Semi-Volatile Organic Compounds Characterization at the Fresno Supersite during Wintertime Stagnation Episodes

Barbara Zielinska and Lynn Rinehart
Desert Research Institute
Reno, NV 89512

California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS)

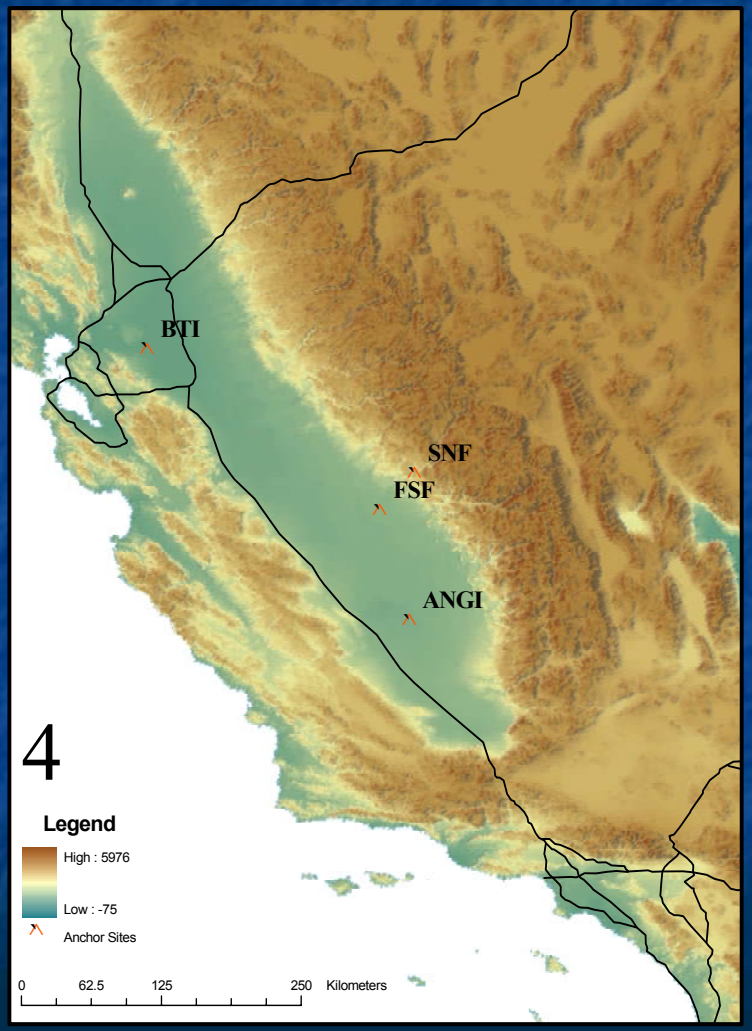
- The general purpose of CRPAQS was to improve scientific understanding of excessive PM levels in Central California Valley
- The overall objective of this work was to provide data on ambient concentrations of organic compounds in the CRPAQS study domain

Project Design:

- The project was conducted over a period of three years with field studies commencing in 12/1/99 and ending on 2/3/01
- 15 Winter IOP days between 12/15/2000 and 2/6/2001 on the basis of meteorological forecasts:
  - 12/15/00-12/18/00
  - 12/26/00-12/28/00
  - 01/4/01-01/7/01
  - 01/31/01-02/3/01

Sampling:

- Four "anchor" sites – Angiola (ANGI), Fresno Supersite (FSF), Bethel Island (BTI), and Sierra Nevada Foothills (SNF)
- FSF: 0000-0500 (inversion tightening), 0500-1000 (fresh emissions), 1000-1600 (dispersion), 1600-2400 (inversion layer formation) PST
- Other sites: 0500-1600 and 1600-0500 PST



Sample Collection and Analysis

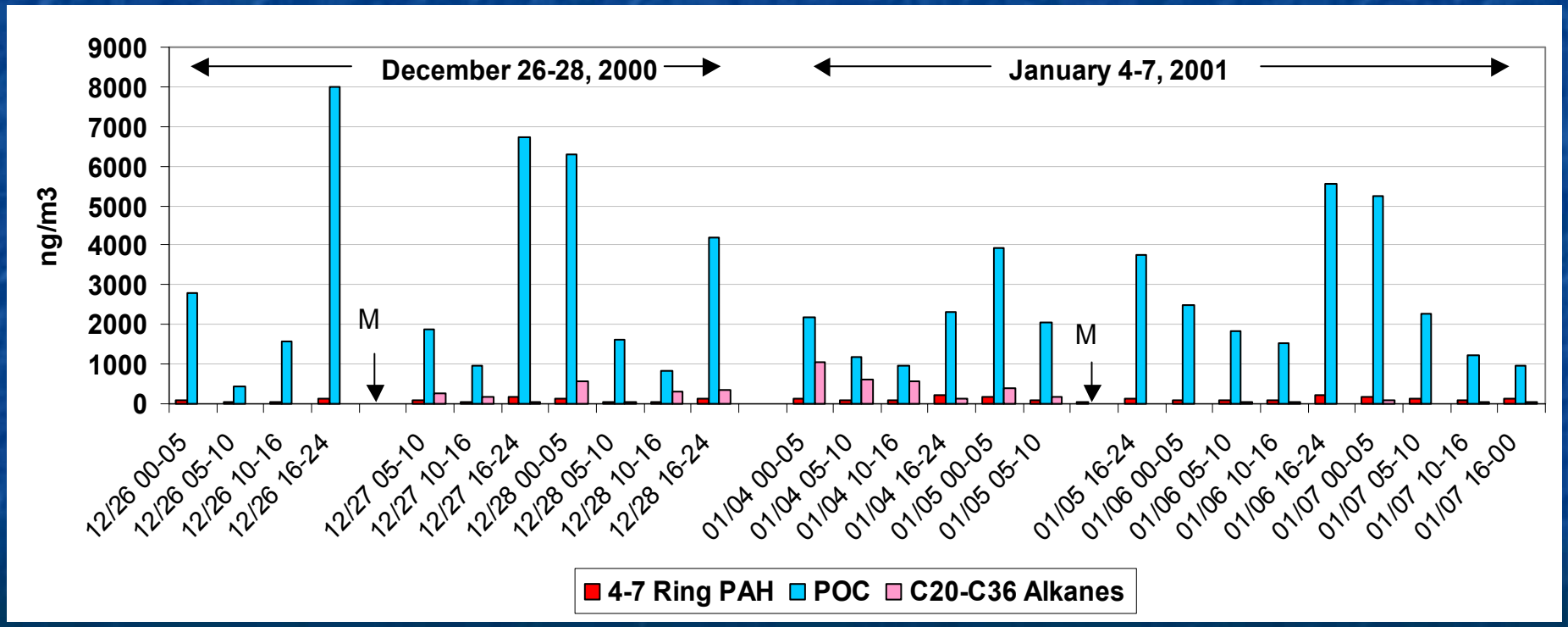
- Collection:
  - DRI sequential Fine Particle/Semi-Volatile Organic Compounds (FP/SVOC) sampler, with PM2.5 inlet operating at 113 L/min
  - TIGF filters followed by PUF/XAD/PUF cartridges
- Extraction:
  - deuterated internal standards added to filter-sorbent pair
  - microwave extraction with DCM followed by acetone
- Analysis:
  - ½ by EI GC/MS for PAH, hopanes/steranes, and alkanes
  - ½ derivatized with bis(trimethylsilyl) trifluoroacetamide (BSTFA) and analyzed by CI GC/MS with isobutane
  - GC/MS: Varian Saturn 2000 Ion Trap

Analysis, cont.

