

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

Presented by:

Pam Milmoe & Adam Eisele

A. Eisele^{1,2}, M. Hannigan¹, J. Milford¹, D. Helmig², P. Milmoe³, D. Tanner²

¹Department of Mechanical Engineering, University of Colorado, Boulder, CO 80309-0427

²Institute of Arctic & Alpine Research, University of Colorado, Boulder, CO 80309-0450

³Boulder County Public Health, Environmental Health Division, Boulder, CO 80304-1824

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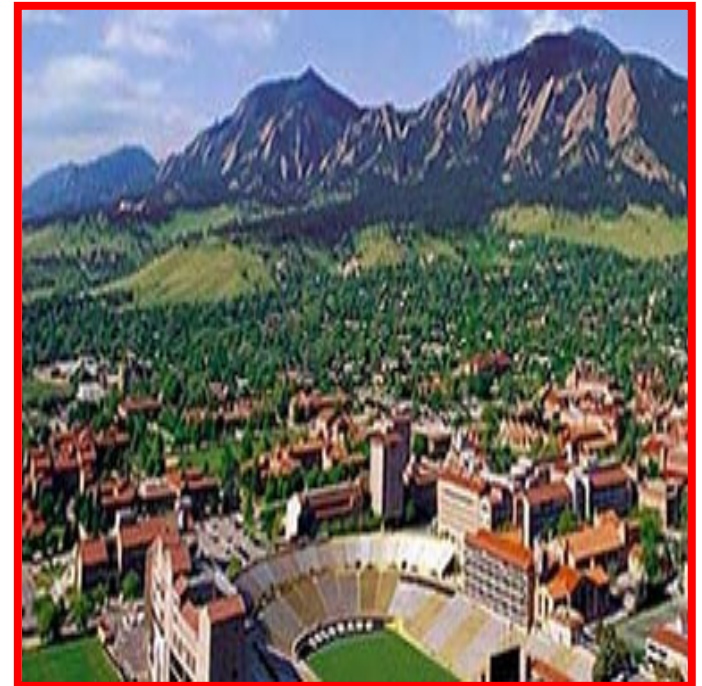
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Roadmap

- **Motivation**
- **Project Objectives**
- **Quality Assurance**
- **Data Analysis**
- **Source Apportionment**
- **Modeling Results**
- **Conclusions**
- **Recommendations**

Motivation

- **Anderson Study in 1996 found higher aldehyde concentrations in Boulder than Denver**
- **Oil & natural gas production activities in neighboring counties increased and began to pose potential health risks**
- **Denver Metro Area (DMA) experiences high ozone concentrations and is currently designated as non-attainment for failing to meet the 8-hr ozone NAAQS set by the EPA**



(www.colorado.edu)

Successful Partnerships

- **BCPH, University of Colorado, & EPA Region 8 collaborated to form project team that collected one year of detailed air toxics measurements**
- **A number of students were trained & educated on measuring air quality; two of which now work at EPA**
- **Public Health staff gained valuable monitoring knowledge and experience and provided valuable information to residents**

Boulder County Public Health Air Toxics Website

The screenshot shows a web browser window with the address bar displaying <http://www.bouldercounty.org/health/environ/airquality/outdoorair/airToxics.htm>. The page header includes the Boulder County logo and the text "Boulder County Colorado Government Online" and "Public Health". A navigation menu contains links for "BC Home", "Services", "Health Home", "Programs", "Health Services", "Employment", and "Search".

The main content area is titled "Air Quality" and includes the URL www.BoulderCountyAir.org. A breadcrumb trail reads: "You are here: Health Home > Environmental Health > Air Quality > Outdoor Air > Air Toxics Monitoring".

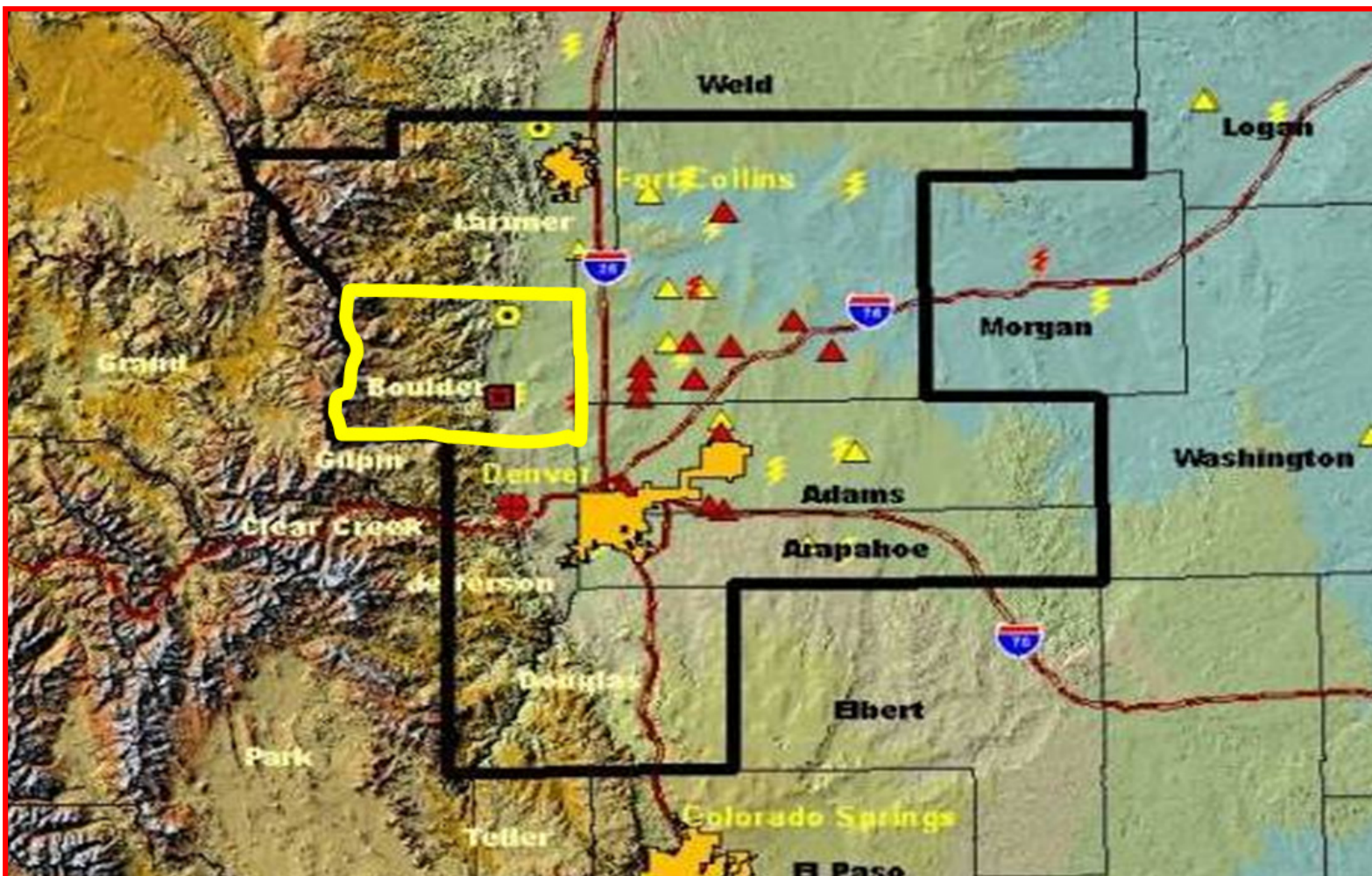
The left sidebar contains a search box and a list of services: "A-Z Services", "Health Home", "Environmental Health", "Indoor Air Quality", "Asbestos", "Lead", "Mold, Mildew", "Radon", "Pollutant Sources", "Outdoor Air Quality", "Alternative Transportation", "Clean Air Consortium", "Burning Info / Permit Request", "About Program", "Current Activity", "Frequently Asked Q's", and "Mission".

The main text area features the heading "Public Health to Monitor Air Quality in Boulder County" and a paragraph dated April 2006: "April 2006 - Boulder, CO – Boulder County Public Health (BCPH), will begin monitoring forty air toxics at five locations throughout the county beginning this winter, thanks to a grant from the U.S. Environmental Protection Agency. The last monitoring study in Boulder County, conducted in 1996, provided monitoring of just three air toxins at one Denver and two Boulder County locations." This is followed by a paragraph explaining that concentrations of pollutants were higher in Boulder than in Denver and that secondary pollutants are being formed.

Three sidebars on the right provide additional information: "Locations" with a map and "Select map to enlarge" link; "Air Toxics" with links to "Understanding Air Toxics and Pollutant Sources (PDF 1722 KB)" and "2005 Community-Scale Air Toxics Monitoring Grant Proposal (PDF 180 KB)"; and "Contact Air Toxics" with the address "Air Quality Program, 3450 Broadway, Boulder, CO, 80304" and phone number "(303) 441-1564".

