

# On-Road Motor Vehicle Emissions including $\text{NH}_3$ , $\text{SO}_2$ and $\text{NO}_2$

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Sacramento, CA  
June 17, 2010

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# **On-Road Emission Measurements of Reactive Nitrogen Compounds from Three California Cities**

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Environmental Science & Technology 44(9), 3616-3620, 2010.

# Acknowledgments

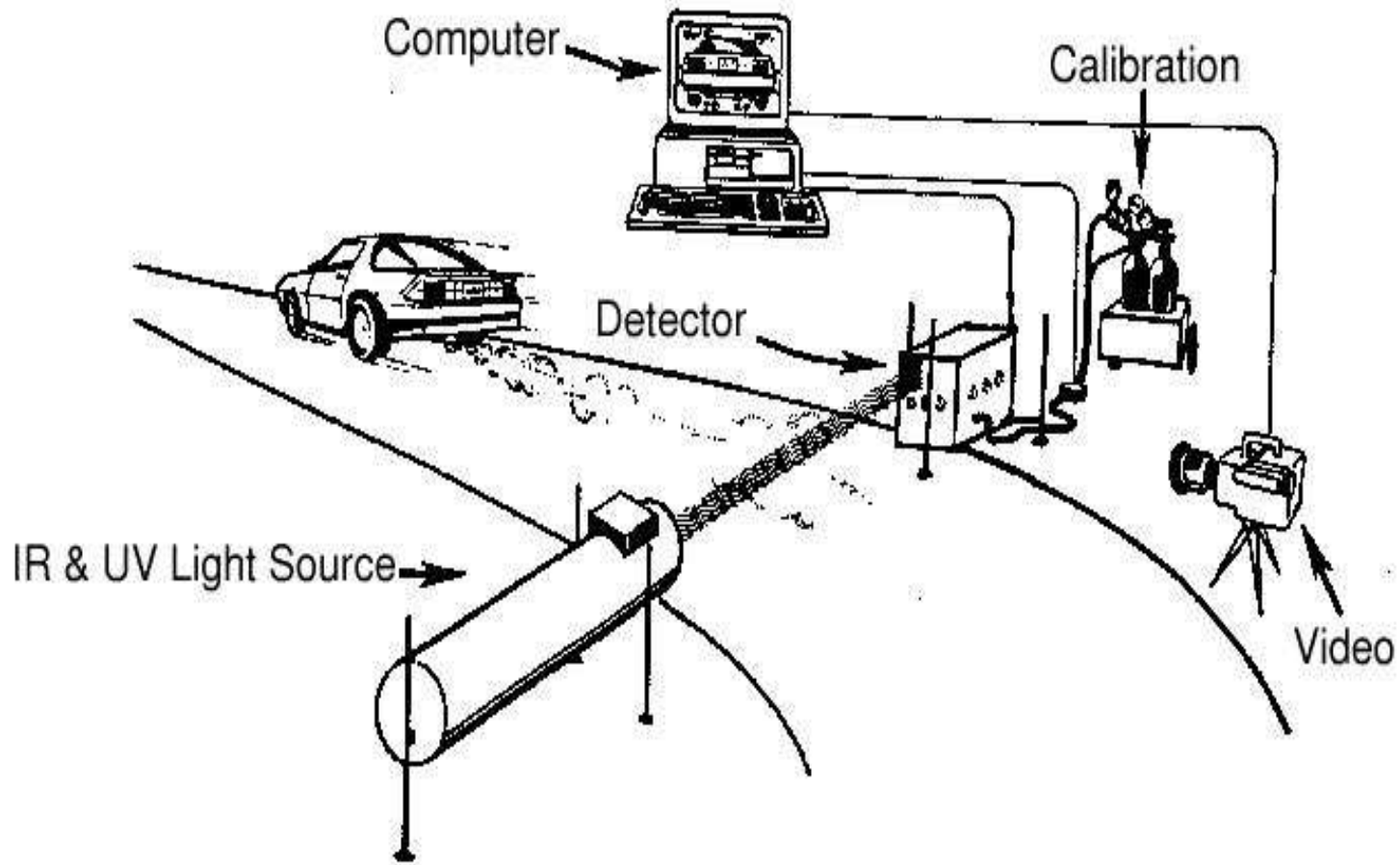
- **Sponsor**

- California Air Resources Board under contract no. 07-319.

- **Support**

- Dr. Tao Zhan
- University of Denver
- Mr. Floyd Little of Caltrans Fresno
- Ms. Annette Bishop
- Mr. Rocky Carlisle

# CO, HC and NO Remote Sensing



***Now with  $NO_2$ ,  $SO_2$ ,  $NH_3$ , smoke***

# Brief History of Vehicle Remote Sensing

- 1973 *Vehicle Inspection Instrumentation*, Hoshizaki, Wood and Kemp, Report to CARB.
  - REMOVE reported CO, HC, and NO ratioed to  $[\text{CO}+\text{CO}_2]$  in the IR. Was battery powered and gave results on 3 analog meters. Worked sometimes for CO and HC up to 20mph. **Results were never published in the literature!**
- 1983 *The remote measurement of traffic generated CO*, Chaney, JAPCA.
  - Demonstrated the capabilities to measure individual vehicle CO plumes with a roadside detector.
- 1987 DU demonstrates the Fuel Efficiency Automobile Test 1000 instrument.
  - Liquid  $\text{N}_2$  cooled InSb detectors for CO and  $\text{CO}_2$ .
  - Added video image capture and a detector for HC in 1989

# Vehicle Remote Sensing History (cont.)

- 1989 General Motors (Stephens et al) develops an on-road sensor
- 1990 FEAT 3000 instrument developed
  - Four peltier cooled detectors CO, CO<sub>2</sub>, HC and Ref
- 1991 Hughes Aircraft tests a sensor using an FTIR
- 1994 RSD1000 First commercial remote sensor
  - FEAT 3000 upgraded with NDUV NO
- 1997 FEAT 3000 upgraded with a dispersive UV spectrometer for NO
- 2005 FEAT 3000 upgraded to twin spectrometers to measure NO, SO<sub>2</sub>, NH<sub>3</sub> and NO<sub>2</sub>