- Analysis for:
  - 2-7 Ring PAH, from naphthalene to coronene
  - Alkane and cycloalkanes from C_{18} to C_{36}
  - Hopanes/Steranes
  - Methoxylated phenol derivatives (syringols and guiacols)
  - Organic acids and diacids C_4 to C_{24}
  - Anhydrosugars (levoglucosan and mannosan)
  - Cholesterol & B-sitosterol

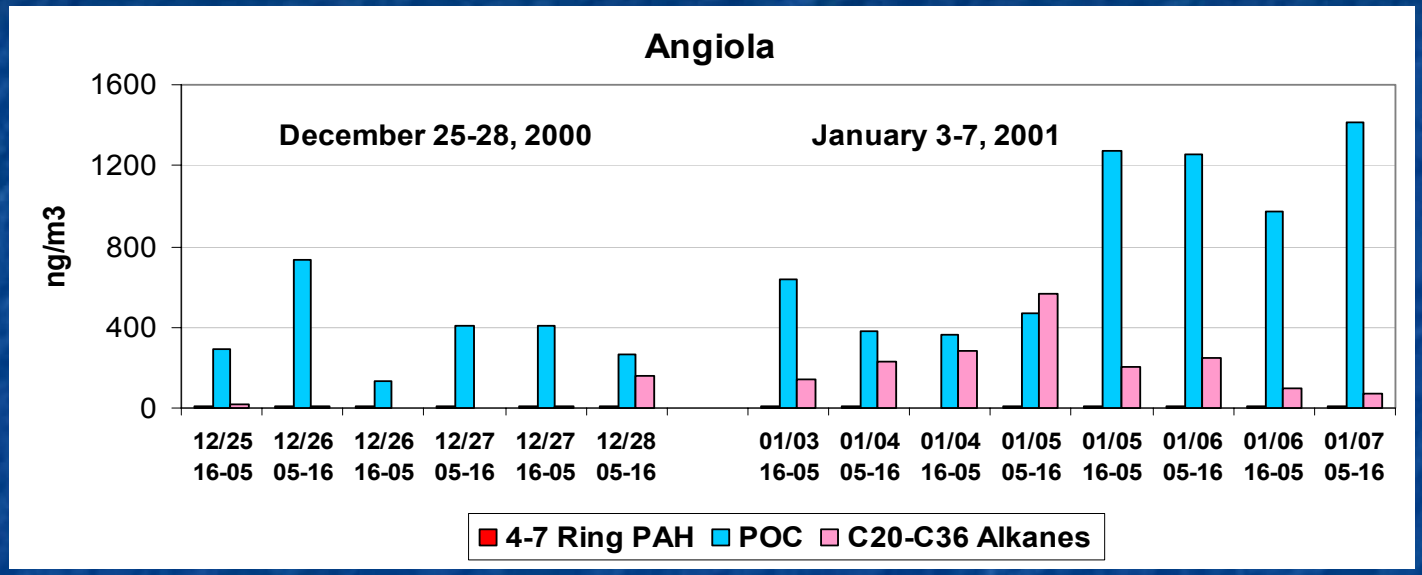
POC

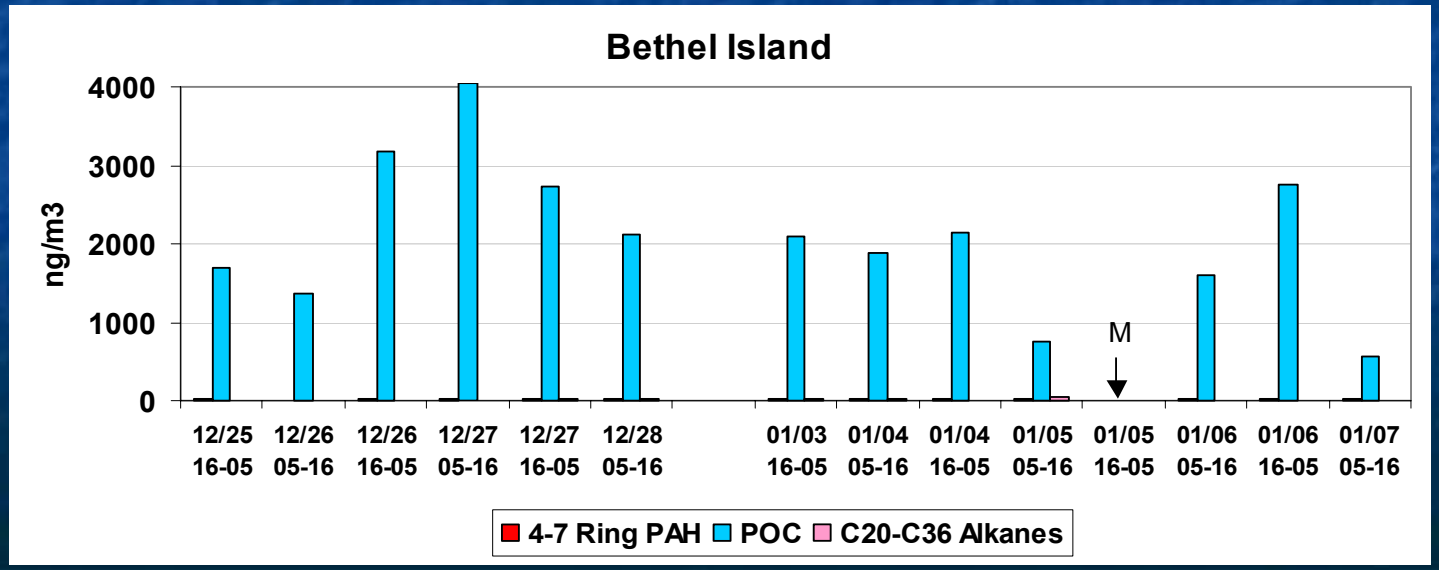
Abundance of Particle-Associated Organics - Fresno



