



Denver Department of Environmental Health Division of Environmental Quality

Airing on the Side of Caution:

The Denver Air Toxics Assessment – Phase III: 2005-06 Air Toxics Monitoring

August 5, 2008



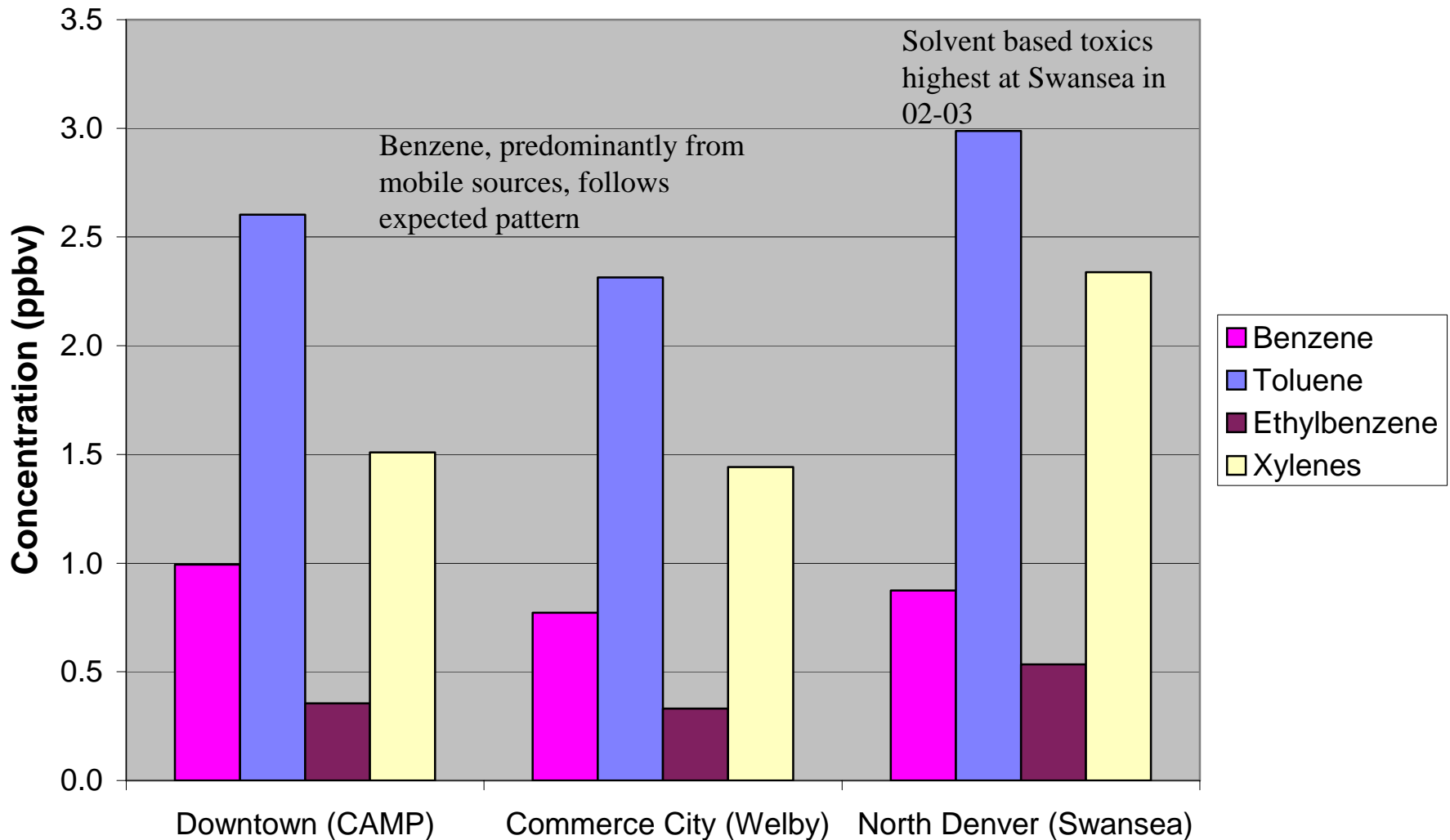
**Denver
Environmental Health**

Background

- Denver developed air toxics modeling platform beginning in 1999
 - For pollutants with medium-high confidence in emission inventories, benzene and carbon monoxide, good model-to-monitor comparisons were observed
- EPA Community Based Air Toxics Monitoring Program
 - Allows for non-traditional look at spatial and temporal differences within a small area
 - Allows for additional insight into “hot spots”

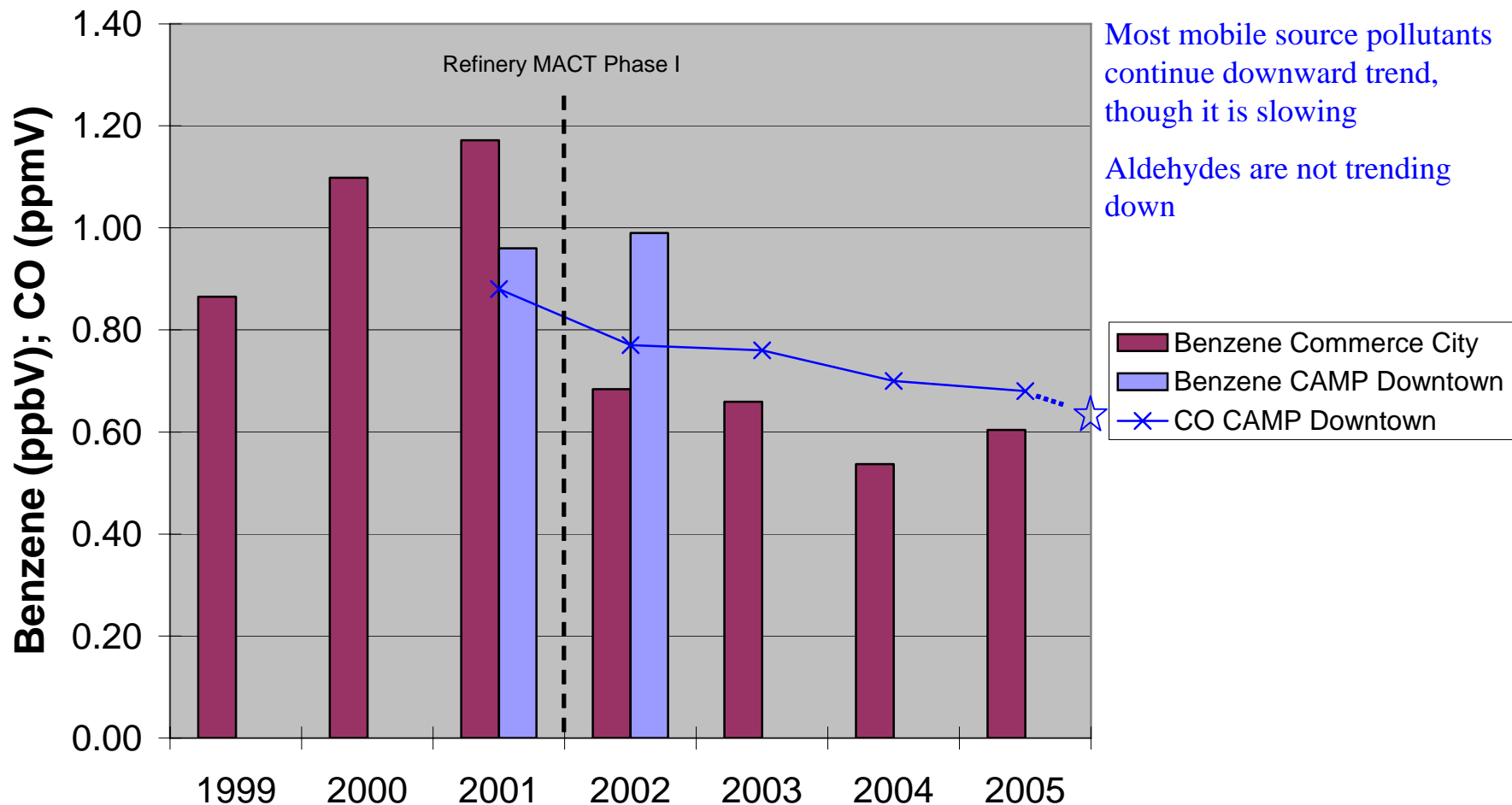
What Does Historic VOC Data Tell Us?