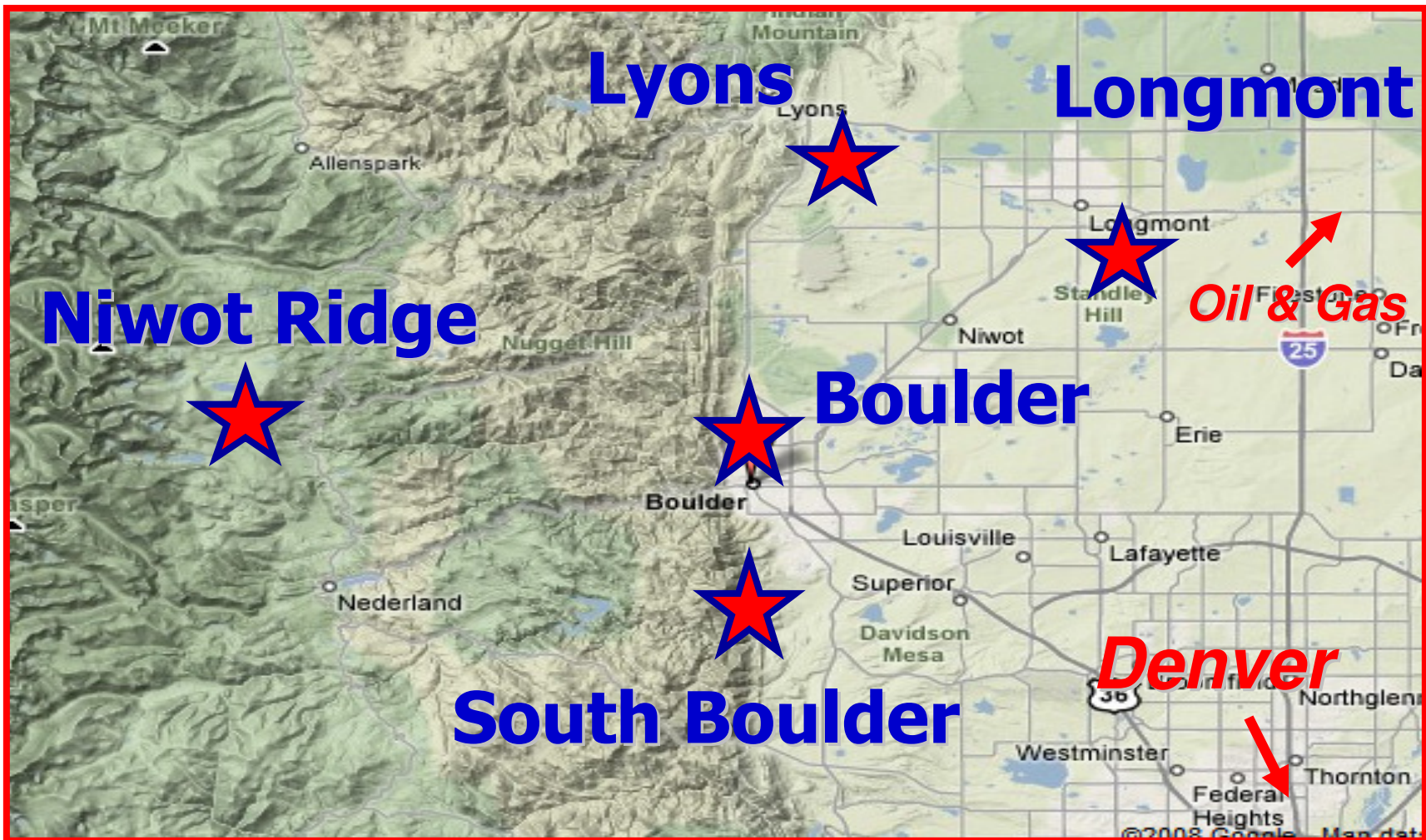
<http://www.bouldercounty.org/health/environ/airquality/outdoorair/airToxics.htm>

DMA NFR Nonattainment Area



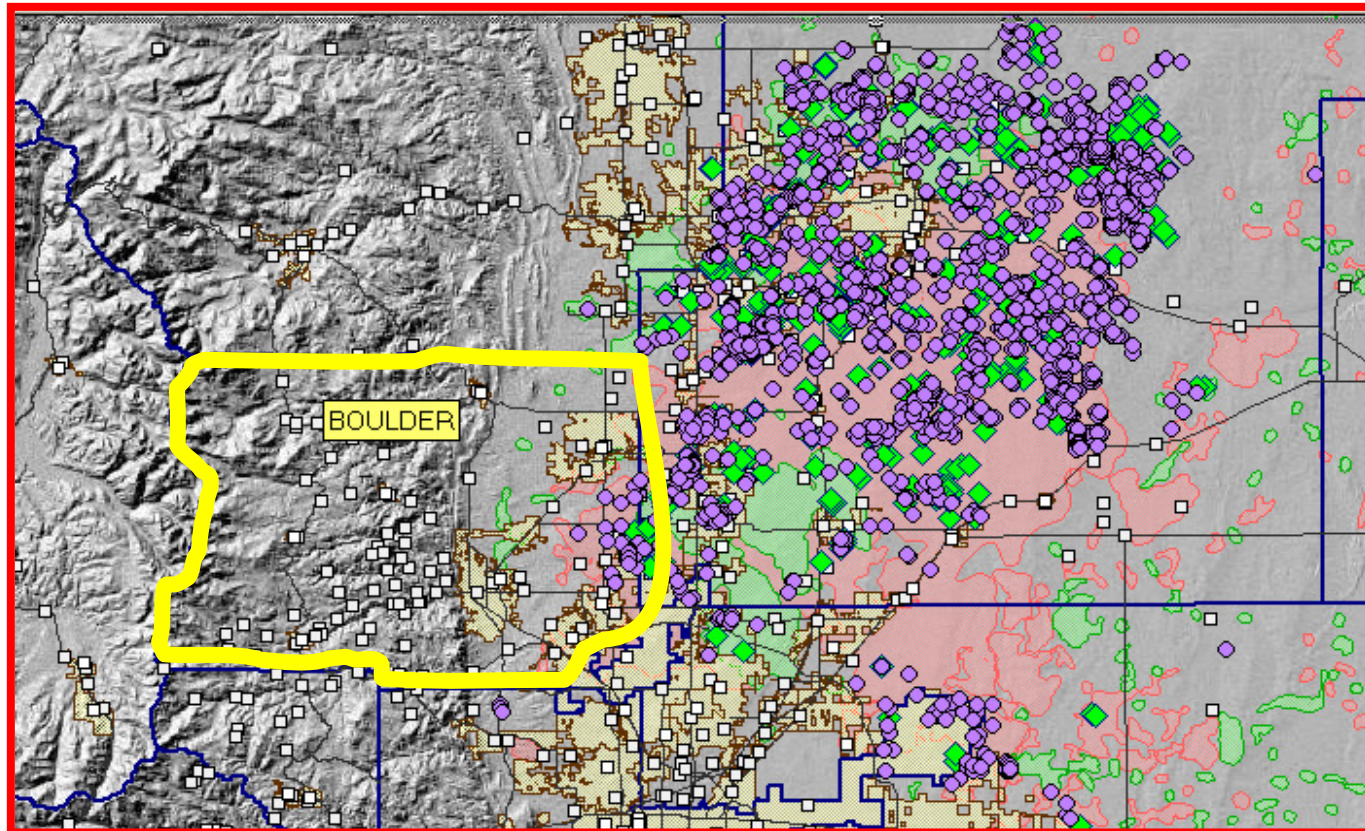
(EPA Region 8, 2004)

5 Sampling Locations



(2008 Google Maps)

Adjacent Oil & Gas Activities



(COGCC, 2008)

 Existing Permits

 Pending Permits

Project Objectives

- Delineate concentrations of local scale VOCs, carbonyls, & ozone
- Develop a baseline reference for longer-term measuring
- Evaluate and improve ambient air quality exposure & community-scale dispersion models
- Aid in air quality management strategies in Boulder County & Denver DMA NAA

What Did We Do?

Mar 1, 2007 – Feb 24, 2008

Sampling

- VOCs (27)
 - Carbonyls (8)
- 24hr integrated sample every 6th day @ each location
- Eight consecutive 3hr samples every 6th day @ one location

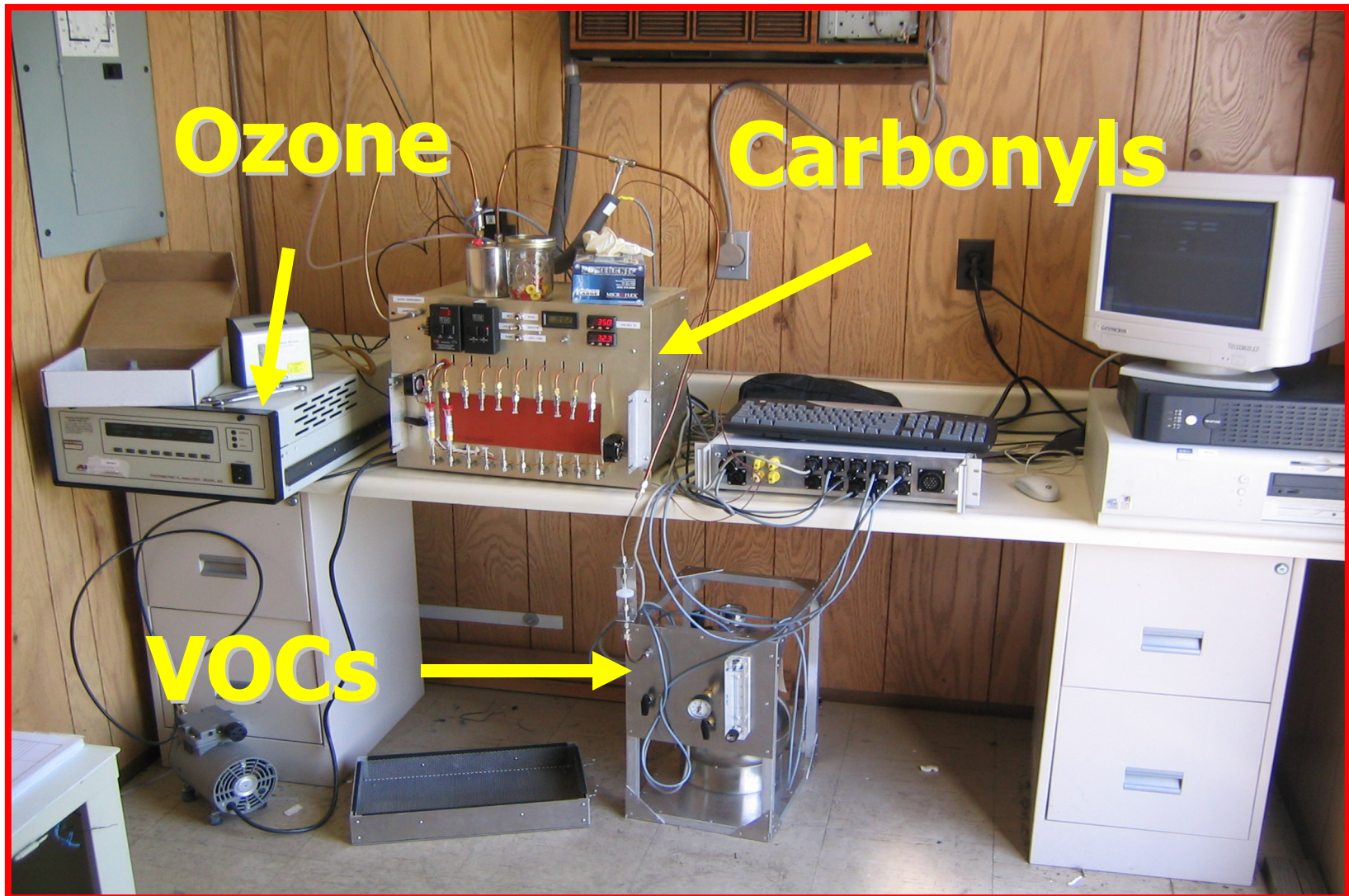
In-Situ Measurements

- Ozone
 - Meteorological Data
- continuous, 5 minute avg

Air Toxics Monitored

- **VOCs (*EPA Method TO-15*)**
 - benzene, toluene, ethylbenzene, xylenes, hexane, & styrene
- **Carbonyls (*EPA Method TO-11A*)**
 - formaldehyde, acetaldehyde, & acrolein
- **Ozone (*40 CFR, Part 50 App. D*)**