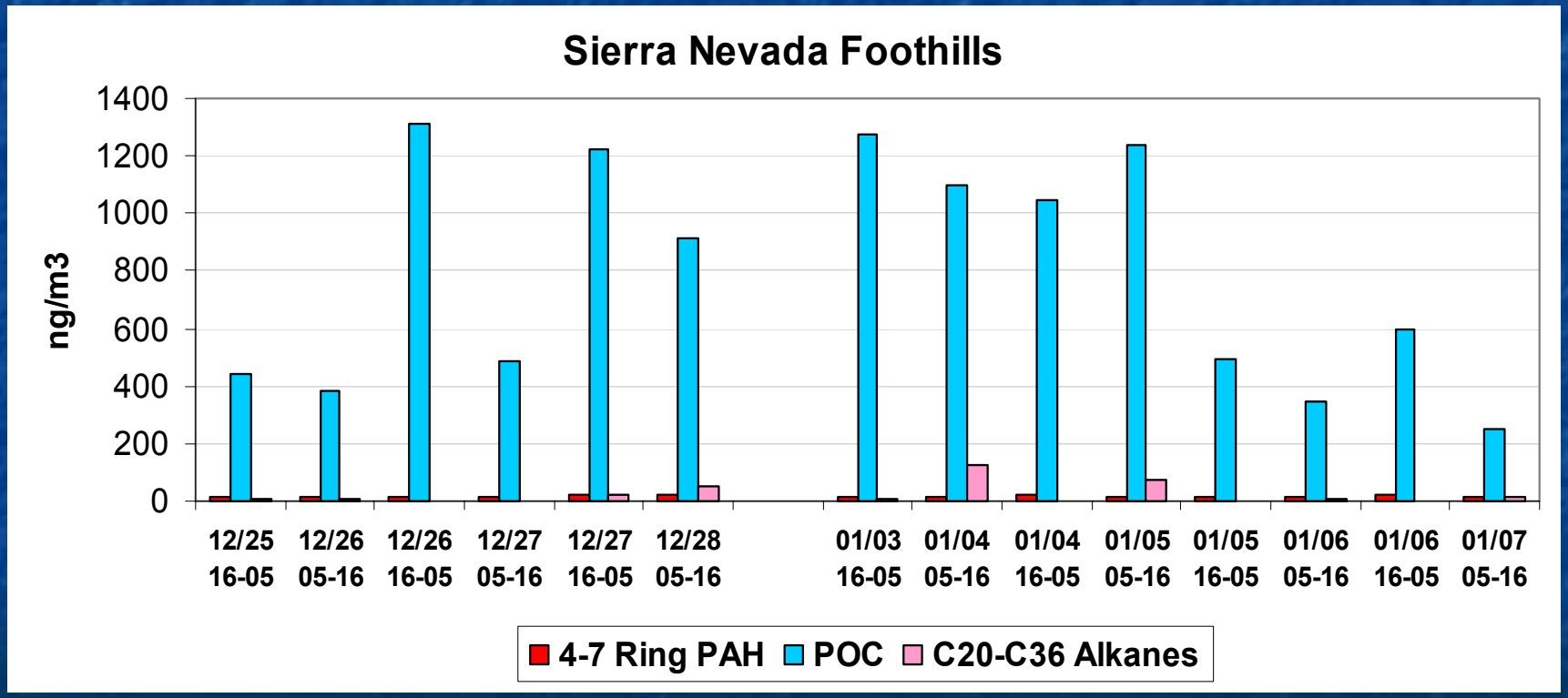
M=missing sample

Particulate Organics – Other Sites

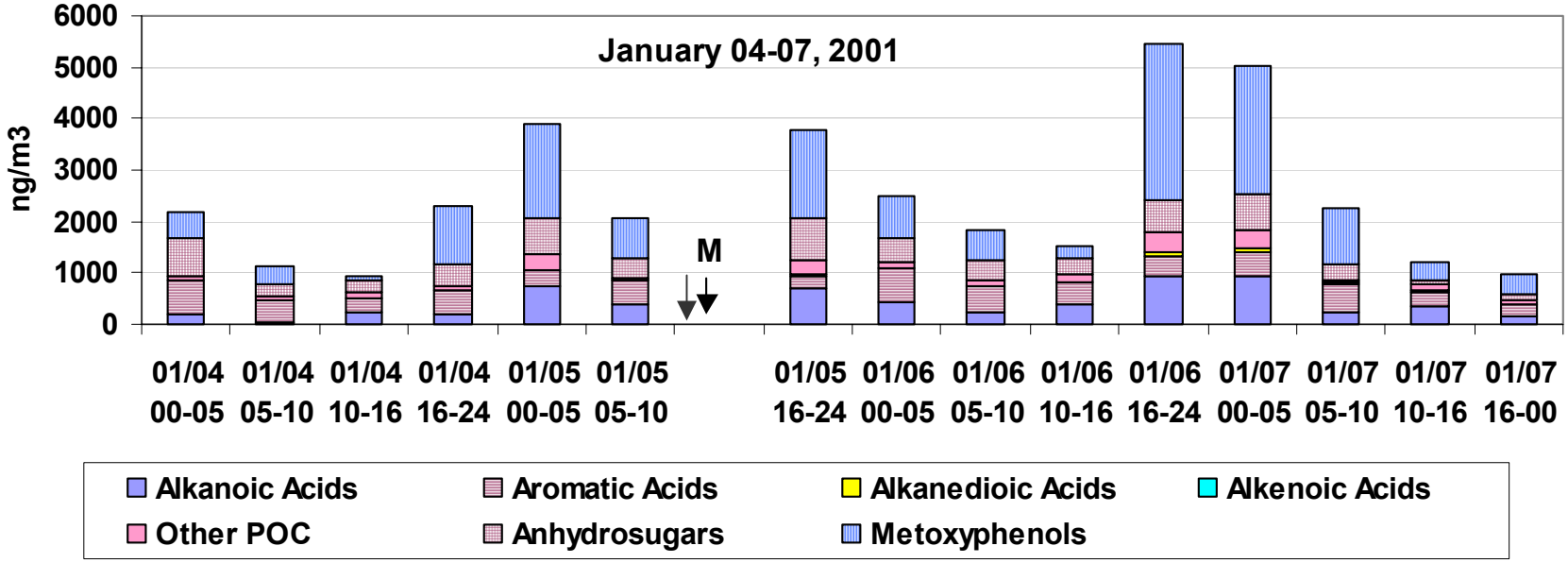


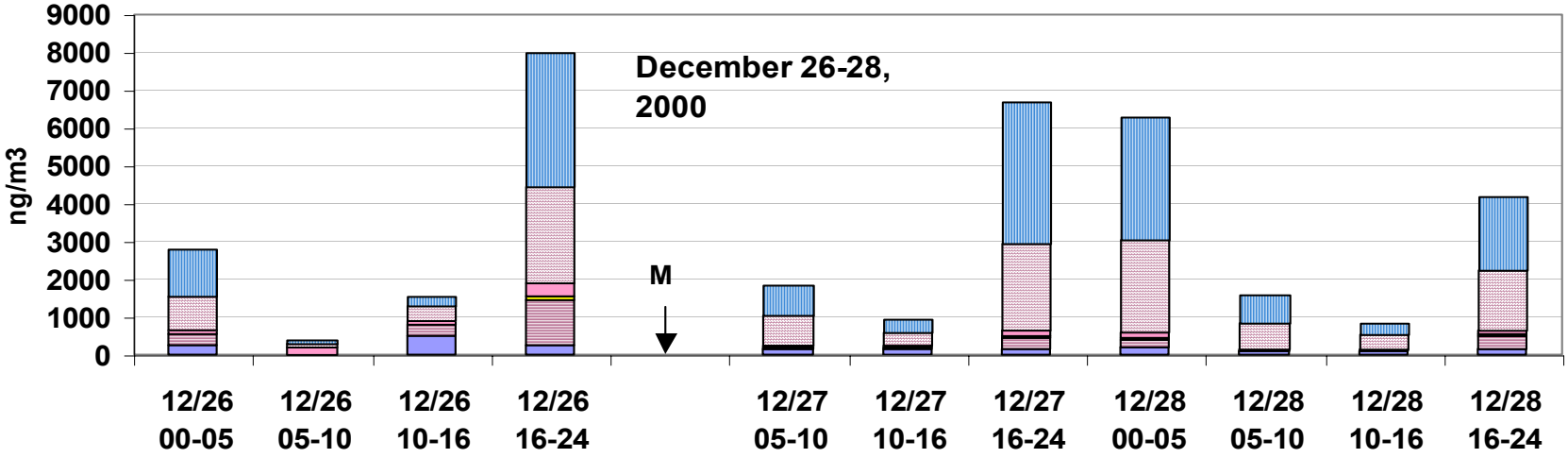


Particulate Organics, cont.