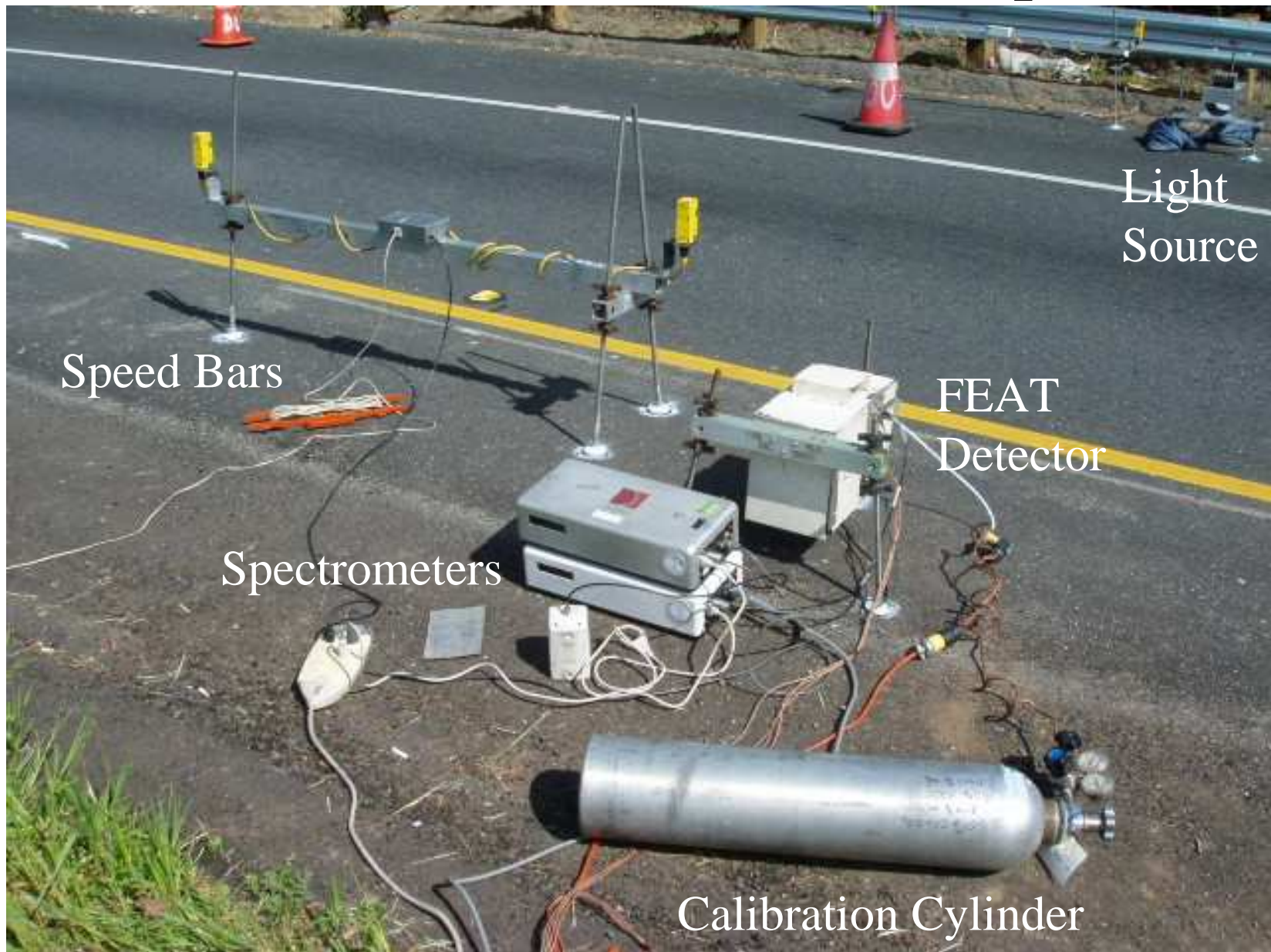
# Roadside Instrument Setup



Speed Bars

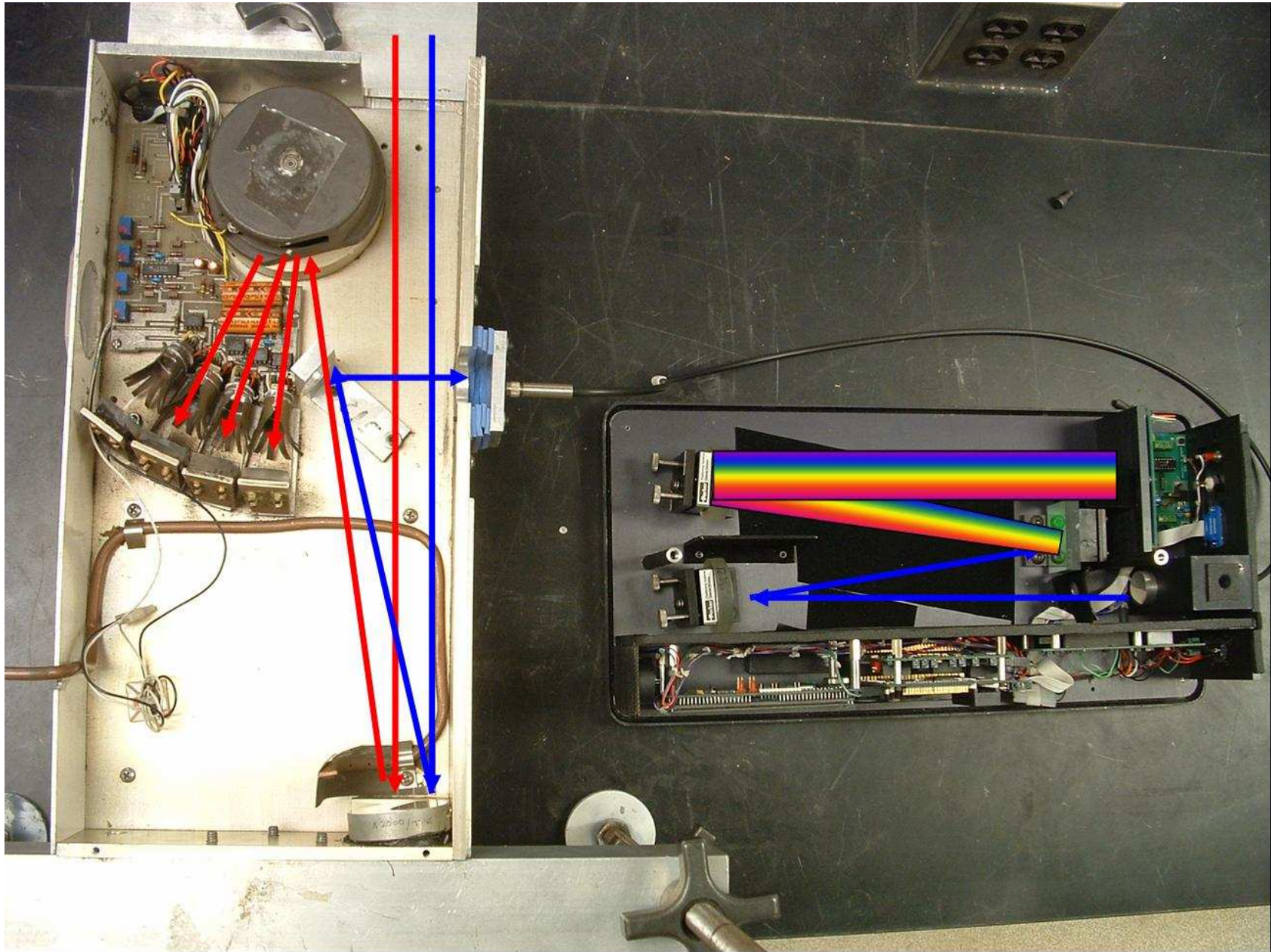
Light Source

# Roadside Instrument Setup





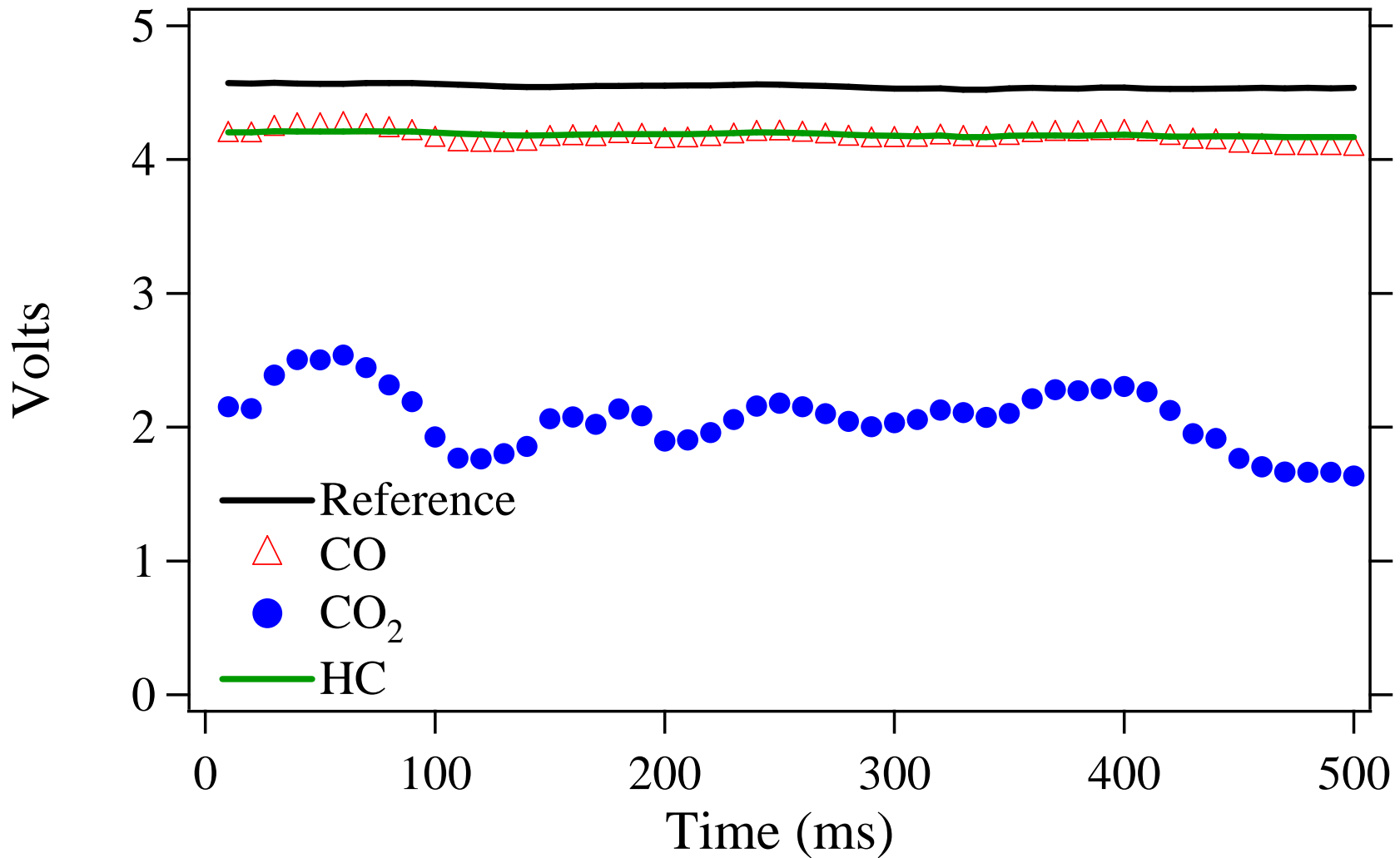
# FEAT Detector and Mono IR/UV Light Paths