Sampling Instrumentation



Overall Data Completeness

VOCs

~85%

Carbonyls

~94%

Ozone

~95%

Includes 3-hour and 24-hour samples

Percent of Samples Detected

Carbonyls

	3-hr	24-hr
formaldehyde	75	100
acetaldehyde	55	100
acrolein	2	77
acetone	68	100
propionaldehyde	28	94
crotonaldehyde	1	12
butyraldehyde	63	99
benzaldehyde	3	33

VOCs

	3-hr	24-hr
n-butane	100	100
n-pentane	99	98
hexane	97	94
toluene	99	98
octane	69	68
ethylbenzene	90	88
m&p-xylene	95	97
o-xylene	72	72
nonane	65	66

24-hr VOC Duplicates

Analyte	# of samples	Average RPD
n-butane	35	12
trans-2-butene	10	20
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
2,3-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

24-hr Carbonyl Duplicates

Analyte	# of samples	Average 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%

Eight 3-hr samples vs. 24-hr samples

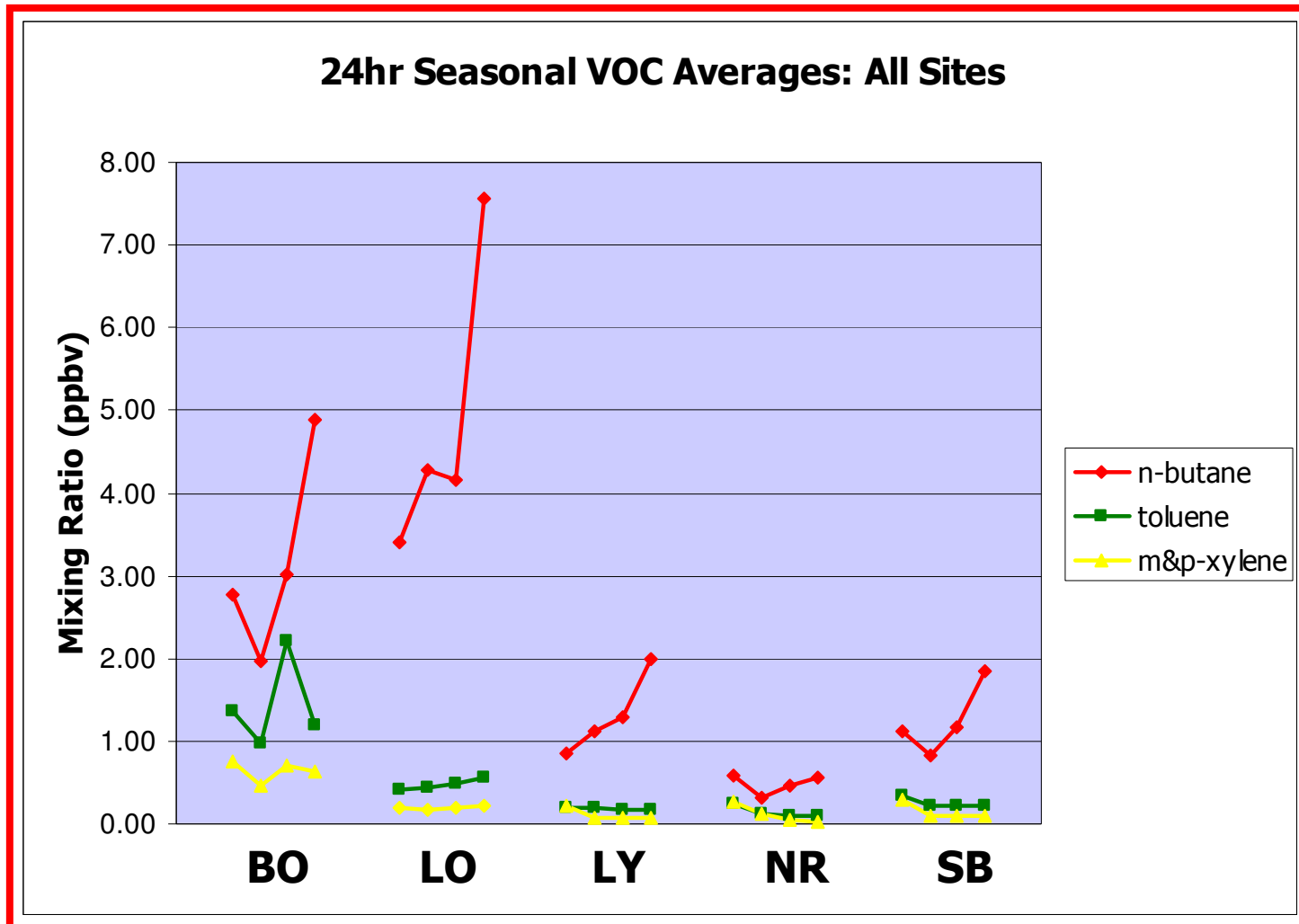
Average Absolute RPD of Eight 3-hr Samples vs. 24-hr Samples		
	n	Absolute RPD (%)
formaldehyde	40	10.2
acetaldehyde	40	20.2
acetone	40	19.3



Average RPD of Eight 3-hr Samples vs. 24-hr Samples		
	n	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

