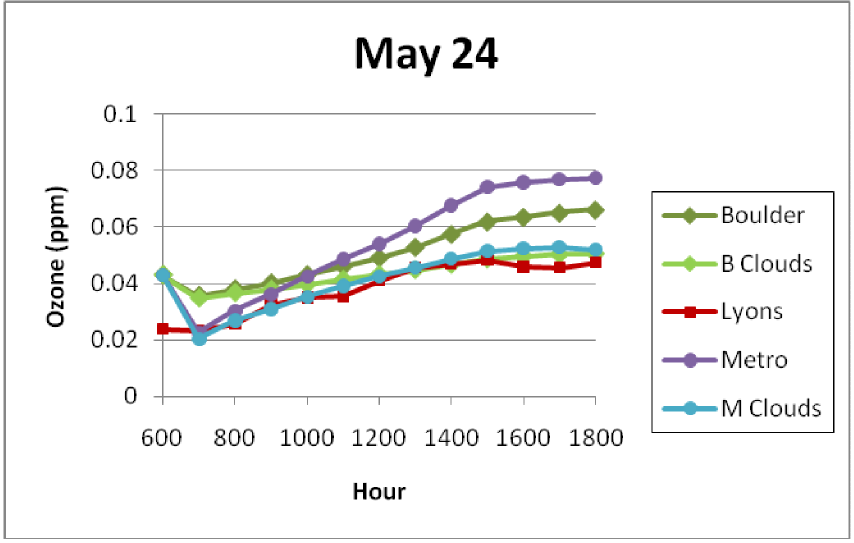
6.1.3 Cloud Cover Adjustment Results for Ozone

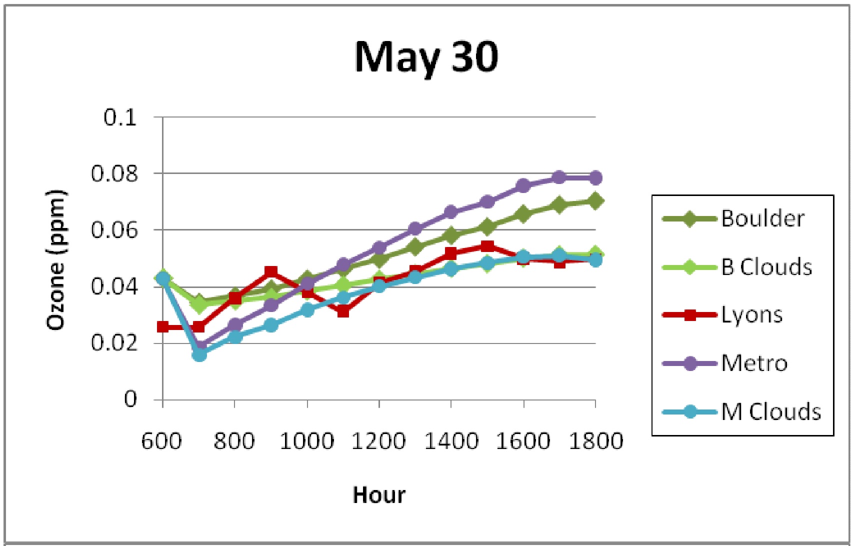
A method for adjusting the photolysis rates based on cloud cover was tested for the seven days of the study that had significant cloud cover; the adjustment was performed for both the Boulder and Metro cases. The cloud cover adjustment was accomplished by reducing the base photolysis rates by an amount appropriate to the average percentage cloud cover for the day. Because photolysis rates versus zenith angle are constants in the OZIPR model, it was not possible to make an hourly cloud cover adjustment.

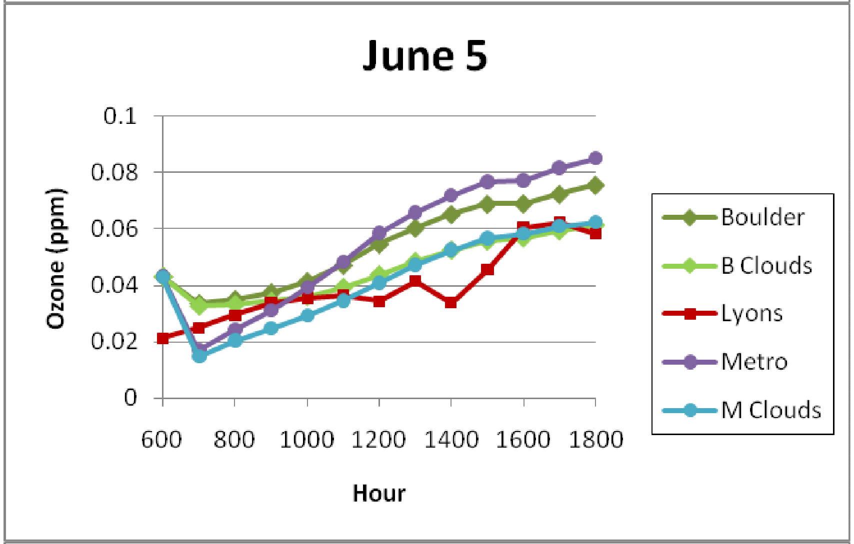
The cloud cover adjustment method proved quite successful, reducing the predicted ozone concentrations by a reasonable amount. Ozone concentrations predicted by the model were reduced by as much as 23 ppb for the Boulder case and 43 ppb for the Metro case on the cloudiest days. The greater decrease for the Metro case is evidence of the fact that when photochemical production is limited, reactions leading to the destruction of ozone compete more strongly in highly polluted areas.

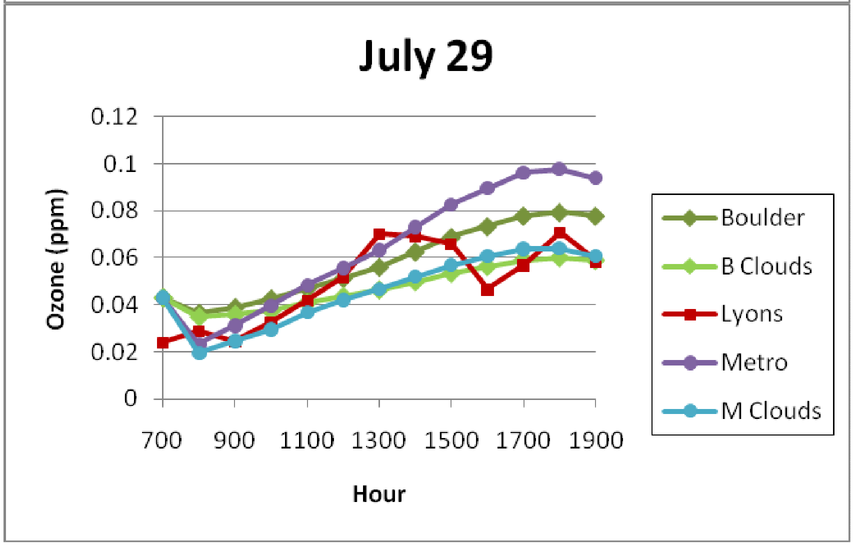
The seven days for which the cloud cover adjustment was tested are shown in Figure 6.4. Base and cloud adjusted model results are shown for Boulder and Metro cases, as well as the measured ozone concentrations at Lyons for comparison.






May 30
Ozone (ppm)
0.1
0.08
0.06
0.04
0.02
0
600
800
1000
1200
1400
1600
1800
Hour
Boulder
B Clouds
Lyons
Metro
M Clouds


June 5
Ozone (ppm)
0.1
0.08
0.06
0.04
0.02
0
600
800
1000
1200
1400
1600
1800
Hour
Boulder
B Clouds
Lyons
Metro
M Clouds


July 29
Ozone (ppm)
0.12
0.1
0.08
0.06
0.04
0.02
0
700
900
1100
1300
1500
1700
1900
Hour
Boulder
B Clouds
Lyons
Metro
M Clouds

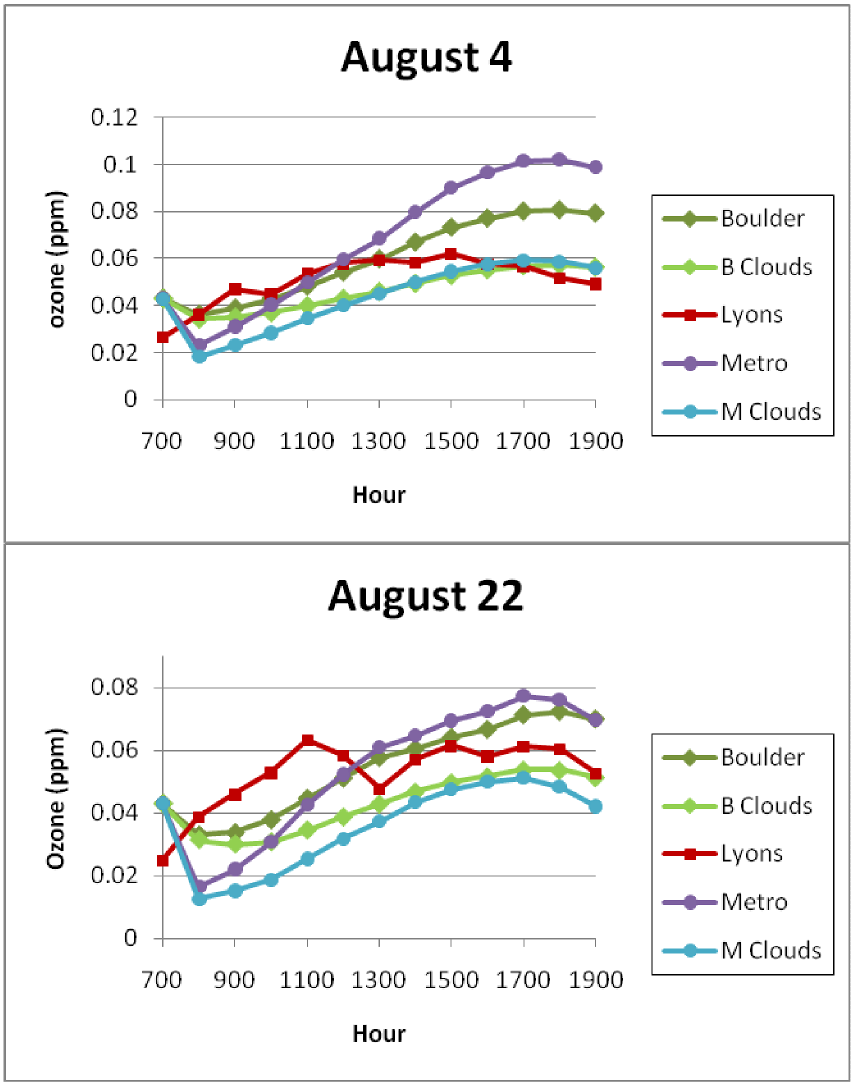


Figure 6.4: Predicted ozone concentrations with cloud cover adjustment and comparison to concentrations observed at Lyons, CO

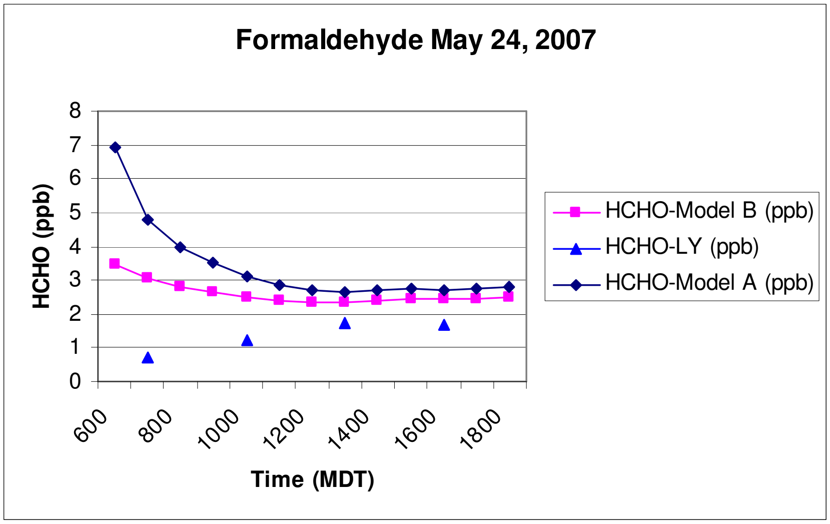
With the exception of August 22, the cloud cover adjusted results for both the Boulder and Metro cases are clearly a better fit to the measured results than either of the full-sun model results. On August 22, the measured ozone lies between the cloud-adjusted and full-sun models. This could be evidence that the averaged daily cloud cover is not very representative of the true meteorology on this day, which was sunny in the morning and very cloudy after noon. It could also indicate that the NCDC reported cloud cover on this day, which is a subjective parameter, may have in fact overestimated the amount of radiation blocked by the clouds.

On May 6 and May 24, the Metro model with clouds appears to fit the measured ozone results the best. On May 30, August 4, and August 22, the Boulder model with clouds produces the best agreement. For June 5 and July 29 it is difficult to determine which of the cloud models presents the best fit, with Boulder slightly over-predicting and Metro slightly under-predicting the ozone measured at Lyons. These results suggest that on certain days, the concentrations of ozone precursors in Boulder County may be more representative of a pollution plume carried from the Metro area than of emissions from Boulder County itself.

6.1.4 Model Results for Carbonyls

The OZIPR model was designed to simulate ozone production. As part of its description of the gas-phase chemistry of ozone formation, the model incorporates photochemical production and loss of formaldehyde (HCHO) and acetaldehyde (ALD2), which are intermediates in ozone chemistry. Results for these carbonyl species were also output from the model runs described above, and were compared to carbonyl measurements made as part of this study. Comparisons for the carbonyl compounds were limited to the standard Boulder model case, which assumed the emissions that originate in the modeled region of Boulder County are the ones that contribute to photochemistry in the county. Adjusting for cloud cover had only a modest effect on HCHO concentrations, so only results for the unadjusted model runs are shown here.

Figure 6.5 compares HCHO concentrations predicted with the OZIPR model to concentrations measured at the Lyons site in northern Boulder County, for three spring and summer days when three-hour average carbonyl measurements were made at the Lyons site. In addition to the standard Boulder case with inputs as described in section 3.1 of this report, a modified case was also run with the initial HCHO concentration multiplied by one-half, to examine the influence of this model parameter. As discussed in section 3.1, the concentrations of volatile organic compounds including HCHO in the standard case were estimated from measurements made by CDPHE at the NREL monitoring site in 2003. The standard case is identified as Model A in Figure 6.5 and the case with the reduced HCHO initial condition as Model B. The model results shown in the figure represent hourly average concentrations and are compared with the sequence of four three-hour average concentrations covering the modeled daytime period.



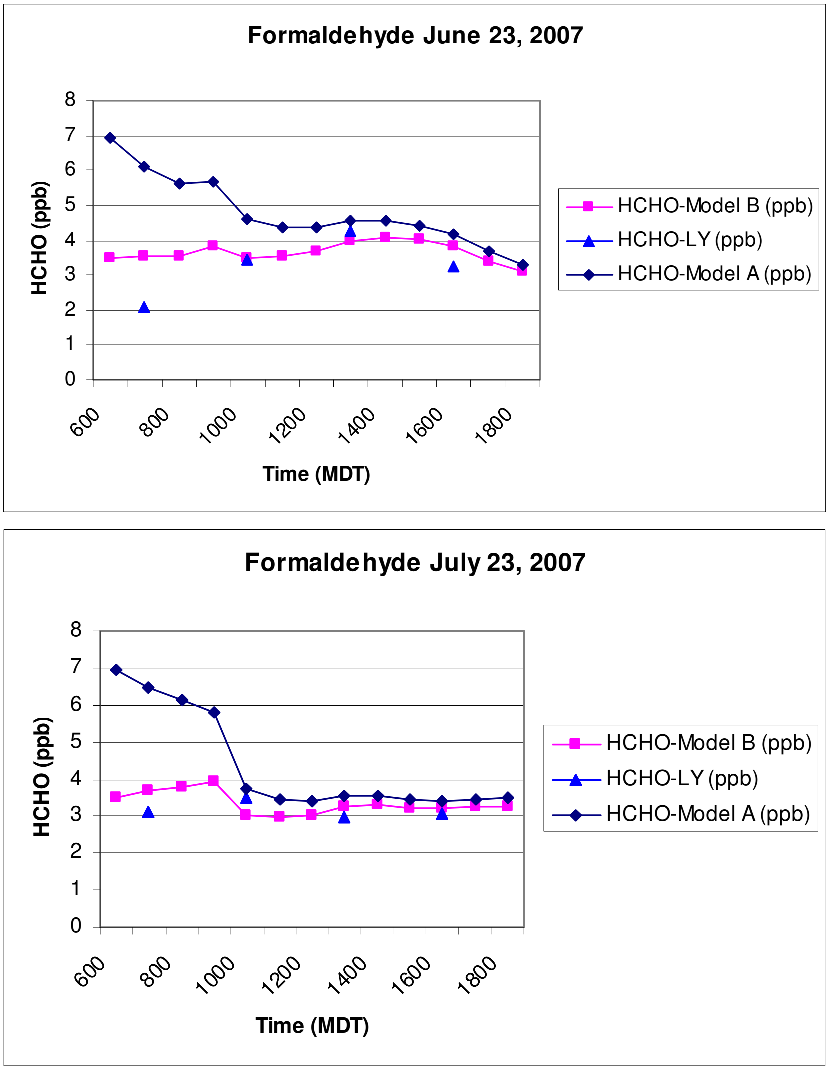


Figure 6.5: Comparison of OZIPR predictions and observed HCHO concentrations at Lyons, CO

Figure 6.5 suggests the initial HCHO concentrations used in the standard Boulder case runs are overestimated, as the agreement between modeled and observed HCHO improves significantly when the initial concentrations are reduced. Compared to the modeled HCHO concentrations, ozone concentrations are much less sensitive to the initial HCHO concentration, because HCHO is only one of the volatile organic compounds that contributes to ozone formation.

Figure 6.6 expands the comparison of modeled and observed HCHO concentrations to additional days and monitoring sites, using the 24-hour average HCHO measurements from this study. An important limitation of the comparison is that 24-hour average measurements are being compared to 12-hour average modeled concentrations, because the OZIPR model can only be used to simulate daytime pollutant concentrations. Considering all of the 3-hour average HCHO data obtained for the months of May, June, July and August, the average measured ratio of daytime (6 a.m. –

6 p.m.) HCHO concentrations to 24-hour average concentrations is about 1.2, so based on this observation the modeled daytime results would be expected to be about 20% higher than 24-hour average values.