2002-03 CDPHE Air Toxics Monitoring Data



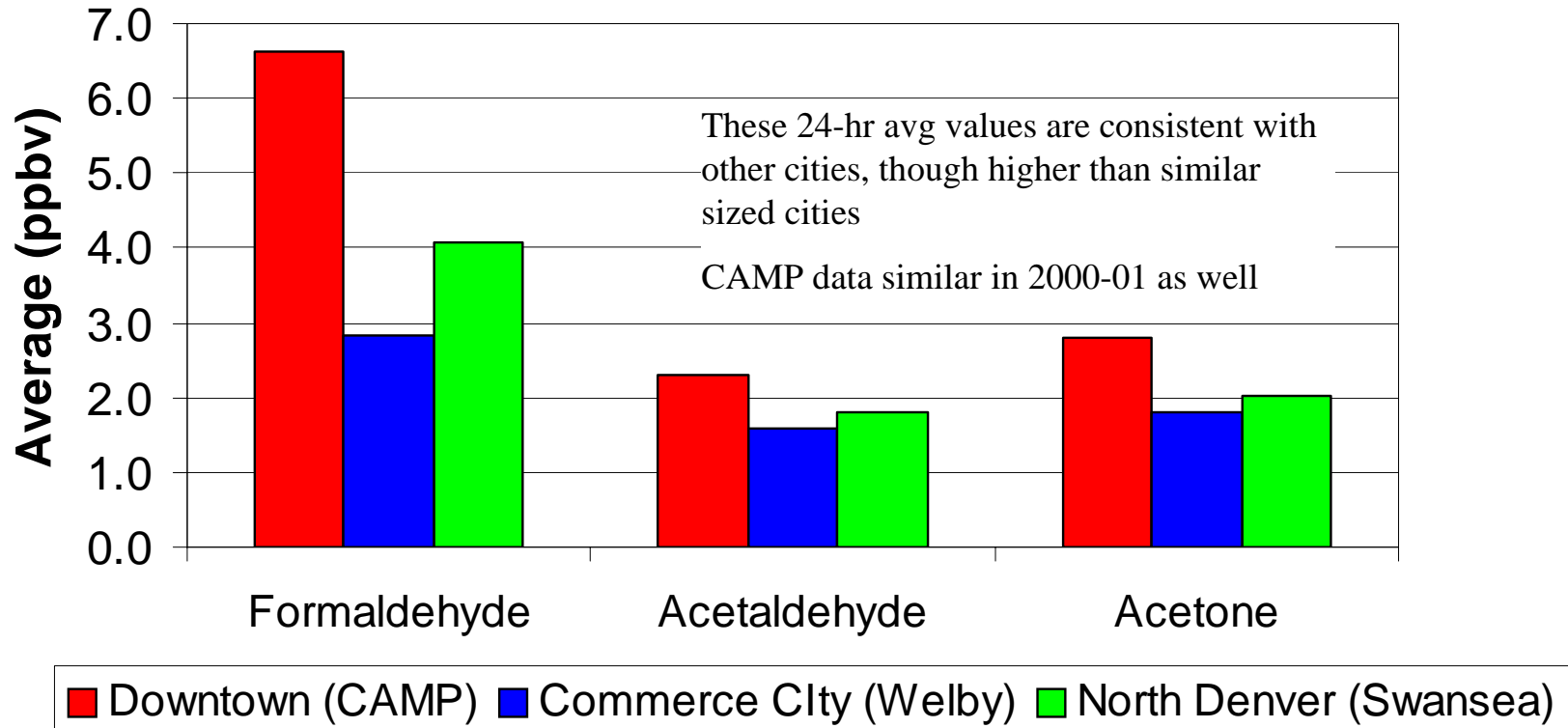
Historic VOC Data (continued)

Benzene and Carbon Monoxide Trends in Denver 1999-2005



Historic Carbonyl Data

Denver 2002/03 --- Carbonyls - average



- Formaldehyde and acetaldehyde are expected to be formed largely through secondary photochemical reactions
- Differences between sites similar to benzene (primary emissions)

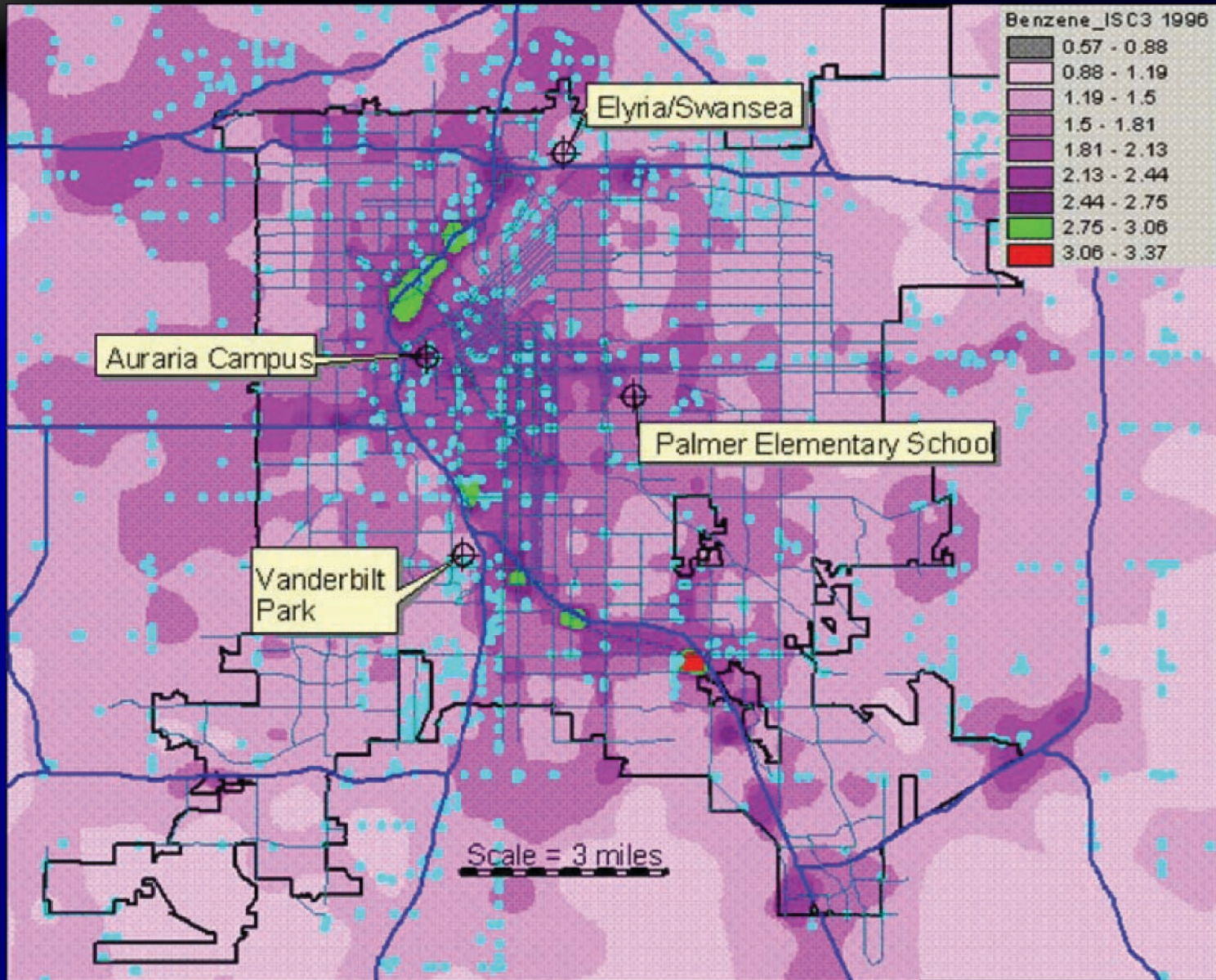
Denver Air Toxics Monitoring

- Monitoring: Jun 05 – May 06
- 4 sites in Denver County
- VOC: 24-hr, 4-hr, < 1-hr (continuous)
- Carbonyls: 24-hr, 4-hr
- Portable Trailer Site:
 - 9 months at Auraria, 3 months at Swansea
 - Aethalometer (black carbon) & autoGC worked well
- Result = DATA OVERLOAD!