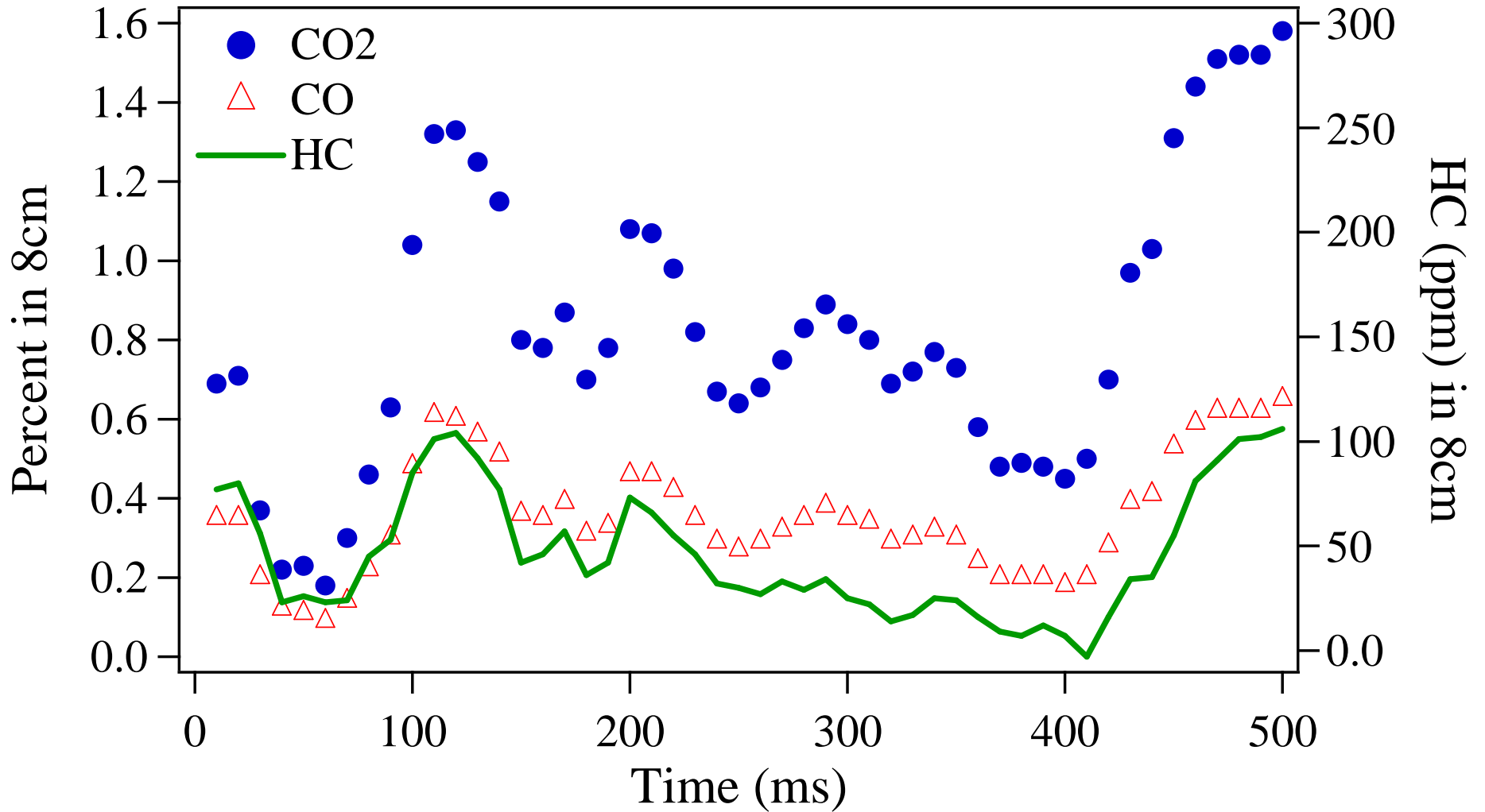
# HOW FEAT WORKS

- FEAT does not MEASURE anything.
- It is a comparator.
- It compares the pollutant ratios (CO/CO<sub>2</sub>, HC/CO<sub>2</sub>, NO/CO<sub>2</sub> etc.) in the vehicle exhaust to the pollutant ratios in a certified cylinder.
- RATIOS are what we measure; all other results such as fuel specific emissions (grams/gallon or g/kg) are derived from the measured ratios.