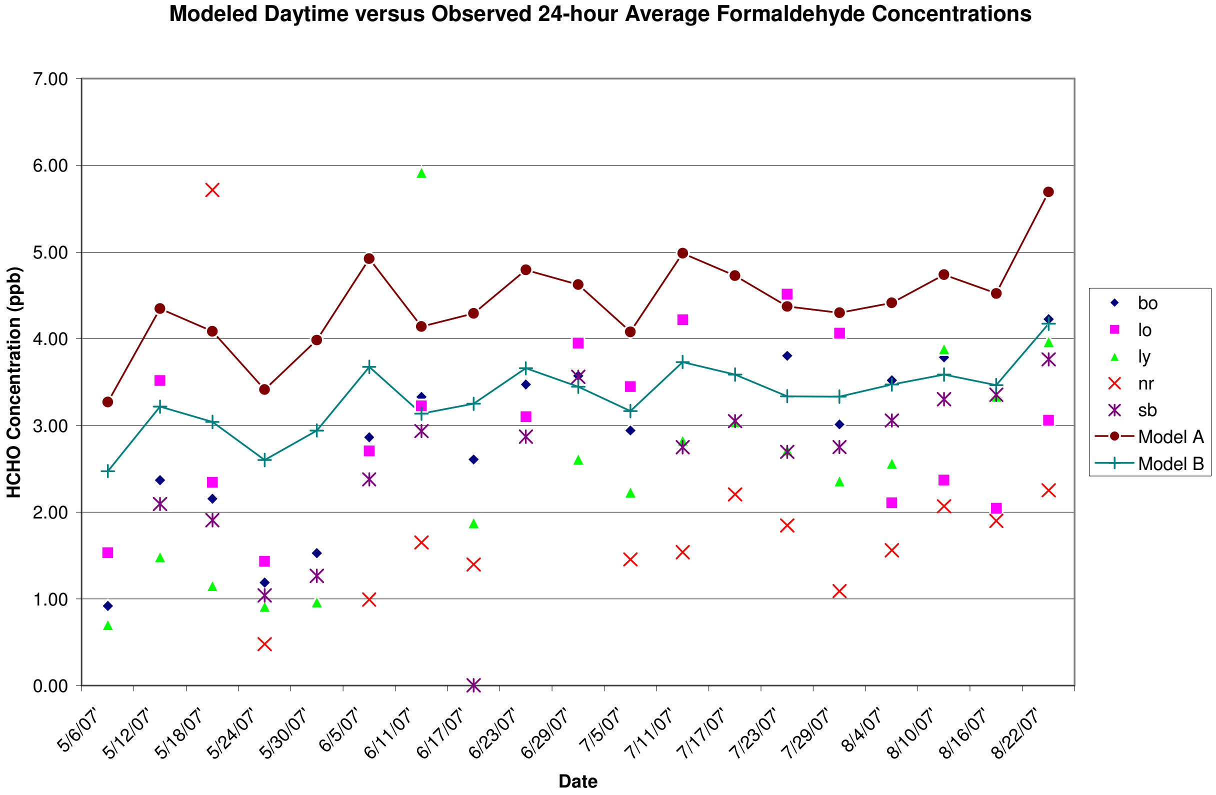
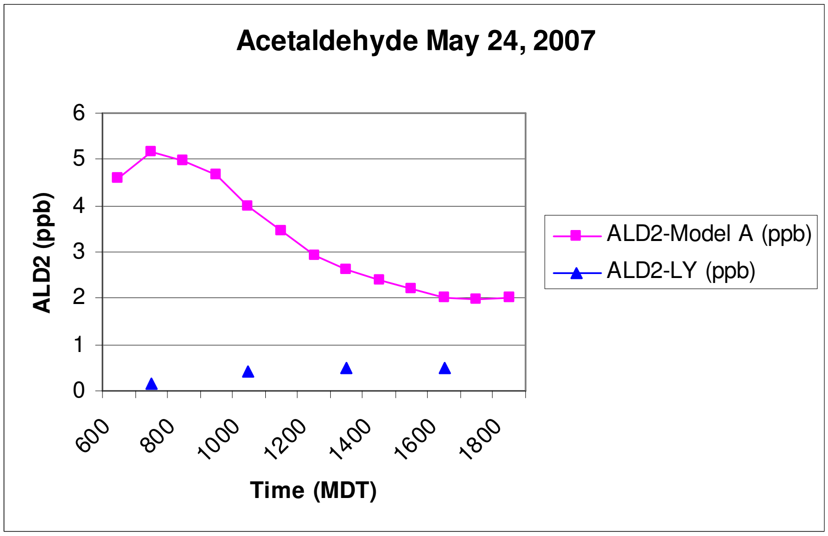
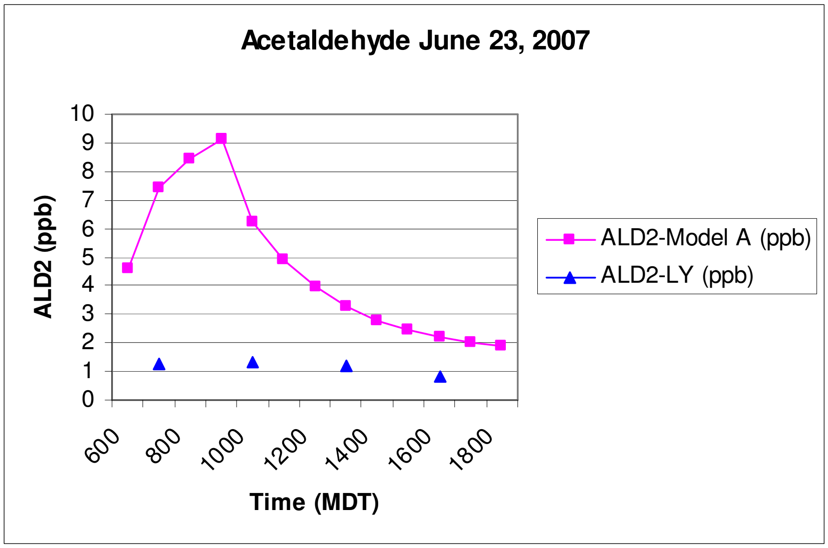


Figure 6.6: Comparison of OZIPR predictions and observed HCHO concentrations at all monitoring sites. Bo: Boulder; LO: Longmont; LY: Lyons; NR: Niwot Ridge; SB: South Boulder

As shown in Figure 6.6, model B with the reduced HCHO initial condition predicts HCHO concentrations that are within the range of the measured concentrations on most days, and are skewed toward the upper end of the observations as expected from the daytime versus 24-hour average comparison. Model A generally overestimates the HCHO concentrations.

Figure 6.7 compares acetaldehyde (ALD2) concentrations predicted with the OZIPR model to concentrations measured at the Lyons site in northern Boulder County, for the same three days for which HCHO comparisons are presented in Figure 6.5. The model results shown for ALD2 are only for the standard Boulder case, with the original initial concentrations of ALD2 (and HCHO) as described in section 3.1. As in Figure 6.5, model results shown in Figure 6.7 represent hourly average concentrations and are compared with the sequence of four three-hour average concentrations covering the daytime period. Figure 6.7 indicates that the model predicts much higher acetaldehyde concentrations for eastern Boulder County than observed at the Lyons monitoring sites on all three days. Overestimated initial concentrations in the model could account for some of the discrepancy, but because the difference persists throughout the day this does not appear to be the primary explanation.





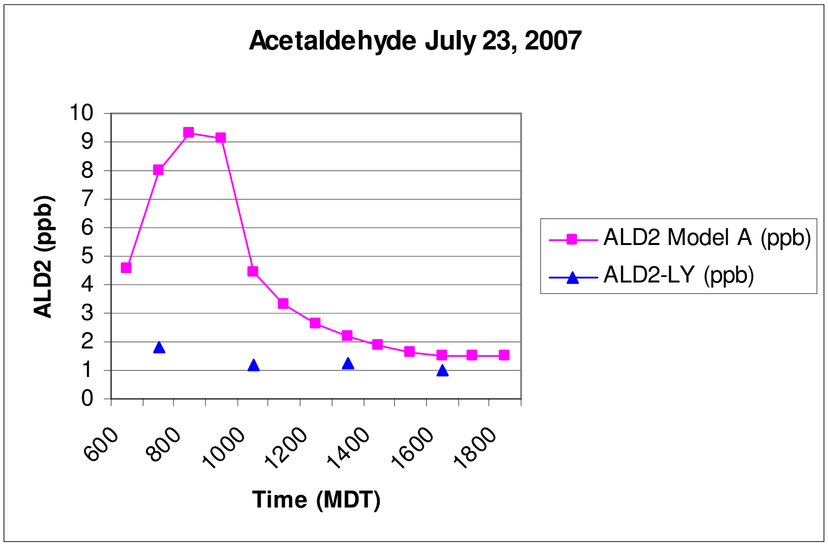


Figure 6.7: Comparison of OZIPR predictions and observed acetaldehyde concentrations at Lyons, CO

Figure 6.8 compares modeled acetaldehyde concentrations with observed concentrations from all of the monitoring sites for all of the days modeled with OZIPR. As with HCHO, an important limitation of the comparison for acetaldehyde is that 24-hour average measurements are being compared to 12-hour average daytime concentrations from the model. In this case, however, for the months of May, June, July and August, the average measured ratio of daytime (6 a.m. – 6 p.m.) acetaldehyde concentrations to 24-hour average concentrations is 1.05, so the use of different averaging periods should introduce relatively little bias into the comparison. Over the summer, the modeled acetaldehyde concentrations are about a factor of three higher than the average of the concentrations measured at the five Boulder County monitoring sites.

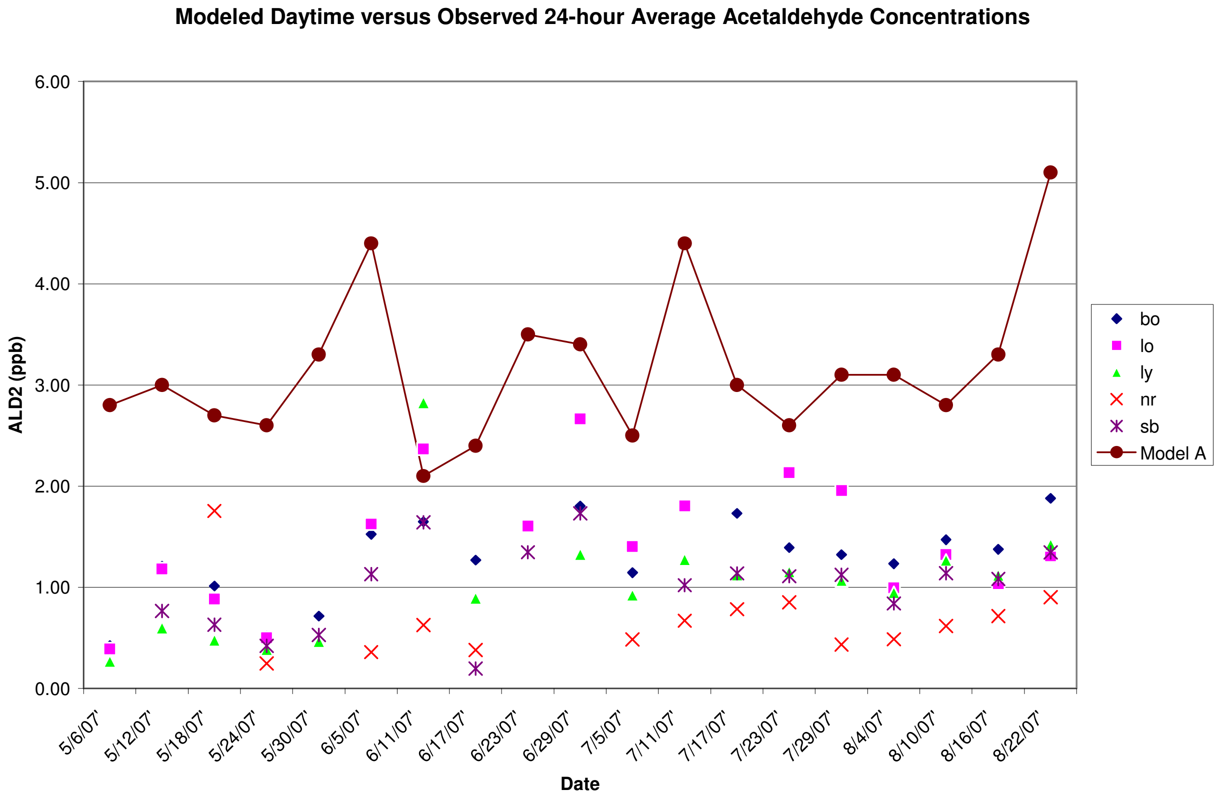


Figure 6.8: Comparison of OZIPR predictions and observed acetaldehyde concentrations at all monitoring sites. BO: Boulder; LO: Longmont; LY: Lyons; NR: Niwot Ridge; SB: South Boulder

The difference between the modeled and observed acetaldehyde concentrations could be due to overestimation of acetaldehyde in the initial conditions and aloft concentrations used in the model, or overestimation of emissions of acetaldehyde or its precursors. As discussed in the next chapter, acetaldehyde concentrations measured in this study are markedly lower than those reported in other studies of carbonyl concentrations in the Denver metropolitan area. We relied on these earlier observational studies in deriving inputs to the OZIPR model; they may not accurately represent conditions in Boulder County in 2007. Another possible explanation of the discrepancy is that acetaldehyde concentrations measured in the BCPH study are too low. However, as discussed in chapter 5, quality assurance checks performed throughout the study provide confidence in the measurements made in the BCPH study.

6.2 Dispersion Modeling Results (Contributed by Gregg Thomas and Sabrina Williams, Denver Department of Environmental Health)

Annual average predicted concentrations were generated using AERMOD for benzene, toluene, ethylbenzene, total xylenes, formaldehyde, acetaldehyde, n-butane, n-pentane, and n-hexane. These same compounds were measured and detected frequently in the

Boulder air toxics study. The Niwot Ridge monitoring location was not in the AERMOD model domain and is therefore not included in this discussion.

Caveats must be applied when comparing predicted and observed concentrations. Notable caveats include the following:

1. Predicted concentrations using emissions inventories for the years 2002 (nonroad mobile and area sources), 2005 (onroad mobile sources), and 2006 (point sources and oil and gas exploration) were compared with observations collected from March 2007 through February 2008. 2005 emissions from non-road mobile and area sources were likely less than 2002, and 2007-08 emissions (if we were to match the Boulder air toxics monitoring timeline) were less than 2005 emissions. An estimated impact of this effect is described below.

2. Meteorological data from 2002-2006 was used to compare with 2007-2008 data. The meteorological data was also collected in Denver, 26 miles southeast of Boulder. This is not expected to influence annual average concentrations to a significant degree, though there can be significant differences on individual days.

3. For n-butane and n-pentane, emissions estimates used with AERMOD reflect only oil and gas emissions, not those from other sources such as motor vehicles.

Air toxics monitoring has been conducted for the past decade as part of the remediation efforts at the Rocky Mountain Arsenal CERCLA site near Commerce City, CO. To understand potential impacts from off-site sources, benzene and toluene were routinely monitored. To understand the magnitude of cumulative emissions reductions over time, air toxics monitoring data from 2002, 2005, and 2007 are compared at two neighboring community sites.

In Commerce City, benzene decreased 29 percent between 2002 and 2007, and toluene decreased 14 percent. In Montbello (Denver), benzene and toluene decreased 40 percent and 49 percent, respectively between 2002 and 2007. These are significant reductions in a short time frame. Between 2005 and 2007, benzene decreased by 20 percent at each monitor. Regarding caveat #1 above, the impact of comparing circa 2005 emissions with 2007 Boulder air toxics data is that AERMOD was shown to under predict to a lesser degree than would otherwise occur if using an “apples-to-apples” inventory year. Unfortunately, peer-reviewed inventories tend to lag by up to three years.

Past model validation of the Denver air toxics assessment using 1996 and 2002 emissions inventories (with apples-to-apples monitoring data), revealed that in the urban core (but not Boulder), ISCST3 and AERMOD both under predicted by a factor of 1.5 – 2.5 for pollutants with medium-high confidence, such as benzene and carbon monoxide (Thomas, 2004; Thomas et al., 2007). These pollutants are primarily emitted (65-70%) by onroad mobile sources. More importantly, the models did correctly predict the spatial distribution of pollutants, signifying that the methodology used to develop spatial surrogates was appropriate.

The under prediction bias of the AERMOD and ISC3 was expected due to the fact that neither model has a "memory" of emissions, meaning that pollutants emitted in the previous hour are not carried over to the next as they are advected downwind. Pollution episodes in the Denver-Boulder region are characterized by aged emissions moving back and forth along the Platte River valley combined with "fresh" emissions. A similar under prediction bias was expected for AERMOD when compared with the Boulder air toxics data.

Measured and predicted annual average BTEX concentrations are listed in Table 6.2. For benzene, AERMOD under predicts by a factor of 7-9. For toluene and ethylbenzene AERMOD under predicts by a factor of 7-13. For total xylenes, AERMOD underpredicts by a factor of 12-30. The difference in the degree of under prediction between benzene and the other aromatic compounds may be due to sampling or analytical bias, bias in emissions estimates, or errors in background concentrations assumed in the model. Historical air toxics monitoring data at other locations in the U.S. and vehicle exhaust VOC mass fractions from dynamometer tests generally show a benzene:toluene ratio of roughly 0.5:1, which is lower than the ratio of concentrations monitored in the Boulder County study. Further investigation of this discrepancy may be warranted.

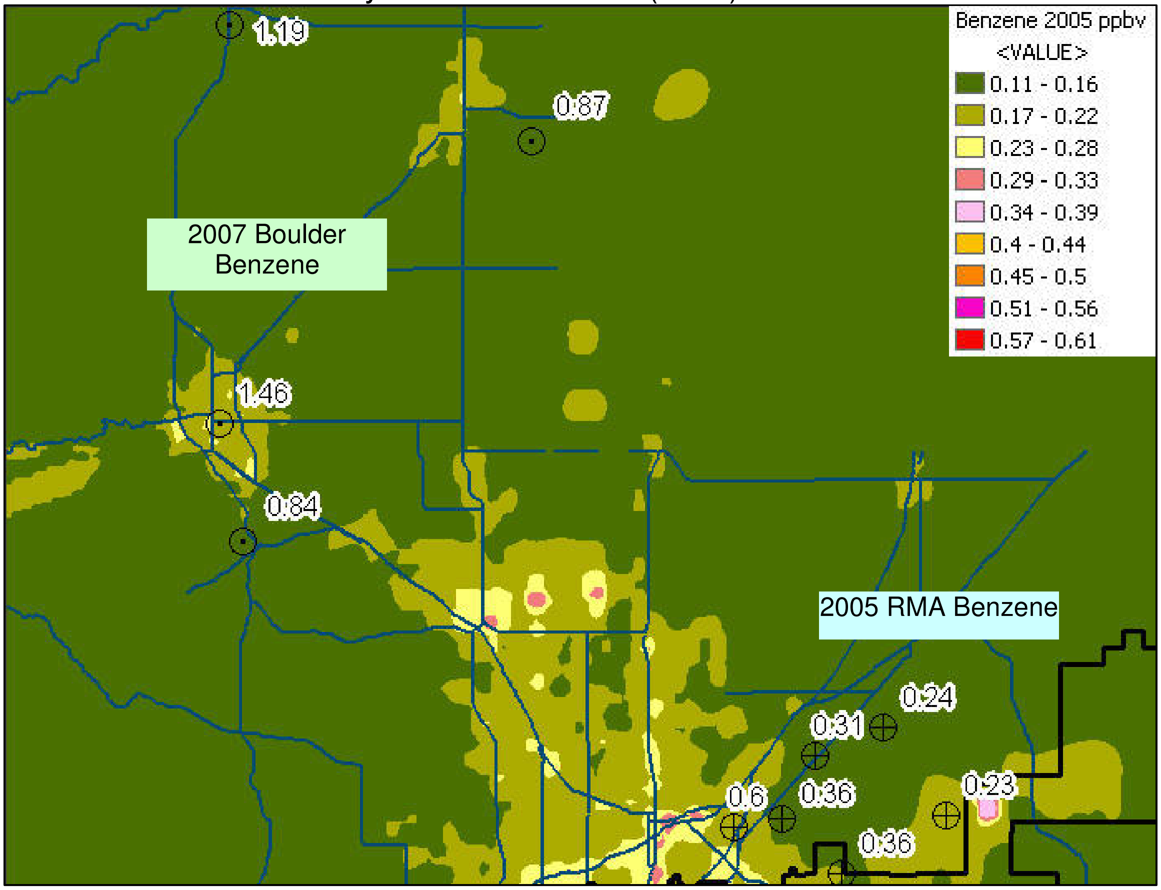
Table 6.2. 2007 observed (obs) and 2005 predicted (AERMOD) BTEX concentrations (ppbV)

Site	Obs Benzene avg	AERMOD Benzene[1] avg	Obs Toluene avg	AERMOD Toluene avg	Obs Ethyl-benzene avg	AERMOD Ethyl-benzene avg	Obs Total Xylenes avg	AERMOD Total Xylenes avg
Boulder Fire Station	1.46	0.20	1.52	0.20	0.21	0.03	0.86	0.03
Longmont	0.87	0.13	0.46	0.04	0.08	0.01	0.25	0.02
Lyons	1.19	0.13	0.20	0.02	0.07	0.01	0.15	0.009
South Boulder	0.84	0.11	0.26	0.02	0.07	0.005	0.19	0.004

[1] Includes regional background of 0.1 ppbv

Figure 6.9 shows AERMOD predicted benzene concentrations with circa 2005 emissions. Observed benzene concentrations are shown for Boulder (2007) and at the Rocky Mountain Arsenal (RMA) CERCLA site (2005). For benzene, AERMOD under predicts at the RMA sites by a factor of 2-3. However, if the regional background for benzene of 0.1 ppbV is excluded, then AERMOD under predicts local benzene concentrations by a factor of 4-8.

