# Using PAMS Data to Assess Potential Control Strategies to Reduce Ozone

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# Outline

- Background
- What ozone precursors need to be reduced?
  - NO<sub>x</sub> vs. volatile organic compound (VOC) limitations
  - Weekday/weekend concentration differences
- What VOC sources are most important?
  - Source apportionment
  - Emissions inventory (EI) evaluation
- What have been the effects of control programs on ambient concentrations?
  - Reformulated gasoline (RFG) implementation and fuel volatilization reduction effects
  - Fleet turnover effects



# What Is PAMS?



- EPA required more extensive monitoring of ozone and its precursors in areas with persistently high ozone levels.
- States established ambient air monitoring sites called Photochemical Assessment Monitoring Stations (PAMS) to collect and report VOCs, NO<sub>x</sub>, ozone, and meteorological parameters.
- These data help analysts to better understand the underlying causes of ozone, to devise effective remedies, and to measure improvement.

### PAMS Site Types and Objectives



- Build VOC database for evaluation of control strategies and modeling efforts
- Provide data for model and El evaluation
- Track trends

# **PAMS Site Types and Analyses**



Site Types 2 (Maximum emissions) and 3 (Maximum ozone) provide the most value in terms of the number and value of monitoring objectives they cover.



# What Ozone Precursors Should Be Reduced?

Emission control strategies are based on assessments of whether an area is "VOC-limited" or "NO<sub>x</sub>-limited."



At high VOC/NO<sub>x</sub> ratios, ozone formation is limited by the availability of  $NO_x$  – reducing  $NO_x$ reduces ozone.

At low ratios, ozone formation is limited by the availability of VOCs.



### Daily Data Are Best for Investigating Day-of-Week Variations





Morning nonmethane hydrocarbon (NMHC)/NO<sub>x</sub> ratios, NO<sub>x</sub> concentrations (ppb), and benzene concentrations (ppbC) at an urban site by day of week. Monday = 1, Sunday = 7.



## Source Apportionment

# What source types may be contributing to ambient VOC concentrations?



Azusa (Los Angeles Basin), 2001-2003





# **Composition by Wind Sector**



With winds from the Houston Ship Channel, concentrations are much higher and reactive species are a higher wt.% than with winds from the freeway.



### **Comparison to Emissions Inventory**

Mobile sources at two Los Angeles area sites may be underestimated in the emissions inventory:

- Site 1 = 57% EI, 74% PMF
- Site 2 = 52% EI, 77% PMF





Results (2000–2001) are consistent with a ratio analysis suggesting that emissions inventory acetylene, toluene, and xylenes are underestimated.

# Assessing Changes in Fuel Composition



RFG resulted in ambient benzene reductions.

#### **Fuel Volatilization Changes**

Reid Vapor Pressure changes: Afternoon butane and pentane concentrations (ppbC) show a decline.







### Fleet Turnover Effects

Ambient VOC trends match VOC reductions from fleet turnover effects:

- Harley et al. (2006) showed that a 4% per year decline in benzene, for example, was attributable to fleet turnover.
- Ambient VOC data from PAMS and air toxics sites across the US show about a 5% per year decline (2003–2008).

Chlorinated VOCs 1,4-Dichlorobenzene Carbon Tetrachloride Chloroform Chloromethane Dichloromethane Methyl Chloroform Tetrachloroethene Trichloroethene Hydrocarbons 1,3-Butadiene 2,2,4-Trimethylpentane X Benzene Ethylbenzene Х Isopropylbenzene N-Hexane o-Xylene X X Styrene Toluene **Oxygenated VOCs** Acetaldehyde X Formaldehyde Methyl Tert-Butyl Ether Propionaldehyde X Metals Arsenic PM 25 Lead PM 25 Manganese PM 2.5 Nickel PM 25 20 -20 -10 10 0 Percentage Change per Year Median Percentage Change per Year 90th 10th Percentile Percentile



# Summary

PAMS data are useful to support SIP development

- Identify whether NO<sub>x</sub> or VOC (or both) should be controlled
- Identify sources to control (source apportionment)
- Evaluate/improve emissions inventory and models
- Investigate effectiveness of control programs
- Track trends in ozone, and in ozone precursors



### Resources

- PAMS data analysis workbook:
  - http://www.epa.gov/airquality/pams/analysis/index.html
  - PDFs to be posted on AMTIC
- Past work:

http://www.epa.gov/oar/oaqps/pams/

 More recent work on air toxics: <u>http://www.epa.gov/ttn/amtic/airtoxpg.html</u>