Lessons Learned

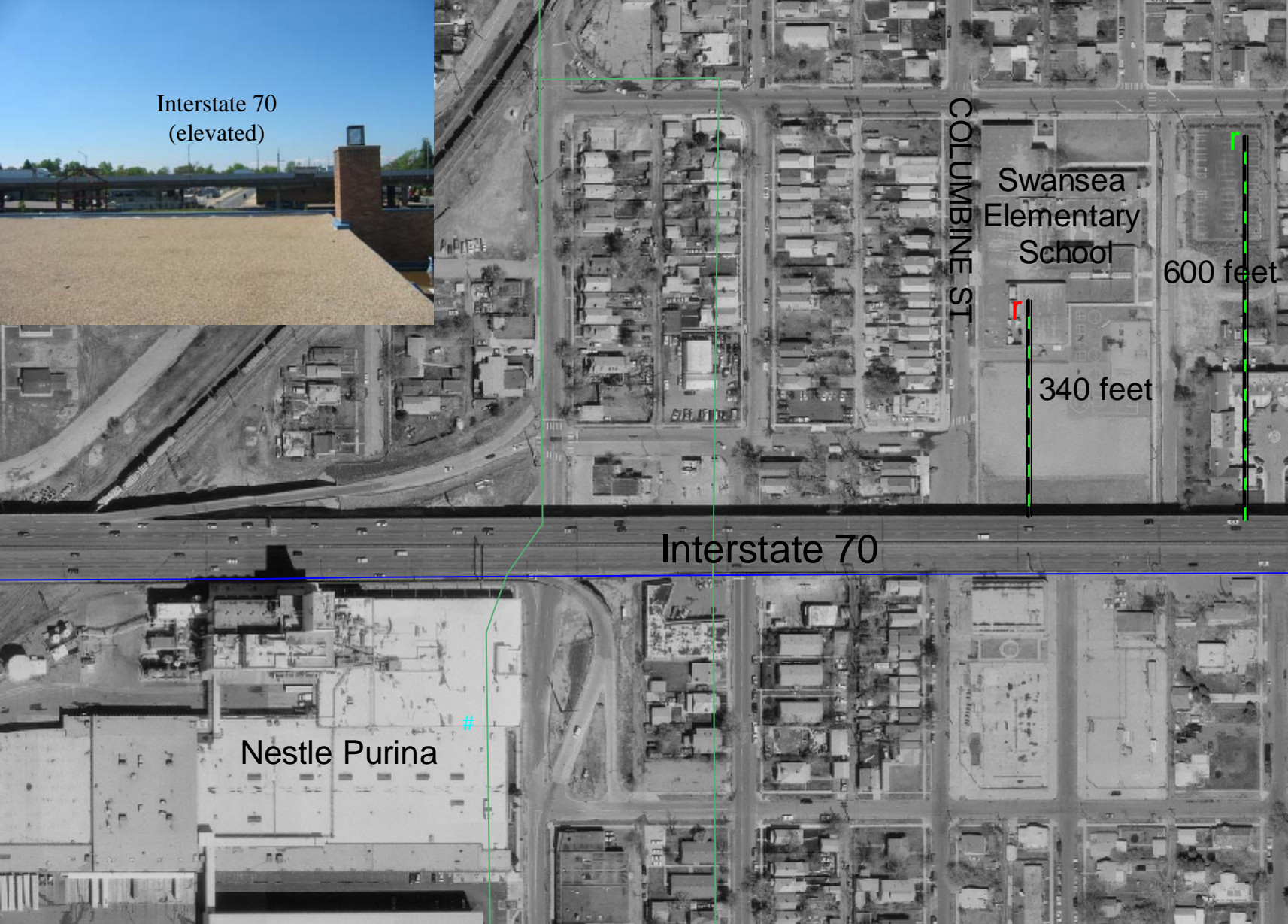
- Building our own samplers was a huge learning experience
 - Had 5 weeks to build and deploy after contract signed
 - Samplers at all sites changed at least once
- With numerous sample collection frequencies, staying on top of analyses was challenging
- Data processing was much more time consuming than anticipated
- Proficiency test audits should have come early in the project