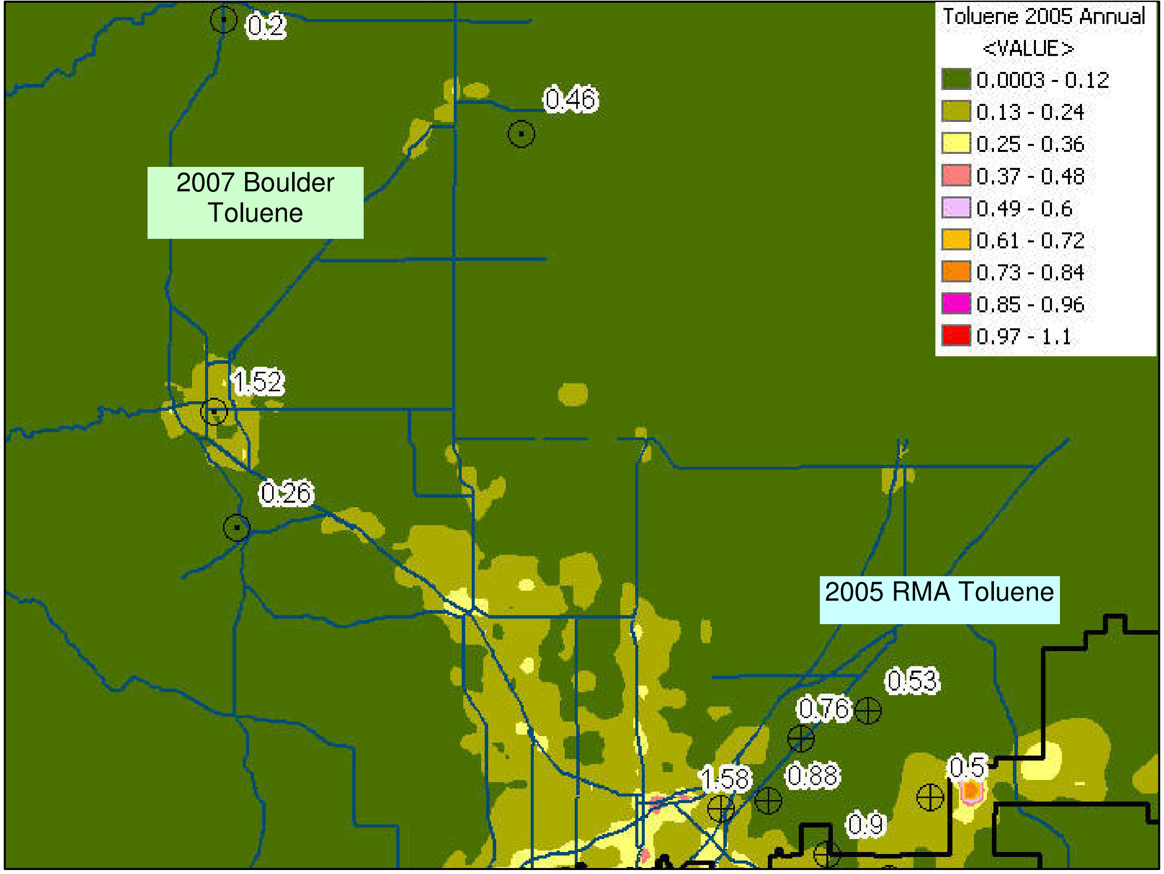
Figure 6.9. Predicted 2005 benzene (color plot) with 2007 Boulder observed benzene and 2005 Rocky Mountain Arsenal (RMA) observed benzene



Including regional background concentrations only for benzene follows the methodology employed in the 1996 (0.15 ppbV), 1999 (0.13 ppbV), and 2002 (0.17 ppbV) National Air Toxics Assessments (NATA). The 2002 NATA, which was out for government agency review in December 2008, now includes background concentrations for toluene of 0.23 ppbV, whereas the 1996 and 1999 NATA had zero background for toluene as assumed in this study. Remote location North American background concentrations listed in McCarthy et al. (2006) are much lower for benzene than assumed in any of the NATAs (0.04 ppbv). McCarthy et al. do not list background concentrations for toluene. DDEH selected a value (0.1 ppbV) for the background concentration of benzene between those given by EPA (1999) and McCarthy et al (2006). A higher value such as that used in the 2002 NATA (0.17 ppbV) would improve predicted to observed ratios, to within a factor of two using the RMA data.

Figure 6.10 shows AERMOD predicted toluene concentrations with circa 2005 emissions and with background concentrations set to zero. Again, observed toluene concentrations are shown for Boulder (2007) and at the RMA CERCLA site (2005). The Boulder toluene data compare well against the RMA data, with relatively high concentrations in downtown Boulder but lower concentrations in the suburban/rural areas. From Table 6.2, toluene is under predicted by AERMOD by a factor of 7-13. Compared to the RMA data in Figure 6.9, AERMOD under predicts by a factor of 6-10. If a regional background toluene concentration of 0.23 ppbV as used in the 2002 NATA was included, AERMOD would appear to under predict by a factor of 3-5.

Figure 6.10: Predicted 2005 toluene (color plot) with 2007 Boulder observed toluene and 2005 Rocky Mountain Arsenal (RMA) observed toluene



Mobile source dominated pollutants will largely resemble Figures 6.9 and 6.10. Formaldehyde and acetaldehyde are primarily emitted by mobile sources, but are also generated via photochemical reactions in the atmosphere. Photochemical modeling studies have estimated that 85-95 percent of ambient formaldehyde/acetaldehyde is formed secondarily, depending on the season. EPA box model studies using the OZIPR model with 1996 emissions for Denver suggest about 87 percent of annual formaldehyde is formed secondarily.

AERMOD was run using the 2005 emissions inventory for formaldehyde and acetaldehyde. The median concentration across the region was then calculated and a multiplier of 6.69 (87 percent / 13 percent) was applied to estimate the secondary contribution for each pollutant. The regional secondary concentration was then added to the primary concentration to generate the results in Table 6.3.

AERMOD, including secondary concentration estimates, under predicts formaldehyde by a factor of about 3 and acetaldehyde by a factor of 5-7. The 1996 and 1999 NATA used a background formaldehyde concentration of 0.2 ppbV, but had a zero background concentration for acetaldehyde. The 1996/1999 NATA background concentration estimates were used for this analysis. The 2002 NATA now uses a background formaldehyde concentration of 1.01 ppbV and a background acetaldehyde concentration of 0.5 ppbV.

If 2002 NATA background concentrations were used in place of the lower 1996/1999 values, total predicted formaldehyde and acetaldehyde concentrations would be within a factor of 1.5 of observed concentrations. In fact, background concentrations dominate the total ambient concentration. This is a significant change, but without documentation to understand how these background concentrations were calculated for different regions of the state, methodology similar to previous years is employed here. It is possible that background estimates for the 2002 NATA are really estimated secondary concentrations.

Table 6.3. 2007 observed (obs) and 2005 predicted (AERMOD + secondary) formaldehyde and acetaldehyde concentrations (ppbV)

Site	Obs Form-aldehyde avg	AERMOD Form-aldehyde avg[1]	Obs Acet-aldehyde avg	AERMOD Acet-aldehyde avg
Boulder Fire Station	2.26	0.70	0.99	0.18
Longmont	1.82	0.60	0.96	0.15
Lyons	1.57	0.60	0.62	0.14
South Boulder	1.63	0.60	0.66	0.14

[1] Includes regional background of 0.2 ppbv

Butane, pentane, and to a lesser degree hexane have significant contributions from the oil and gas exploration sector, and were included in this analysis to examine the spatial distribution of primary pollutants from oil and gas production. For the emissions inventory used in this study, butane and pentane emissions were assumed to be solely attributable to the oil and gas sector. Butane and pentane are components of gasoline and in reality are emitted ubiquitously across the Denver-Boulder region, so the

AERMOD results are expected to underestimate their concentrations. Due primarily to their low toxicity, however, mobile source emissions are not routinely estimated for butane and pentane.

The oil and gas VOC emissions estimates used in this study were estimated for 2006 to support photochemical modeling required for the development of an ozone State Implementation Plan (SIP). VOC emissions were then speciated using data obtained from condensate tank testing conducted in 2002. Table 3.10 lists butane and pentane emissions for 2006. As noted above, zero background concentrations were assumed for butane, pentane, and hexane.

Table 6.4 lists observed and predicted concentrations of butane, pentane, and hexane. For mobile source dominated pollutants like benzene and toluene, where confidence in the inventory is medium to high, AERMOD under predicts by a factor of 2-10. For butane and pentane, AERMOD is under predicting by a factor of 50-100 or more. For hexane, a pollutant with about 50 percent of emissions from mobile sources, AERMOD under predicts by a slightly lower factor of 18-60.

Colorado, since first discovering oil and gas VOC emissions were an important source sector affecting ozone in 2002, has struggled to properly characterize oil and gas VOC emissions. Ozone model performance evaluations using the CAMx photochemical model indicate a large degree of under prediction for oil and gas dominated VOCs, like ethane and butane. Regulations to control oil and gas VOC emissions did go into effect in 2007 that controlled ozone season VOC emissions by 75 percent across the system, versus about 50 percent control in 2006. Accounting for this change would worsen the already poor predicted-to-observed ratios for butane, pentane, and hexane. For the inventories used in this assessment, it is likely that total VOCs from oil and gas are underestimated, as documented by Morris et al. (2008).

Table 6.4. 2007 observed (obs) and 2005-06 predicted (AERMOD) butane, pentane, and hexane concentrations (ppbV)

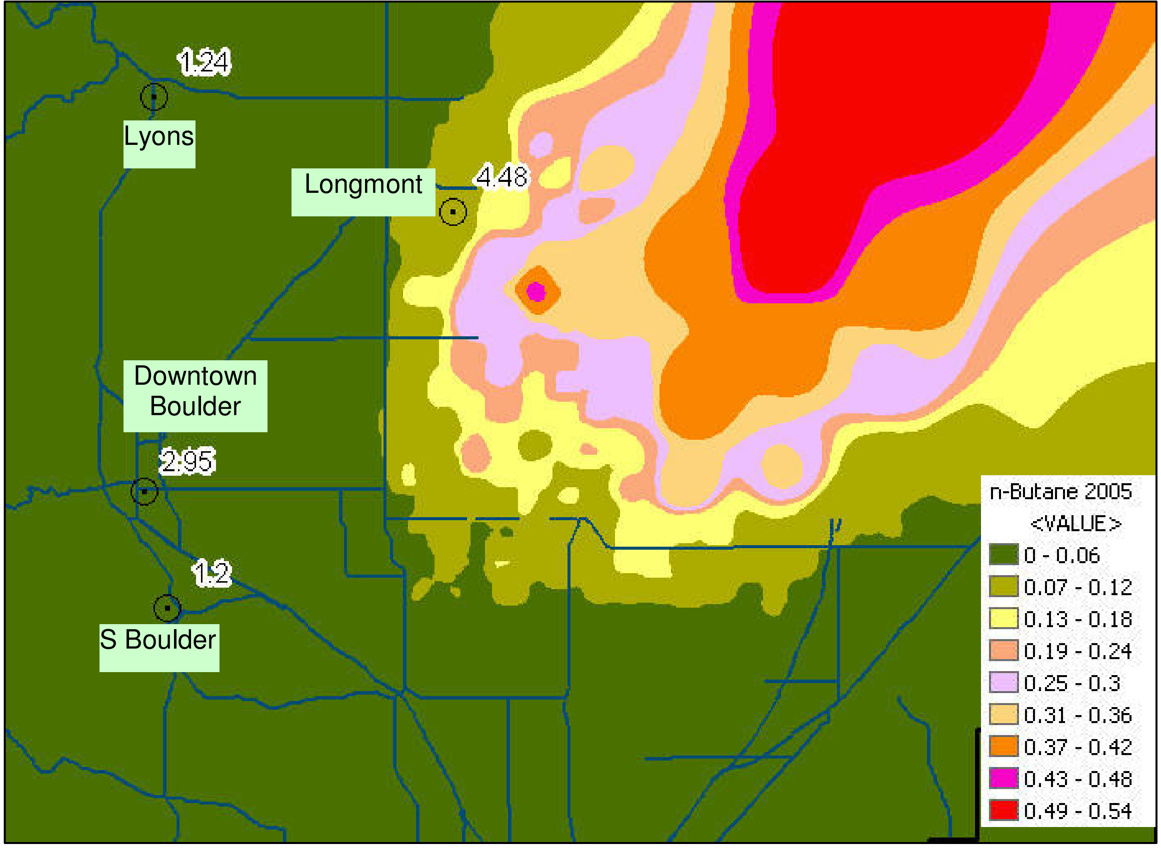
Site	Obs Butane avg	AERMOD Butane avg	Obs Pentane avg	AERMOD Pentane avg	Obs Hexane avg	AERMOD Hexane avg
Boulder Fire Station	2.95	0.002	1.35	<.001	0.71	0.04
Longmont	4.48	0.09	1.66	0.02	0.62	0.01
Lyons	1.24	0.001	0.46	<.001	0.21	0.005
South Boulder	1.20	0.001	0.44	<.001	0.21	0.005

Figure 6.11 shows predicted and observed n-butane concentrations. Notice the sharp difference in spatial distribution from benzene and toluene, which are mobile source dominated. AERMOD annual average concentrations are under predicted by more than a factor of 50. This under prediction error may be due in part to underestimation of background concentrations coming into the area, as well as underestimation of local emissions. The observed concentrations show that eastern Boulder County has the highest concentration. This monitor is on the edge of the Denver-Julesburg basin. In

fact, at several times throughout the sampling campaign, rigs were actively drilling wells within 0.5 miles of this site.

While oil and gas emissions at these apparently large magnitudes are expected to contribute regionally to ambient concentrations, it appears that there is also an un-inventoried mobile source or gasoline component as well, as evidenced by the large spread in concentrations between the downtown Boulder and Lyons or South Boulder sites.

Figure 6.11: Predicted 2006 n-Butane (color plot) with 2007 Boulder observed n-Butane (ppbV)



6.2.1 Dispersion Modeling Summary

For pollutants where we have medium to high confidence in the emissions inventories, AERMOD under predicts by a factor of 2-10 across the Denver-Boulder region. Pending issues with estimates of regional background concentrations could improve predicted-to-observed ratios. For most pollutants, the predicted spatial distribution of emissions seems to match the distribution of observed concentrations.

Predicted butane, pentane, and hexane concentrations match poorly with observed concentrations. AERMOD under predicts by a factor of 50 or more. This reflects the omission of mobile source emissions of butane and pentane from the modeling inventory, but may also indicate a significant under estimation of VOC emissions from oil and gas sources and underestimation of a regional background contribution.

Finally, circa 2005 emissions inventories were used in this assessment. However, observed concentrations from the RMA CERCLA site between 2002 and 2007 showed significant decreases in mobile source pollutants. Comparing 2005 emissions with 2007 observations in Boulder is expected to show better predicted-to-observed ratios than would otherwise be seen if comparing “apples-to-apples.” That is why the 2005 RMA data were of value in performing model-to-monitor comparisons.

7 DATA ANALYSIS

7.1 SEASONAL VARIATIONS

7.1.1 Carbonyls

Carbonyls are introduced into the atmosphere from both primary emissions and secondary formation. Figure 7.1 shows a time series plot of 24-hour formaldehyde values across all five sites. Increased concentrations for all carbonyls were observed during summer months, suggesting secondary formation. Secondary formation is enhanced by increased sunlight and solar radiation that is present during summer months. Overall, the Boulder and Longmont sites had the greatest concentrations of carbonyls. South Boulder and Lyons had similar concentrations throughout the study. Niwot Ridge typically had the lowest carbonyl values, with the exception of acetone.

Figure 7.1: Time series plot of 24-hour formaldehyde samples taken at all sites

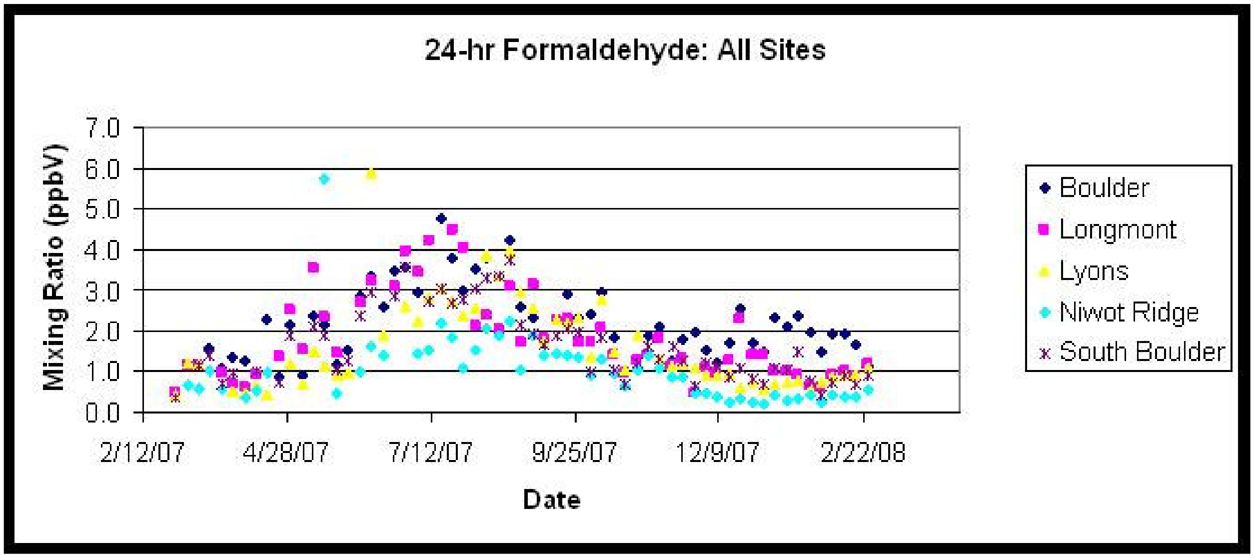
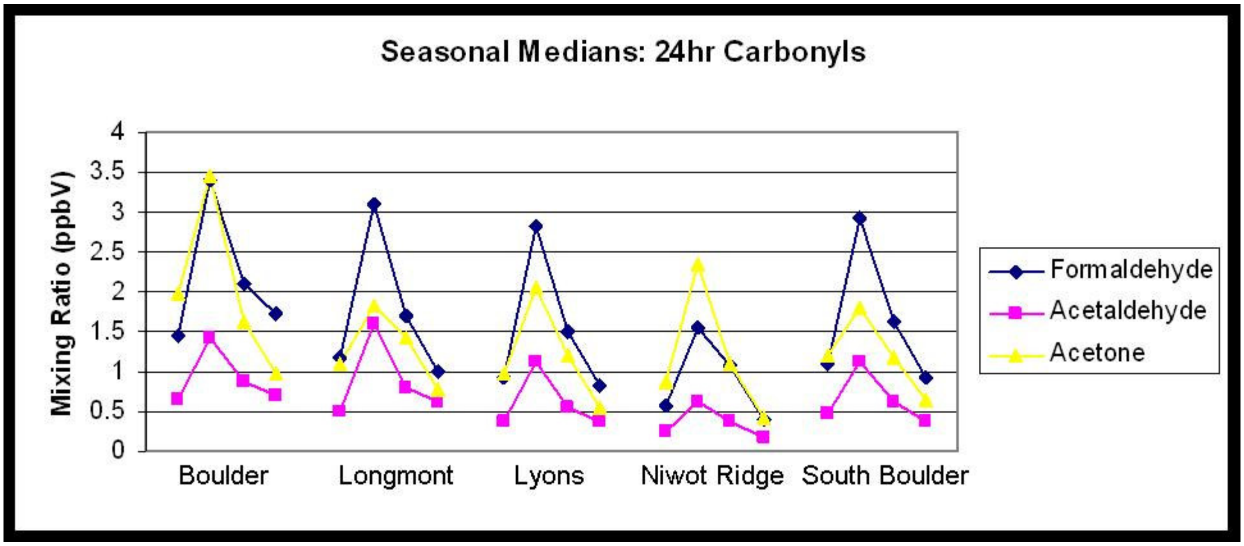


Figure 7.2 shows seasonal medians for formaldehyde, acetaldehyde, and acetone 24-hour samples. Formaldehyde, acetone, and acetaldehyde were the most abundant carbonyls across all sites during the study. Each data point on Figure 7.2 represents a season, with spring being the first data point. Spring includes March, April, and May. Summer includes June, July, and August. Fall includes September, October, and November. December, January, and February are included in winter. The greatest concentrations occurred during the summer months, with formaldehyde medians ranging from 1.5 ppbV (Niwot Ridge) to nearly 3.5 ppbV at Boulder. Acetone was the

most abundant carbonyl at the Niwot Ridge site, suggesting possible upslope transport and reflecting its longer atmospheric lifetime. The Niwot Ridge site had the lowest formaldehyde and acetaldehyde concentrations. Acetaldehyde medians ranged from 1.5 ppbV (Niwot Ridge) to nearly 3.5 ppbV (Boulder).

Figure 7.2: Seasonal median values for 24-hour carbonyl samples



7.1.2 VOCs

Unlike carbonyls, VOCs are introduced into the atmosphere as primary emissions only. Figure 7.3 shows a time series plot of 24-hour n-butane values across all five sites. VOC concentrations were not as dependent on season as carbonyls, with relatively stable values throughout the year. Overall, the Boulder and Longmont sites had the greatest concentrations of VOCs. South Boulder and Lyons had similar concentrations throughout the study. Niwot Ridge typically had the lowest VOC values.