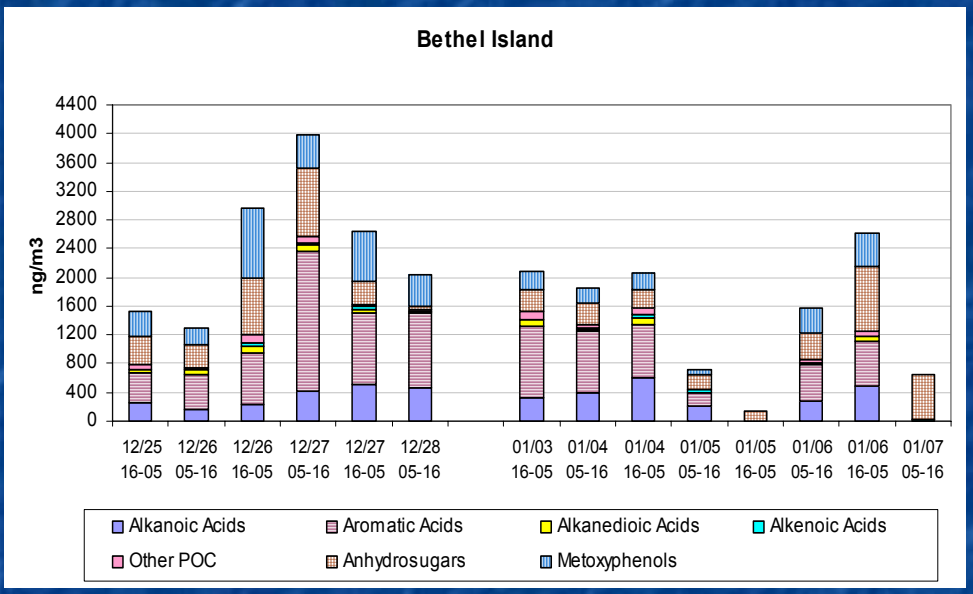


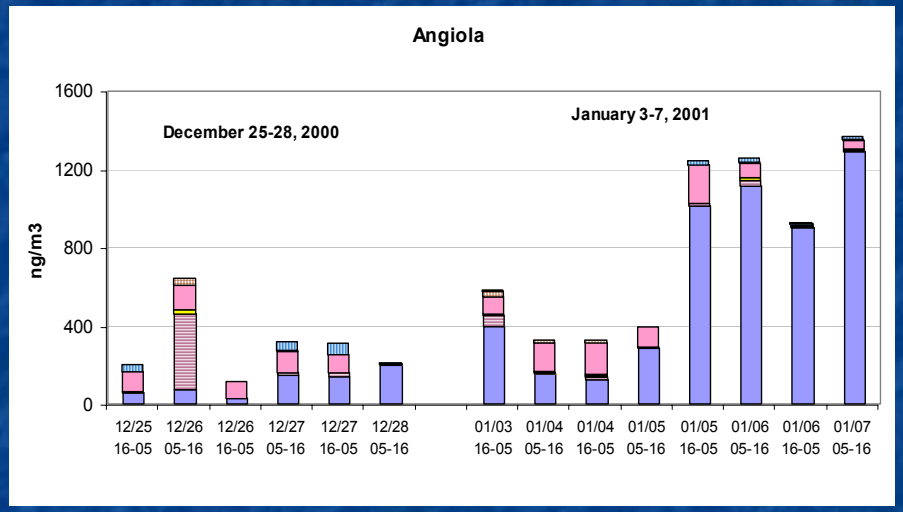
POC Composition - Fresno

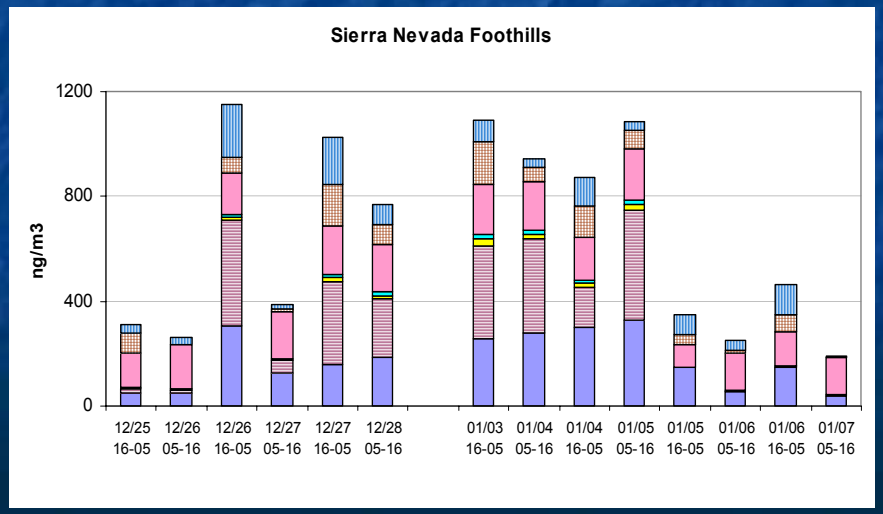




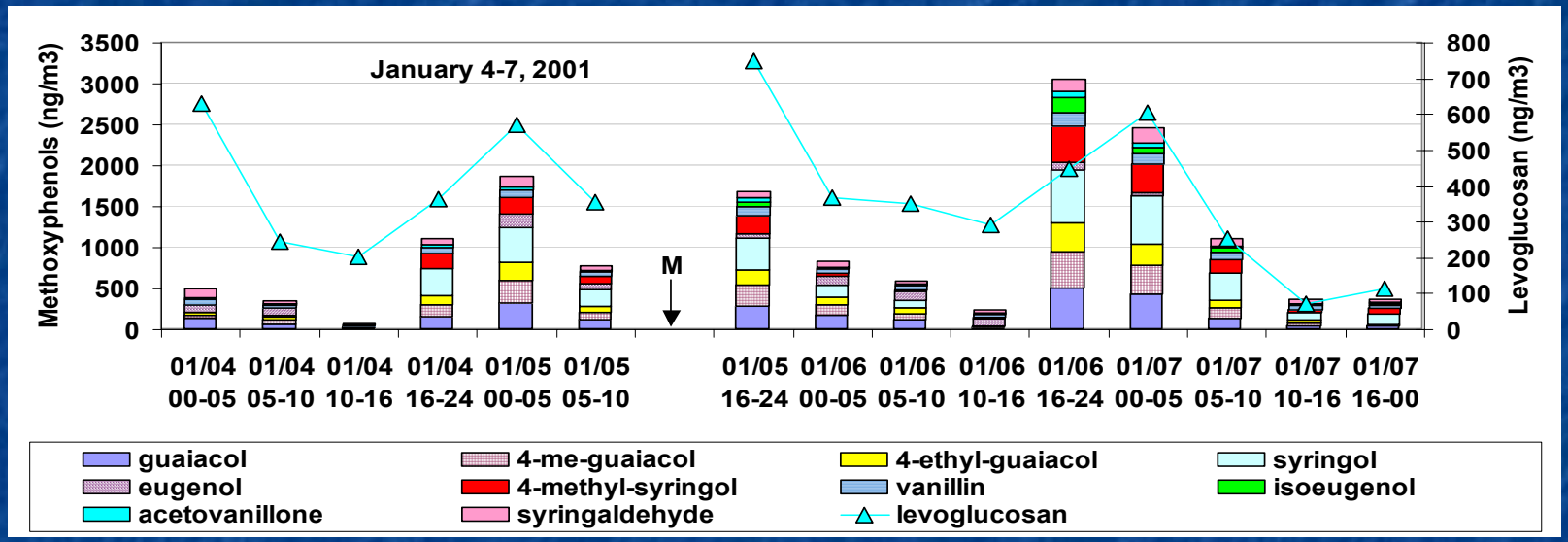