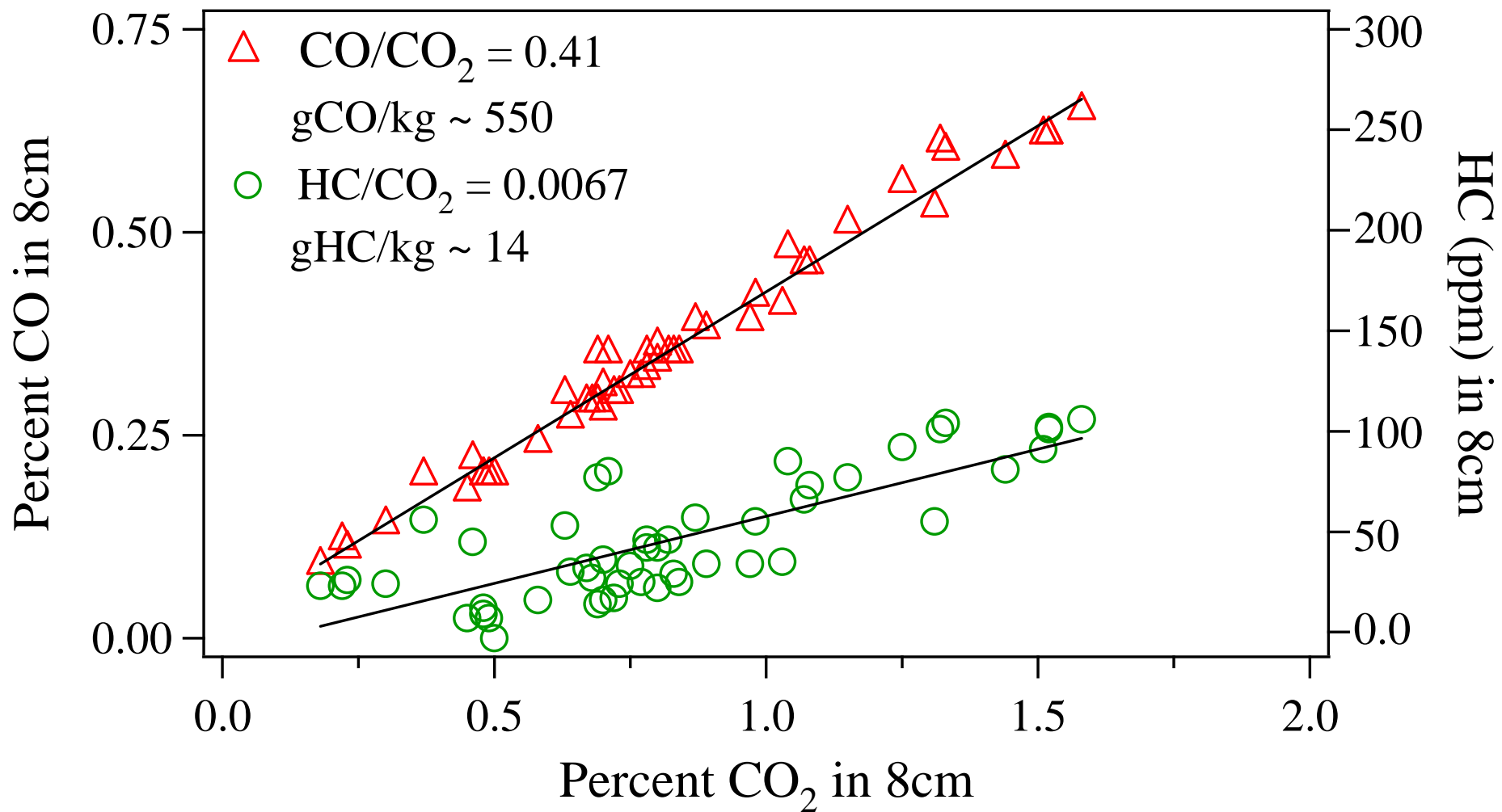
# IR Plume Signal vs. Time



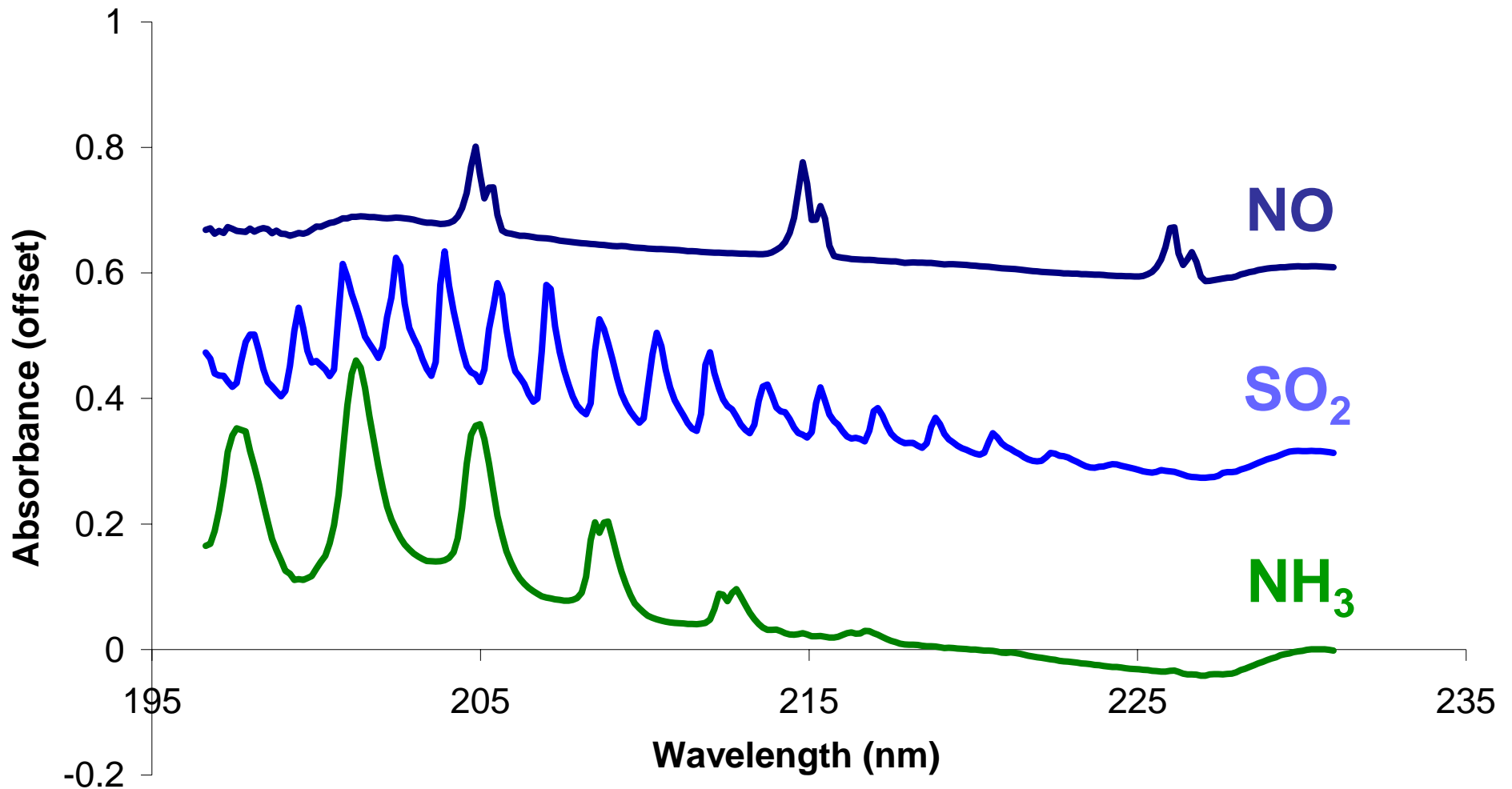
# Pollutant Readings vs Time



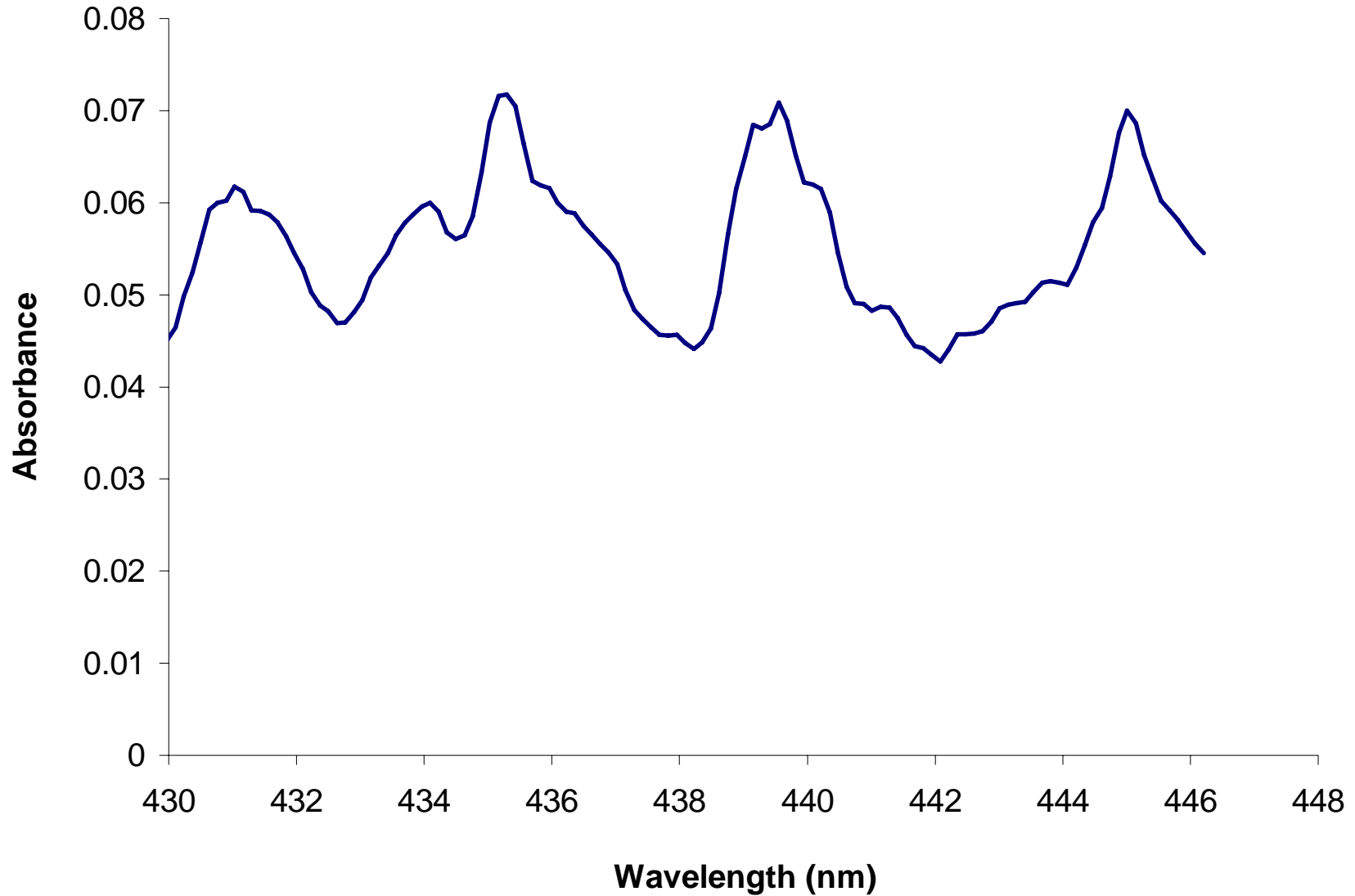
# Pollutant Ratio Plots



# UV Dispersive Spectroscopy



# NO<sub>2</sub> Spectrum from FEAT Remote Sensor





0.01

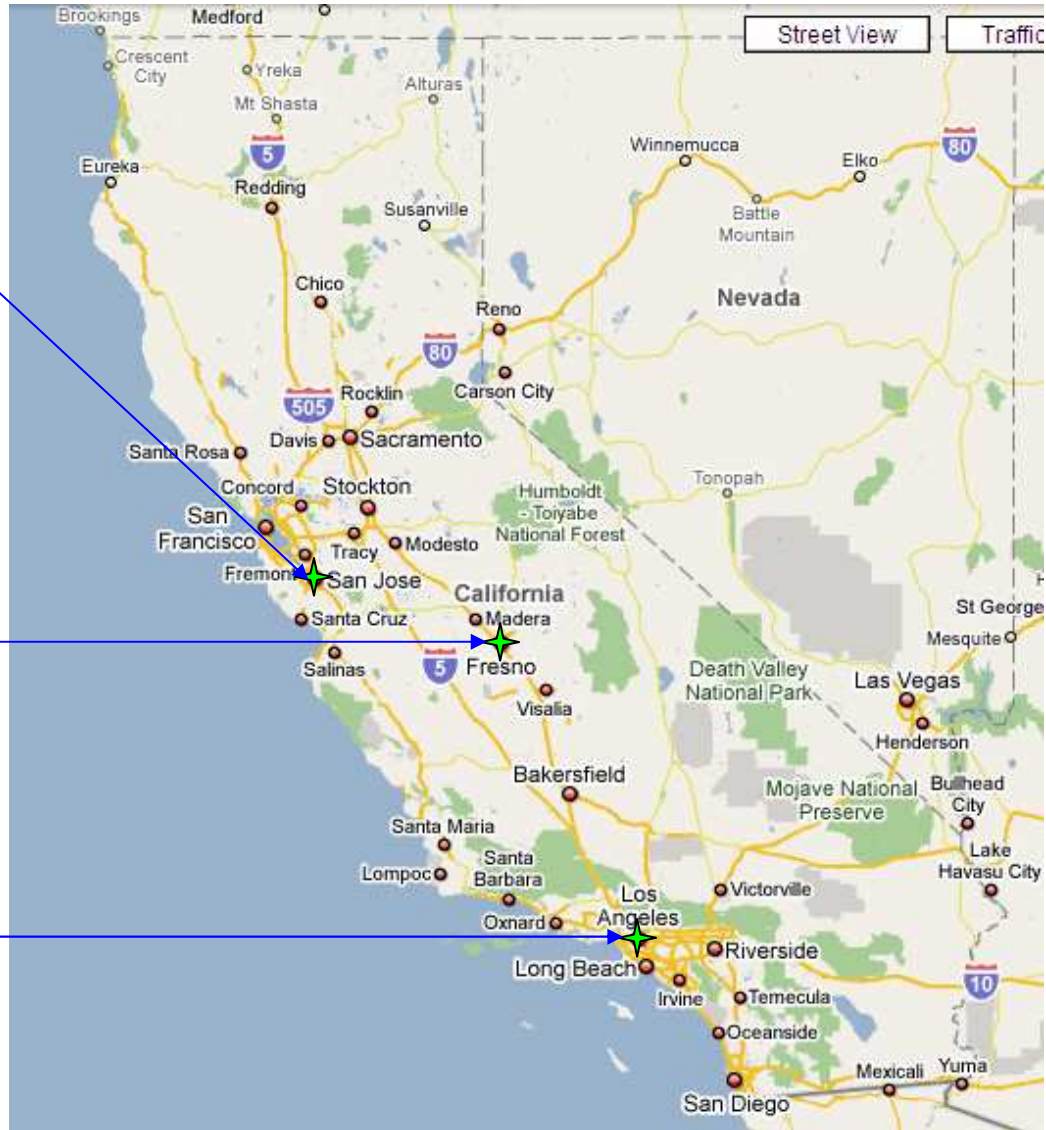
0.004

0.0011

15.05



# Three Field Sampling Sites



Field Sampling: March, 2008

# San Jose Site / Nb I-280 to Nb I-880



March 4 – 7, 2008

Attempts / Valid Gas / Matched

31,116 / 25,371 / 24,978

Mean CO – 16.6 g/kg

Mean HC – 1.5 g/kg

Mean NO – 2.6 g/kg