Figure 7.3: Time series plot of 24-hour n-butane samples taken at all five sites

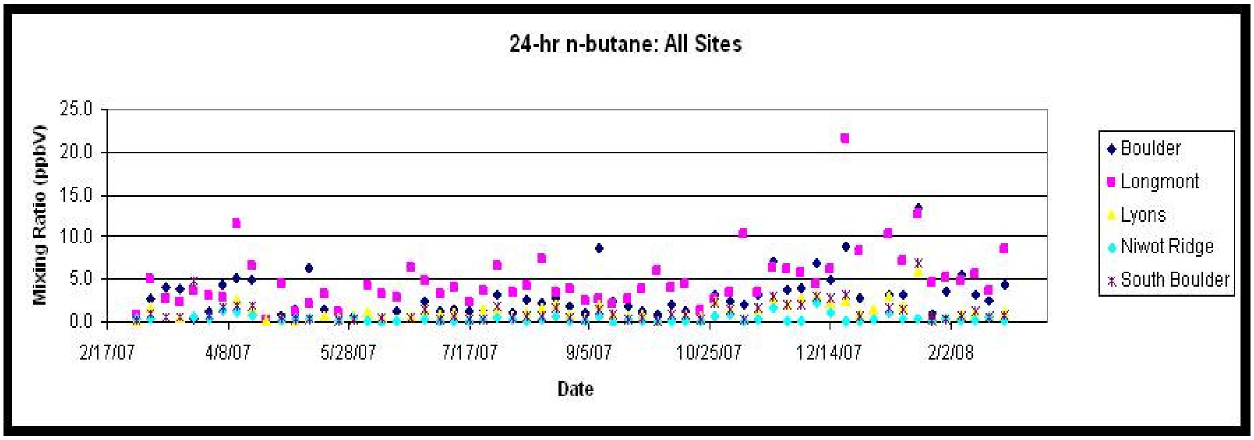


Figure 7.4 shows seasonal medians for n-butane, toluene, and m&p-xylene 24-hour samples. n-butane and n-pentane were the most abundant VOCs across all sites during the study. Similar to Figure 7.2 above, each data point on Figure 7.4 represents a season, with spring being the first data point. Concentrations of lighter alkanes, compounds associated with evaporative emissions, were the greatest at the Longmont site. Oil and gas exploration activities, with a heavy presence in neighboring Weld County, are believed to contribute significantly to the light alkane burden. Overall, the Niwot Ridge site had the lowest concentrations of VOCs. N-butane median concentrations ranged from 0.3 ppbV (Niwot Ridge) to nearly 6 ppbV.

Figure 7.4: Seasonal median values for 24-hour VOC samples

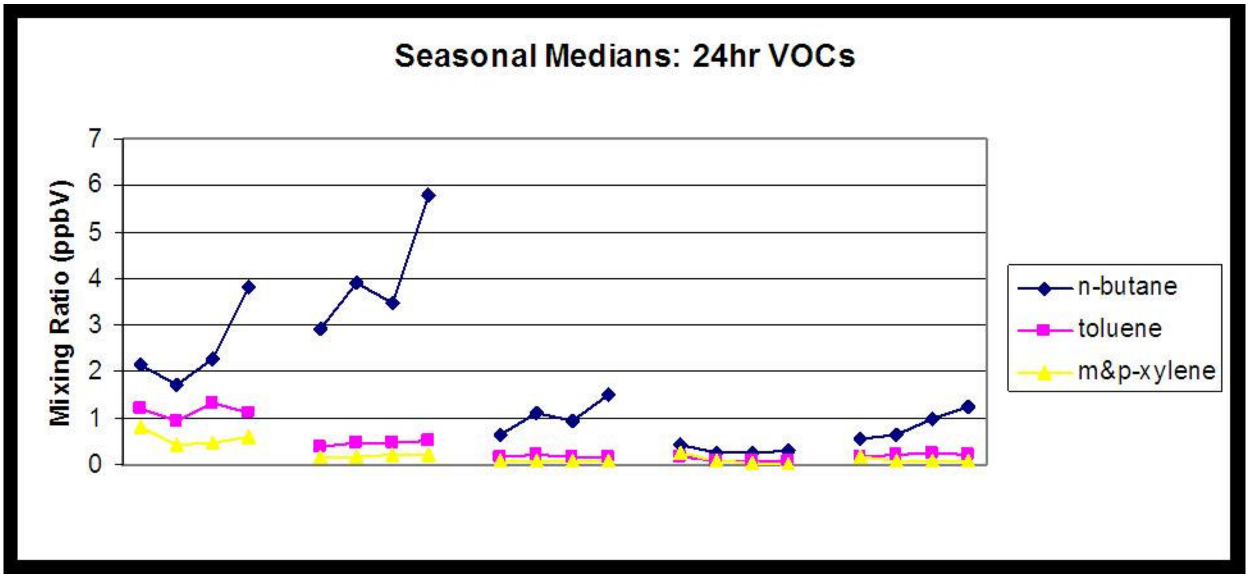


Table 7.1 shows the seasonal 24-hour median concentrations at the Longmont and South Boulder sites. Median formaldehyde and acetaldehyde concentrations were lowest in the winter season. n-butane median concentrations were the lowest in spring and greatest in winter. Toluene and m&p-xylene median concentrations remained stable throughout the year.

Table 7.1: Seasonal 24-hour median concentrations for select carbonyls and VOCs at Longmont and South Boulder

Seasonal 24-hr Median Concentrations (in ppbV)								
	Longmont				South Boulder			
	Spring	Summer	Fall	Winter	Spring	Summer	Fall	Winter
formaldehyde	1.17	3.10	1.70	1.01	1.09	2.93	1.62	0.92
acetaldehyde	0.50	1.61	0.80	0.62	0.47	1.13	0.64	0.39
n-butane	2.90	3.89	3.47	5.81	0.55	0.64	1.00	1.27
toluene	0.40	0.45	0.49	0.51	0.17	0.22	0.24	0.22
m&p-xylene	0.22	0.17	0.22	0.20	0.15	0.09	0.09	0.10

7.1.3 Ozone

As formation of ground level ozone is driven by UV radiation, the summer months typically yielded the greatest concentrations of ozone. Figure 7.5 shows that ozone concentrations were greatest during the summer months at the Boulder site. However, Figure 7.6 indicates that the Niwot Ridge site experienced less seasonality with similar ozone concentrations occurring outside of summer from April until August. The 1-hour medians at Niwot Ridge showed less overall variation throughout the year than at all other sites. An elevated boundary layer causing higher background concentrations could be a possible explanation for the ozone behavior at Niwot Ridge. Figure 7.7 shows the IQR covers a large range of ozone values at the Longmont site, which is due to the large diurnal ozone swings that occurred at the that site throughout the year.

Figure 7.5: Monthly 1-hr ozone averages at Boulder

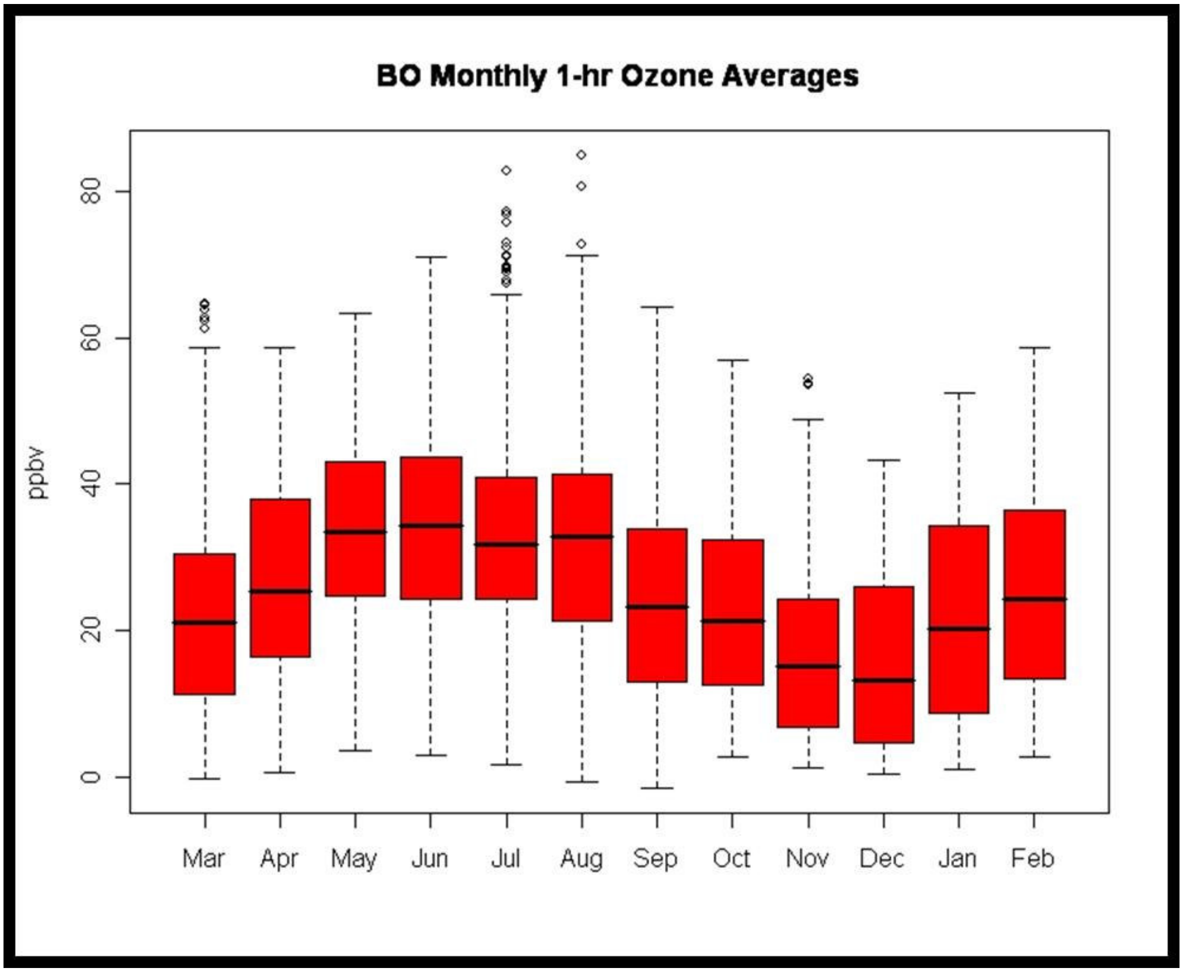


Figure 7.5 shows a large range of ozone values that stretch from nearly zero ppbV to 80 ppbV that occurred at the Boulder site. The lower ends of the whiskers reach near zero ppbV, suggesting the presence of NOx and it’s affinity to react with ozone.

Figure 7.6: Monthly 1-hr ozone averages at Niwot Ridge

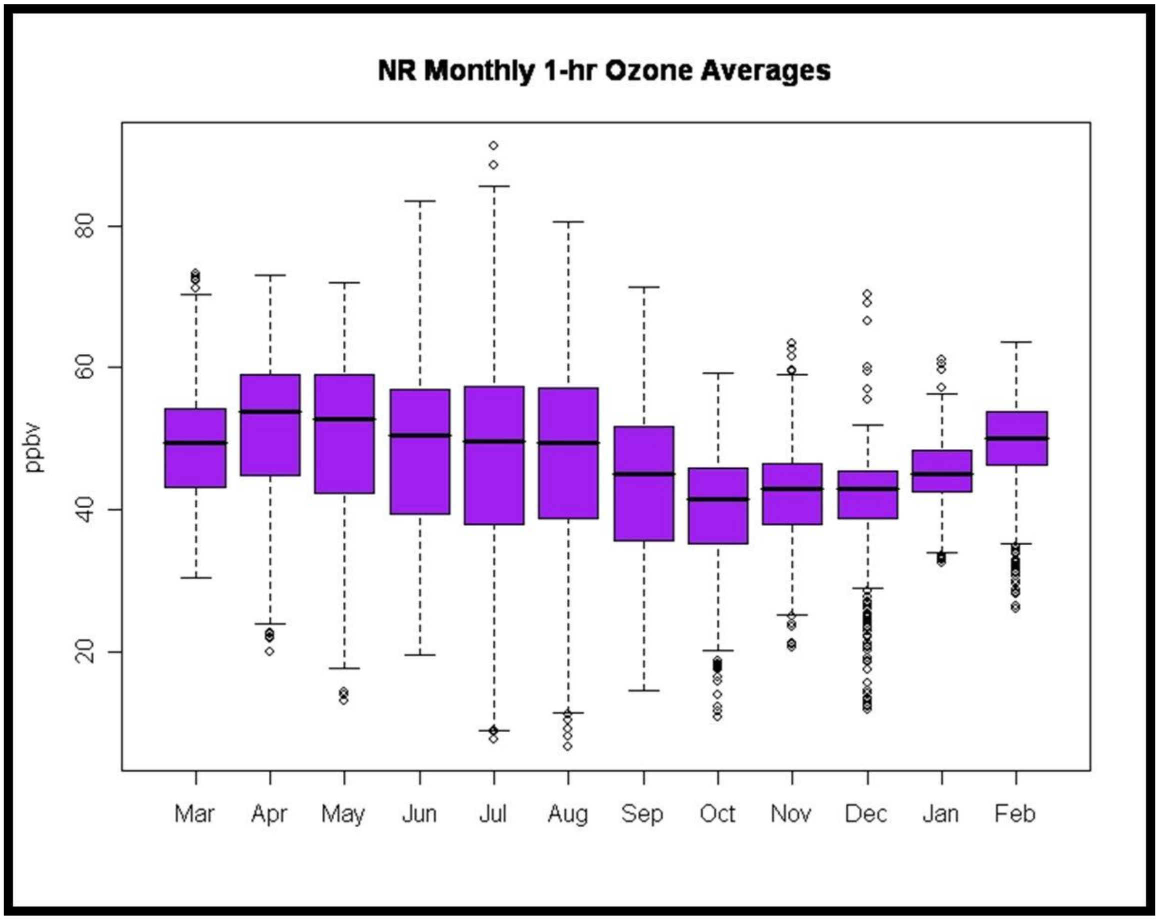


Figure 7.6 shows similar median values throughout the year and smaller IQR values with respect to the other sites. Contrary to the Boulder site with local NOx sources, the lower end of the 1-hour ozone at Niwot Ridge values do not regularly approach zero ppbV.

Figure 7.7: Monthly 1-hr ozone averages at Longmont

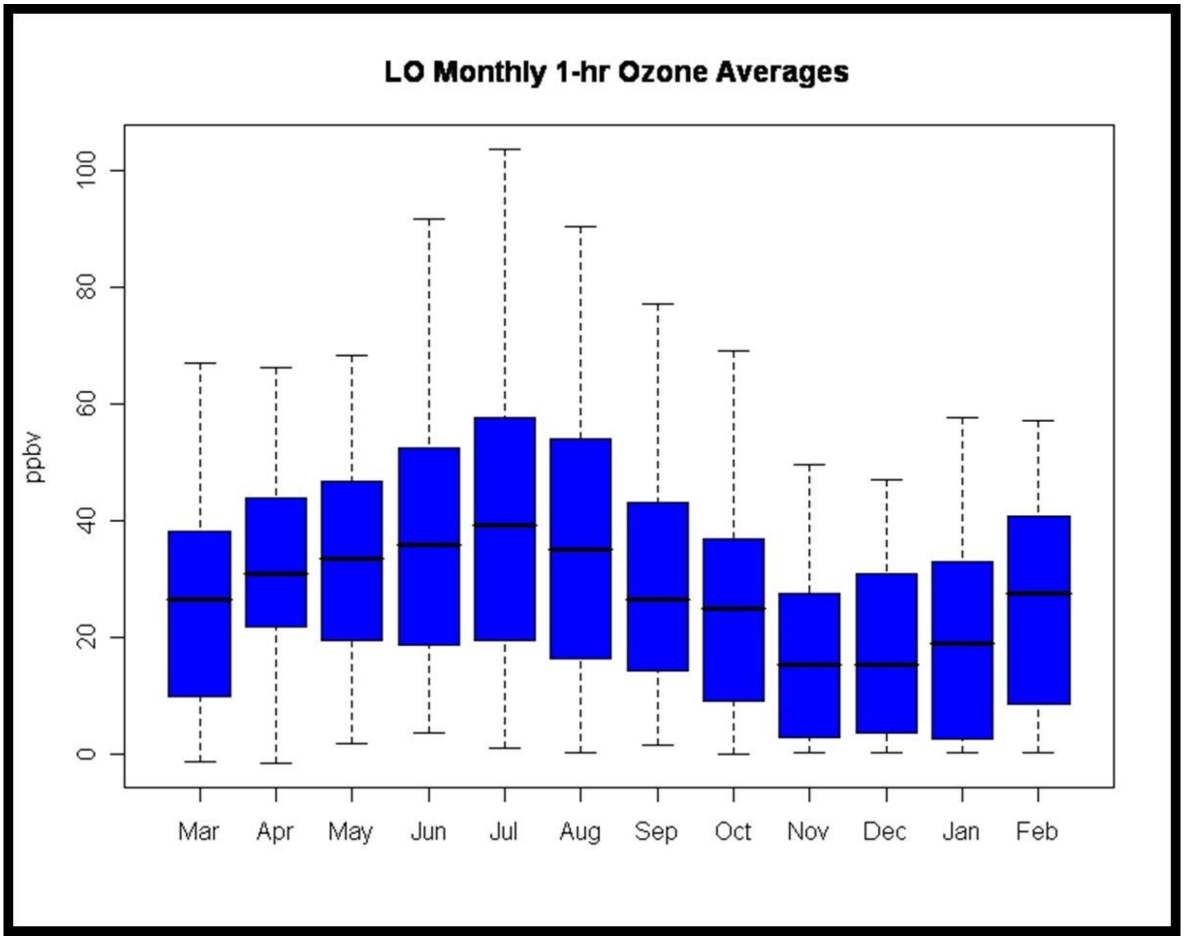


Figure 7.7 shows the 1-hour ozone probability values that occurred at the Longmont site. The whiskers stretch from zero ppbV to at least 75 ppbV for many months, suggesting both ozone titration and significant generation. This is especially true in the summer months.

At the Longmont site, the Lyons site, and the South Boulder site, 8-hour ozone averages exceeded the secondary ozone standard of 0.08 ppmV (80 ppbV) on at least one occasion. July and August were two months when ozone concentrations were typically the highest. Figures 7.8 and 7.9 display the 1-hour and the 8-hour ozone averages during July and August 2007 at the Longmont site and the Niwot Ridge site, respectively. Although the Niwot Ridge site did not show any exceedences of the 8-hour standard, values approached the proposed new 8-hour ozone standard of 0.075 ppmV (75 ppbV). Longmont, Lyons, Boulder, and South Boulder all had 8-hour average values that exceeded the new 75 ppbV standard on numerous instances.