POC Composition – Other Sites

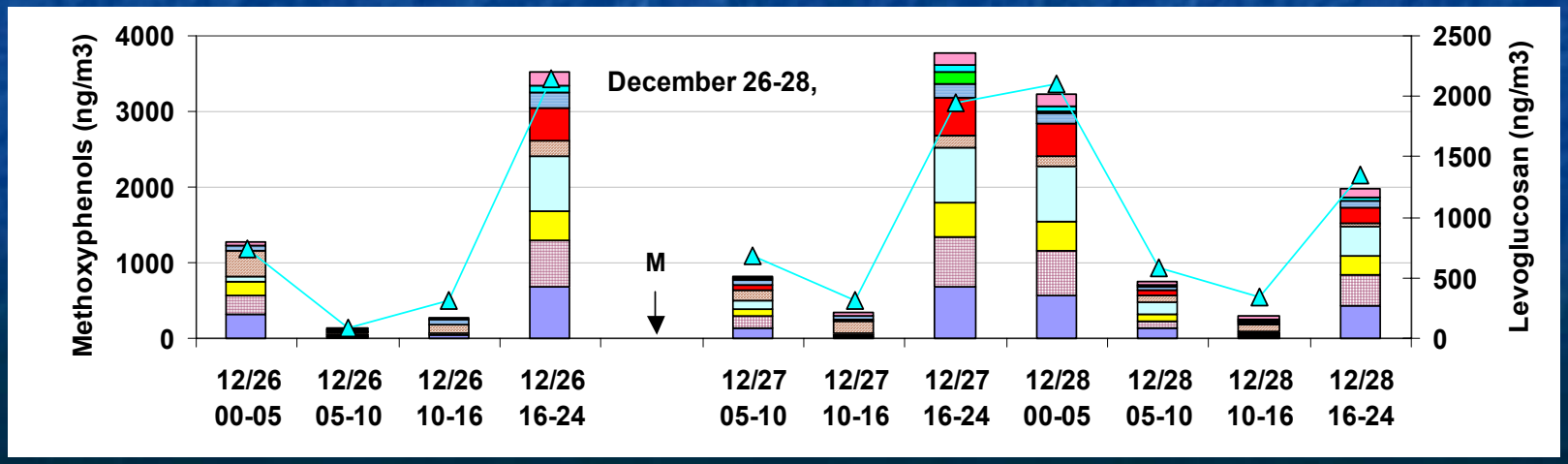




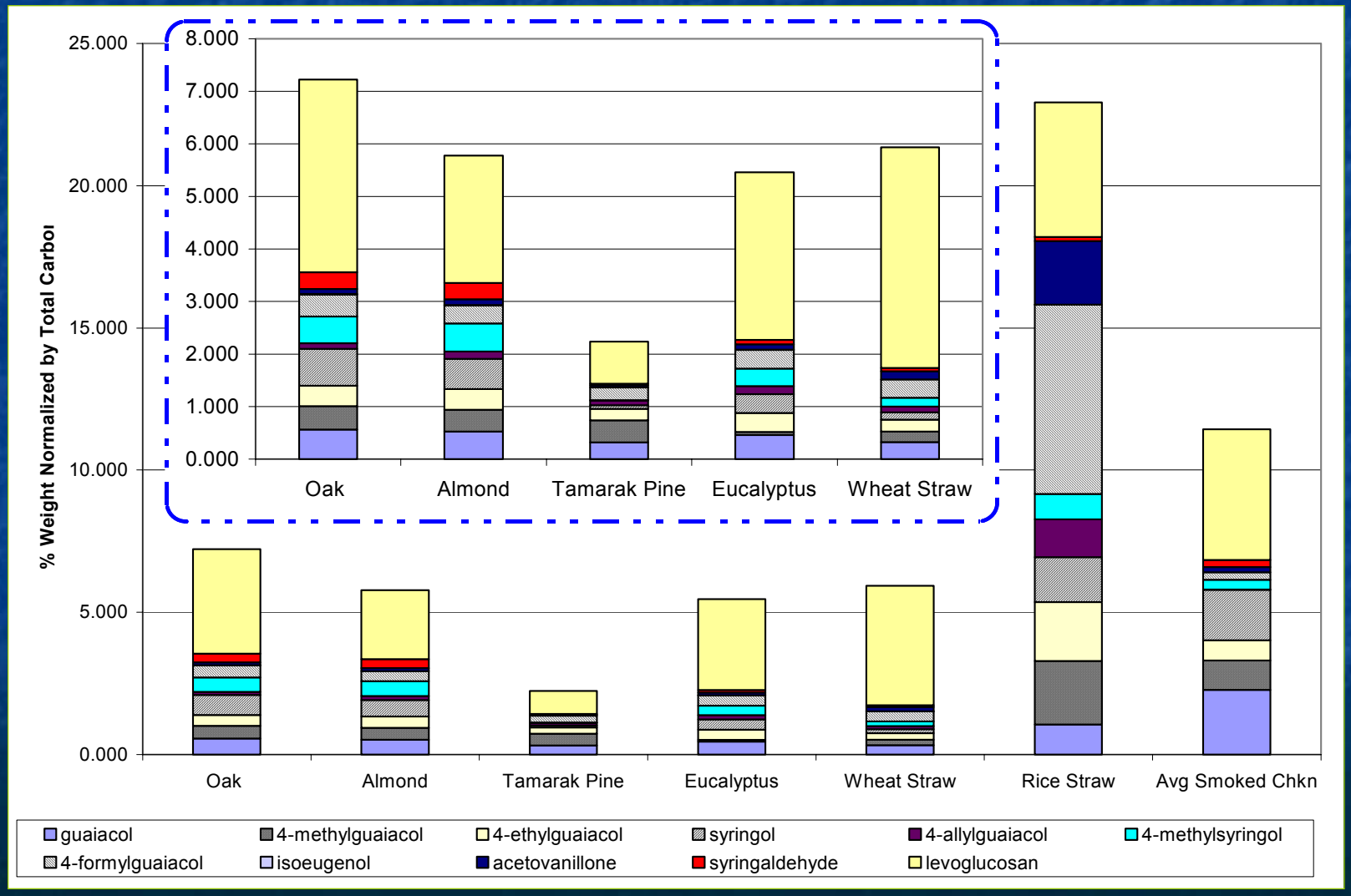


Methoxyphenols and Levoglucosan-Fresno