Denver Monitoring Locations



- Expected Rankings: Auraria, Swansea, Vanderbilt, Palmer

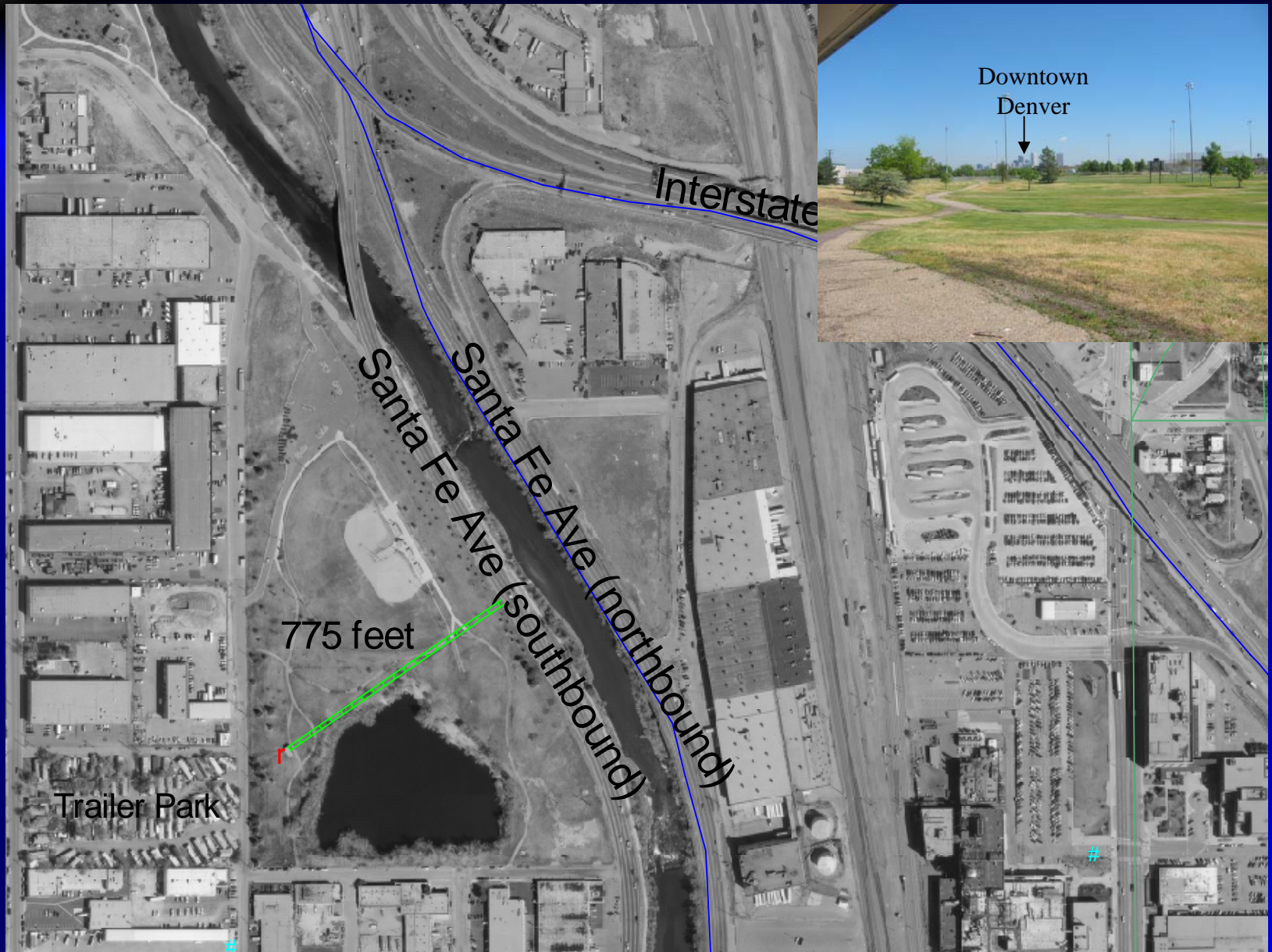
Swansea Elementary



Palmer Elementary



Vanderbilt Park

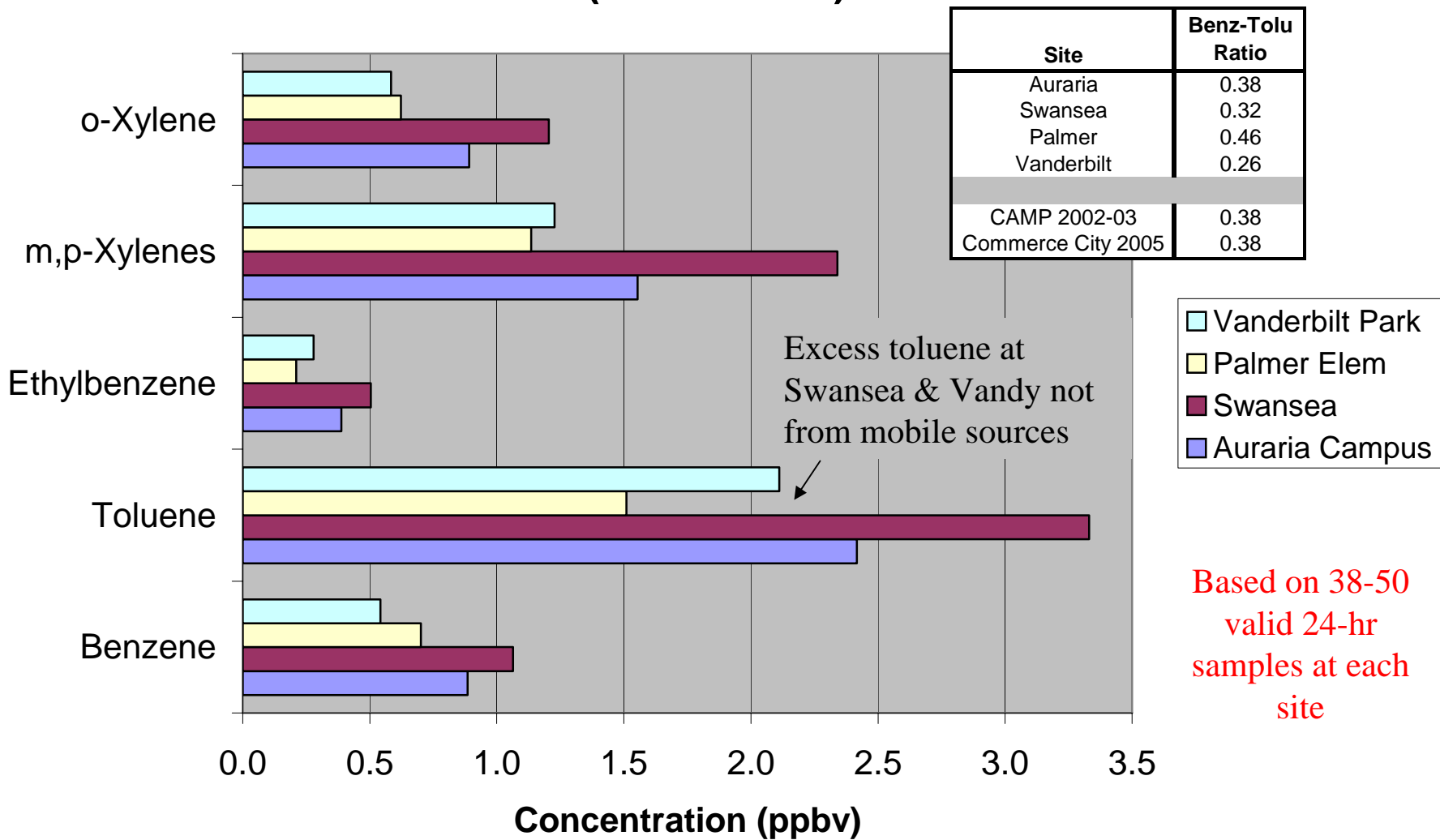


Auraria Campus



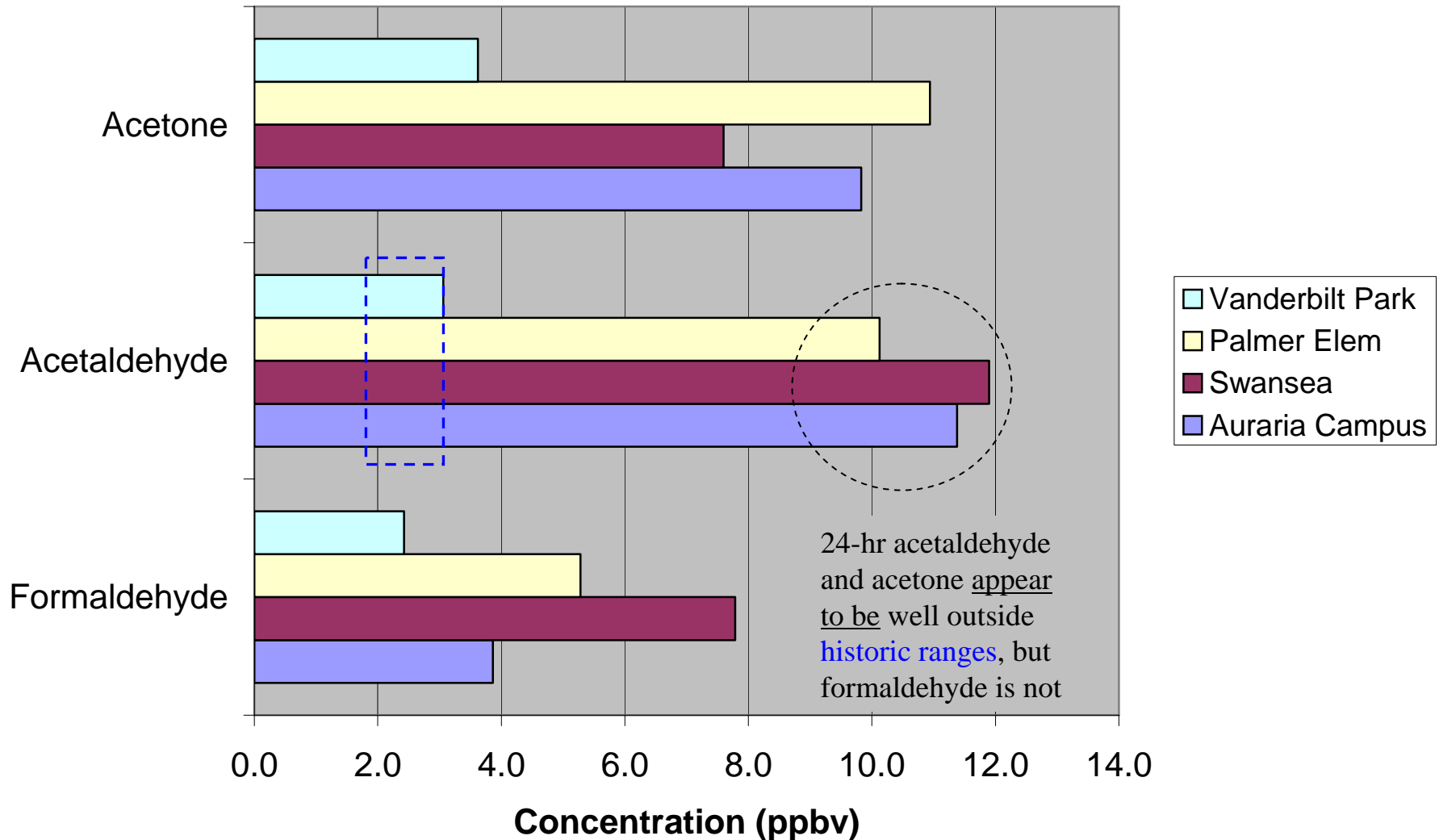
24-hr TO-17 Median BTEX Results

2005-06 Denver Median BTEX Concentrations (24-hr tubes)



24-hr Median Carbonyl Results

2005-06 Denver Median Carbonyl (24-hr TO-11a)