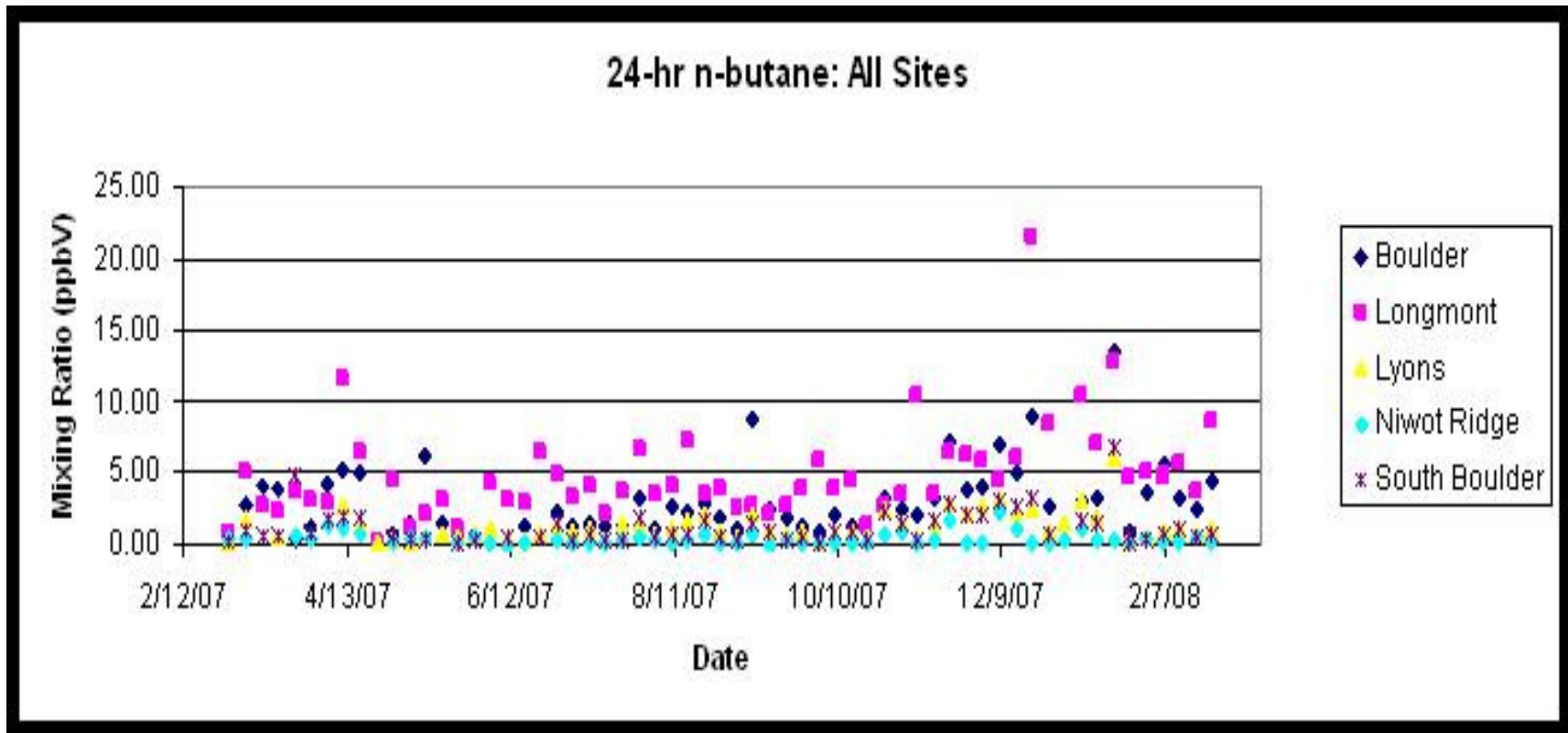


Seasonal Averages: VOCs



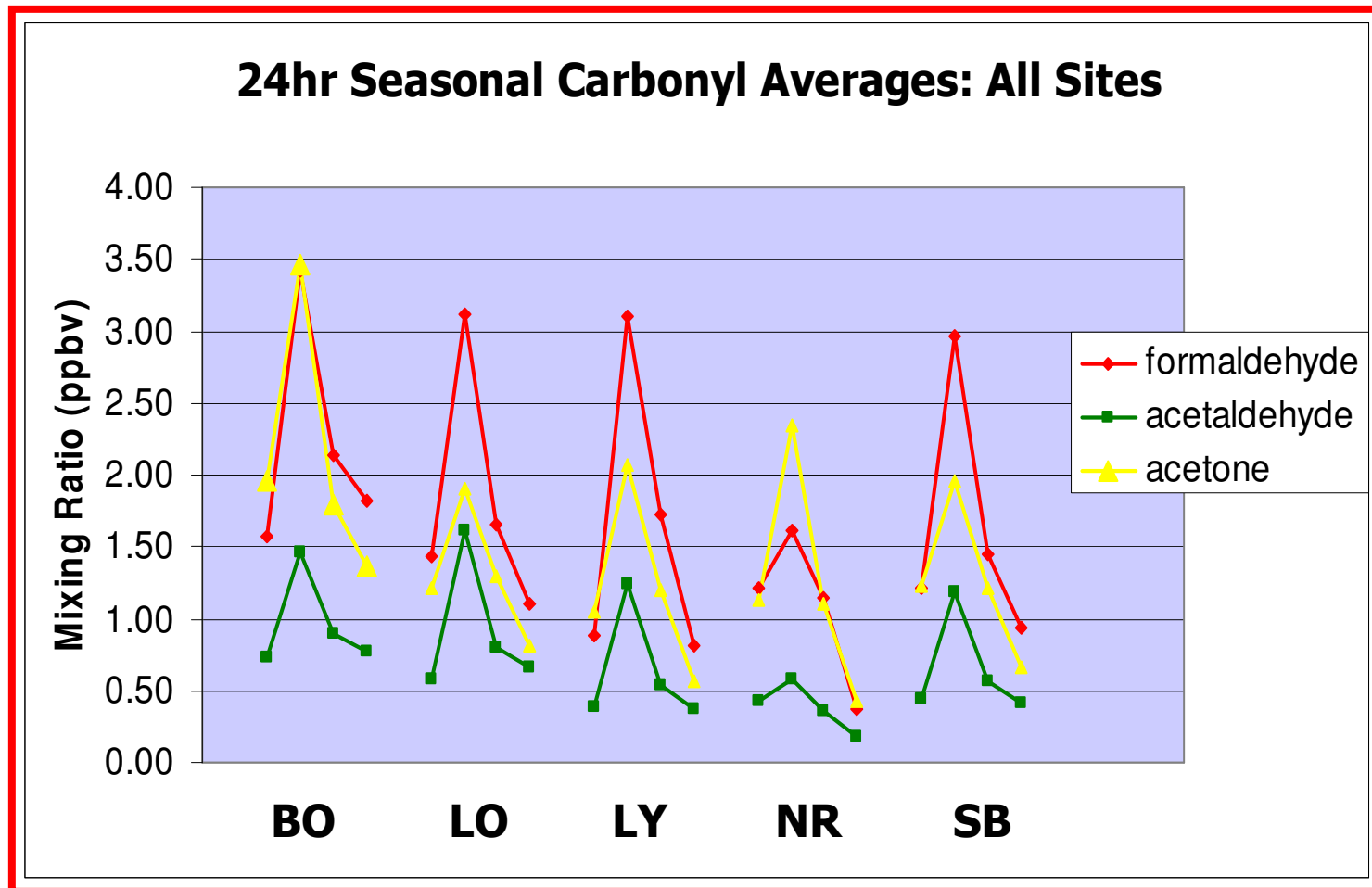
Each dot represents a season, starting with spring

24-hr n-butane



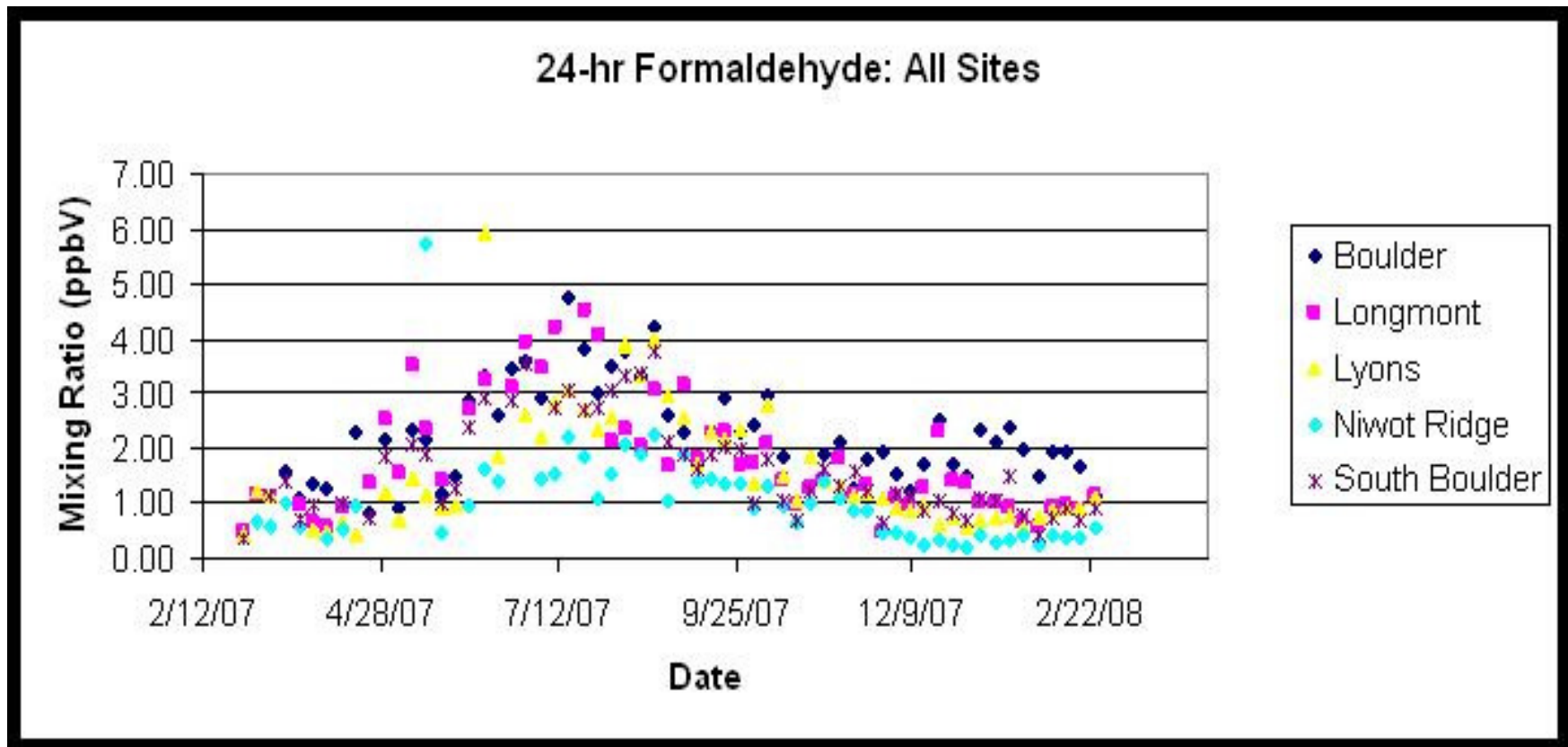
Overall, VOC concentrations were not seasonally dependent

Seasonal Averages: Carbonyls



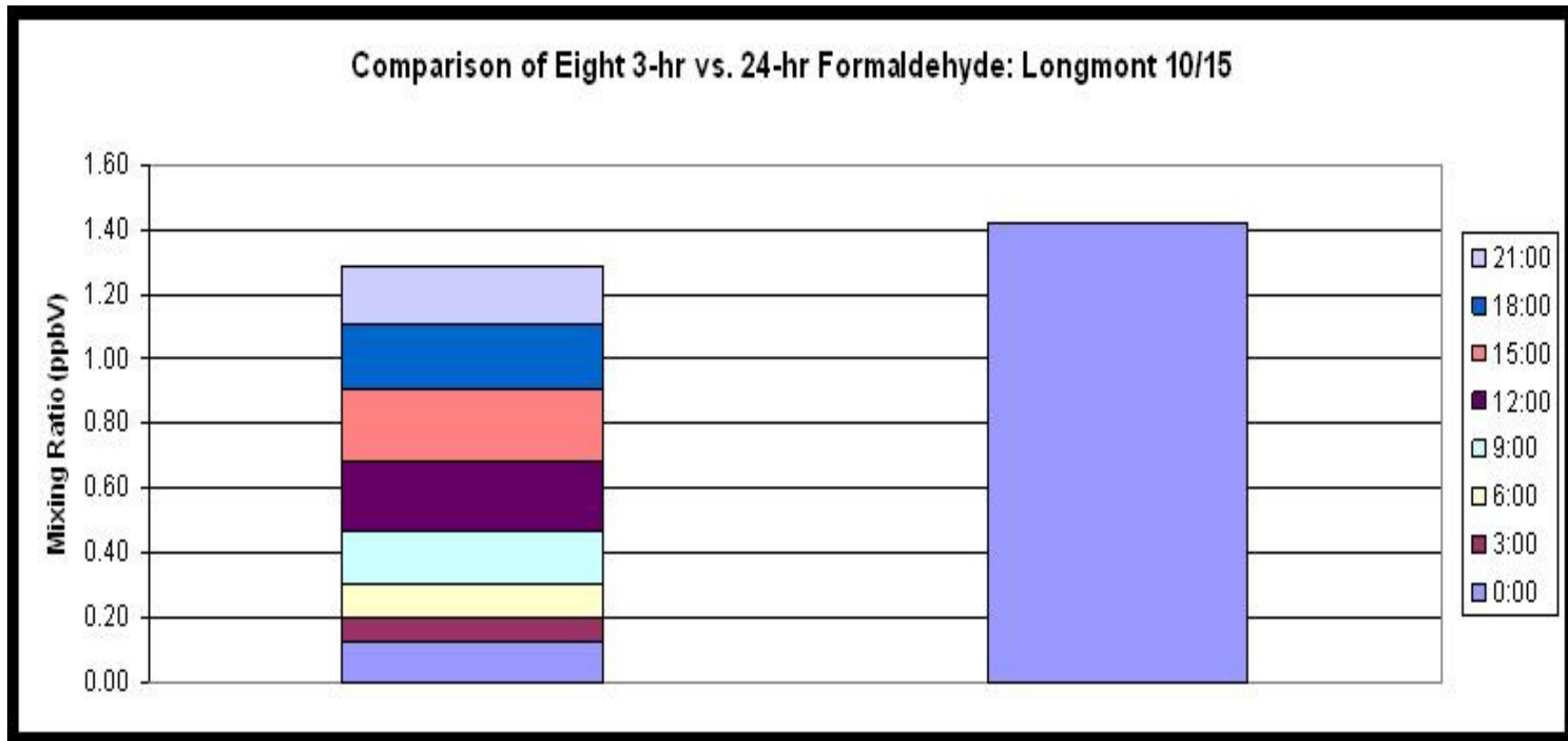
*Each dot represents a season, starting with spring*²¹