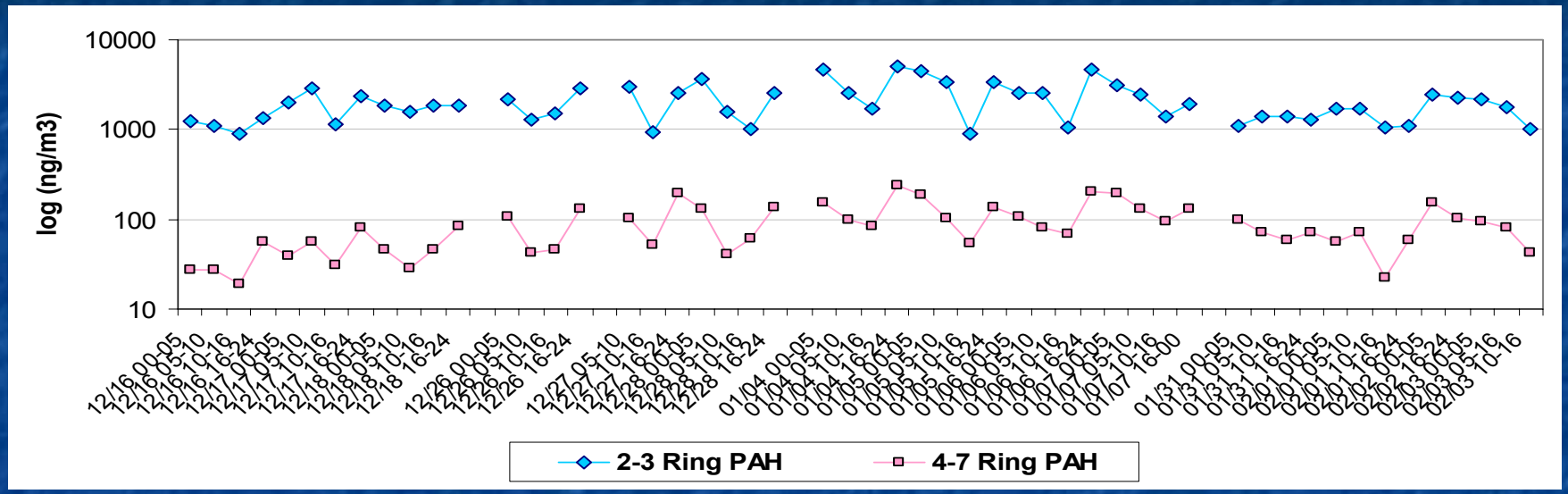


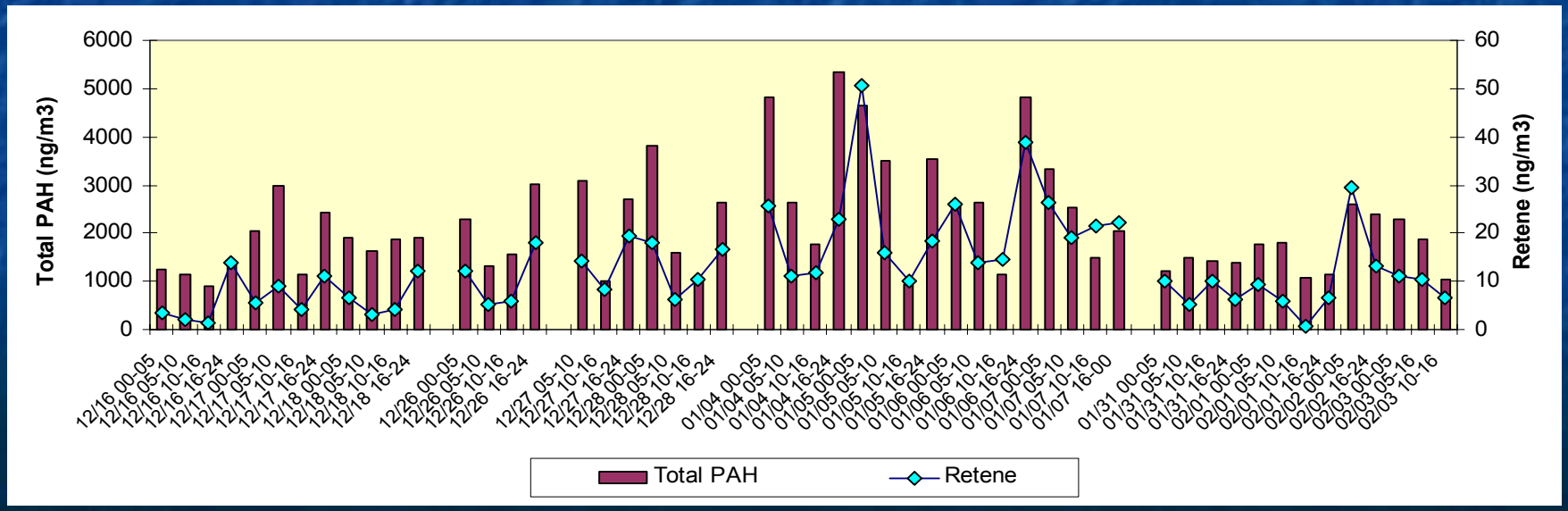


Levoglucosan & Selected Methoxy Phenols Abundance in Residential Woods & Agricultural Straws