Figure 7.8: 1-hour and 8-hour ozone averages at Longmont in July and August 2007

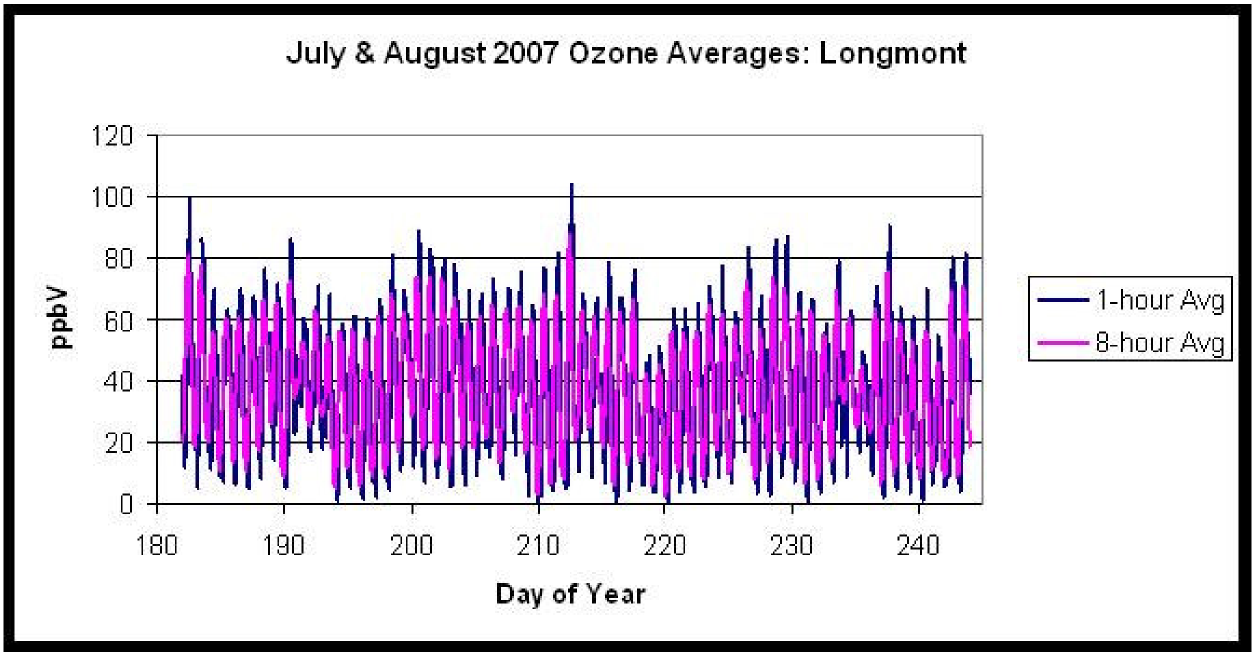
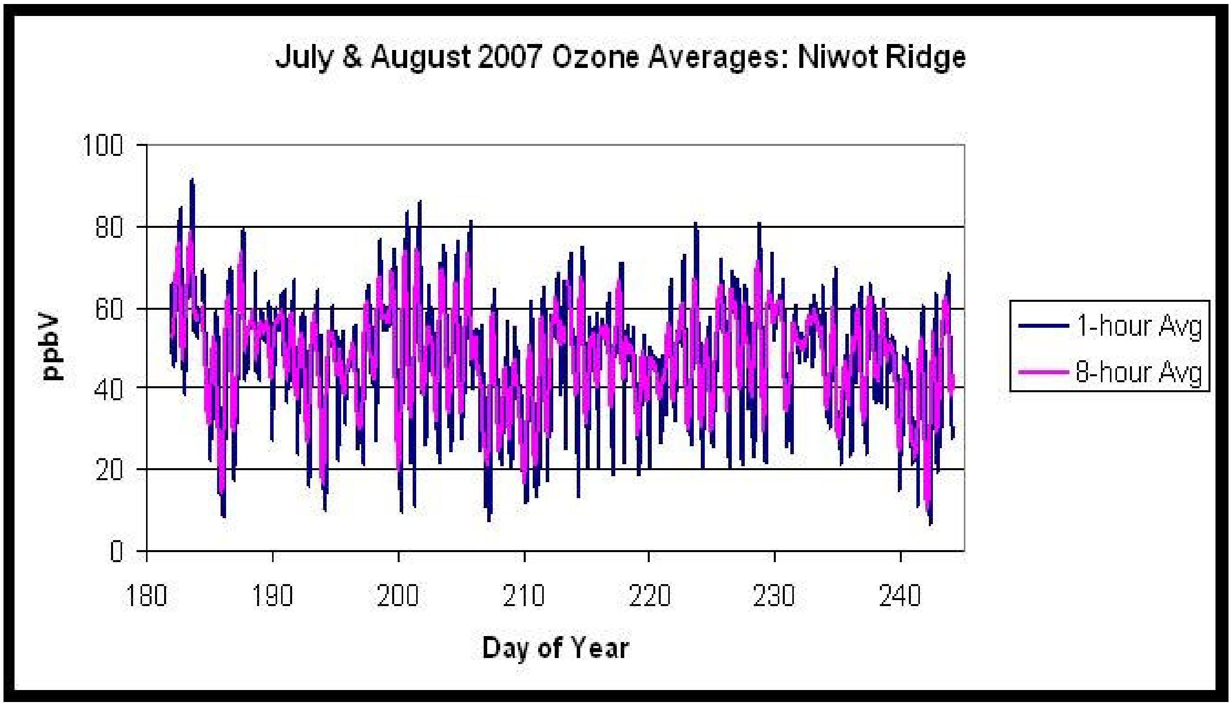


Figure 7.9: 1-hr and 8-hr ozone averages at Niwot Ridge in July and August 2007



Boxplots of 1-hour ozone and summer time series plots of 1-hour for all sites in the Boulder Study are included in Appendix G.

7.2 SOURCE CONTRIBUTIONS AND RELATIONSHIPS

7.2.1 Pairwise Correlations

7.2.1.1 Carbonyls

A potential indicator of common sources of air pollutants is whether they trend together by concentration. This is especially true when time resolved data are available to discern whether pollutants share the same spatial or temporal patterns.

Figure 7.10 shows the overall pairwise correlation between 24-hour acetaldehyde versus formaldehyde concentrations at all sampling locations. The two compounds share a good correlation with an overall R^2 value of 0.82 using a linear fit, suggesting that the same sources or meteorological patterns are contributing to their ambient concentrations.

Figure 7.10: Acetaldehyde versus Formaldehyde pairwise correlation of 24-hour mixing ratios at all sites

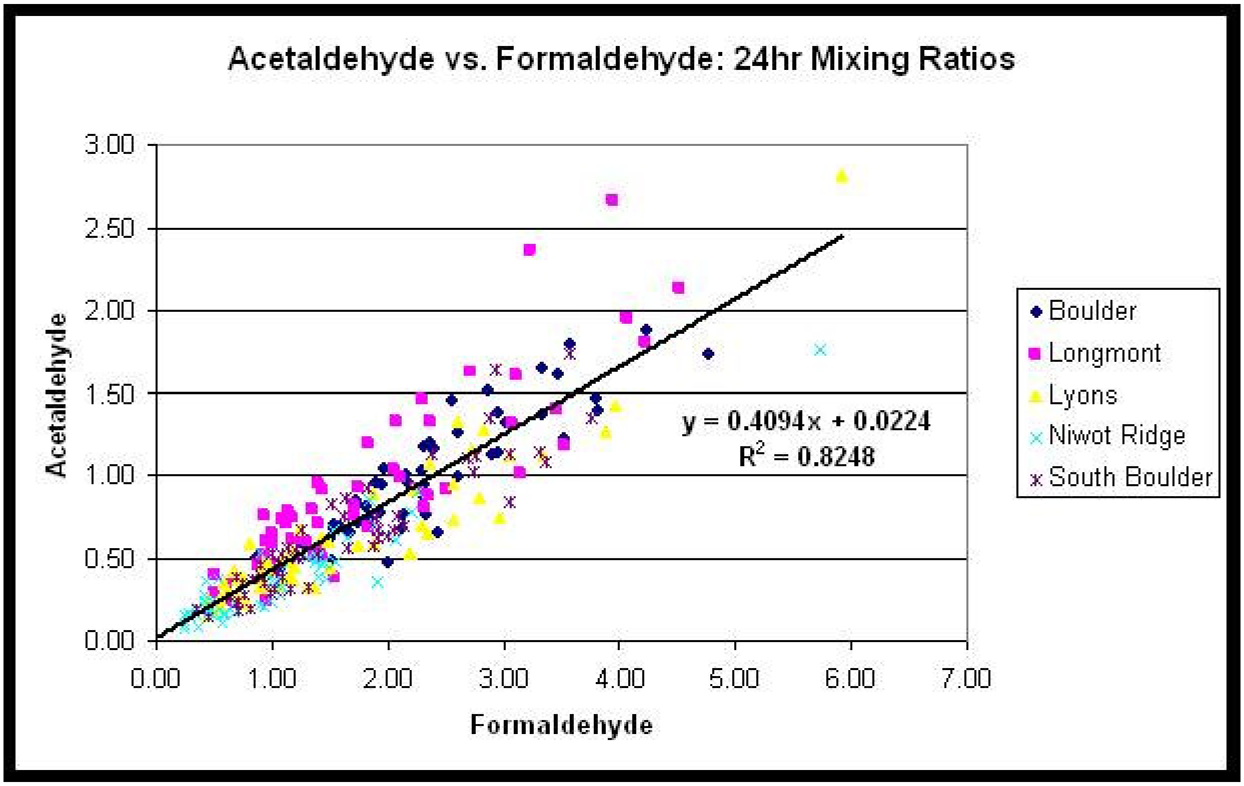
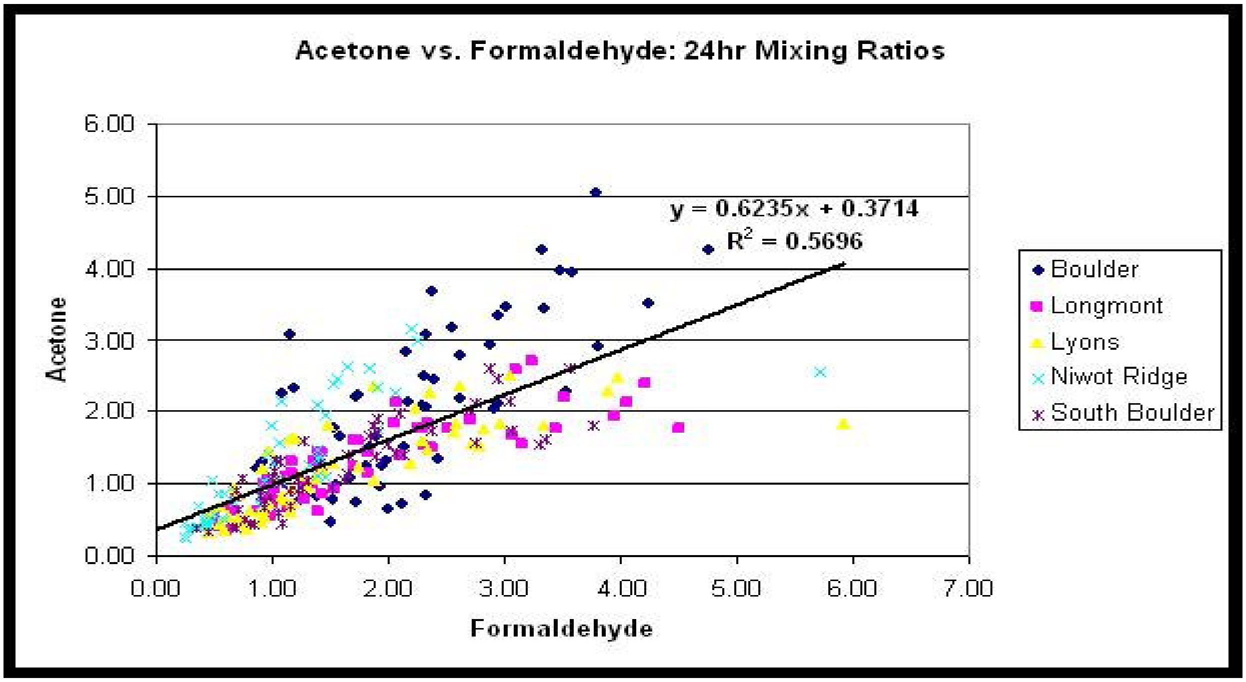


Figure 7.11 shows the overall pairwise correlation between 24-hour acetone versus formaldehyde concentrations at all sampling locations. The two compounds do not correlate as well as acetaldehyde and formaldehyde, with an overall R^2 value of 0.57. The weaker correlation between acetone and formaldehyde suggests that some different sources or meteorological patterns could be contributing to their ambient concentrations.

Figure 7.11: Acetone versus Formaldehyde pairwise correlation of 24-hour mixing ratios at all sites



As the previous figures take an overall correlation of data from all sites, Table 7.2 shows the correlations of acetaldehyde versus formaldehyde and acetone versus formaldehyde at the individual sites. The 2006 Denver Air Toxics Study showed R^2 values of 0.96 for Auraria and 0.93 for Swansea for acetaldehyde versus formaldehyde. Acetaldehyde/formaldehyde R^2 values at Swansea and Auraria in the Denver Study were greater than acetaldehyde/formaldehyde R^2 values in the Boulder Study, suggesting that the two compounds are more likely coming from the same source at the Denver sites than at the Boulder sites. The R^2 values of acetone/formaldehyde for the Boulder Study sites were lower than the acetaldehyde/formaldehyde R^2 values, suggesting that acetone and acetaldehyde may have additional sources influencing their behavior.

Table 7.2: R^2 values from individual sites of acetaldehyde/formaldehyde and acetone/formaldehyde ratios

R^2 Values From 24-hr Samples: Boulder 07-08 Study					
	Boulder	**Longmont**	**Lyons**	**Niwot Ridge**	**South Boulder**
acetaldehyde/formaldehyde	0.83	0.78	0.87	0.89	0.85
acetone/formaldehyde	0.53	0.73	0.62	0.58	0.73

7.2.1.2 VOCs

Figure 7.12 shows the pairwise correlation between 24-hour n-pentane versus n-butane concentrations at all sampling locations. The two compounds share a good correlation with an overall R^2 value of 0.84 using a linear fit, suggesting the same sources and/or meteorological factors are contributing to their ambient concentrations.

Figure 7.12: n-pentane versus n-butane pairwise correlation of 24-hour mixing ratios at all sites

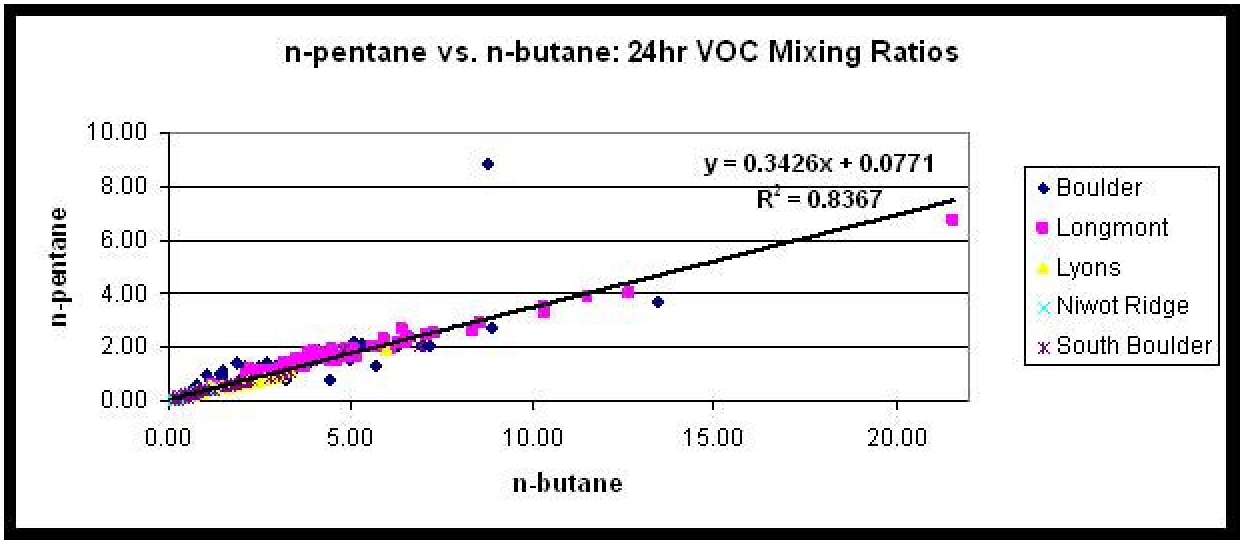
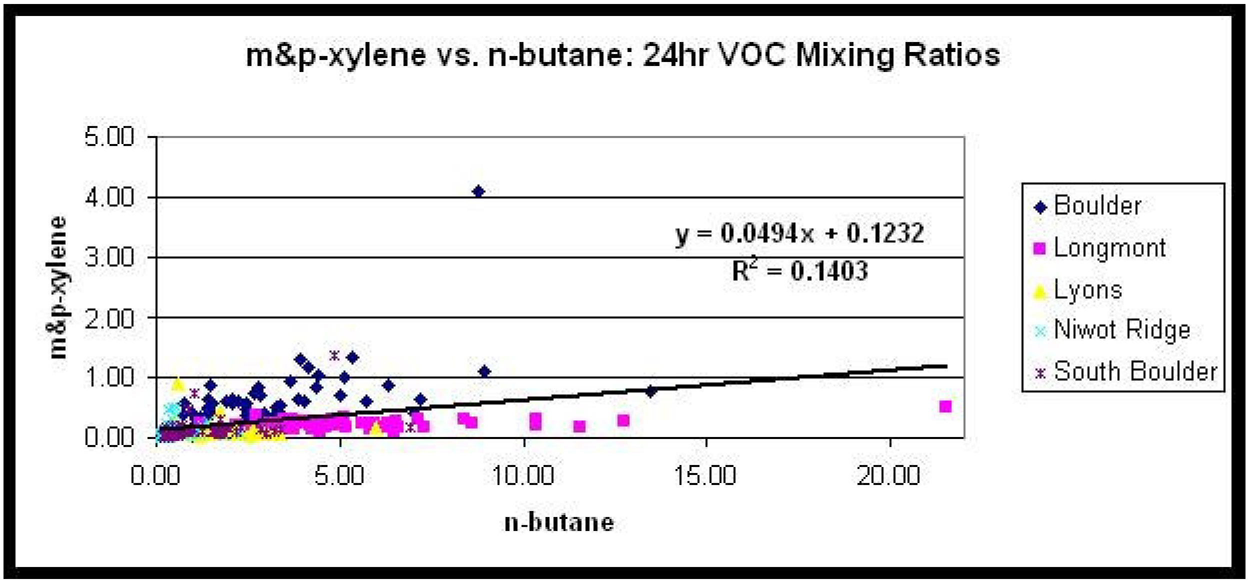


Figure 7.13 shows the pairwise correlation between 24-hour m&p-xylene versus n-butane concentrations at all sampling locations. The two compounds do not correlate as well as n-pentane versus n-butane, with an overall R^2 value of 0.14. This R^2 value shows a poor correlation between m&p-xylene versus n-butane, suggesting that different sources could be contributing to their ambient concentrations.

Figure 7.13: n-pentane versus n-butane pairwise correlation of 24-hour mixing ratios at all sites



As the previous figures show an overall correlation of data across all sites, Table 7.3 shows the correlations of n-pentane versus n-butane and m&p-xylene versus n-butane for individual sites. The m&p-xylene/n-butane R^2 values were very low across all sites, which suggest that it is unlikely that m&p-xylene and n-butane are coming from the same pollution source.

Table 7.3: R^2 values from individual sites of n-pentane/n-butane and m&p-xylene/n-butane ratios

Boulder Study R^2 Values From 24-hr Samples					
	Boulder	**Longmont**	**Lyons**	**Niwot Ridge**	**South Boulder**
n-pentane/n-butane	0.52	0.98	0.97	0.92	0.97
m&p-xylene/n-butane	0.27	0.28	0.00	0.01	0.15

Table 7.4 shows a correlation matrix for 24-hour carbonyls and VOCs collected on the same days at the Boulder site. Values greater than 0.65 are in bold, indicating a strong correlation. Carbonyls correlated well with respect to each other, but did not correlate well with VOCs. Most VOCs also correlated well with each other. The 2006 Denver Study saw stronger carbonyl/VOC correlations, suggesting that carbonyls measured in Denver are most likely primarily emitted rather than secondarily formed. The lack of strong correlation of carbonyls and VOCs in Boulder suggests that secondary formation of carbonyls dominates over primary emissions.

Table 7.4: A correlation matrix that includes carbonyls and VOCs at the Boulder site

Correlation Matrix: 24-hr Carbonyls and VOCs at Boulder									
	formaldehyde	acetaldehyde	acetone	n-butane	n-pentane	toluene	octane	ethylbenzene	m&p-xylene
formaldehyde	1								
acetaldehyde	**0.91**	1							
acetone	**0.69**	**0.75**	1						
n-butane	-0.13	0.02	-0.04	1					
n-pentane	-0.06	0.01	0.02	**0.71**	1				
toluene	-0.13	-0.06	-0.06	0.56	**0.85**	1			
octane	-0.08	0.00	0.03	0.63	**0.97**	**0.85**	1		
ethylbenzene	-0.06	0.01	0.15	0.51	**0.91**	**0.83**	**0.95**	1	
m&p-xylene	-0.12	-0.06	0.07	0.53	**0.92**	**0.83**	**0.96**	**0.99**	1

7.2.1.3 Ozone

Table 7.5 shows a correlation matrix including the R^2 values from 1-hour ozone across all five sites, with values greater than 0.65 emboldened. The South Boulder correlated fairly well with the Boulder, Lyons, and Niwot Ridge sites. The Niwot Ridge site did not correlate well with the other sites, with the greatest R^2 value being 0.49 at the South Boulder site. The lack of strong correlation of the Niwot Ridge with the other sites is likely due to the background nature of the site. It is located at an elevation near 10,000 feet and relatively far from other pollution sources.