24-hr Formaldehyde



Carbonyl concentrations were greatest in summer months

Eight 3-hr vs. 24-hr Formaldehyde: Longmont



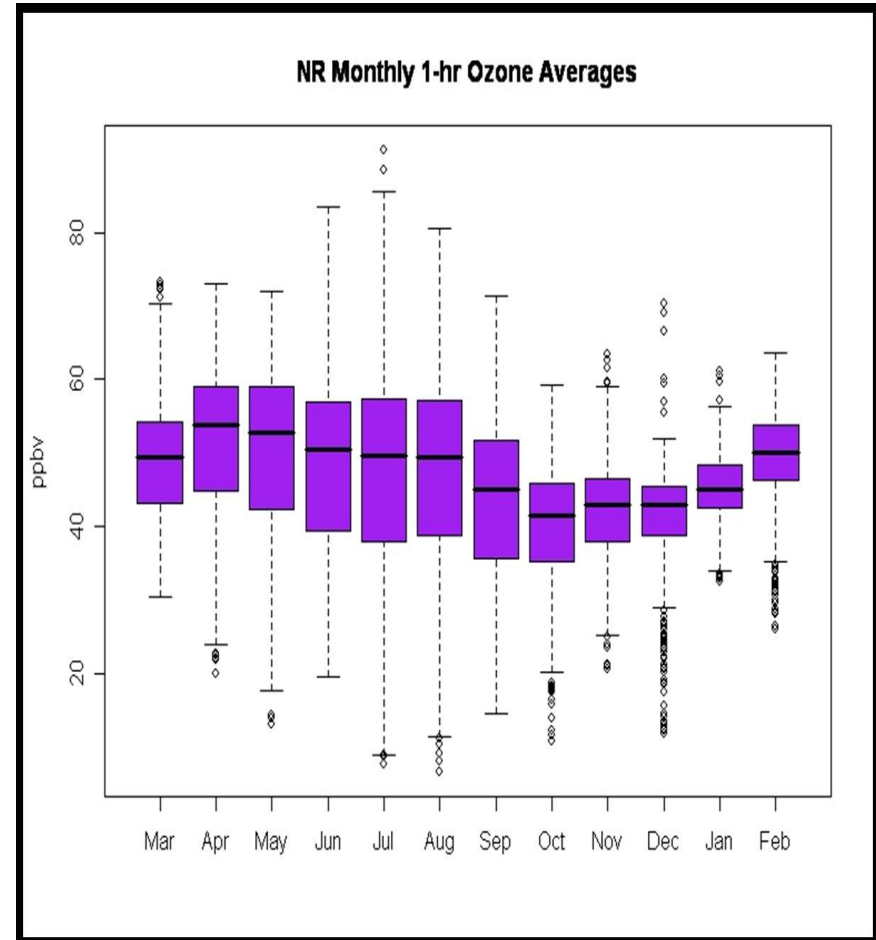
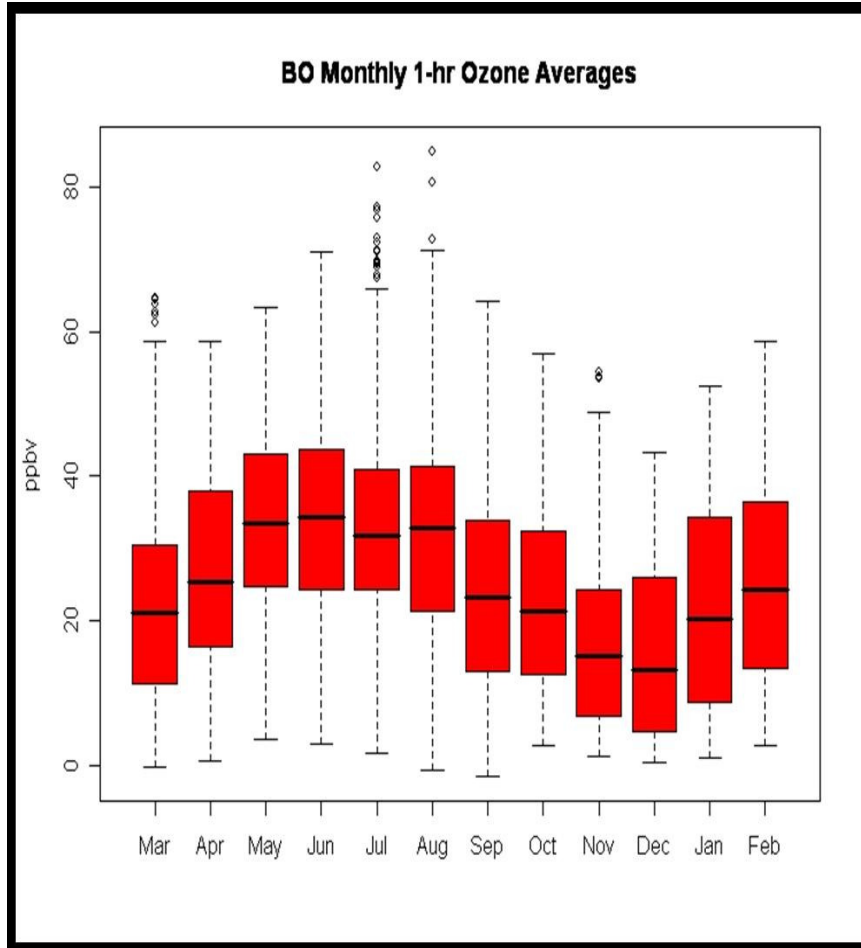
The sum of the eight 3-hr samples compared fairly well to the one 24-hr sample collected during the same period ²³

Ozone Correlation Matrix

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

The Niwot Ridge background site had the lowest correlation values when compared to the Front Range sites

Seasonal 1-hr Ozone Averages



Seasonal variations at Boulder & Niwot Ridge

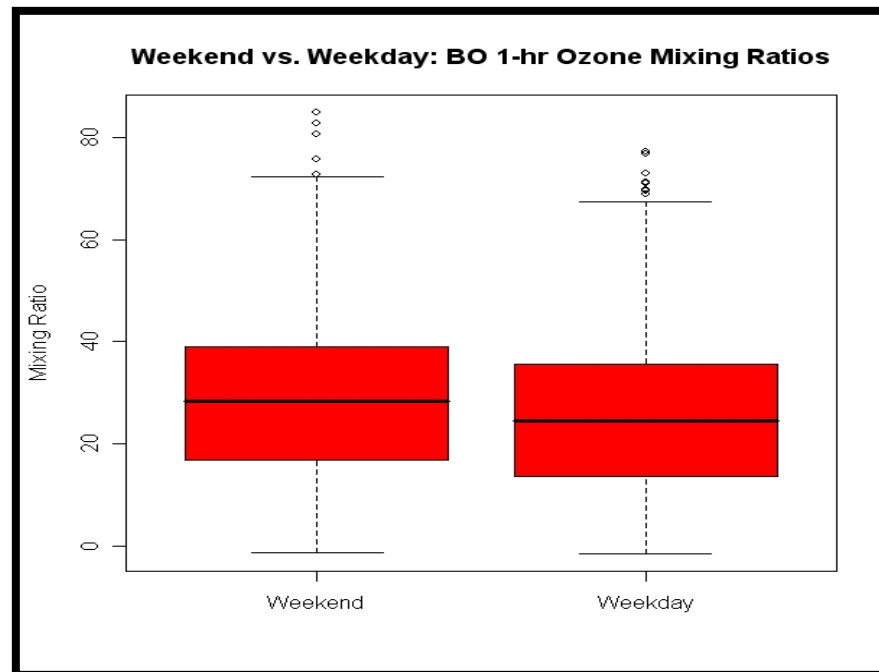
Weekend vs. Weekday Analysis

- Compared weekend vs. weekday samples for VOCs, carbonyls, and ozone to better understand the impact of mobile source traffic

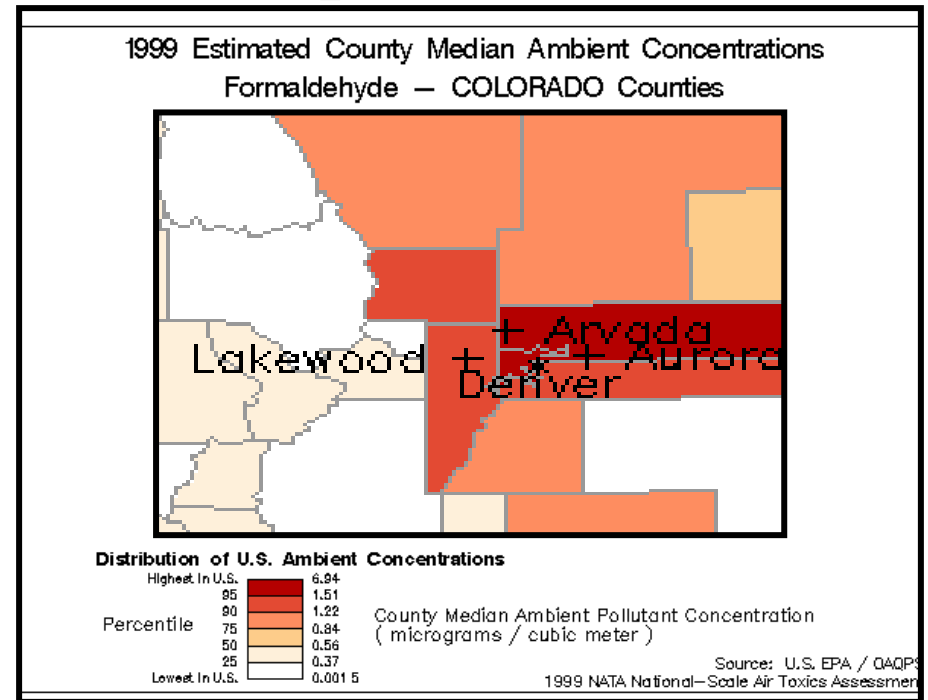
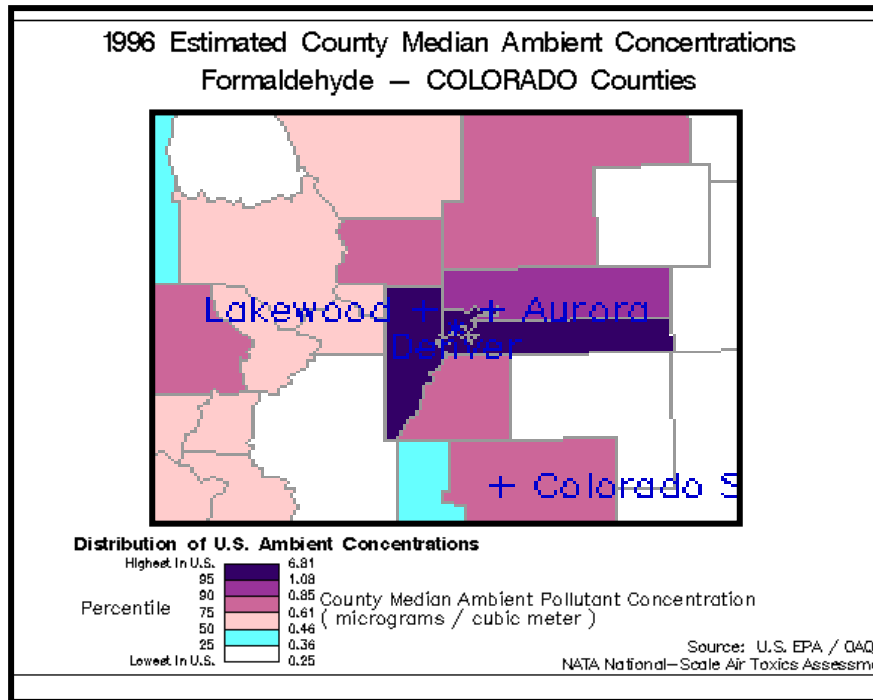
Weekend vs. Weekday 24-hr Median Concentrations (in ppbV)				
	Boulder		Niwot Ridge	
	Weekday	Weekend	Weekday	Weekend
formaldehyde	2.15	2.10	0.96	0.67
acetaldehyde	0.95	0.81	0.36	0.28
n-butane	2.45	3.32	0.29	0.39
toluene	1.21	0.95	0.11	0.11
m&p-xylene	0.58	0.44	0.06	0.06