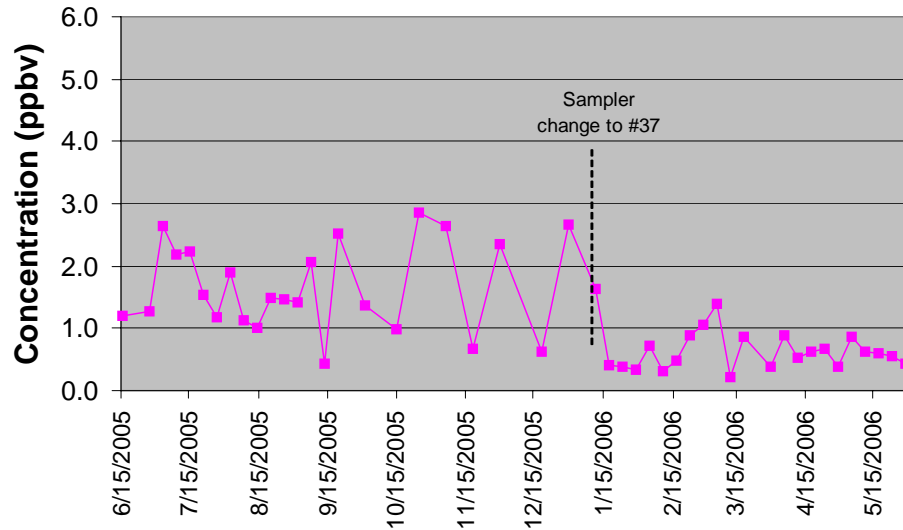


Possible Causes for Out of Range Data

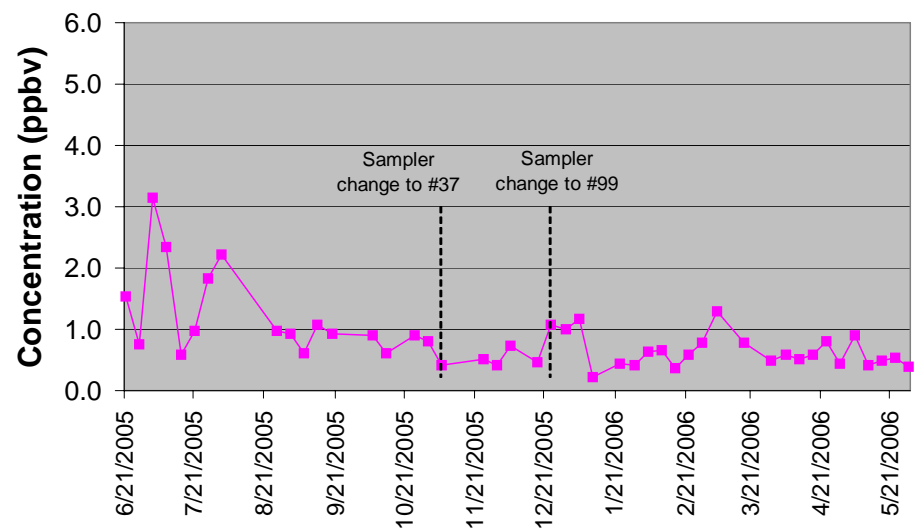
- VOC and carbonyl samplers changed at least once at all sites (Fall 2005)
- Rooftop samplers (Swansea and Palmer) were unsheltered – roof got hot
- Early rooftop samplers were small and boxes generated heat (~55 C) due to pump
- Carbonyl cartridges stored inside sampler box; not so for VOC tubes; react with heat?
- Early flow controllers may have been affected by heat or voltage interference

Early versus Late Generation Samplers

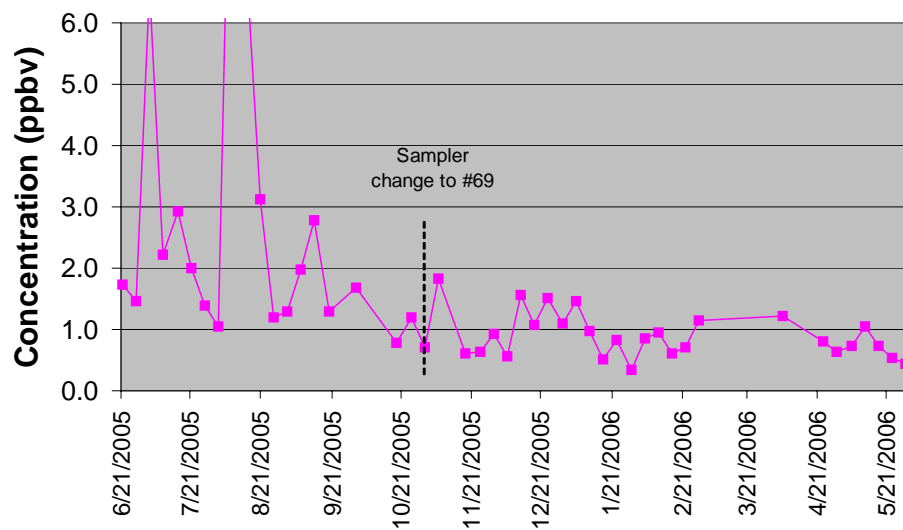
24-hr Tube Benzene Auraria



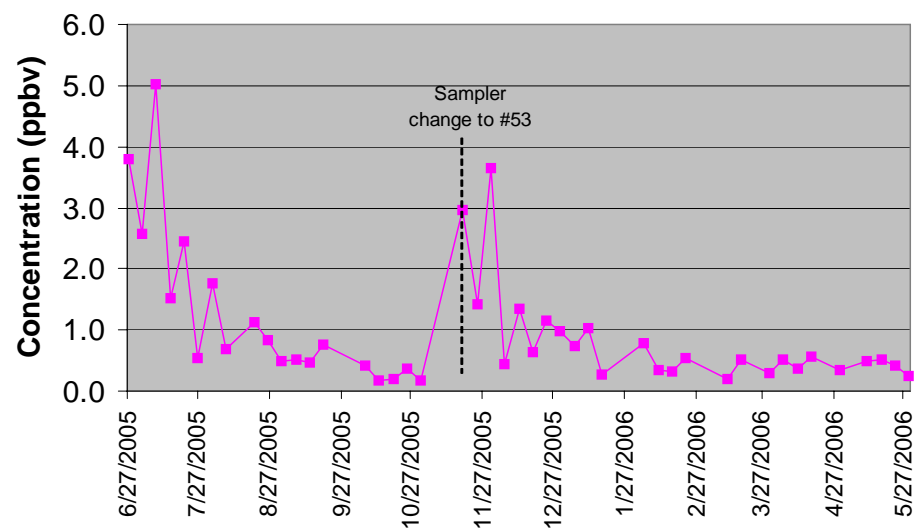
24-hr Tube Benzene Palmer



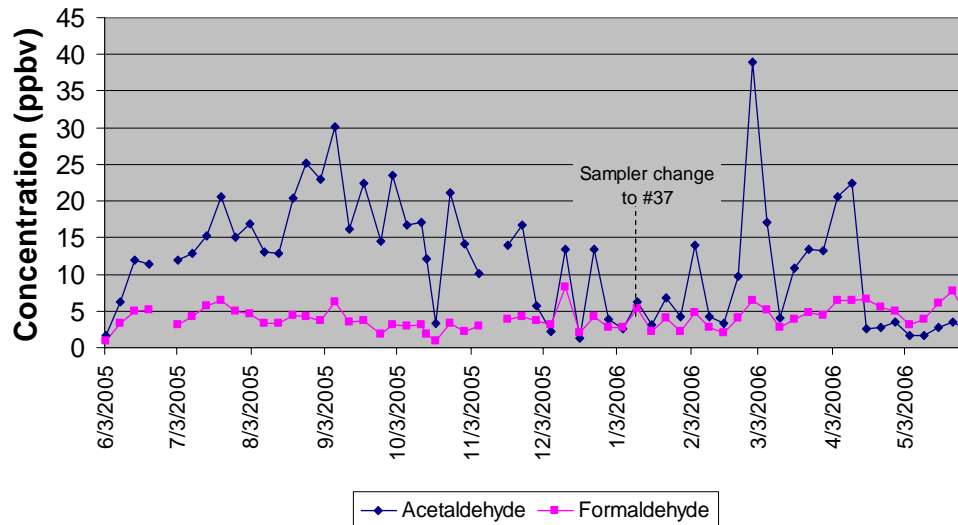
24-hr Tube Benzene Swansea



24-hr Tube Benzene Vanderbilt



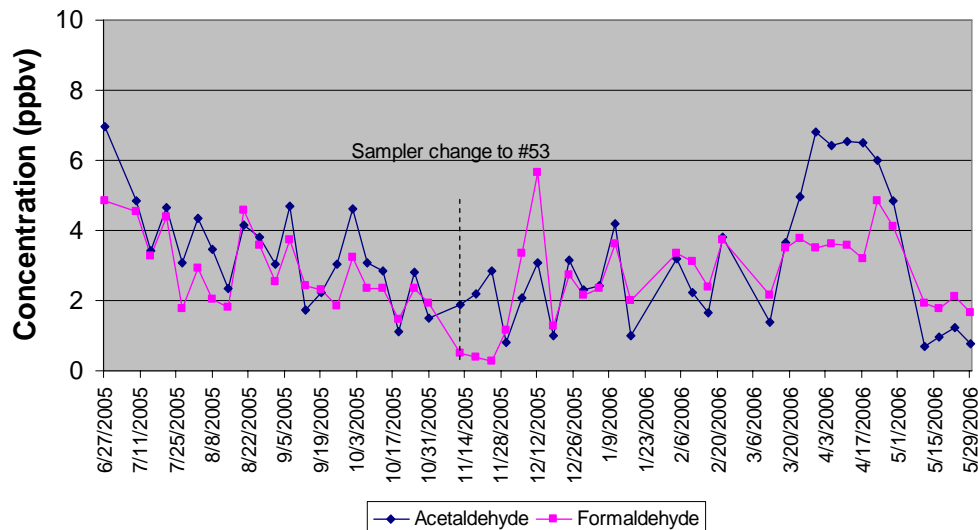
24-hr Formaldehyde and Acetaldehyde Auraria



Formaldehyde steady throughout – probably not a sampler flow issue

If lab analysis were the issue, would probably manifest itself in Vanderbilt results (and in 4-hr tubes)