Table 7.5: A correlation matrix that includes 1-hour ozone values at all sites

Correlation Matrix: 1-hr Ozone Values					
	Boulder	Longmont	Lyons	Niwot Ridge	South Boulder
Boulder	1				
Longmont	0.62	1			
Lyons	**0.77**	0.71	1		
Niwot Ridge	0.34	0.37	0.41	1	
South Boulder	**0.72**	**0.69**	**0.78**	0.49	1

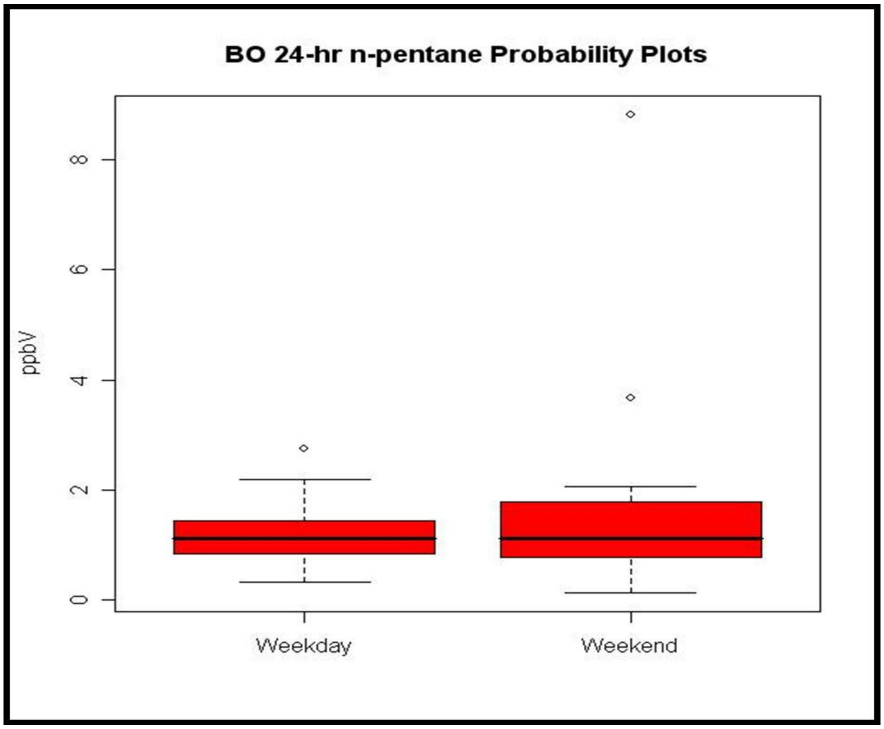
7.3 WEEKDAY VS. WEEKEND COMPARISONS

7.3.1 Carbonyls and VOCs

An analysis was performed with carbonyl and VOC data to determine if there was a significant difference between samples taken during weekdays and weekends.

However, this analysis was challenging due to the low number of weekend samples. Following the EPA 1-in-6 day sampling schedule from the beginning to the end of the study, only 20 sampling days fell on the weekend out of the 61 total scheduled sampling days. Data coverage was not 100%, so the number of weekend samples was less than 20 at each site. However, a general analysis was performed for both carbonyls and VOCs by analyzing the median values of weekday and weekend values. Significant differences between median values were not observed. Figure 7.14 shows boxplots for weekday and weekend values for 24-hour n-pentane samples at the Boulder site. Each boxplot in Figure 7.14 shows a similar median for n-pentane, which is also true for a majority of the carbonyl and VOC compounds that were quantified.

Figure 7.14: Weekday and weekend boxplots for 24-hour n-pentane median concentrations at the Boulder site



Boxplots, or box and whisker plots, display the inter-quartile range (IQR) of a data set that falls within the box, where all other data falling outside of the IQR are represented with whiskers and outlier points. The line located inside of the box represents the median of the data set, while the bottom extent of the box represents the 25th percentile and the upper extent of the box representing the 75th percentile.

Table 7.6 compares the weekend and weekday samples for two carbonyls and three VOCs at the Boulder and Niwot Ridge sites. n-butane medians were greater on the weekend, while weekday medians for formaldehyde and acetaldehyde were greater than weekend values. Weekday versus weekend values of toluene and m&p-xylene were essentially the same at the Niwot Ridge site. A comparison of weekday versus weekend 3-hour samples was not performed due to the limited number of samples collected.

Table 7.6: A comparison of weekend and weekday 24-hour samples at Boulder and Niwot Ridge

Weekend vs. Weekday 24-hr Median Concentrations (in ppbV)				
	Boulder		**Niwot Ridge**	
	Weekday	**Weekend**	**Weekday**	**Weekend**
formaldehyde	2.15	2.10	0.96	0.67
acetaldehyde	0.95	0.81	0.36	0.28
n-butane	2.45	3.32	0.29	0.39
toluene	1.21	0.95	0.11	0.11
m&p-xylene	0.58	0.44	0.06	0.06

7.3.2 Ozone

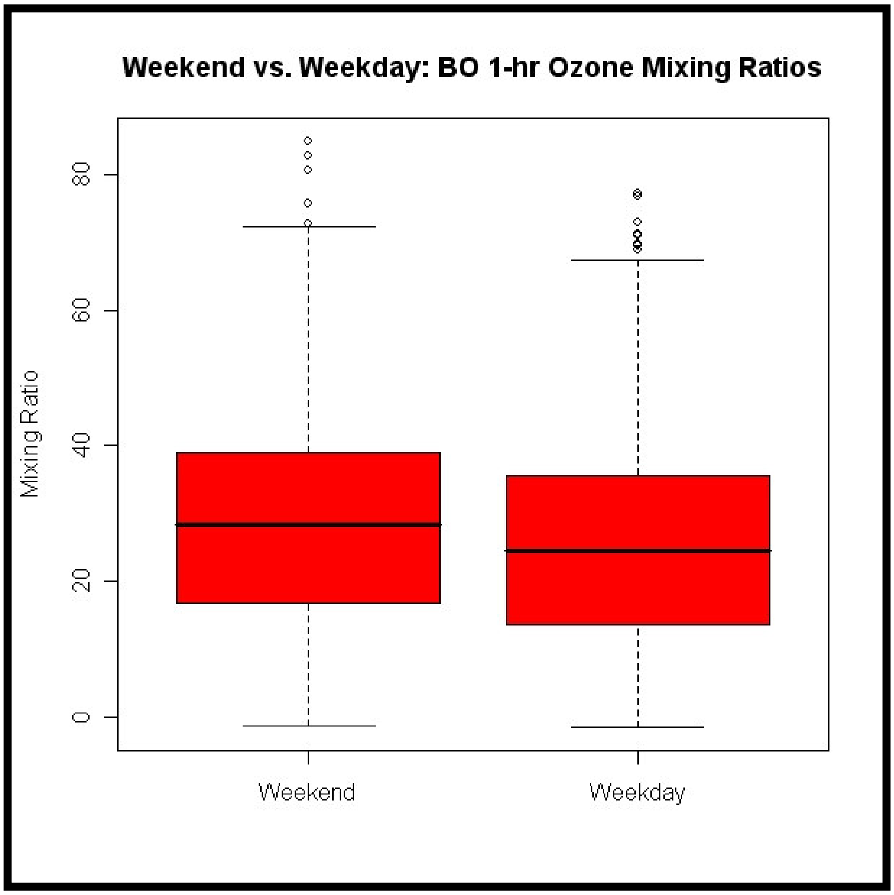
An analysis was also performed on hourly ozone values collected during the study across all five sites. Table 7.7 shows the annual 1-hour medians for weekdays and weekends across all five sites. At Longmont, Lyons, Niwot Ridge, and South Boulder, median weekend and weekday values were within 1.3 ppbV of each other. At Boulder, the weekend value of 28.0 ppbV was 3.1 ppbV greater that the weekday value of 24.9 ppbV.

Table 7.7: Annual ozone medians from 1-hr averages across all five sites – March 1, 2007 through February 29, 2008

Annual 1-hr Ozone Medians at Each Site (in ppbV)									
Boulder		**Longmont**		**Lyons**		**Niwot Ridge**		**South Boulder**	
Wknd	**Wkdy**	**Wknd**	**Wkdy**	**Wknd**	**Wkdy**	**Wknd**	**Wkdy**	**Wknd**	**Wkdy**
28.0	24.9	28.4	27.3	39.0	38.0	46.6	45.9	39.6	38.3

Figure 7.15 shows a boxplot of the weekend versus weekday 1-hour ozone values at the Boulder site. The greatest difference between the weekend/weekday values occurred at this location. Boxplots comparing weekend versus weekday 1-hour ozone mixing ratios for each of the five sites are included in Appendix G.

Figure 7.15: Boxplot of weekday versus weekend 1-hour ozone mixing ratios at the Boulder site



7.4 *PRINCIPAL COMPONENTS ANALYSIS*

Principal Components Analysis (PCA) was performed on 24-hour carbonyl and VOC samples for each site as a source apportionment tool. PCA is a multivariate technique that is applied to arrays of pollution variables for the purpose of pointing out potential pollution sources as well as each variable's mutual interrelation (Thurston et al, 1985). PCA runs were completed to evaluate relationships of VOCs only and a combination of VOCs and carbonyls. PCA for 3-hour samples was not performed due to the limited data set of 3-hour samples. An average of 57 observations were used in the PCA for each site.

7.4.1 VOCs

Table 7.8 shows the correlation matrix for eleven of the more abundant VOCs measured at the Longmont site. Many of the alkanes correlated well with respect to each other, suggesting that they are emitted from the similar sources.

Table 7.8: Correlation matrix for 24-hour VOCs samples collected at the Longmont Site

	n-butane	**n-pentane**	**3-methylpentane**	**hexane**	**heptane**	**toluene**	**octane**	**ethylbenzene**	**m&p-xylene**	**o-xylene**	**nonane**
n-butane	**1**										
n-pentane	**0.99**	**1**									
3-methylpentane	**0.84**	**0.87**	**1**								
hexane	**0.94**	**0.95**	**0.85**	**1**							
heptane	**0.94**	**0.97**	**0.84**	**0.99**	**1**						
toluene	0.53	0.59	**0.68**	**0.65**	**0.84**	**1**					
octane	**0.74**	**0.76**	**0.78**	**0.79**	**0.95**	**0.69**	**1**				
ethylbenzene	0.16	0.21	0.25	0.24	0.38	0.58	0.24	**1**			
m&p-xylene	0.32	0.38	0.46	0.40	**0.67**	**0.82**	0.48	0.59	**1**		
o-xylene	0.42	0.47	0.45	0.46	**0.67**	**0.82**	0.62	0.62	**0.80**	**1**	
nonane	0.46	0.47	0.33	0.50	0.58	0.42	0.49	0.40	0.48	0.36	**1**

Figures 7.16, 7.17, and 7.18 show the results from a PCA run that included 24-hour VOC samples taken at Longmont. Eleven VOC compounds were selected for the analysis because of their abundance.

Figure 7.16 displays a scree plot of the eigenvalues of each factor for the Longmont VOC run. Four factors were retained in this particular analysis, which account for a majority of the variance in the data set. Each retained factor relates to a potential pollution source or another common influence, such as meteorology.

Figure 7.16: Factor Scree Plot - Longmont VOCs

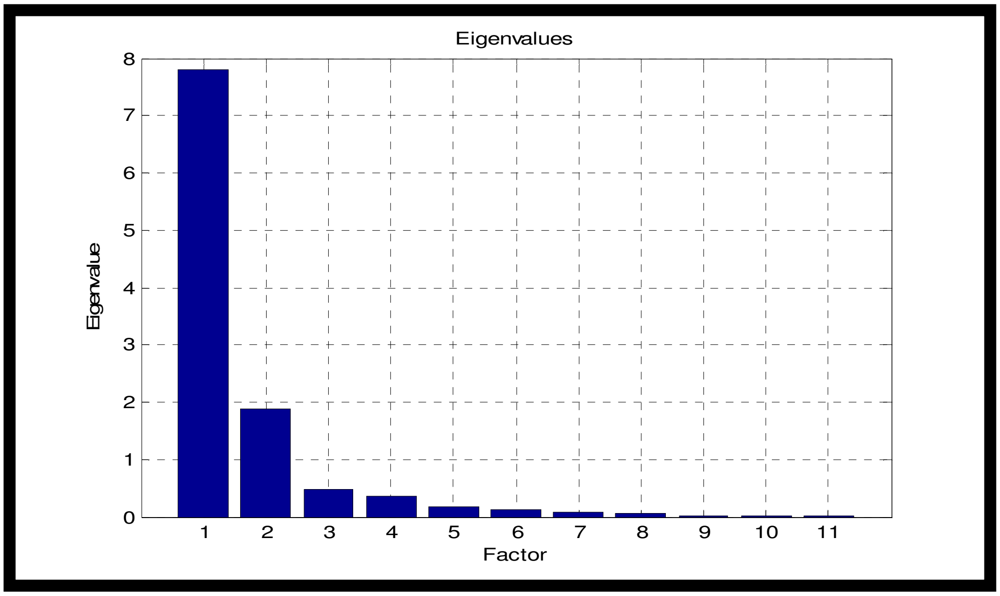
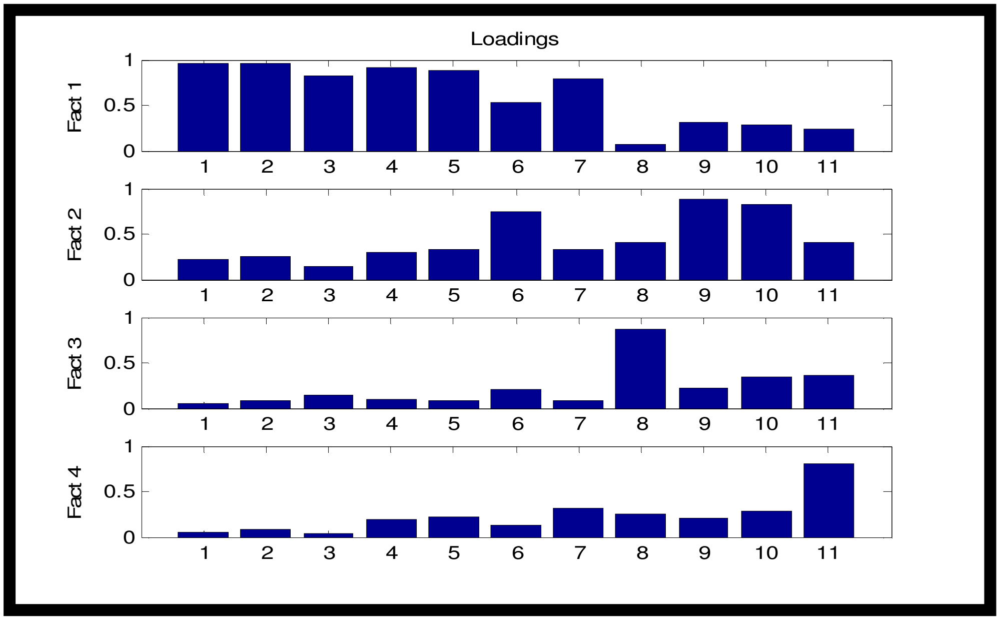


Figure 7.17 shows the individual compound loadings for each factor. Individual compounds with high loadings for a specific factor are believed to come from a similar source. Table 7.9 shows the individual compound that corresponds to each loading value.

Figure 7.17: Factor Loadings - Longmont VOCs



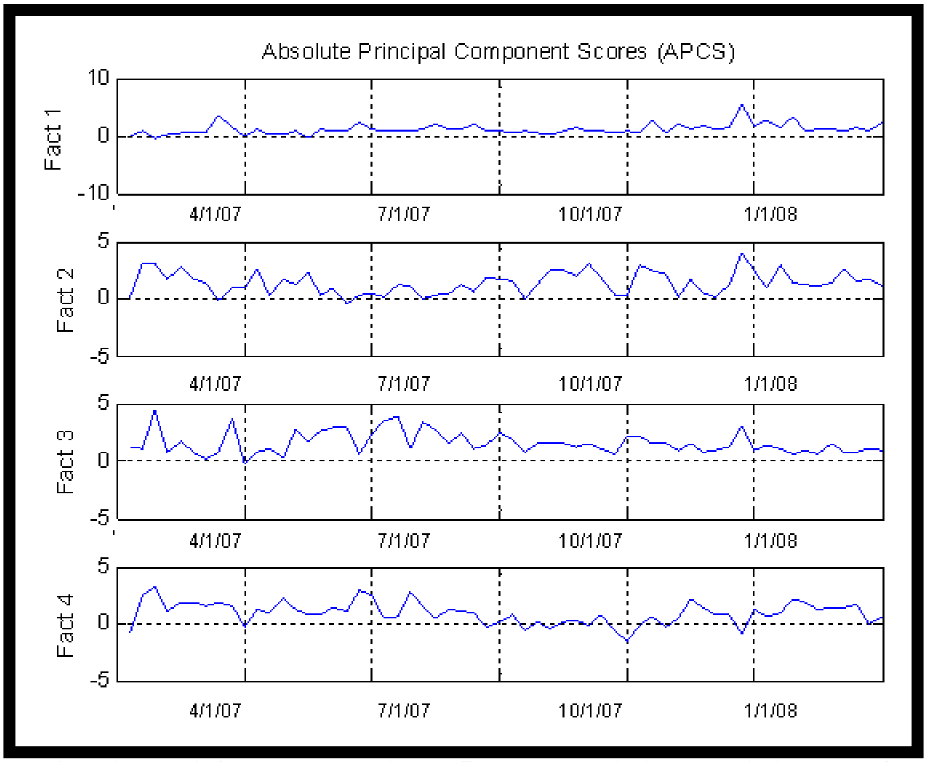
Light alkanes, toluene, and octane heavily load on Factor 1. Compounds such as n-butane and n-pentane are found in evaporative emissions of gasoline vapor and natural gas condensate (Mukund et al., 1995). Longmont is located near oil and natural gas production activities, so Factor 1 suggests that these production activities are significantly contributing to the variation in ambient VOC concentrations at the Longmont site. Aromatic compounds including toluene and xylenes load largely on Factor 2. These compounds are significant components of motor vehicle exhaust (Lin et al., 1994). Factors 3 and 4 show that one individual compound loads heavily on the respective factor, suggesting a local source of that individual compound or possible sampling/analytical problems that may have occurred.

Table 7.9: VOC Factor Loadings

Loading	Compound
1	n-butane
2	n-pentane
3	3-methylpentane
4	hexane
5	heptane
6	toluene
7	octane
8	ethylbenzene
9	m&p-xylene
10	o-xylene
11	nonane

Figure 7.18 shows the Absolute Principal Components Scores (APCS) for each of the retained factors. APCS are adjusted principal component scores that are more easily interpreted than Varimax-rotated scores, which are the standard output of PCA. The APCS are plotted as a time series that corresponds to the dates samples were taken. From the time series plot for each factor, time periods can be identified where the factor had the greatest influence on VOC concentrations. Factor 1, which potentially relates to evaporative emissions, appears to have had especially high impact in April 2007 and January 2008.

Figure 7.18: Absolute Principal Components Scores: Longmont VOCs



(Note: Factor 1's scale extends from +10 to -10, whereas Factors 2, 3, and 4 have a scale that ranges from +5 to -5)

Eleven VOCs were included in the PCA runs for each site in the Boulder Study. Two potential pollution sources, evaporative emissions and mobile source emissions, were identified from the PCA results. However, source identification was not always possible in the VOC PCA runs. A dominant pollution source was not identifiable from the PCA run for the Boulder site. Evaporative emissions followed by mobile source exhaust were identified from the PCA run at the Lyons site and the Niwot Ridge site. The PCA run for the South Boulder site showed that VOC markers for mobile source exhaust followed by evaporative emissions loaded heavily on the first and second factors, respectively.

7.4.2 Combined VOCs and Carbonyls

PCA runs including eleven VOCs and five carbonyls collected during the same sampling periods were completed to evaluate if relationships exist between certain VOCs and carbonyls. Secondary formation of carbonyls was identified as a potential source using these PCA inputs, which was not possible in the carbonyl-only PCA runs.

Table 7.10 shows the correlation matrix for five of the abundant carbonyls and eleven of abundant VOCs measured at the Longmont site. The five carbonyls correlated well with respect to each other, the evaporative emission VOC markers correlated well with each other, and the mobile source exhaust VOC markers correlated fairly well. The three groups of potential sources agree with PCA results for the combined 24-hour carbonyls and VOCs.

Table 7.10: Correlation matrix for 24-hour VOCs and carbonyl samples collected at the Longmont Site

	formaldehyde	**acetaldehyde**	**acetone**	**propionaldehyde**	**butyraldehyde**	**n-butane**	**n-pentane**	**3-methylpentane**	**hexane**	**heptane**	**toluene**	**octane**	**ethylbenzene**	**m&p-xylene**	**o-xylene**	**nonane**
formaldehyde	**1**															
acetaldehyde	**0.87**	**1**														
acetone	**0.88**	**0.82**	**1**													
propionaldehyde	**0.83**	**0.91**	**0.88**	**1**												
butyraldehyde	**0.84**	**0.87**	**0.80**	**0.84**	**1**											
n-butane	-0.05	0.16	0.00	0.03	0.15	**1**										
n-pentane	0.04	0.25	0.11	0.13	0.24	**0.99**	**1**									
3-methylpentane	0.22	0.46	0.26	0.35	0.43	**0.86**	**0.89**	**1**								
hexane	0.07	0.28	0.15	0.17	0.27	**0.96**	**0.99**	**0.89**	**1**							
heptane	0.06	0.27	0.17	0.18	0.28	**0.93**	**0.96**	**0.88**	**0.99**	**1**						
toluene	0.11	0.25	0.24	0.18	0.24	**0.72**	**0.77**	**0.73**	**0.81**	**0.82**	**1**					
octane	0.04	0.23	0.14	0.14	0.30	**0.84**	**0.88**	**0.82**	**0.91**	**0.94**	**0.77**	**1**				
ethylbenzene	0.47	0.56	0.49	0.45	0.47	0.31	0.37	0.48	0.43	0.44	**0.66**	0.42	**1**			
m&p-xylene	0.02	0.17	0.18	0.09	0.16	0.57	0.61	0.55	**0.66**	**0.67**	**0.91**	0.63	**0.68**	**1**		
o-xylene	0.10	0.21	0.22	0.13	0.17	0.55	0.60	0.56	**0.66**	**0.67**	**0.92**	**0.67**	**0.76**	**0.94**	**1**	
nonane	0.18	0.32	0.25	0.20	0.32	0.48	0.54	0.54	0.61	**0.66**	**0.67**	**0.69**	0.64	**0.68**	**0.76**	**1**

Figure 7.19 displays a scree plot of the eigenvalues of each factor for the Longmont VOC and carbonyl run. Five factors were retained in this particular analysis, accounting for a majority of the variance in the data set.