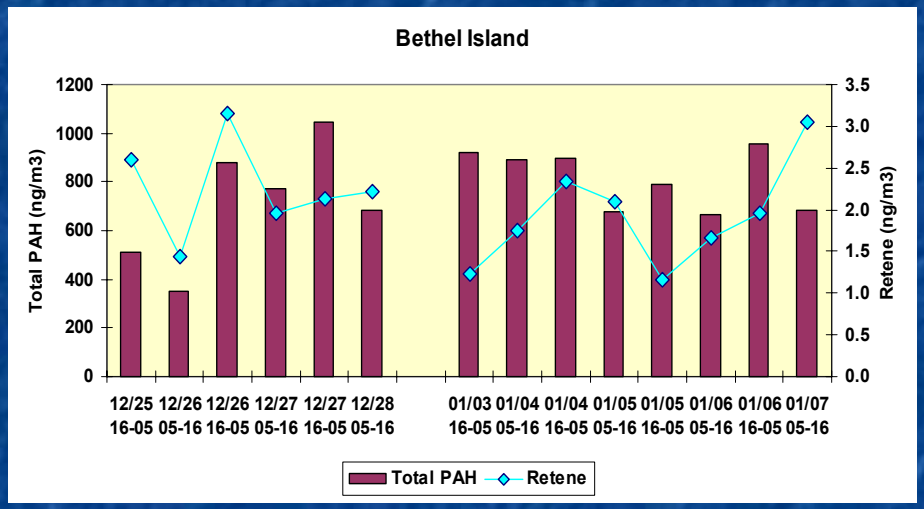


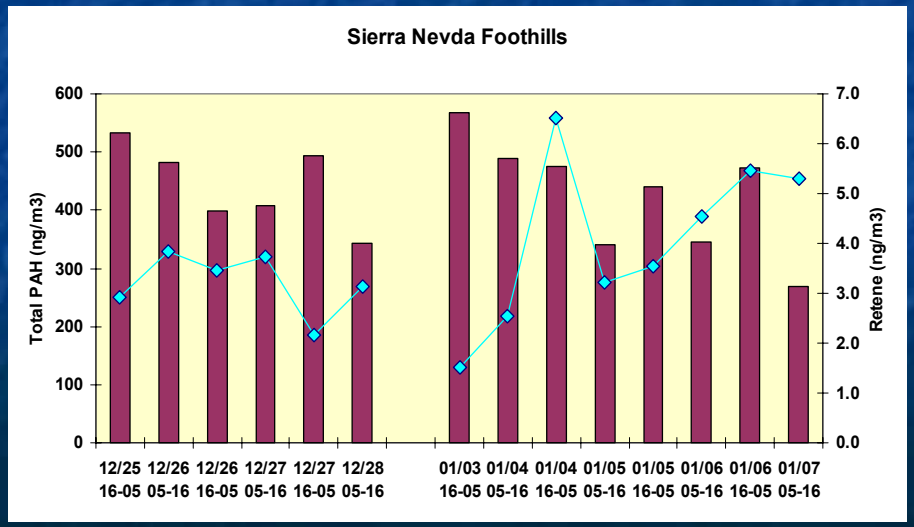
PAH - Fresno

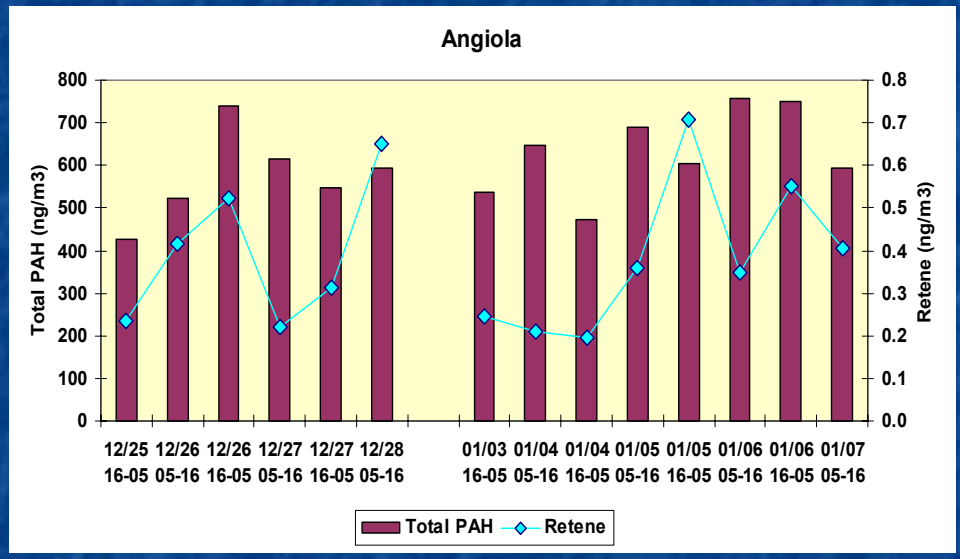

log (ng/m3)
10000
1000
100
10
2-3 Ring PAH
4-7 Ring PAH


Total PAH (ng/m3)
6000
5000
4000
3000
2000
1000
0
Retene (ng/m3)
60
50
40
30
20
10
0
Total PAH
Retene