Weekend vs. Weekday Ozone

Annual 1-hr Ozone Medians at Each Site (in ppbV)									
<u>Boulder</u>		<u>Longmont</u>		<u>Lyons</u>		Niwot Ridge		<u>South Boulder</u>	
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



1996 & 1999 EPA NATA for Formaldehyde



(www.epa.gov/nata/mapconc.html)

1996 NATA: 0.61–0.85 $\mu\text{g}/\text{m}^3$

1999 NATA: 1.22-1.51 $\mu\text{g}/\text{m}^3$

2007-2008 Boulder County Median: **1.50 $\mu\text{g}/\text{m}^3$**

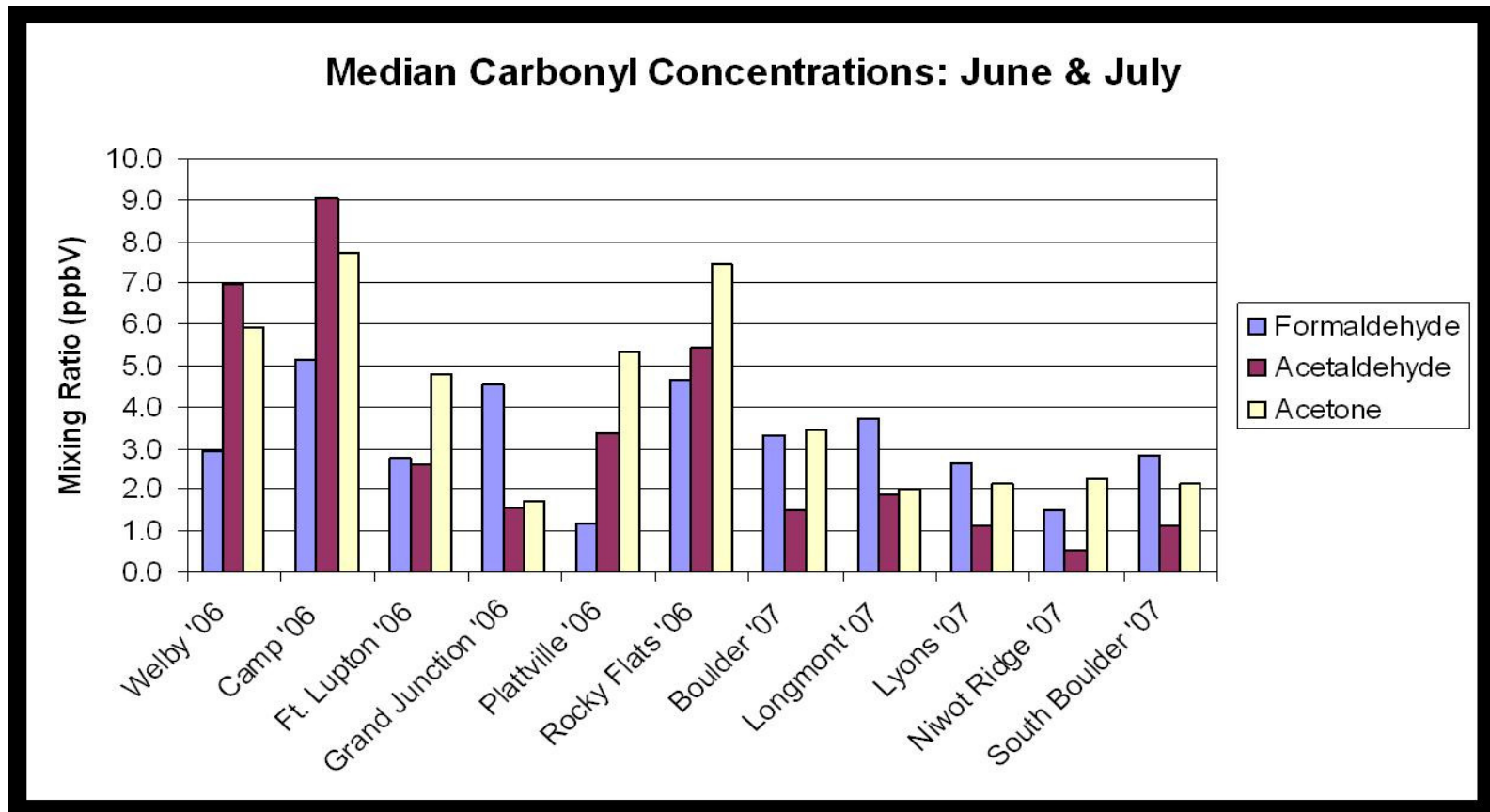
DDEH 05-06 vs. BCPH 07-08

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

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

Overall, BCPH values were less than the Denver Study

CDPHE 2006 Summer Study



BCPH values were also less than the 2006 CDPHE data

Source Apportionment

- **Pairwise correlation analysis**
- **Principal Components Analysis (PCA)**

24-hr Carbonyl Correlation Matrix: Boulder Site

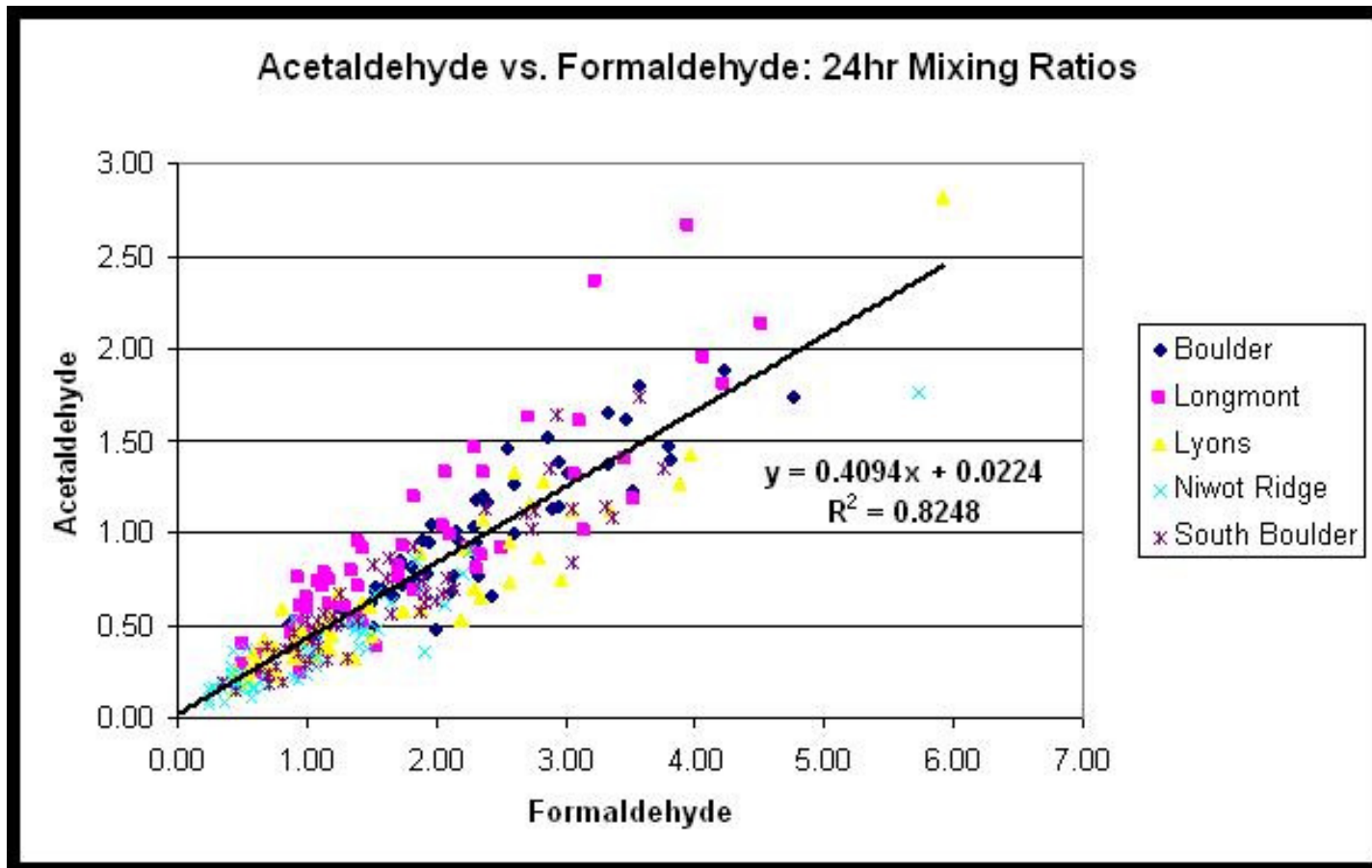
	formaldehyde	acetaldehyde	acrolein	acetone	propionaldehyde	crotonaldehyde	butyraldehyde	benzaldehyde
formaldehyde	1							
acetaldehyde	0.91	1						
acrolein	0.10	0.30	1					
acetone	0.73	0.78	0.08	1				
propionaldehyde	0.86	0.89	0.22	0.78	1			
crotonaldehyde	0.23	0.23	0.05	0.12	0.25	1		
butyraldehyde	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