Mean SO<sub>2</sub> – 0.06 g/kg

Mean NH<sub>3</sub> – 0.5 g/kg

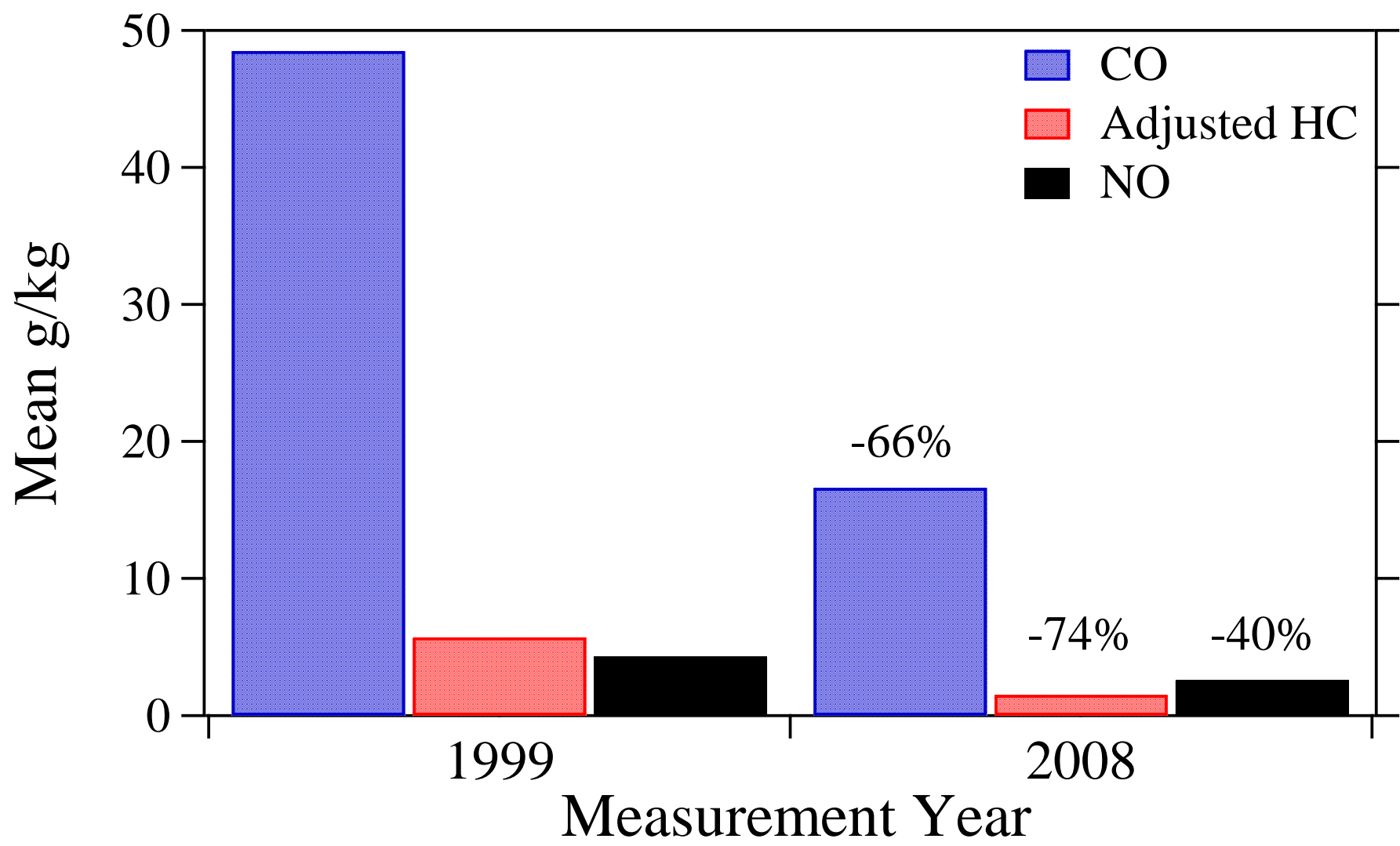
Mean NO<sub>2</sub> – 0.05 g/kg

Mean MY – 2000.6

Mean Speed – 30.6 mph

Mean Accel – 1.0 mph/s

# San Jose Historical Emissions Comparison



# Fresno Site / Nb US-41 to Nb US-180

March 8 – 14, 2008

Attempts / Valid Gas / Matched

15,656 / 15,048 / 13,365

Mean CO – 20 g/kg

Mean HC – 2.9 g/kg

Mean NO – 2.9 g/kg

Mean SO<sub>2</sub> – 0.09 g/kg

Mean NH<sub>3</sub> – 0.5 g/kg

Mean NO<sub>2</sub> – 0.14 g/kg

Mean MY – 1999.8

Mean Speed – 25.4 mph

Mean Accel – 0 mph/s