24-hr Formaldehyde and Acetaldehyde Vanderbilt



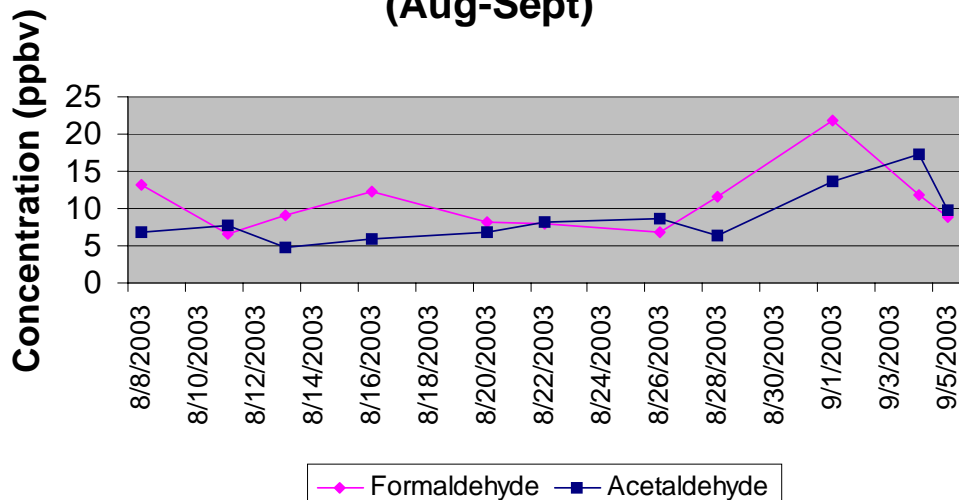
Formaldehyde and acetaldehyde at Vanderbilt Park within historic ranges throughout

Sampler was sheltered and not prone to heating issues

Acetaldehyde occasionally greater than formaldehyde, goes somewhat against historic data

Other Short-term Carbonyl Data

2003 6-9am Carbonyls Downtown CAMP (Aug-Sept)

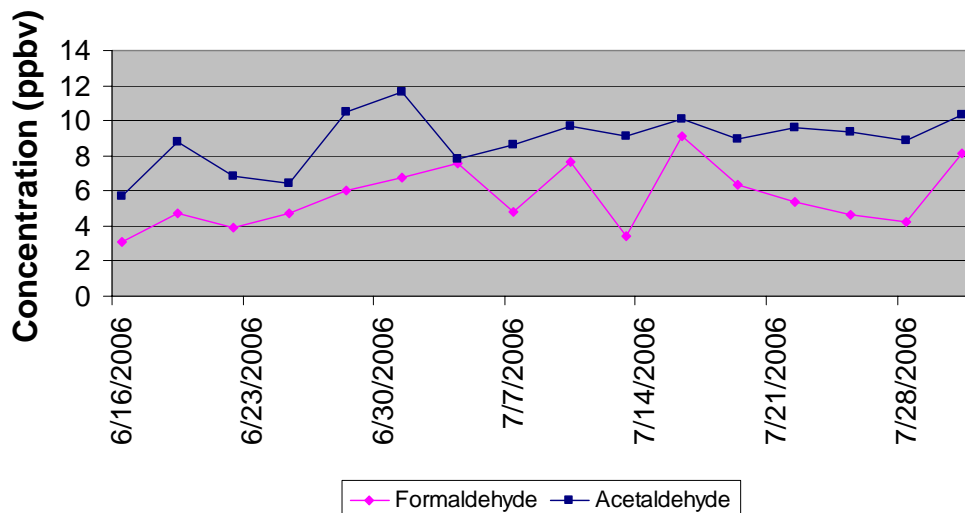


CDPHE aldehydes in both years are higher than expected for 6-9am average

Expect most aldehydes to be formed photochemically

Same lab analyzed samples in 2003 and 2006

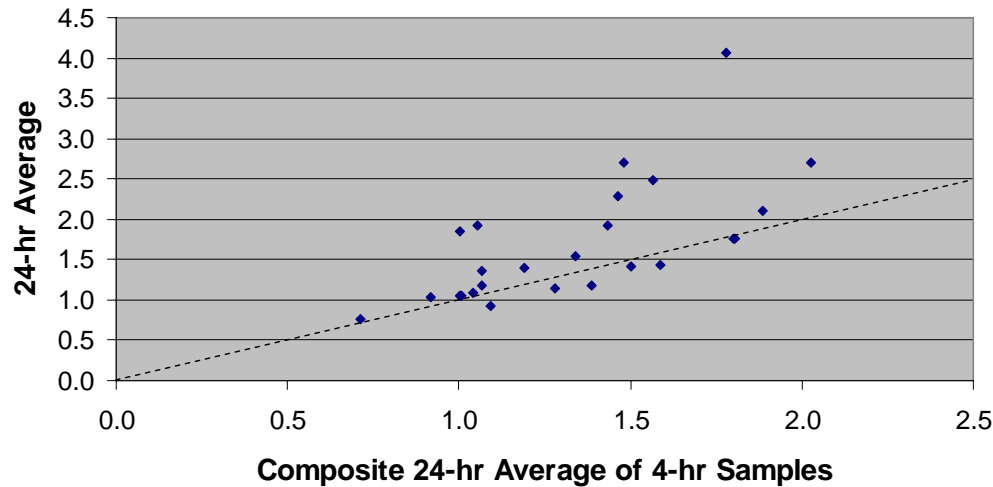
2006 6-9am Carbonyls Downtown CAMP (Jun-Jul)



Lots of confusion re: acetaldehyde concentrations though tend to believe 2000-01 and 2002-03 annual average 24-hr data

Mobile Trailer Site and Multiple Methods Proved Valuable

Acetaldehyde Method Comparison @ Trailer Site



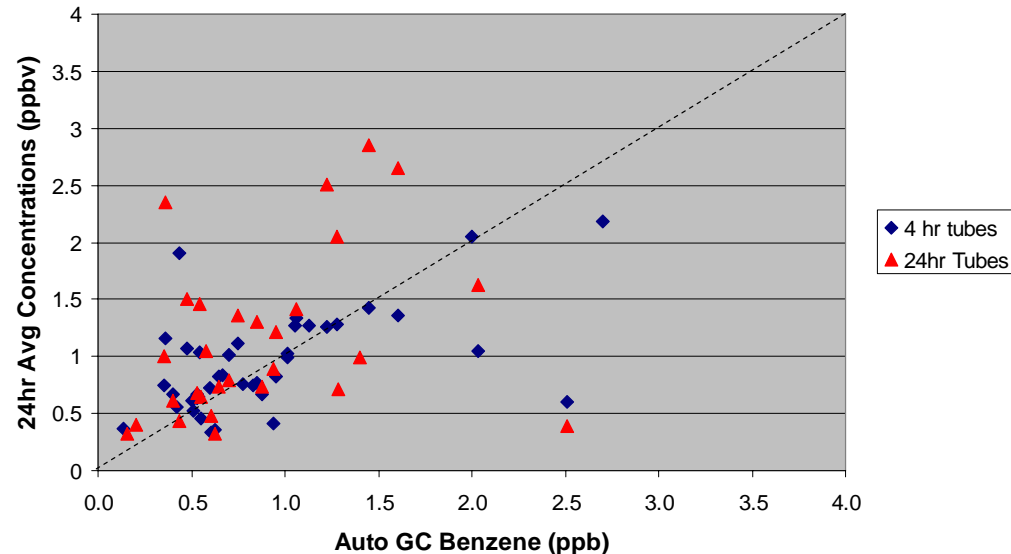
Have high confidence in autoGC and 4-hr VOC data