Figure 7.19: Factor Scree Plot - Longmont VOCs & Carbonyls

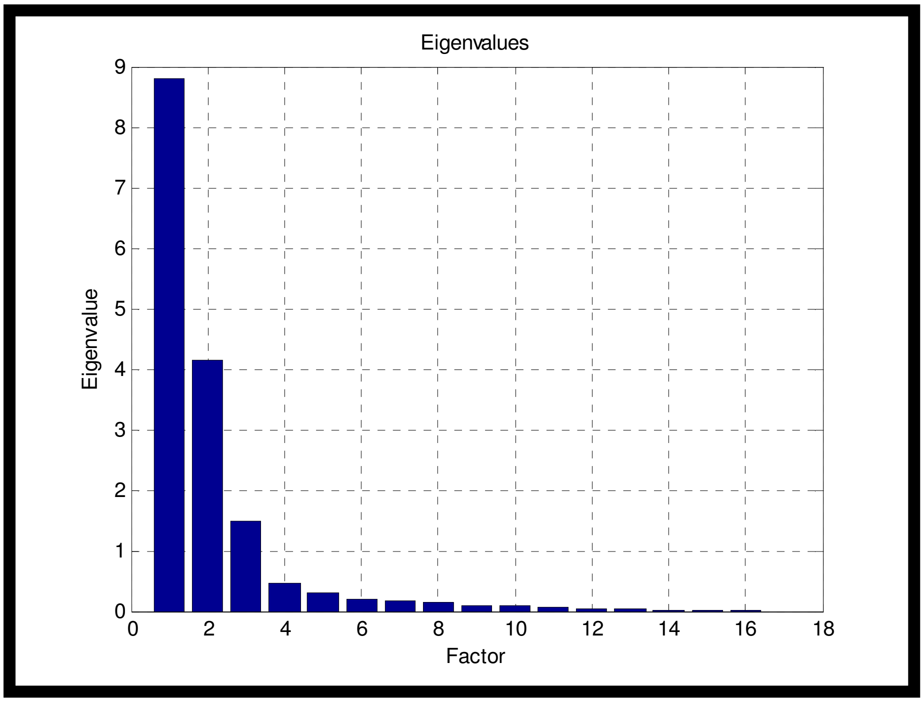
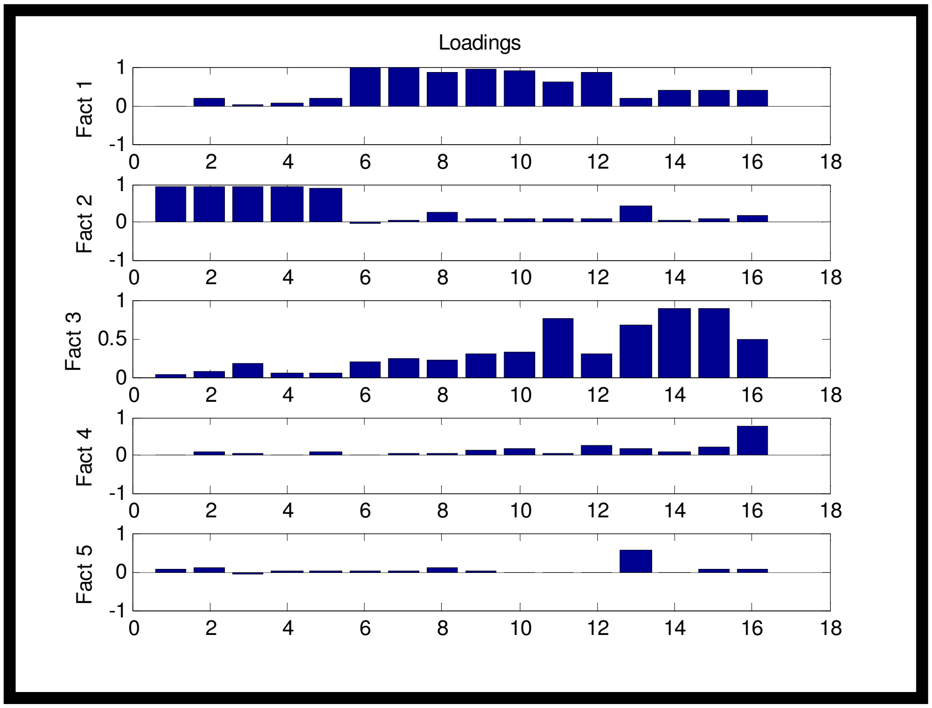


Figure 7.20 shows the individual compound loadings for each factor. Individual compounds with high loadings for a specific factor are believed to come from a similar source. Table 7.11 shows the individual compound that corresponds to each loading value.

Figure 7.20: Factor Loadings - Longmont VOCs & Carbonyls



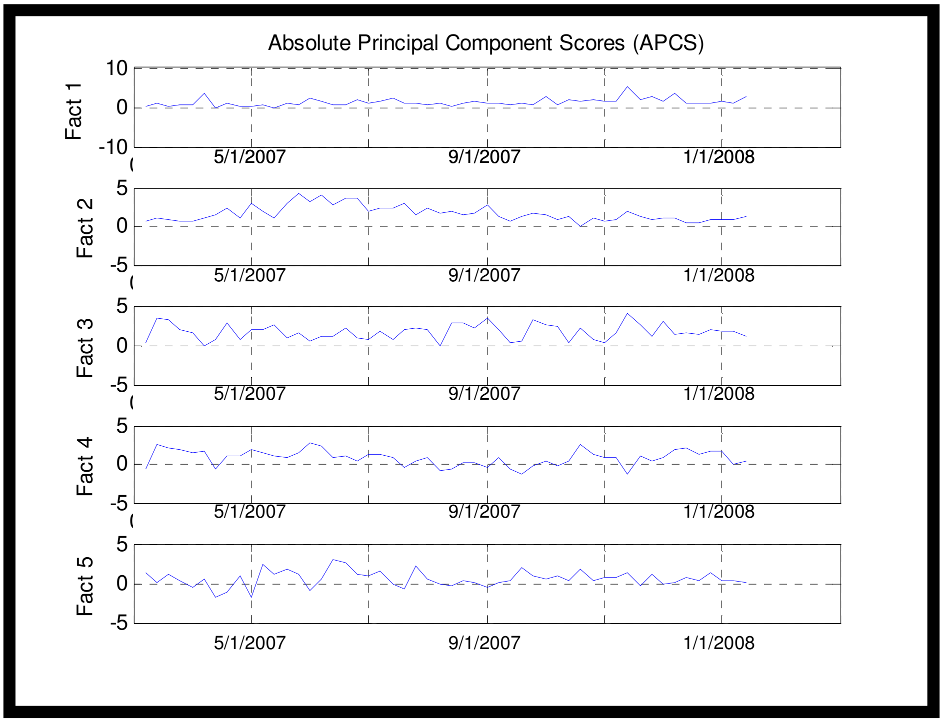
Alkane compounds heavily load on Factor 1. These compounds are associated with evaporative emissions. A similar result was observed in the VOC-only PCA run for the Longmont site, suggesting the impact from oil and gas exploration activities. Carbonyl compounds load largely on Factor 2, suggesting that secondary formation of carbonyls is influencing this factor in addition to primary emissions. Factor 3 is heavily impacted by aromatic compounds including xylenes and ethylbenzene. As mentioned earlier, these compounds are common to mobile source emissions. Factor 4 is influenced by nonane and Factor 5 is influenced by ethylbenzene. It is unlikely that one particular source would only emit these compounds, which suggests potential sampling and/or analytical errors.

Table 7.11: VOC & Carbonyl Factor Loadings

Loading	Compound
1	formaldehyde
2	acetaldehyde
3	acetone
4	propionaldehyde
5	butyraldehyde
6	n-butane
7	n-pentane
8	3-methylpentane
9	hexane
10	heptane
11	toluene
12	octane
13	ethylbenzene
14	m&p-xylene
15	o-xylene
16	nonane

Figure 7.21 shows the APCS for each of the retained factors. Factor 1, which may relate to evaporative emissions, was not affected largely in any particular season. Factor 2 was impacted the greatest during the summer months. This confirms that secondary formation of carbonyls in the warmer months affects the Longmont site. Factors 3, 4, and 5 were not impacted largely during any particular time period.

Figure 7.21: Absolute Principal Components Scores: Longmont Carbonyls



(Note: Factor 1's scale extends from +10 to -10, whereas Factors 2,3,4 and 5 have a scale that ranges from +5 to -5)

Mobile source emissions, secondary formation, and evaporative emissions are impacting each of the Boulder County sites in varying degrees. Additional pollution sources are likely impacting each site, but not necessarily on the magnitude of the three identified sources. Table 7.12 lists the rank of potential sources impacting each site generated from the PCA results of the 24-hour combined carbonyl and VOC runs.

Mobile source pollution affected the Boulder and South Boulder sites the most, likely due to the nearby roadways at each location. The Longmont site is located near oil and gas production areas and was impacted mostly by evaporative emissions, which are expected to come primarily from natural gas condensate. The Lyons and Niwot Ridge sites were affected mostly by secondary formation of carbonyl compounds, suggesting increased photochemistry. Complete PCA results for all sites are included in Appendix H.

Table 7.12 shows the potential pollution source rank (based on contributions to variance in the data) generated from the combined 24-hour carbonyl and VOC PCA runs

Table 7.12: Potential pollution source rank for each site

Potential Pollution Source Rank by Site			
	1st	**2nd**	**3rd**
Boulder	Mobile Source	Secondary Formation	Evaporative
Longmont	Evaporative	Secondary Formation	Mobile Source
Lyons	Secondary Formation	Evaporative	Mobile Source
Niwot Ridge	Secondary Formation	Mobile Source	Evaporative
South Boulder	Mobile Source	Evaporative	Secondary Formation

7.5 COMPARISON OF BCPH OBSERVED CONCENTRATIONS TO PREVIOUS STUDIES

Previous studies measuring ambient carbonyls and/or VOCs have been made since 1987 in the Denver Metro Area including Boulder County. Until 2004, it appears that no long-term carbonyl monitoring efforts had been made. Several shorter-term studies of carbonyls and VOCs have been made in the Denver Metro Area and were used for comparative purposes. In many cases the sample times and durations varied, which makes direct comparison difficult. Regardless, the overall results of these studies are presented in this section.

From December 1987 through mid-April 1998, Larry Anderson of the University of Colorado at Denver collected formaldehyde and acetaldehyde samples in downtown Denver in response to the implementation of a mandated oxygenated fuel program along Colorado’s Front Range. 24-hour and 4-hour average samples were collected in this study, with six consecutive 4-hour samples being collected from 16:00 until 16:00. From March 2007 through February 2008, BCPH collected carbonyl samples at five locations in Boulder County. 24-hour and 3-hour average samples were collected in this study. For comparative purposes, the ranges of average concentrations from the 1987 – 1998 Denver Study are compared to average concentrations from the 2007 – 2008 Boulder Study in Table 7.13. It should be noted that the ranges of 3-hour samples listed in Table 7.13 include maxima and minima from eight samples periods in the Boulder Study, as opposed to maxima and minima values from three sampling periods in the Denver Study. It should also be noted that 4-hour average samples were collected during the Denver Study, while 3-hour average samples were collected during the Boulder Study.

Table 7.13: 1987-1988 Denver Study and 2007-2008 Boulder Study of average carbonyl concentration ranges

Denver 1987-1988 and Boulder 2006-2007 Average Carbonyl Concentrations (ppbV)				
	Denver 87-88 4hr	**Boulder 07-08 3hr**	**Denver 87-88 24hr**	**Boulder 07-08 24hr**
formaldehyde	1.0 – 18.0	0.0 – 9.4	2.6 – 10.0	0.2 – 5.9
acetaldehyde	0.5 – 10.0	0.0 – 3.1	1.7 – 3.5	0.1 – 2.8

In all cases, the formaldehyde and acetaldehyde concentration ranges measured in the Denver Study were greater than the concentrations measured in the Boulder Study.

In 1996, Anderson et al. monitored carbonyls at three locations in Boulder and one location in Denver as part of a study that looked into the correlations of carbonyls with carbon monoxide (CO). Two of the 1996 Boulder sampling locations were near 2007 Boulder Air Toxics Study sites, as the 1996 Boulder Marine Street location (Marine) was near the 2007 Boulder site and the 1996 CU Mountain Research Station location (C1) was near the 2007 Niwot Ridge site. Six 4-hour winter samples were collected 24 hours per day, seven days per week from the Denver Auraria, Marine, and the Boulder 28th Street locations in 1996 from February 7 to March 8. Six discrete 4-hour samples were collected every other day from the 28th Street location during the same sampling period. Winter carbonyl data from the Denver Auraria location had been collected from November through February over a nine year time period beginning in 1987. Six 4-hour carbonyl data were collected at Marine, Auraria, and C1 during the 1996 summer period, July 11 through September 1. For comparison purposes, carbonyl concentration ranges measured at the Boulder and Niwot Ridge sites for winter and summer during the 2007-2008 Boulder Study were included in Table 7.14. Table 7.14 shows the average carbonyl concentration ranges from the 1996 Anderson Study and 2007-2008 Boulder Study. It should be noted that Table 7.14 compares 1996 4-hour average concentration ranges to 2007-2008 concentration ranges.

Table 7.14: Boulder 1996 4-hour average and Boulder 2007-2008 3-hour average carbonyl concentration ranges

Boulder 1996 4-hr Average and Boulder 2007-2008 3-hr Average Carbonyl Concentration Ranges (in ppbV)						
	Winter 1996	Winter 2008	Summer 1996	Summer 2007	Summer 1996	Summer 2007
	Marine	Boulder	Marine	Boulder	C1	Niwot Ridge
formaldehyde	0.4-7.4	0.8-3.8	0.8-7.2	1.8-5.7	0.1-17.3	0.0-2.5
acetaldehyde	0.1-18.7	0.3-2.0	0.6-21.7	0.5-2.5	1.0-53.1	0.0-1.5
acetone	0.1-44.6	0.6-2.8	0.1-39.2	1.2-18.6	0.1-66.9	0.3-5.2

Carbonyl concentrations in the table above from the 1996 Anderson Study were considerably higher than the concentrations in the 2007-2008 Boulder Study, especially at the Niwot Ridge/C1 site. Differences may reflect actual changes in concentration levels across the time period, as well as changes in sampling and analysis methods. Sampling instrumentation used in the 2007-2008 Boulder Study was fully automated while maintaining constant cartridge temperature and flowrate. Proficiency testing of formaldehyde and acetaldehyde quantification was performed with an independent laboratory during the 2007-2008 Boulder Study, with successful quantification of both compounds.

In both 1996 and 1999, the EPA performed National-Scale Air Toxics Assessments (NATA) across the country in an effort to comprehensively evaluate the risk of cancer and other serious health effects from breathing air toxics. Monitoring data, atmospheric dispersion models, and population statistics are collectively used to generate results for a NATA. Formaldehyde, acetaldehyde, and benzene were included in the 1996 and 1999 assessments. Modeled county median results from the Denver Metro Area show similar values for these compounds. Table 7.15 provides the modeled results from the two assessments. The NATA results were reported in mass concentration units.

Table 7.15: EPA 1996 and 1999 NATA results versus BCPH 2007-2008 results

NATA and BCPH Median Mass Concentration Values (µg/m^3)			
	NATA Results		**BCPH Results**
	1996	**1999**	**2007-2008**
Formaldehyde	0.61-6.91	0.94-6.94	0.04-12.75
Acetaldehyde	0.52-4.57	0.91-4.26	0.03-6.91
Benzene	1.14-4.76	0.71-4.93	0.00-41.34

(http://www.epa.gov/ttn/atw/natamain/index.html)

The 1996 and 1999 NATA results were given as median mass concentration ranges for individual counties that fall within the Denver Metro Area. The mass concentration ranges from the NATA modeling results do not include maximum and minimum values, whereas the monitored concentrations from the Boulder Study include these values. Mass concentration ranges from all five sites of the Boulder Study were summarized and in the table above. Median mass concentrations of formaldehyde, acetaldehyde, and benzene in the Boulder Study were 1.35 µg/m^3, 0.91 µg/m^3, and 2.38 µg/m^3, respectively. These median concentrations fell within the range of the NATA results from 1996 and 1999.

The DDEH sampled carbonyls, VOCs, and black carbon from June 2005 through May 2006. VOCs and carbonyls were sampled every six days from midnight to midnight, following EPA Compendium Methods TO-17 and TO-11A respectively. Table 7.16 shows the median 24-hour average concentrations of select air toxics from the four DDEH Study sites. Table 7.17 shows the 2007-2008 24-hour median concentrations from the five BCPH Study sites.

Table 7.16: DDEH 2005-2006 Study results for 24-hr carbonyl and VOC samples

DDEH 2005-2006 Air Toxics Study: 24-hr Median Concentrations (in ppbV)				
	Auraria	**Swansea**	**Palmer**	**Vanderbilt**
formaldehyde	3.86	7.79	5.28	2.43
acetaldehyde	11.38	11.90	10.12	3.06
acrolein	0.07	0.07	0.07	0.07
benzene	0.89	1.06	0.70	0.54
toluene	2.42	3.33	1.51	2.11
m&p-xylene	1.55	2.34	1.14	1.23
o-xylene	0.89	1.21	0.62	0.58

Table 7.17: BCPH 2007-2008 Study results for 24-hr carbonyl and VOC samples

BCPH 2007-2008 Air Toxics Study: 24-hr Median Concentrations (in ppbV)					
	Boulder	**Longmont**	**Lyons**	**Niwot Ridge**	**South Boulder**
formaldehyde	2.14	1.42	1.18	0.94	1.27
acetaldehyde	0.90	0.76	0.47	0.34	0.56
acrolein	0.05	0.04	0.02	0.00	0.02
benzene	0.95	0.77	0.55	0.68	0.57
toluene	1.98	0.47	0.15	0.11	0.20
m&p-xylene	0.57	0.19	0.08	0.06	0.10
o-xylene	0.17	0.06	0.03	0.00	0.03

Formaldehyde, acetaldehyde, toluene, and xylene median concentrations in the DDEH Study were considerably higher than concentrations measured in the Boulder Study. These differences may relate to the urban setting of the Denver sampling sites and the suburban setting of the Boulder sites. Vehicular traffic and industrial sources of emissions are greater in Denver than in Boulder. Acrolein median concentrations were similar between the two studies, with median concentrations across all sites less than 0.07 ppbV. Benzene median concentrations were also similar between the two studies.

In 2006, the CDPHE set up a network of six sampling locations around the state of Colorado that monitored VOCs and carbonyls. The locations consisted of Welby, Denver-Camp, Fort Lupton, Grand Junction, Platteville, and Rocky Flats. The duration of monitoring periods varied from site to site, but all included samples taken during the summer months of 2006. Table 7.18 shows the CDPHE median 3-hour concentrations from the months of June and July 2006. Median 3-hour concentrations from each site in the Boulder Study that were taken during June and July of 2007 data are included in Table 7.19.