# West LA Site / Sb Labrea Blvd. to Eb I-10

March 17 – 21, 2008

Attempts / Valid Gas / Matched

23,579 / 22,072 / 17,953

Mean CO – 21.4 g/kg

Mean HC – 1.8 g/kg

Mean NO – 3.75 g/kg

Mean SO<sub>2</sub> – 0.07 g/kg

Mean NH<sub>3</sub> – 0.8 g/kg

Mean NO<sub>2</sub> – 0.08 g/kg

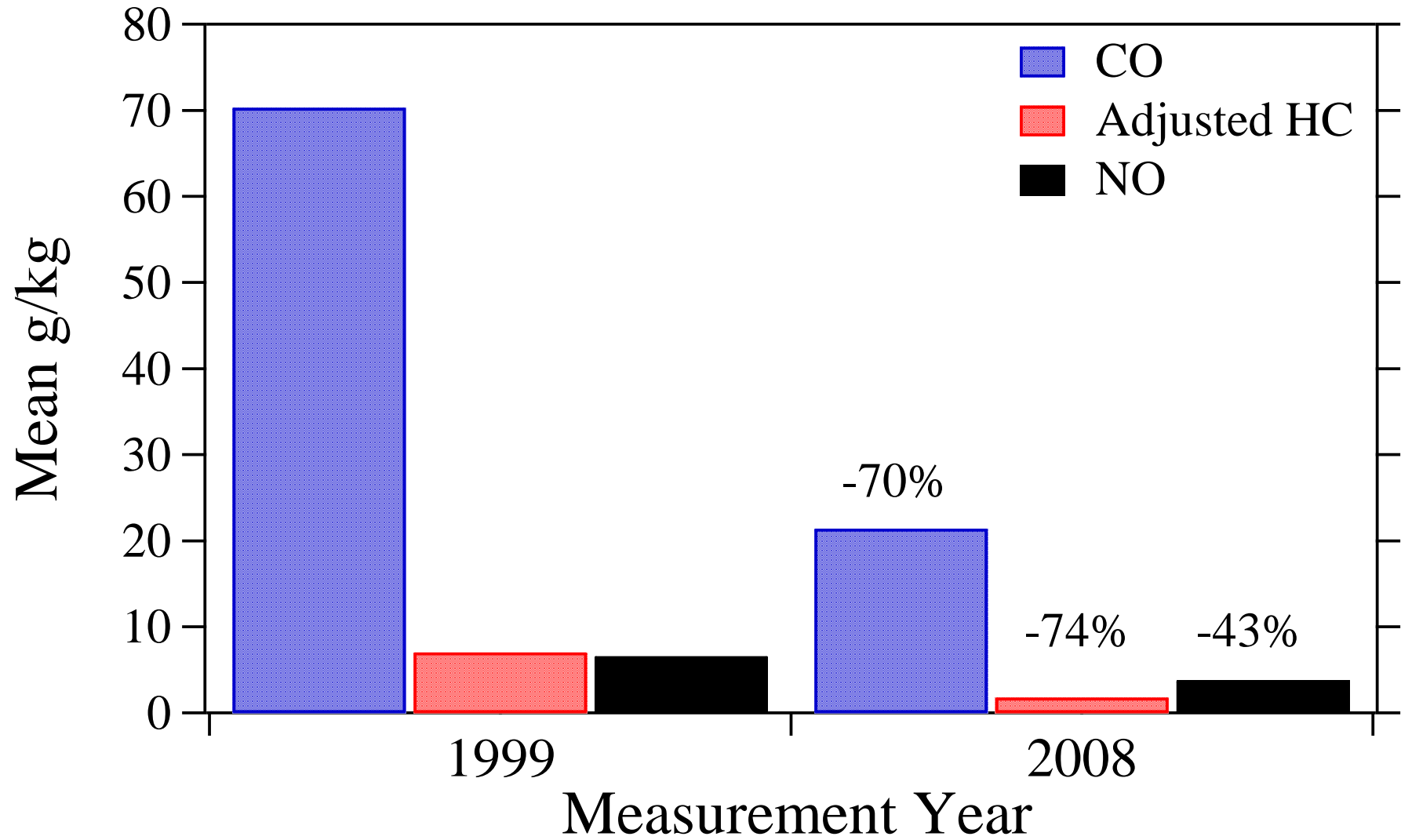
Mean MY – 2001.2

Mean Speed – 17.6 mph

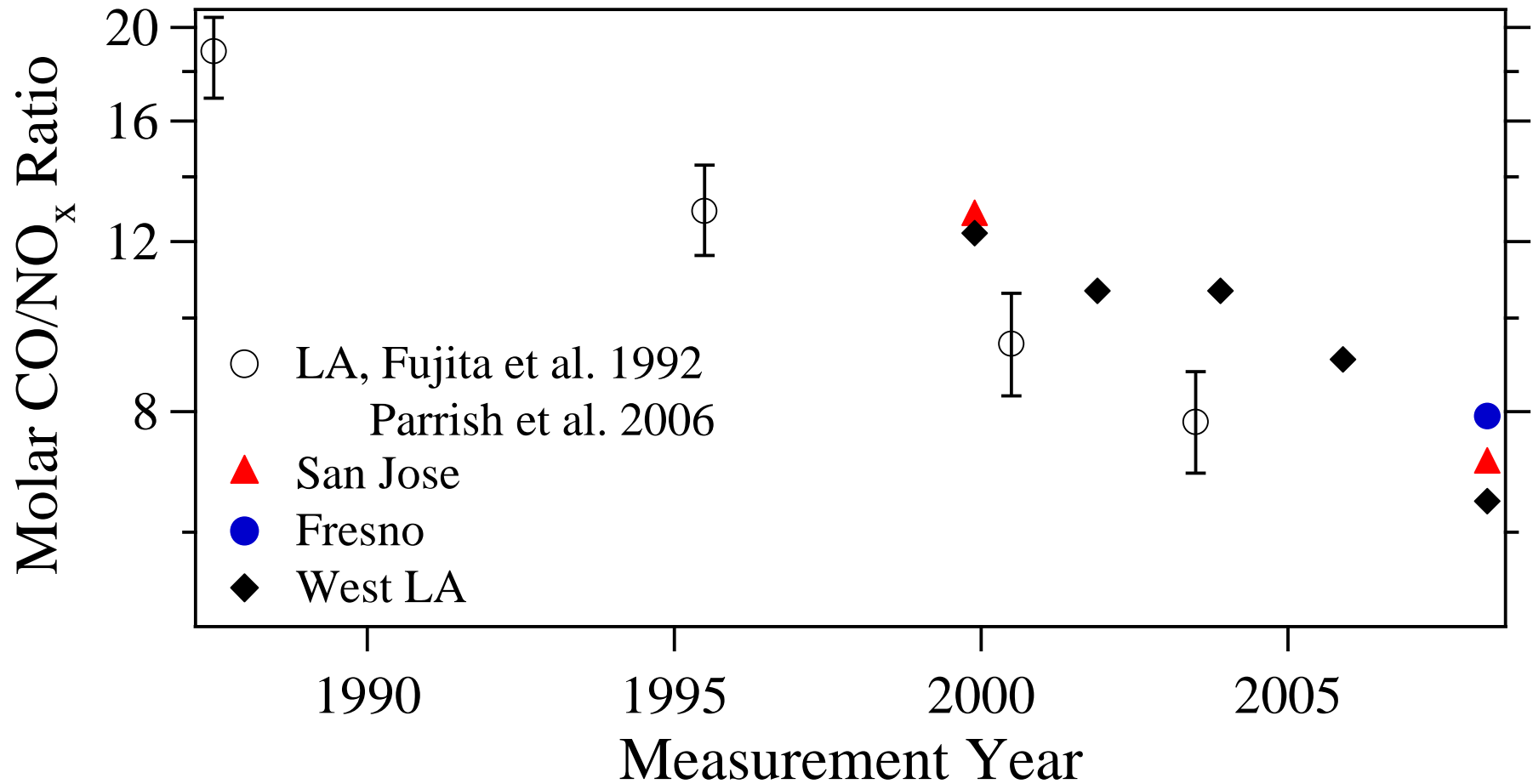
Mean Accel – 1.9 mph/s



# West LA Historical Emissions Comparison

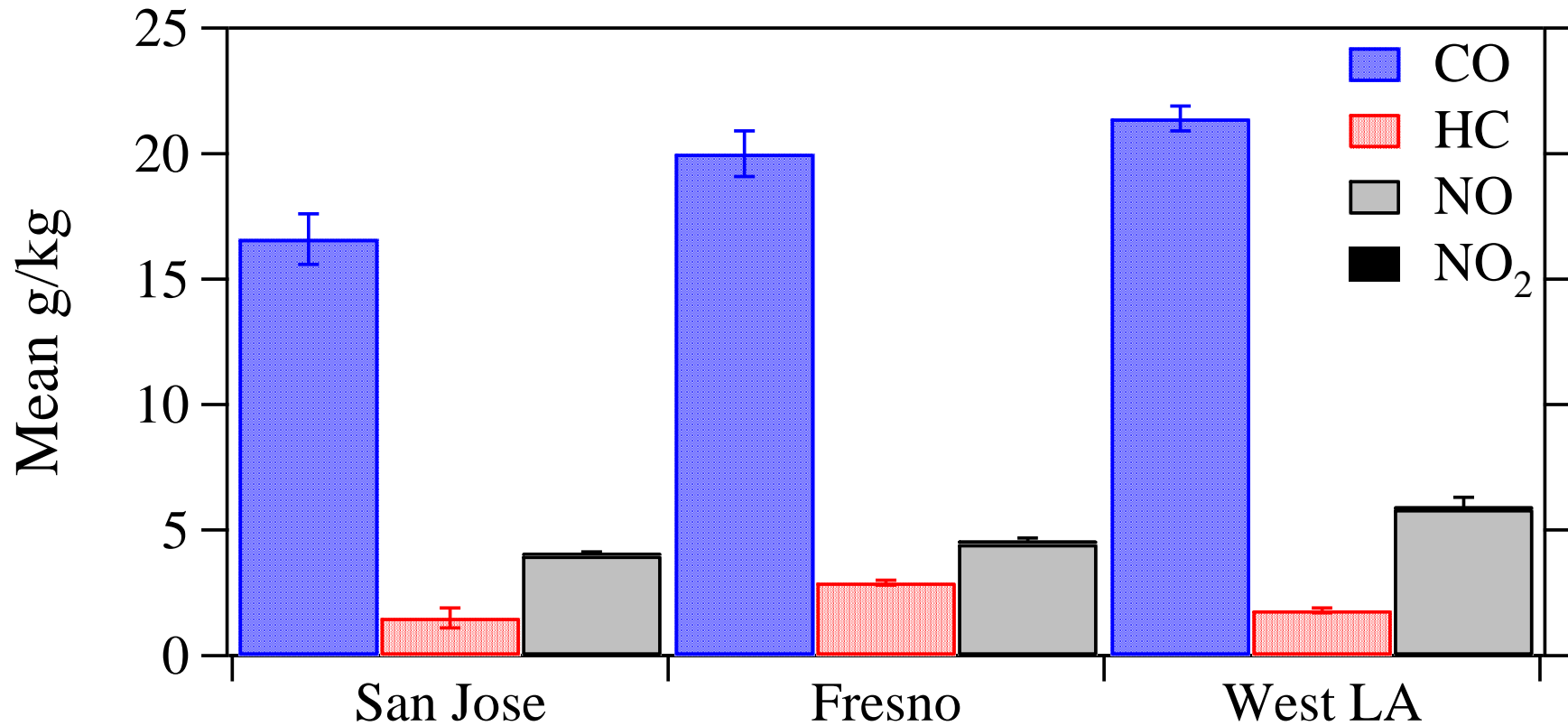


# CO/NO<sub>x</sub> Emissions Trend Comparison



Parrish LA  $-5.5 \pm 0.4\%$     San Jose  $-7.1\%$     WLA  $-7.0 \pm 0.2\%$   