Have high confidence in validated 4-hr carbonyl data

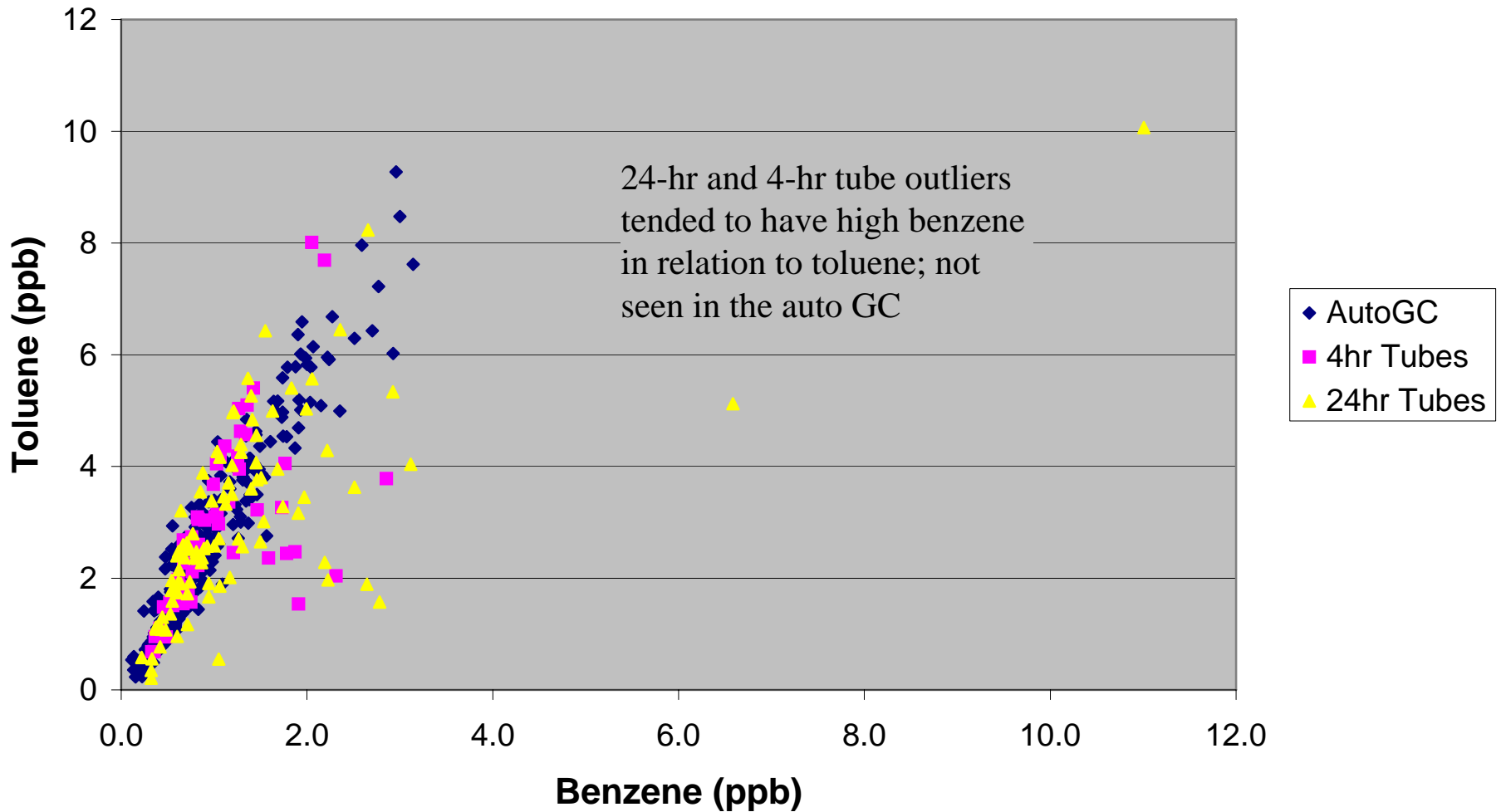
Have high confidence in 24-hr formaldehyde data at all sites

Diurnal VOC methods agreed well; important for evaluating dispersion models, emission inventories, and for future source apportionment

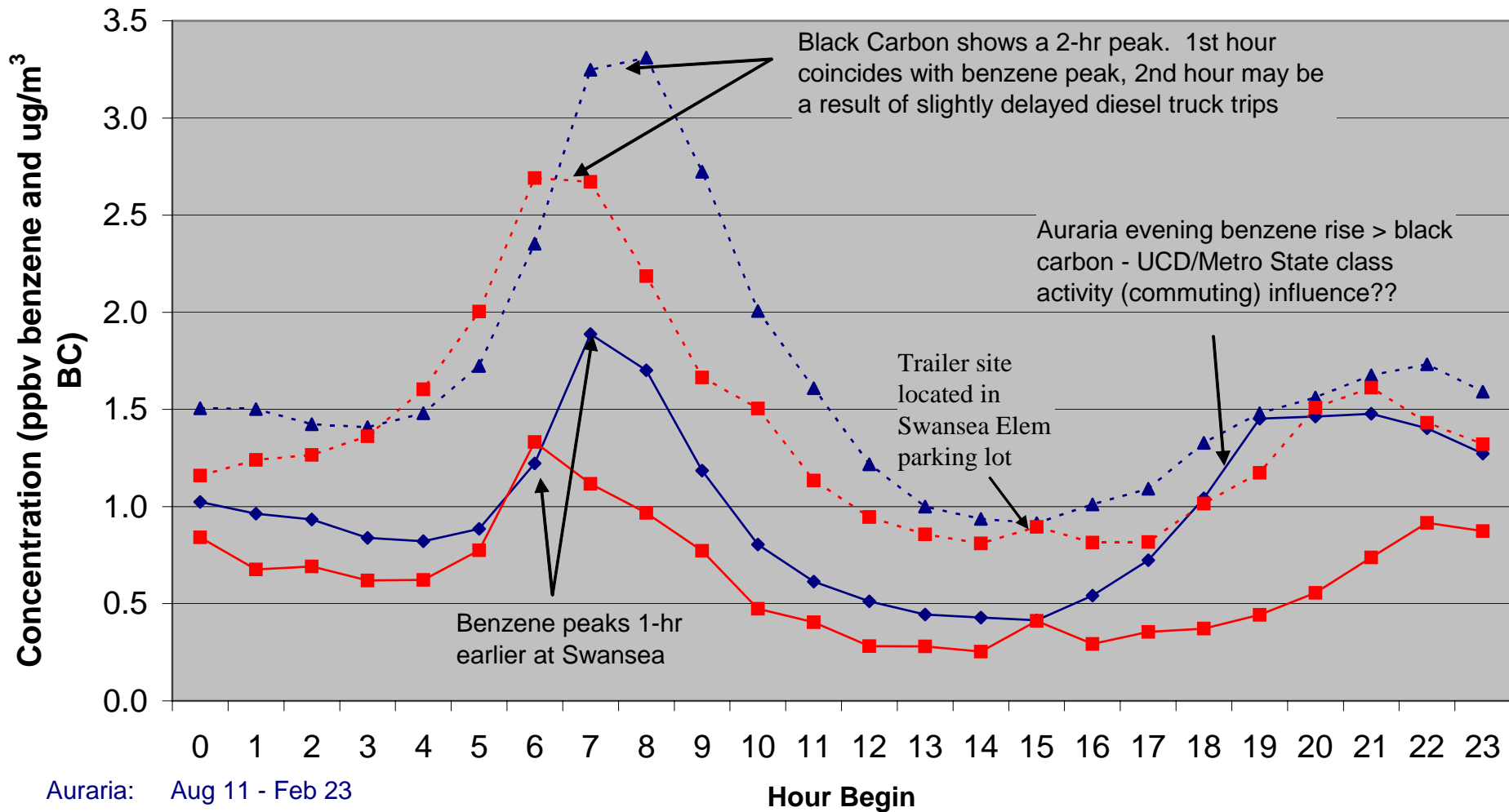
Benzene Method Comparison 4-hr (trailer), 24-hr (rooftop), and autoGC (trailer)