Table 7.18: Summer 2006 results from a CDPHE study of the Denver Metro Area

CDPHE June and July 2006 3-hr Median Concentrations (in ppbV)						
	Welby	**Denver-Camp**	**Fort Lupton**	**Grand Junction**	**Platteville**	**Rocky Flats**
formaldehyde	2.94	5.12	2.77	4.56	1.18	4.65
acetaldehyde	6.99	9.04	2.62	1.55	3.36	5.42
acetone	5.94	7.75	4.81	1.71	5.35	7.42
benzene	1.19	0.73	0.65	0.42	2.03	0.52
toluene	1.32	1.41	1.24	0.68	1.70	0.97
m&p-xylene	0.63	0.54	0.46	0.28	0.57	1.00
o-xylene	0.23	0.22	0.15	0.12	0.16	0.45
n-butane	2.80	2.01	18.88	--	43.00	1.70

Table 7.19: Summer 2007 results from the Boulder County study

BCPH June and July 2007 3-hr Median Concentrations (in ppbV)					
	Boulder	**Longmont**	**Lyons**	**Niwot Ridge**	**South Boulder**
Formaldehyde	3.45	3.29	2.89	1.31	2.98
Acetaldehyde	1.44	1.77	1.23	0.71	1.10
Acetone	3.27	3.44	2.52	2.52	2.62
Benzene	3.15	1.35	1.10	1.63	1.42
toluene	1.51	0.39	0.19	0.13	0.27
m&p-xylene	0.64	0.15	0.08	0.08	0.12
o-xylene	0.22	0.04	0.03	0.02	0.03
n-butane	2.77	2.29	0.75	0.49	0.54

Median 3-hour acetaldehyde and acetone concentrations measured at the CDPHE sites were generally greater than the concentrations measured at the Boulder Study sites. Formaldehyde, m&p-xylene, and o-xylene median concentrations were similar between the two studies. The Fort Lupton and Platteville sites had large n-butane medians, which, due to the low number of observations, may not represent the typical ambient concentrations of n-butane. The median benzene concentrations at the Boulder Study sites in summer 2007 were generally greater than those measured by the CDPHE in the summer of 2006. These median concentration differences between the two studies are likely a result of the urban setting of Denver and the suburban setting of Boulder, but could also reflect sampling and analytical differences between the two studies. Sampling equipment utilized in the two studies to collect carbonyl and VOC samples was different, which likely lead to some analytical differences.

In the past, acetaldehyde values measured in the Denver Metro Area have been significantly greater than formaldehyde values. The acetaldehyde/formaldehyde (C2/C1) ratios determined by these Front Range studies have been much higher than many acetaldehyde/formaldehyde ratios measured in other published studies in the United States and beyond. However, acetaldehyde/formaldehyde ratios measured in the Boulder study are in the range of other studies across the United States, unlike past values measured in Colorado. Table 7.20 shows a comparison of acetaldehyde/formaldehyde ratios from other studies conducted in the western United States and other countries. C2/C1 ratios from the 2005 Denver Study were approximately 2.5, which is greater than the 0.41 C2/C1 average ratio measured during the Boulder Study.

Table 7.20: Acetaldehyde/formaldehyde (C2/C1) ratios measured in other studies in the United States and other countries

Location	**Reference**	**C2/C1**
Hong Kong, China (urban)	Ho et al. (2002)	0.48
Mexico City, Mexico (urban)	Baez et al. (1995)	0.34
Socorro, New Mexico (rural)	Villaneuva et al. (2004)	0.60
Los Angeles, California (suburban)	Grosjean et al. (1996)	0.89
Los Angeles, California (urban)	Grosjean et al. (1996)	0.75
Denver, Colorado (urban)	Thomas et al. (2005)	~2.5
Boulder, Colorado (suburban)	Eisele et al. (this work)	0.41

8 CONCLUSIONS AND RECOMMENDATIONS

8.1 SUMMARY

In 2006, the Boulder County Public Health Department (BCPH) and the University of Colorado at Boulder (CU) received a grant from the United States Environmental Protection Agency (EPA), Office of Air Quality Planning and Standards (OAQPS) to conduct a Community Based Air Toxics Study. The objective of Boulder's Community Based Air Toxics Monitoring grant was to investigate the spatial and temporal characteristics of air toxics across Boulder County, which sits at the foothills of the Rocky Mountains. This was accomplished by monitoring for air toxics at multiple locations for a period of one year.

The sampling portions of this study began in March 2007 and extended through February 2008. The study monitored air toxics concentrations at five different sites located within Boulder County. The sampling sites included an urban area heavily influenced by vehicle traffic, three suburban areas that are influenced by multiple air pollution sources, and a remote background location that sits far from local pollution sources.

BCPH and its partners monitored VOCs, carbonyls, and ozone at five locations to aid in air toxics model evaluation and air toxics source apportionment. The measurements were used to help evaluate the Denver Department of Environmental Health's regional air toxics model. Timely carbonyl and tracer gas measurements enabled the county to better assess the impacts from primary and secondary air toxics pollutant sources in the urban-mountain interface.

Specifically, the study has met the following objectives:

1) Delineate concentrations of local scale air toxics, including ozone.
    a. Build upon previous studies that have identified levels of acetaldehyde and formaldehyde well in excess of those found in more densely urbanized neighboring areas and National Air Toxics Assessment (NATA) predictions.
    b. Add more spatial resolution to the existing ozone monitoring effort undertaken by the Colorado Department of Public Health and the Environment.
    c. Use monitoring and modeling to assess the impact of secondary pollutants and understand the spatial and temporal variations of air toxics at the urban/mountain interface.
2) Evaluate and improve air quality exposure models. Use the spatial and temporal air toxics monitoring data to evaluate the NATA results for Boulder County and an established community-scale air dispersion model.

3) Develop a baseline for longer-term monitoring. Create a monitoring and modeling capability, in partnership with the University of Colorado and the City and County of Denver, which can be built upon in subsequent years.
4) Guide air quality management strategies in Boulder County.

8.2 MONITORING APPROACH

The main objective of this study was to assess the spatial and temporal variations of air toxics in Boulder County. Sampling locations were selected to represent the variety of sources within and adjacent to Boulder County, which ranged from the mobile source dominated downtown sampling location to the rural background location in the foothills of the Rocky Mountains.

With guidance from EPA Region 8, the project team agreed that optimum design for this study, given resource limitations, was to sample at five locations for 24-hour durations on a one-in-six day basis. In addition, ground-level ozone was monitored continuously at four of the locations (as the fifth location was collocated with a state ozone monitor). It was anticipated that five monitoring sites would be sufficient to confirm whether concentrations of HAPs and ozone are uniform throughout Boulder County, or have local variations. In addition to the 24-hour integrated samples, eight 3-hour average VOC and carbonyl samples were collected at one location per sampling period on a rotating schedule. The higher time resolved samples were also collected for one year.

In consultation with EPA, BCPH and its partners selected the monitoring locations based on the proximity to potential pollution sources. The monitoring sites were anticipated to be representative of a range of high and low urban air toxics concentrations. The following five locations were selected as the base sites for the Boulder County Air Toxics Study:

1) *Niwot Ridge*. A remote mountain location to assess both the upwind air and the potential back flush of the urban corridor. The Niwot Ridge Research Station is approximately three miles from the closest road, the Peak-to-Peak Highway.
2) *City of Boulder*. A location in close proximity to the sites previously used in the Anderson study and near two of the busiest traffic intersections in the state.
3) *City of Longmont*. An agricultural area and adjacent to oil and gas exploration to the north to assess the agricultural burning and oil and gas impacts.
4) *City of Lyons*. A small rural location in the mountain foothills to validate a recent health consultation and assess oil and gas activities to the north.
5) *South Boulder Creek State Ozone Monitor*. A rural location along the South Boulder Creek and collocated with a state ozone monitoring station to capture air flows occurring along water drainages and provide insights into transport.

8.3 MODELING AND SOURCE APPORTIONMENT APPROACH

Monitoring data collected during the Boulder County Air Toxics Study were compared with results of modeling performed to describe the fate and transport of air toxic compounds. Dispersion models predict ambient concentrations based on information collected by the user and supplied in the model input file. The DDEH's established air dispersion model was run for a select period based on meteorological characteristics and county-level emission factors within the Denver Metropolitan Area.

OZIPR, a trajectory-type air quality simulation model developed by EPA that provides a detailed description of gas-phase photochemistry but a simple treatment of dispersion, transport, and deposition, was used to relate ozone concentrations to levels of VOC and nitrogen oxide (NOx) emissions. OZIPR was also used to estimate concentrations of formaldehyde and acetaldehyde produced in eastern Boulder County.

Principal Components Analysis (PCA) is a multivariate technique that was applied to arrays of measured pollution variables for the purpose of identifying potential sources, as well as each variable's mutual relationship. PCA was run using 24-hour VOC and carbonyl concentrations measured at each of the five sampling locations. In addition to PCA, pairwise correlations were used to potentially identify common sources of air pollutants. Pairwise correlations were run on 24-hour VOC and carbonyls, as well as 1-hour ozone values.

8.4 FINDINGS

8.4.1 Spatial and Temporal Variability of Air Toxics

Five sampling locations, all located within Boulder County, were utilized to assess spatial variability of air toxics at the rural/mountain interface. Concentrations of VOCs and carbonyls varied from site to site. Local sources appear to impact each site differently and at varying magnitudes. The downtown Boulder site, which is in close proximity to vehicular traffic, showed elevated concentrations of air toxics common to vehicle exhaust. The Longmont site was located near oil and gas exploration activities and showed elevated concentrations of n-butane and n-pentane, two evaporative VOCs found in gasoline vapor and natural gas condensate. The Lyons site was located near vehicular traffic, a cement plant, and oil and gas exploration activities and did not appear to be strongly influenced by one particular source. Compounds with relatively short atmospheric lifetimes, such as m&p-xylene, had the lowest overall concentrations at the background location, Niwot Ridge.

Ozone values varied from site to site as well. The Longmont site would experience rapid ozone production in the morning hours, which would then be followed by near zero concentrations in the nighttime hours. The Niwot Ridge site maintained the most stable ozone concentrations throughout the day, when compared to the other sites. The Lyons site and South Boulder site, located approximately 20 miles apart, shared the greatest correlation coefficient of 0.78. Correlation coefficients of 1-hour ozone averages can be found in Table 7.5.

The seasonal variability between the sites was quite similar for certain air toxics. Formaldehyde, which is primarily emitted and secondarily formed, had concentrations that peaked during the summer months across all five sites. Certain VOCs, such as n-pentane, had the greatest 24-hour mean concentrations in winter at Longmont, Lyons, Niwot Ridge, and South Boulder. However, concentrations of many of the VOCs remained fairly stable throughout the sampling campaign at all of the sites.

Ozone also showed similar seasonal trends across all five locations, with maximum concentrations occurring during June, July and August. When interpreting from a higher time resolution, individual spikes in ozone concentrations were observed during the same hour and day at many of the locations. However, this was not always true. Seasonal trends were also different for ozone across the five sites. While ozone concentrations were greatest in summer months at every location, concentrations varied in other seasons for each site. In particular, the Niwot Ridge site experienced less pronounced seasonality than the other locations.

8.4.2 Comparison of Observed Concentrations to Previous Studies

Generally, reported concentrations of certain air toxics have declined in the Denver Metropolitan Area since the 1980s while others have remained steady. Primary pollutants, such as VOCs, do not show significant trends. Secondary pollutant concentrations of carbonyls appear to have declined, but elevated ozone concentrations continue to be a health concern; particularly as the national health-based standard has been lowered to reflect its effects on public health and the environment. The relationships between ozone precursor emissions inventories and ambient exposures are still emerging. Attaining the EPA primary and secondary ozone standards is a difficult challenge in Boulder County, especially with new regulatory standards set at lower concentrations.

From December 1987 through mid-April 1998, Larry Anderson of the University of Colorado at Denver collected formaldehyde and acetaldehyde samples in downtown Denver in response to the implementation of a mandated oxygenated fuel program along Colorado’s Front Range. For comparative purposes, the ranges of average concentrations form the 1987 – 1998 Denver Study were compared to average concentrations from the 2007 – 2008 Boulder Study. In all cases, the formaldehyde and acetaldehyde concentration ranges measured in the Denver Study were greater than the concentrations measured in the Boulder Study.

In 1996, Anderson et al. monitored carbonyls at three locations in Boulder and one location in Denver as part of a study that looked into the correlations of carbonyls with carbon monoxide (CO). Two of the 1996 Boulder sampling locations were near 2007 Boulder Air Toxics Study sites, as the 1996 Boulder Marine Street location (Marine) was near the 2007 Boulder site and the 1996 CU Mountain Research Station location (C1) was near the 2007 Niwot Ridge site. Carbonyl concentrations from the 1996 Anderson Study were considerably higher than the concentrations in the 2007-2008 Boulder Study, especially at the Niwot Ridge/C1 site.

The EPA performed National-Scale Air Toxics Assessments (NATA) for the country in 1996 and 1999 in an effort to comprehensively evaluate the risk of cancer and other serious health effects from breathing air toxics. Monitoring data, atmospheric dispersion models, and population statistics are collectively used to generate results for a NATA. Formaldehyde, acetaldehyde, and benzene median mass concentrations were included in the 1996 and 1999 assessments, which were compared to median concentration ranges from the current Boulder Study. Median mass concentrations of formaldehyde, acetaldehyde, and benzene in the Boulder Study were 1.35 $\mu g/m^3$, 0.91 $\mu g/m^3$, and 2.38 $\mu g/m^3$, respectively. These median concentrations fell within the range of the NATA results from 1996 and 1999.

The DDEH sampled carbonyls, VOCs, and black carbon in Denver from June 2005 through May 2006. VOCs and carbonyls were sampled every six days from midnight to midnight. Formaldehyde, acetaldehyde, and toluene median concentrations in the DDEH study were considerably higher than concentrations measured in the current study. These large differences may relate to the urban setting of the Denver sampling sites and the suburban setting of the Boulder sites. Vehicular traffic and industrial sources of emissions are greater in Denver than in Boulder. Benzene median concentrations were similar between the two studies.

In 2006, the CDPHE measured VOC and carbonyl concentrations at six State or local air monitoring stations (SLAMS) around Colorado's Front Range. The locations were Welby, Denver-Camp, Fort Lupton, Grand Junction, Platteville, and Rocky Flats. The duration of monitoring periods varied from site to site, but all included samples taken during the summer months of 2006. Median 3-hour acetaldehyde and acetone concentrations measured at the CDPHE sites were generally higher than the concentrations measured at the Boulder Study sites. The median benzene concentrations at the Boulder sites were generally greater than those measured by the CDPHE in the summer of 2006, while median concentrations of formaldehyde and xylenes were similar.

In summary, concentrations of formaldehyde and acetaldehyde measured in the Boulder study were generally lower than those observed in earlier monitoring studies, with especially pronounced differences for acetaldehyde. Prior to the current Boulder study, acetaldehyde/formaldehyde ratios measured in the Denver metropolitan area were much higher than values measured in other studies performed in the United States and abroad. Ratios from the Boulder study are more in line with those measured in other locations. Furthermore, carbonyl sampling and quantification techniques used in this study underwent careful evaluation and incorporated a number of improvements in sampling and analytical protocols, as detailed in Chapter 4. Sampling instrumentation used in the 2007-2008 Boulder Study was fully automated while maintaining constant cartridge temperature and flowrate. Proficiency testing of formaldehyde and acetaldehyde quantification was performed with an independent laboratory during the 2007-2008 Boulder Study, with successful quantification demonstrated for both compounds. Duplicate 24-hour samples collected during the Boulder study show strong agreement, as did the sum of the eight 3-hour samples collected along with the 24-hour samples. Clean field blanks collected during the Boulder Study also support the validity of the current measurements.

8.4.3 Innovative Sampling Techniques

One of the expected outcomes of this project was to determine whether the higher time-resolved sampling approach is a practical and accurate means of assessing exposure to the appropriate hazardous air pollutants.

In order to make this determination, this study assessed the accuracy of collecting a 24-hour integrated sample and, from a collocated sampler, eight consecutive 3-hour integrated samples during the same period.

Overall, there was a good agreement between most 24-hour and eight 3-hour VOC and carbonyl samples. Previous studies indicated poor collection efficiency for carbonyl samples collected using the EPA Compendium TO-11A method. Results from the Boulder County Study showed that, by temperature and mass-flow controlling valves and sampling lines, monitoring carbonyls for 3-hour and 24-hour durations using 2,4-DNPH cartridges is an effective way to accurately quantify ambient carbonyl concentrations.

8.4.4 Model Results

The OZIPR model provides a detailed description of gas-phase photochemistry leading to summertime production of ozone and other secondary pollutants, but uses a simple description of dispersion, transport, and deposition, as it models the area of interest as a single, completely mixed reactor. The model performs well for ozone in eastern Boulder County, taking the Lyons monitor as most representative of average conditions in the area. On the days for which modeling was performed for May – August, 2007, the hourly average ozone concentrations predicted with the model had correlations with observed ozone concentrations at Lyons ranging from 0.6 – 0.96, and bias ranging from -0.0016 ppm to 0.136 ppm. The overestimation bias found on some days was largely eliminated when the model was modified to account for the presence of cloud cover on those days. The OZIPR model was developed to predict ozone concentrations, and is not expected to perform as well for other secondary pollutants such as formaldehyde and acetaldehyde. Even so, when the initial formaldehyde concentration in the model was set at 3.5 ppb, the results from OZIPR agreed reasonably well with formaldehyde concentrations observed in eastern Boulder County. On the other hand, there was a significant discrepancy between the modeled and observed concentrations of acetaldehyde, with modeled concentrations exceeding observed values by about a factor of three.

Results from the dispersion modeling conducted by the Denver Department of Environmental Health indicate that for pollutants where we have medium to high confidence in the emissions inventories, AERMOD under predicts by a factor of 2-10 across the Denver-Boulder region. Pending issues with estimates of regional background concentrations could improve predicted-to-observed ratios. For most pollutants, the predicted spatial distribution of emissions seems to match the distribution of observed concentrations. Butane, pentane, and hexane were modeled to examine the spatial distribution of primary pollutants from oil and gas production. With butane and pentane assumed to be emitted exclusively from the oil and gas sector and assuming zero background concentrations, concentrations modeled with AERMOD were under predicted by a factor of 50 or more, and poorly matched the spatial pattern of observed concentrations.

8.5 RECOMMENDATIONS FOR FUTURE WORK

The Boulder County Community-Scale Air Toxics Project provided high-quality measurements that characterized spatial, temporal, and seasonal variability of VOCs, carbonyl pollutant sources, and ground-level ozone at the urban/mountain interface in Boulder, Colorado. The study also built upon a network of previous studies that have been conducted in the Denver Metro Area since the 1980's. Twenty-seven VOCs and eight carbonyls, eleven of which are recognized as hazardous air pollutants by the EPA, were quantified in this study.

However, it is likely that additional gaseous pollutants are present in the ambient air within Boulder County that were not detectable or quantifiable with the analytical instrumentation used in this study. For future air quality studies conducted in Boulder County, it is recommended that monitoring instrumentation capable of measuring a greater array of compounds at a higher time resolution be utilized. Using a hydrocarbon analytical system with a column capable of detecting/quantifying propane and ethane would provide further insight into impact of oil and gas operations. For any future monitoring, it is suggested that a thorough performance evaluation of the analytical system be conducted prior to sampling to ensure that a full range of target compounds can be properly identified and quantified.

The use of real-time or near real-time monitoring equipment for a future study in Boulder would allow for greater characterization of diurnal patterns and the effects of photochemistry. Continuous measurements oxides of nitrogen (NO and NO_2) collocated with ozone and VOC monitoring would address ground-level ozone formation and titration. Near real-time monitoring would be more comparable to local meteorological measurements, which could aid in tracer analyses and modeling applications. The 3-hour samples collected during the Boulder Study provided greater insight of pollutant concentrations present throughout the day, when compared to 24-

hour samples. If real-time monitoring is not available, 3-hour integrated sampling is recommended.

If a one-year air toxics study is to be conducted in the future and continuous monitoring instrumentation is not available, it is recommended that the sampling frequency be increased to follow at least the EPA 1-in-3 day sampling calendar. The increased sampling frequency would provide greater insight into weekday versus weekend trends and more accurately capture the ambient conditions. Collected data could still be entered into the EPA's National Air Quality System (AQS) database on this sampling schedule.

Utilizing other tools such as the National Oceanic and Atmospheric Administration's HYSPLIT backtrajectory model and local sondes launch data would provide additional information towards atmospheric mixing layer height, which heavily influences ground-level ozone formation.

NATTS proficiency testing (PT) should require a greater number of compounds that require certification, rather than the select few currently required by NATTS. This requirement would include all monitoring networks across the United States. This would help increase the precision and accuracy of data entered into the AQS that is used for comparative purposes. It would also assist the sampling agency by illustrating the strengths and weaknesses of their analytical systems. In addition to NATTS PT, a separate agency should collect split samples in the field to further evaluate how final concentrations compare to each other. This would be especially useful to further assess acetaldehyde sampling and quantification techniques.

Finally, all projects should require EPA and/or state assistance with data uploads to the AQS. This regulatory reporting process for AQS is arduous and time consuming for agencies that do not regularly report data in this format. EPA staff or an approved contractor reserved to facilitate this task would ensure timely and accurate submission of final data.

8.6 REDUCING EXPOSURE TO AIR TOXICS

As results from the Boulder County Air Toxics Study and other local air toxics studies have indicated, mobile sources appear to be an important contributor to air toxics exposures in urban and suburban areas in the Denver Metropolitan Area. Further efforts to reduce mobile source emissions, including increased use of mass transit, should help reduce exposure to air toxics. In addition, EPA programs such as the "Control of Hazardous Air Pollutants from Mobile Sources: Early Credit Technology Requirement" rule and the Clean School Bus USA program, should assist in reducing air toxics risk and exposures. Further efforts are also needed to reduce oil and gas emissions, an important source of ozone precursor emissions in Boulder County.

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