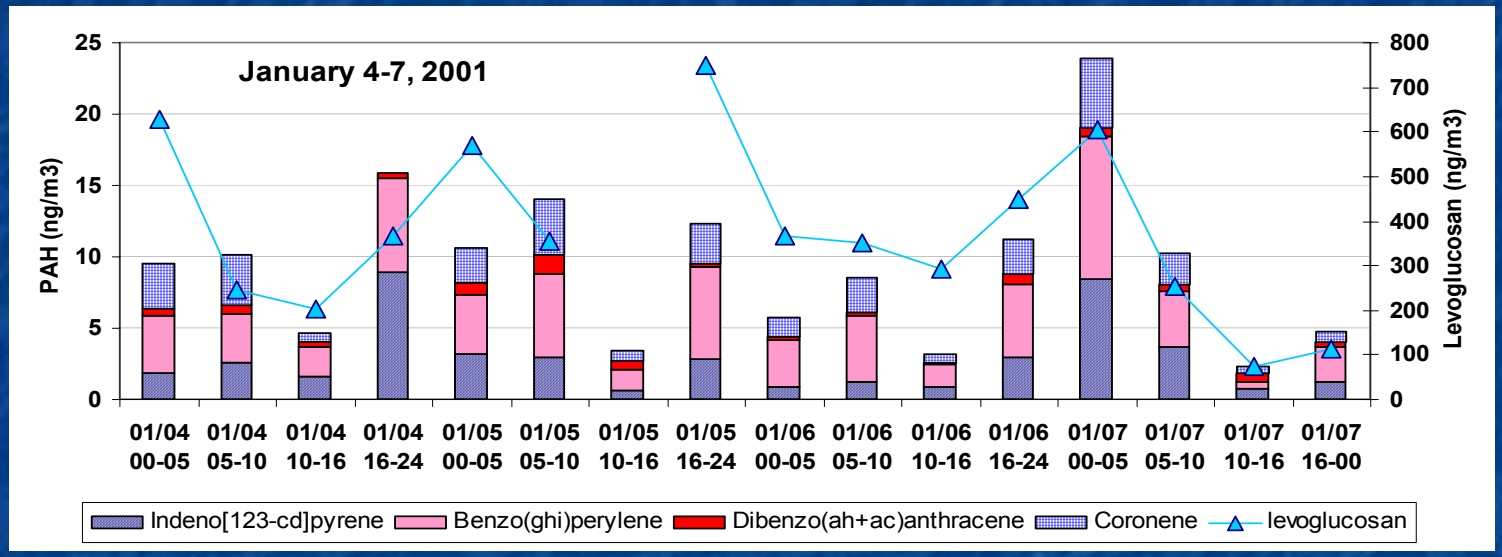
PAH – Other Sites

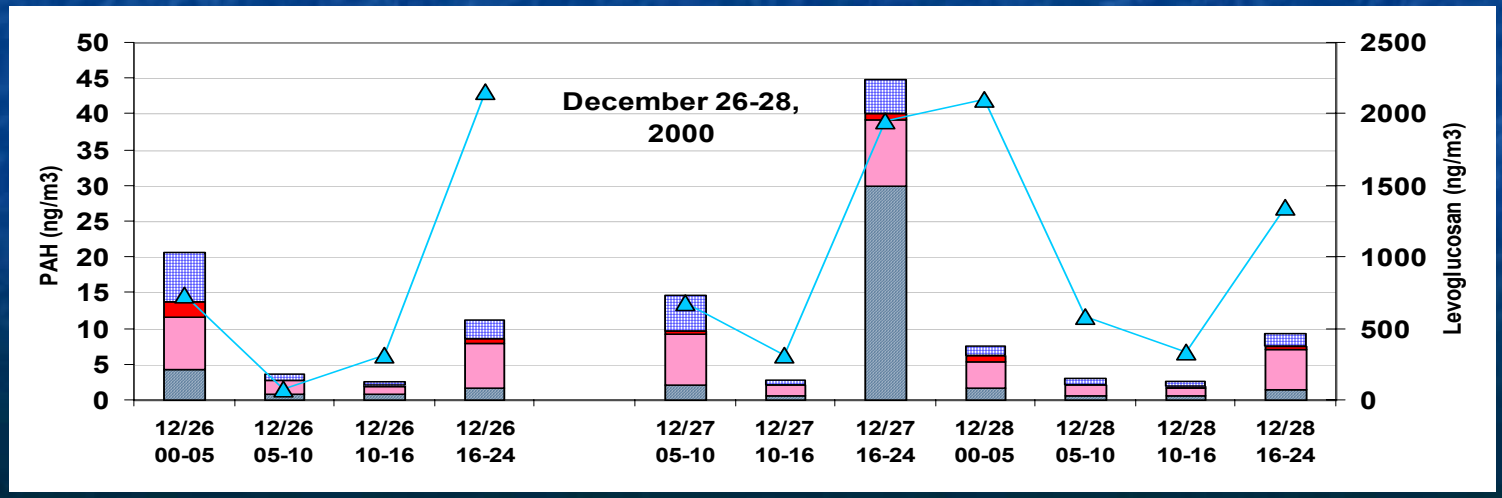




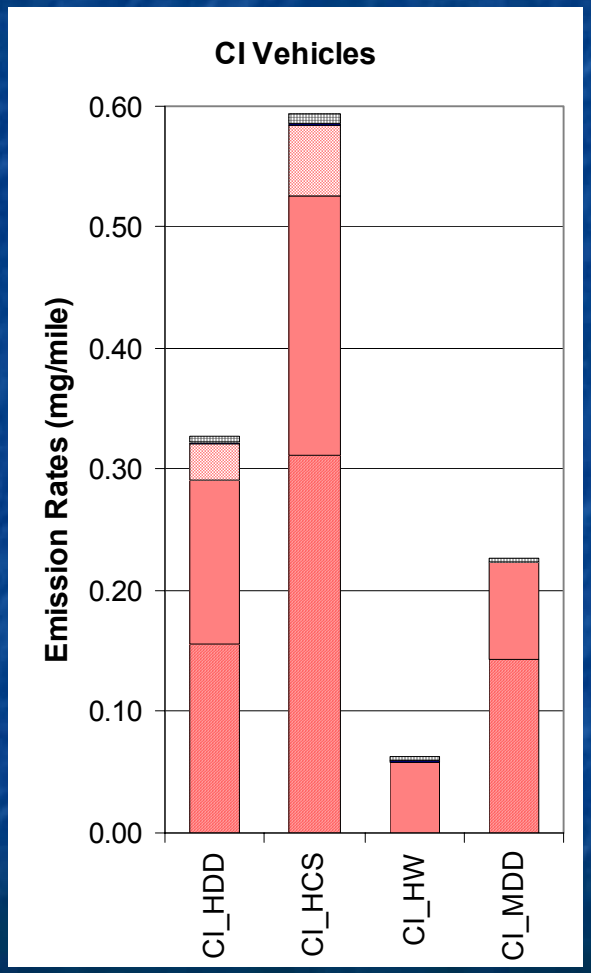


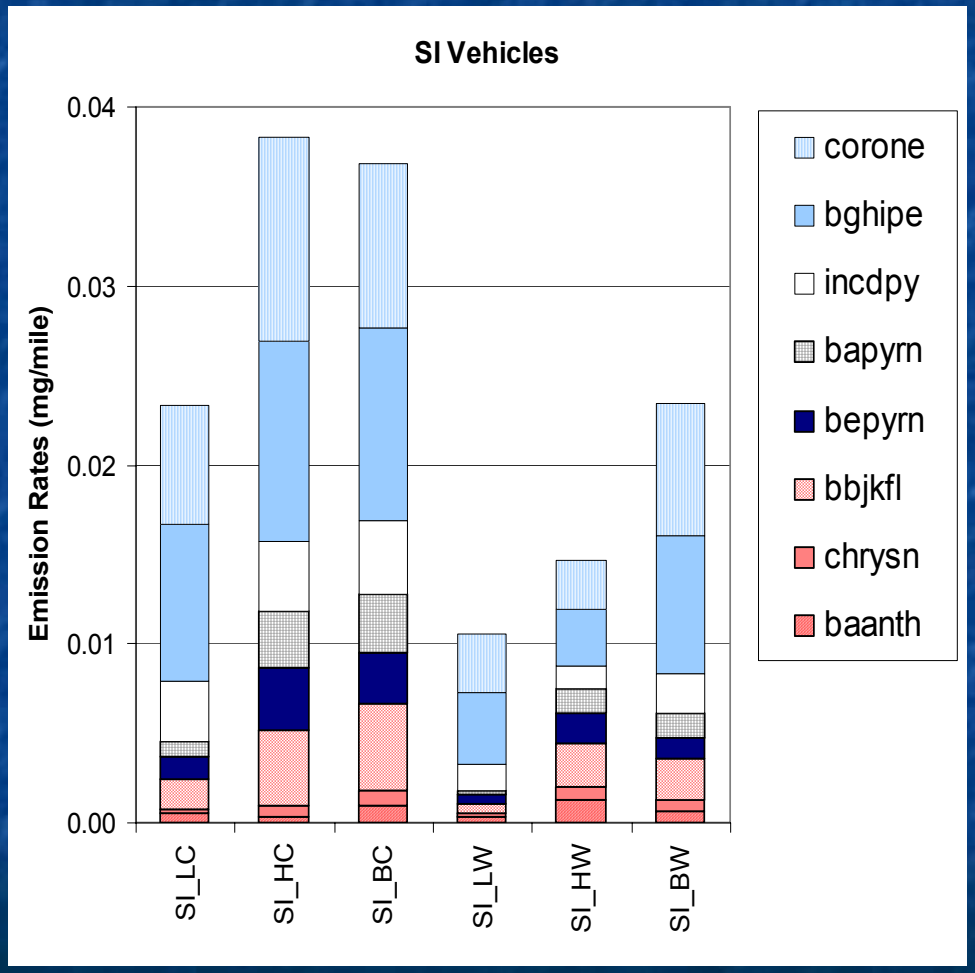
Heavy PAH - Fresno





Heavy PAH in Vehicle Exhaust





Fujita et al., 2005, DOE's gasoline/diesel PM split study

Conclusions:

- Polar organic compounds (POCs) are the major constituents of SVOC in Central California Valley during winter pollution episodes
- In Fresno, Bethel Island and Sierra Nevada Foothills, POCs originate mostly from wood burning. This is not the case for Angiola
- SVOC in Fresno show a clear diurnal variation with highest concentrations observed during sampling periods from 1600 to 2400 and 0000 to 0500 PST that correspond to the formation and tightening of the radiation inversion layer, respectively

Conclusions, cont.

- Retene, a coniferous woodsmoke marker, correlate well with total PAH (R^2=0.6) indicating that the significant portion of PAH originates from wood burning
- However, relatively higher concentrations of indeno[1,2,3-cd]pyrene, benzo(ghi)perylene and coronene during 0500-1000 PST sampling period ("rush hours") indicate the contribution of gasoline vehicle emissions at Fresno Supersite

Acknowledgements:

- Special thanks to Mrs. Karen Magliano of California Air Resources Board for managing this project
- Financial support for this study was provided by the San Joaquin Valley Air Pollution Study Agency
- We thank site's operators for sample collections and the staff of Organic Analytical Laboratory of DRI for sample analyses