24hr Benzene-to-Toluene Method Comparison Auraria and Swansea

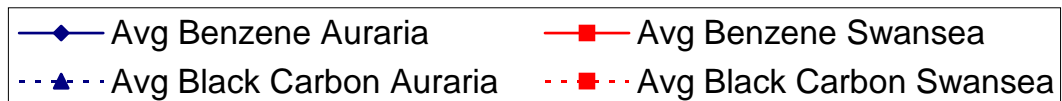


Hourly Average Concentrations Benzene and Black Carbon

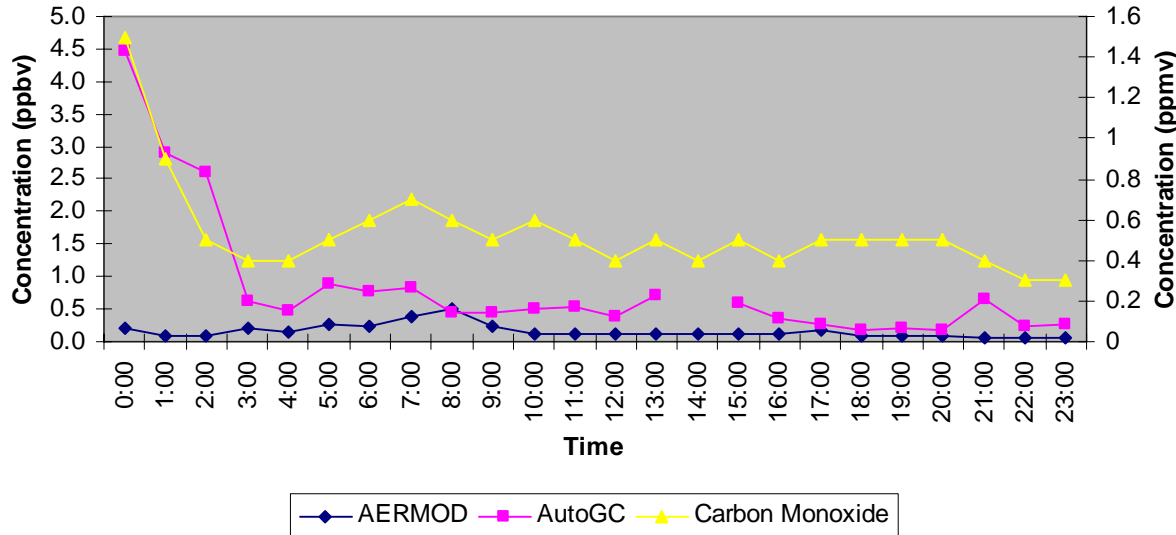


Auraria: Aug 11 - Feb 23

Swansea: Feb 24 - May 16



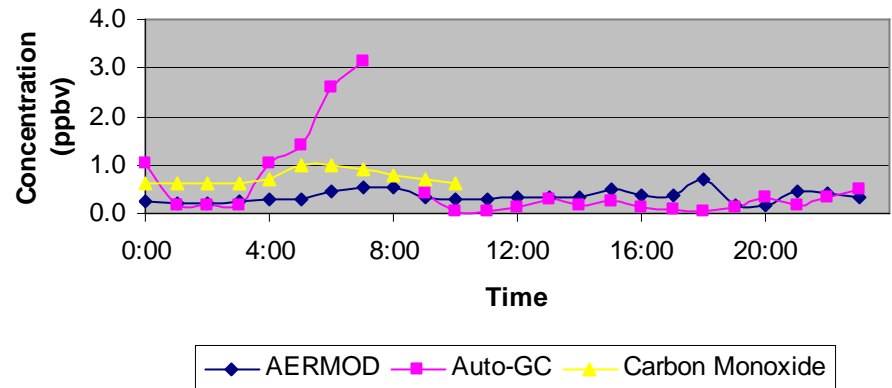
**Predicted vs Observed Benzene Concentrations
Sunday April 23, 2006**



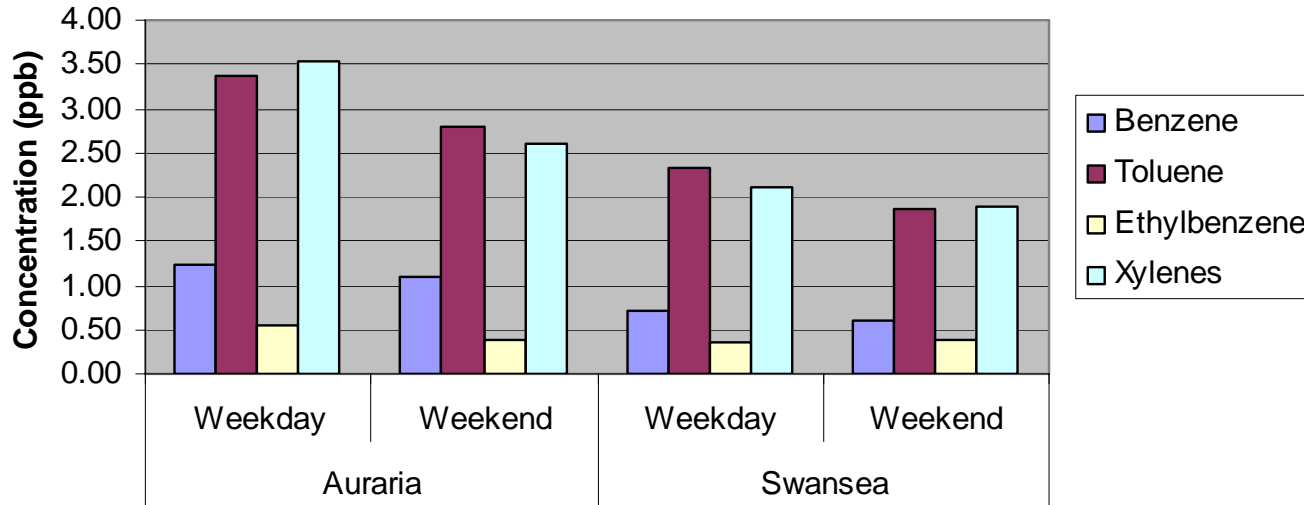
**Rockies vs Giants
game – ended at 10
pm night before**

**N-ly winds all day;
non-mobile source
influence observed
for benzene**

**Predicted vs Observed Benzene Concentrations
Saturday April 29, 2006**

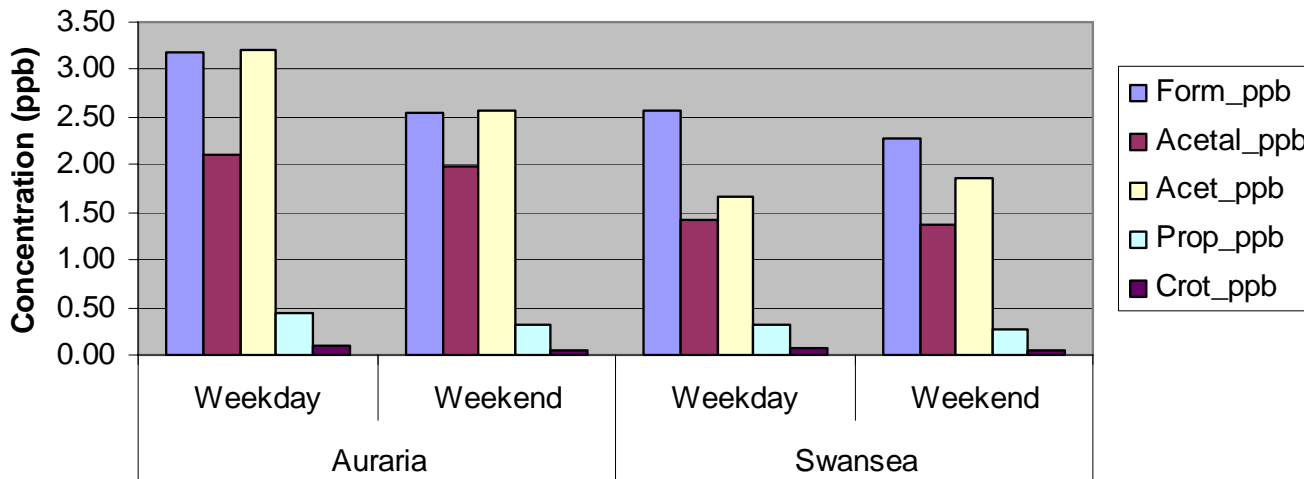


Weekday vs. Weekend



Weekend differences
11%, 17% lower
benzene; 20%, 25%
lower toluene

Weekday vs. Weekend



Weekend differences
25%, 13% lower
formald; 7%, 4%
lower acetald

Conclusions

- Statistically significant biases exist between sites as well as diurnally within a location
 - One air toxics monitor in a metro area is not truly representative of population exposures
- Time resolved data was of great value
 - 24-hr samples give limited insight for source apportionment, evaluation of dispersion model results, and tracking secondary pollutant formation
- Questions still remain about acetaldehyde in ambient air – is the acetald-to-formald relationship changing?

Conclusions (cont.)

- Solvent type emissions (toluene, xylenes) are not fully accounted for in the emissions inventory
 - Vanderbilt Park and Swansea data indicate this
 - Possibly many small sources having large impact
- Black carbon and benzene track well in time but differences are observed
 - Indicator of gasoline versus diesel vehicle patterns
- AutoGC and aethalometer proved to be reliable and effective
 - Cost effective, continuous operation
- EPA Community Air Toxics grants are important for understanding spatial and temporal differences

Next Steps

- Final report of 2005-06 monitoring study complete
- Update Denver air model and evaluate with Boulder County 2007-08 air toxics monitoring

Recommendations

- Future studies should focus on non-methane organic carbon (NMOC) and carbonyls
 - Most air toxics continue to decrease
 - Can still detect BTEX but lighter alkanes as well (important for ozone)
 - TO-15 should not be the preferred method in the West
 - Half the compounds are often not-detected
- Future studies should be designed to test specific hypotheses

Thank You!

- Ken Distler – EPA R8
- Marisa McPhilliamy – EPA R8

- Larry Anderson, Univ. Colorado @ Denver
 - Ning Wigrakasada
 - Steve Moss
 - Jeff Boon

- Deb Bain and Sabrina Williams for their strong commitment to data quality assurance

- APCD for AQS data uploading assistance