Low correlation values were likely a quantification issue

24-hr VOCs Correlation Matrix: Boulder Site

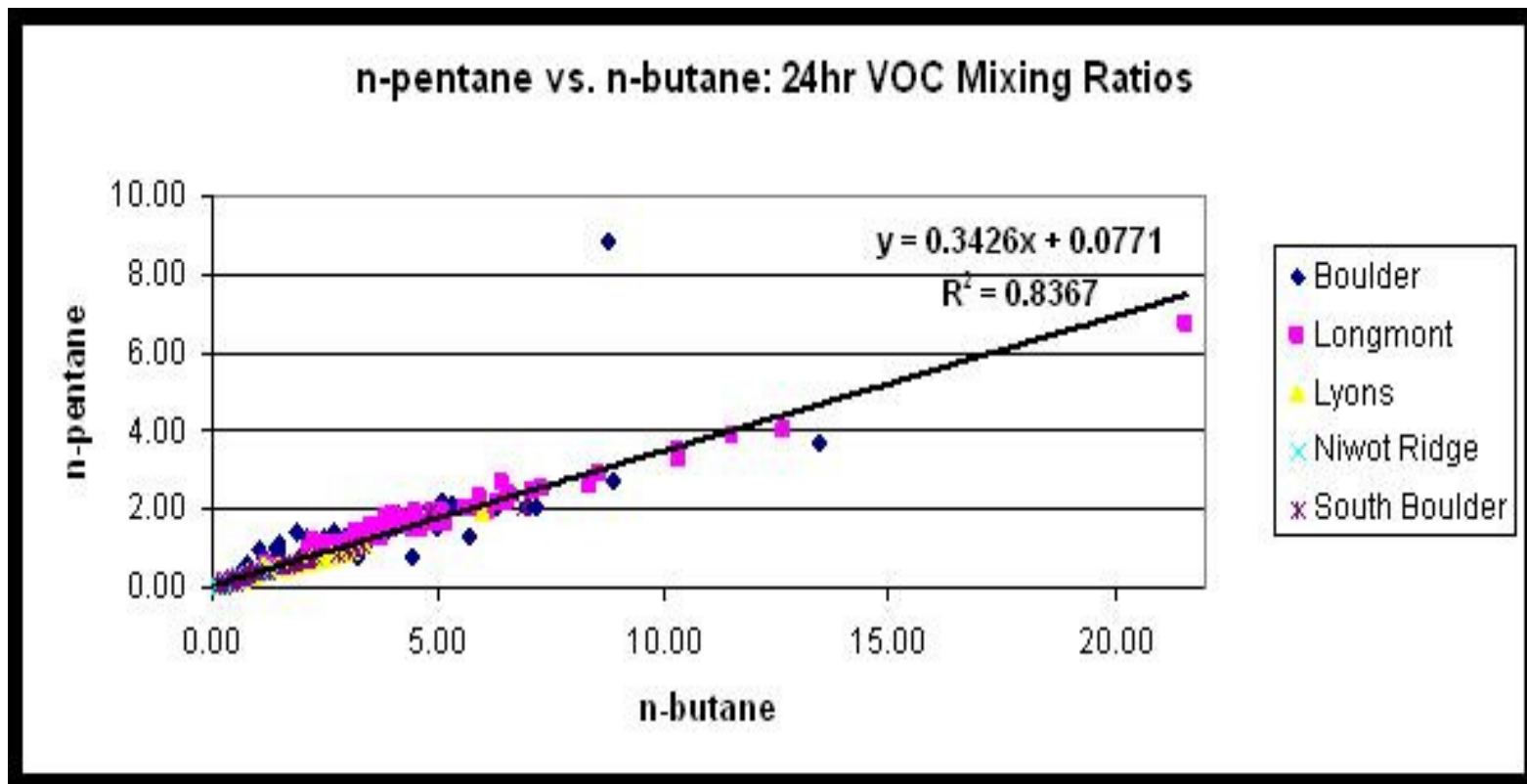
	n-butane	n-pentane	hexane	toluene	octane	ethylbenzene	m&p-xylene	o-xylene	nonane
n-butane	1								
n-pentane	0.71	1							
hexane	0.61	0.98	1						
toluene	0.52	0.84	0.86	1					
octane	0.61	0.95	0.97	0.83	1				
ethylbenzene	0.48	0.89	0.93	0.83	0.93	1			
m&p-xylene	0.51	0.90	0.94	0.83	0.95	0.99	1		
o-xylene	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

Acetaldehyde vs. Formaldehyde



Acetaldehyde & formaldehyde correlated well at all sites

n-pentane vs. n-butane



Strong VOC correlations suggest similar emission sources

Source Profiles

Table 1. Source profiles used in CMB modeling

	Hydroxyl radical rate constant (Carter, 1992) $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Roadway ($n=9$) ppbC % of TNMOC† (Lonneman <i>et al.</i> , 1991)		Gasvap ($n=6$) ppbC % of TNMOC† (Lonneman <i>et al.</i> , 1991)	
		Average	S.D.	Average	S.D.
Sum of 38 species		57.60		60.53	
‡ Ethylene	8.45×10^{-12}	4.55	0.47	0.01	0.01
‡ Acetylene	7.80×10^{-13}	3.94	0.65	0.01	0.02
‡ <i>Iso</i> -butane	2.36×10^{-12}	1.17	0.26	4.66	1.19
‡ <i>n</i> -butane	2.56×10^{-12}	4.31	0.73	19.33	2.17
‡ <i>n</i> -pentane	4.11×10^{-12}	2.80	0.28	8.53	0.60
‡ 2-methylpentane	5.66×10^{-12}	2.55	0.08	3.99	0.45
‡ 3-methylpentane	5.77×10^{-12}	1.49	0.05	2.18	0.28
‡ Methylcyclopentane/ 2, 4-dimethylpentane	8.11×10^{-12}	1.56	0.07	1.37	0.07
‡ Benzene	1.29×10^{-12}	2.86	0.19	0.88	0.13
‡ Cyclohexane/ 2-methylhexane	7.56×10^{-12}	1.09	0.05	0.67	0.11
‡ 2, 2, 4-trimethylpentane	3.72×10^{-12}	2.62	0.22	0.66	0.32
‡ 2, 3, 4-trimethylpentane	8.72×10^{-12}	1.00	0.10	0.17	0.07
‡ Ethylbenzene	7.09×10^{-12}	1.34	0.03	0.10	0.01
* Propylene	2.60×10^{-11}	2.05	0.17	0.13	0.09
* <i>m/p</i> -xylene	1.90×10^{-11}	4.54	0.14	0.29	0.04
* <i>o</i> -xylene/ <i>n</i> -nonane	1.37×10^{-11}	1.96	0.06	0.11	0.01
§ 1-butene	3.11×10^{-11}	1.25	0.09	1.16	0.71
§ <i>Trans</i> -2-butene	6.30×10^{-11}	0.43	0.03	1.82	0.50
§ <i>Cis</i> -2-Butene	5.58×10^{-11}	0.35	0.03	1.62	0.38
§ 1-pentene	3.11×10^{-11}	0.41	0.03	1.32	0.19

(Lin et al., 1994)

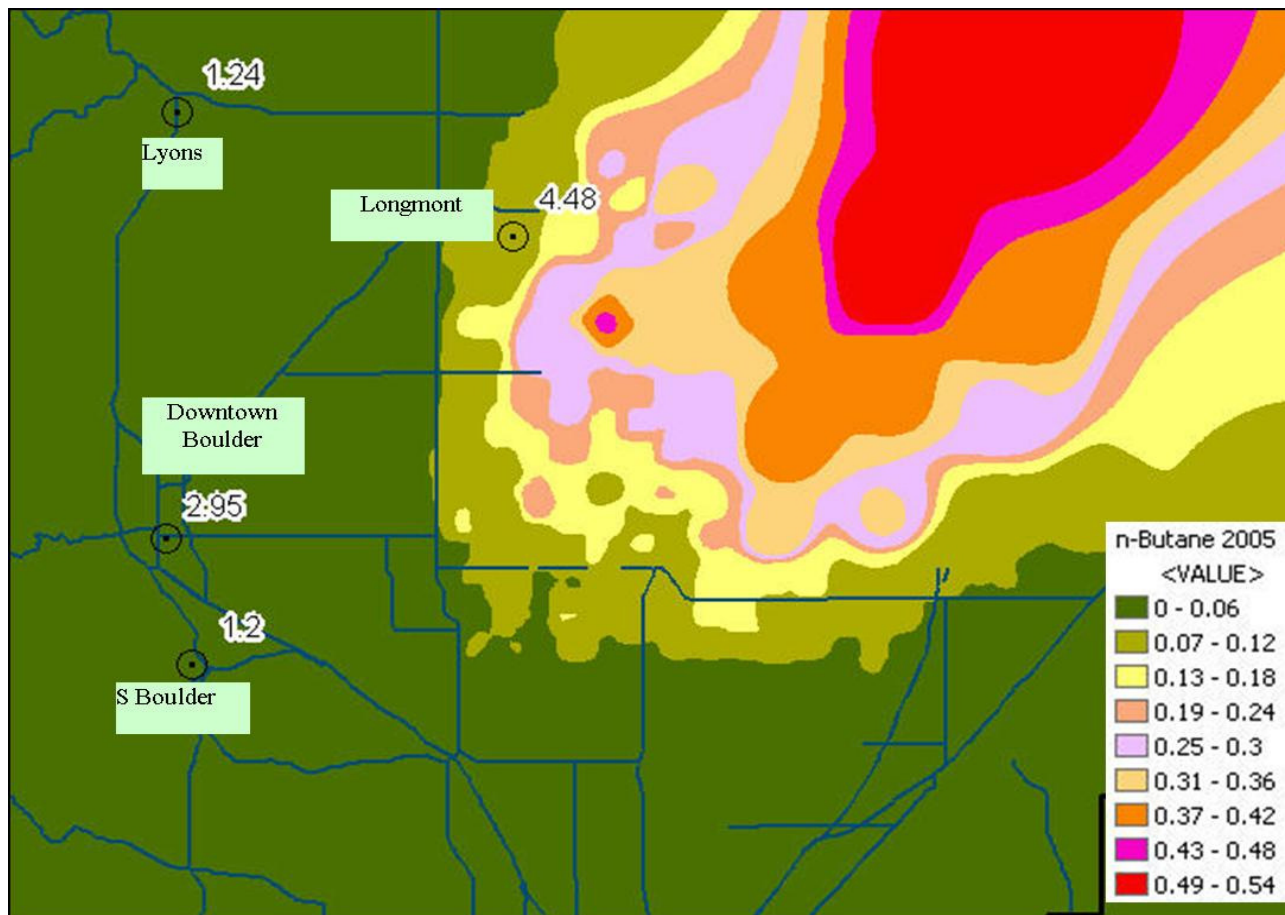
Potential Pollution Source Based on PCA Results (based on variance)