Parrish Nashville  $-8.8 \pm 1.0\%$

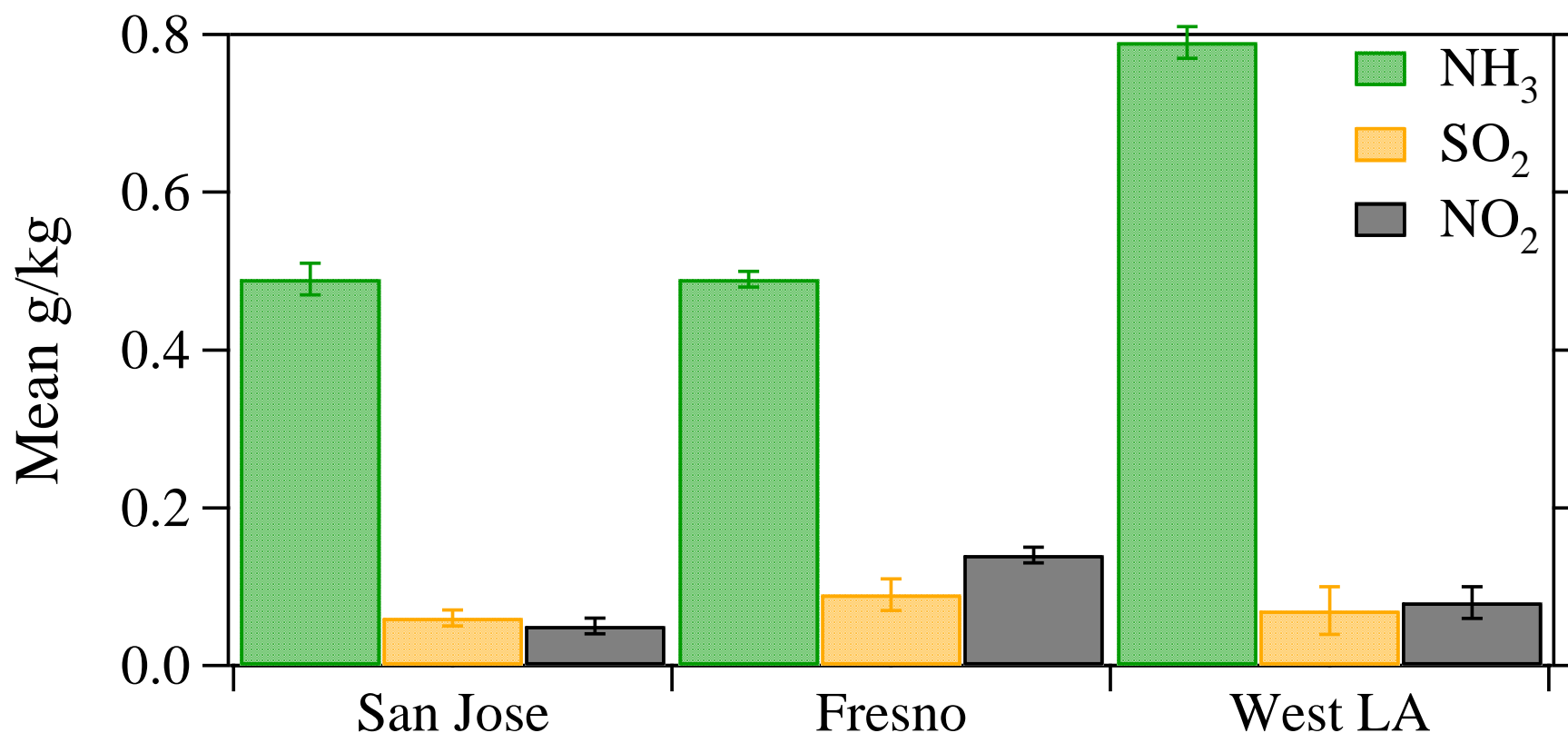
# Summary of Regulated Emissions



Grams of NO reported as grams of NO<sub>2</sub> so bar height equals total NO<sub>x</sub>.  
Error bars are standard errors of the means calculated from the daily means.



# Summary of Specialty Species



Baum et al. (1999) 0.35 g/kg Burgard et al. (2005)  $0.47 \pm 0.02$  and  $0.51 \pm 0.01$

Kean et al (2000 and 2006)  $0.64 \pm 0.04$  and  $0.4 \pm 0.02$

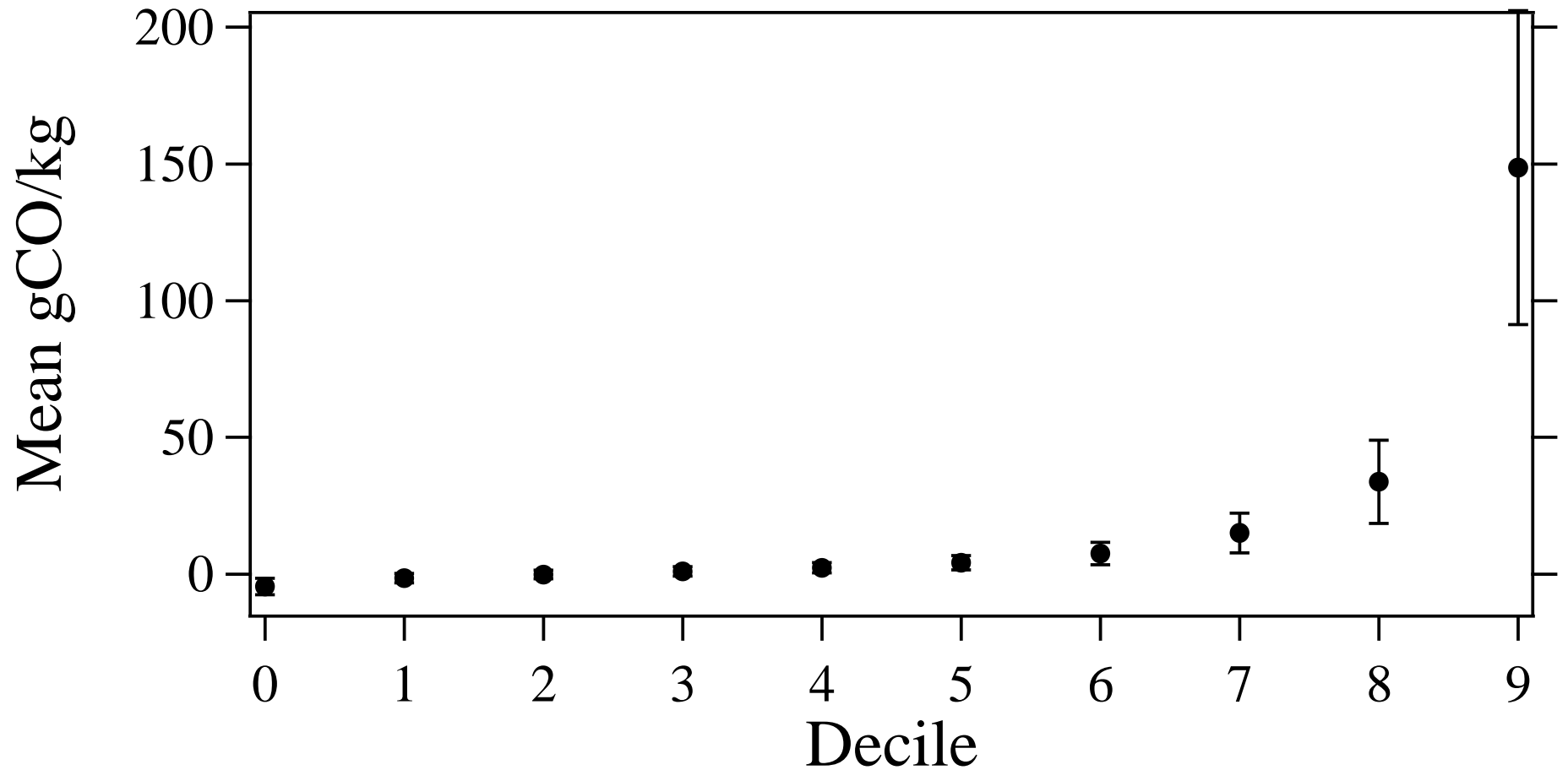
Error bars are standard errors of the means calculated from the daily means.