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

Dispersion Modeling

- **AERMOD & MOBILE6.2 models used**
- **Pollutants included in model**
 - Formaldehyde
 - Acetaldehyde
 - BTEX
 - Hexane
 - Diesel PM

Predicted 2006 n-butane with 2007 Boulder Observed n-butane (ppbV)



Inventories underpredict n-butane direct emissions

Dispersion Model Results

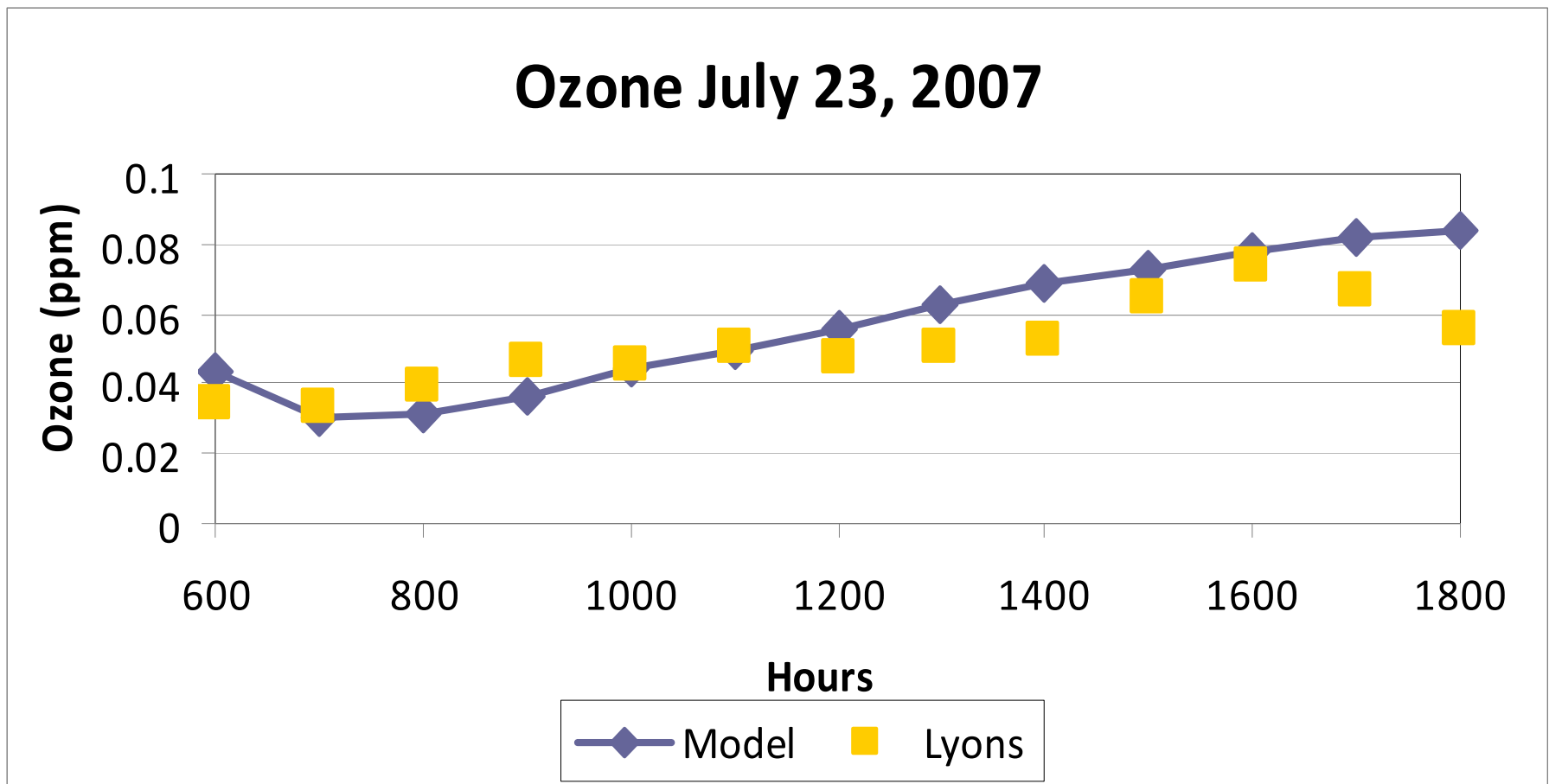
Site	Obs	AERMOD	Obs	AERMOD	Obs	AERMOD
	Butane avg	Butane avg	Pentane avg	Pentane avg	Hexane avg	Hexane avg
Boulder Fire Station	2.95	0.002	1.35	<.001	0.71	0.04
Longmont	4.48	0.09	1.66	0.02	0.62	0.01
Lyons	1.24	0.001	0.46	<.001	0.21	0.005
South Boulder	1.20	0.001	0.44	<.001	0.21	0.005

- **AERMOD generally under predicts by a factor of 2–10 in Denver-Boulder Region**
- **Using local/rural met measurements would improve modeled results**

Photochemical Modeling

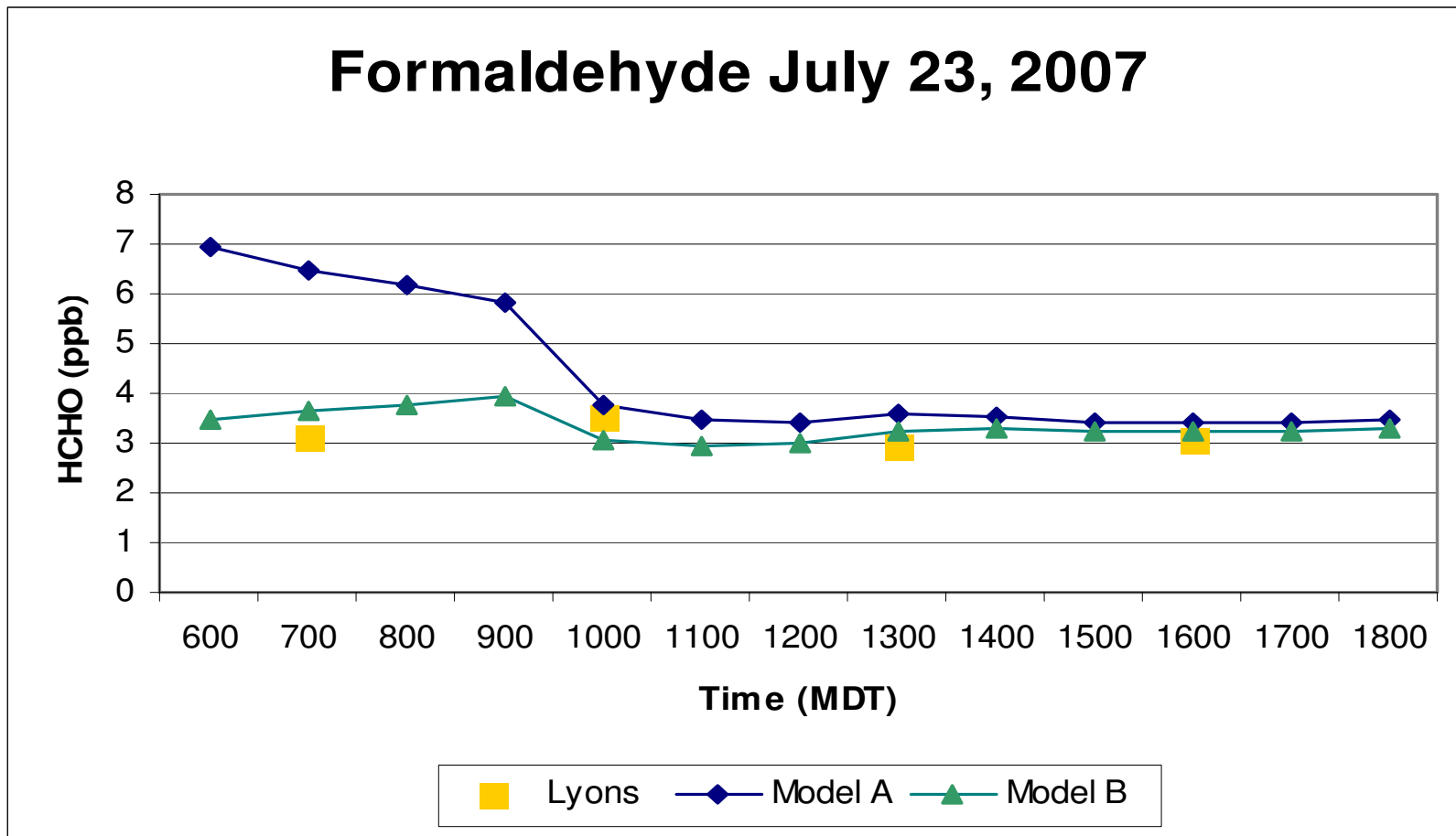
- OZIPR model used to model formation of ozone and secondary pollutants
- Run from May - August 2007 with observed data
- Overall, OZIPR generally overpredicted acetaldehyde concentrations by a factor of 3

Comparison of OZIPR Predictions & Observed Ozone at Lyons, CO



Ozone was simulated reasonably well on most days ⁴²

Comparison of OZIPR Predictions & Observed Formaldehyde at Lyons, CO



Formaldehyde predictions were much closer for Model B

Summary

- **Delineate concentrations of local scale air toxics**
- **Develop a baseline reference for longer-term measuring**
- **Evaluate and improve air quality exposure and dispersion models**
- **Guide air quality management strategies in Boulder County & DMA NAA**

Conclusions

- Overall carbonyl & VOC concentrations in 07-08 were lower than those in the Anderson Studies and other FR studies
- Carbonyl concentrations peaked in the summer months, suggesting increased photochemistry
- VOC concentrations were relatively stable and were not seasonably variable

Conclusions

- From PCA results, mobile source exhaust, natural gas condensate emissions, and meteorology are significant pollution source
- Ozone values varied from site to site, but increased significantly in summer
- Ozone values occasionally exceeded the former/current 8-hr NAAQS values

Recommendations

- Increase sampling frequency for weekend vs. weekday analyses
- Use higher resolution sampling durations for source apportionment
- Use analytical equipment capable of quantifying additional natural gas markers
- Get EPA assistance with AQS uploads

Acknowledgements

- **Boulder County Public Health, Colorado Dept. of Public Health, & EPA Region 8**
- **Jana Milford, Mike Hannigan, & Detlev Helmig**
- **Steve Dutton, Greg Brinkman, David Tanner, Ian Hoffecker, Boulder Fire Rescue, Foothills Baptist Church, Gordon Pierce, Duane Kitzis, Gregg Thomas, Ken Distler, Michael Copeland, Jacques Heuber, Molly Brodin, & Larry Anderson**

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