There are still low hanging emissions...

| Top 1%<br>Contribute | CO  | HC  | NO  |
|----------------------|-----|-----|-----|
| San Jose             | 34% | 17% | 16% |
| Fresno               | 33% | 15% | 15% |
| West LA              | 31% | 38% | 14% |
| Denver 2007          | 27% | 34% | 12% |

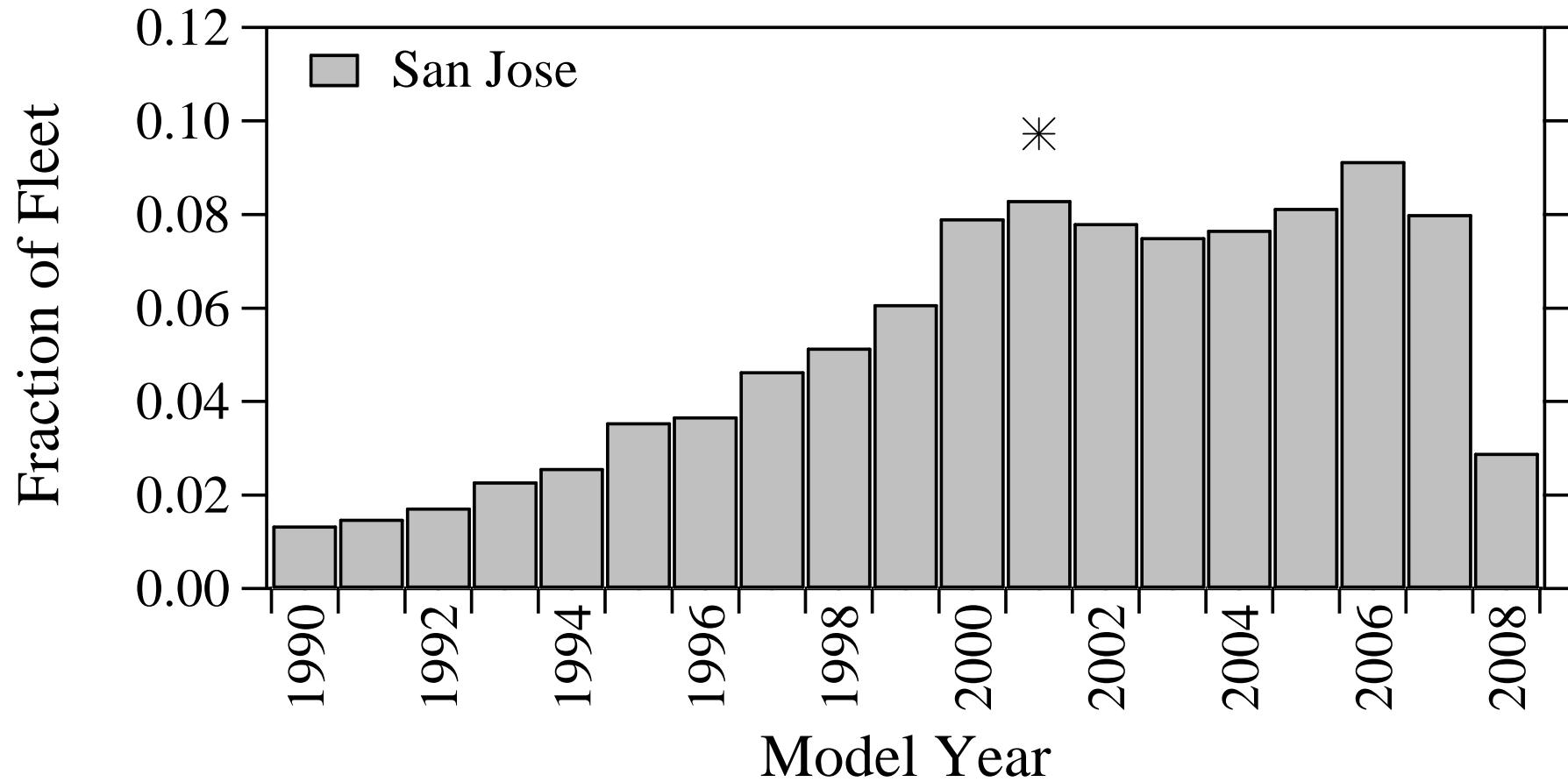
**If a study misses one vehicle out of 100, these are the potential errors in the resulting inventory**

# High Emitter Variability

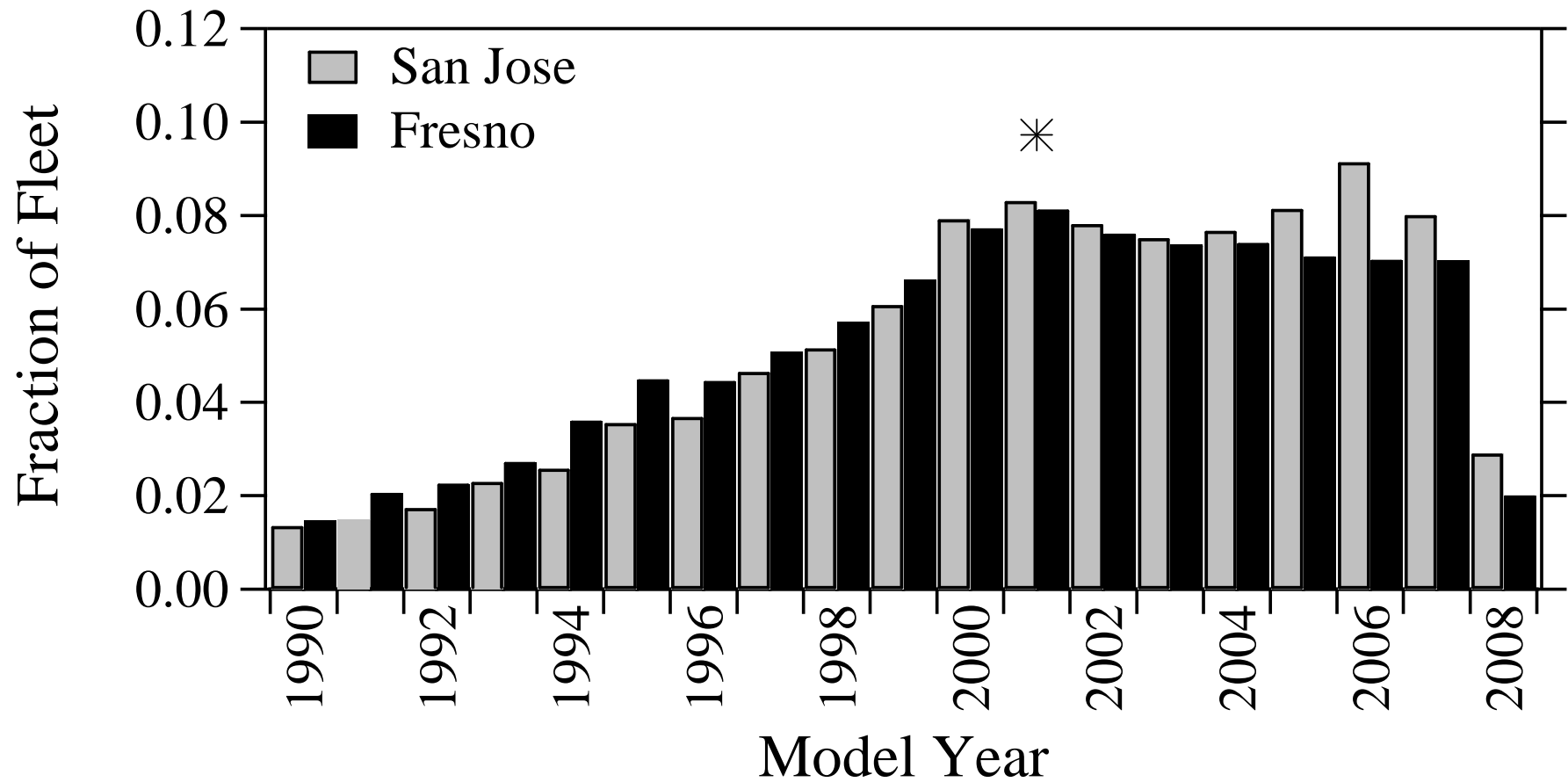


All cities combined and 960 vehicles selected that have at least 3 repeat measurements.

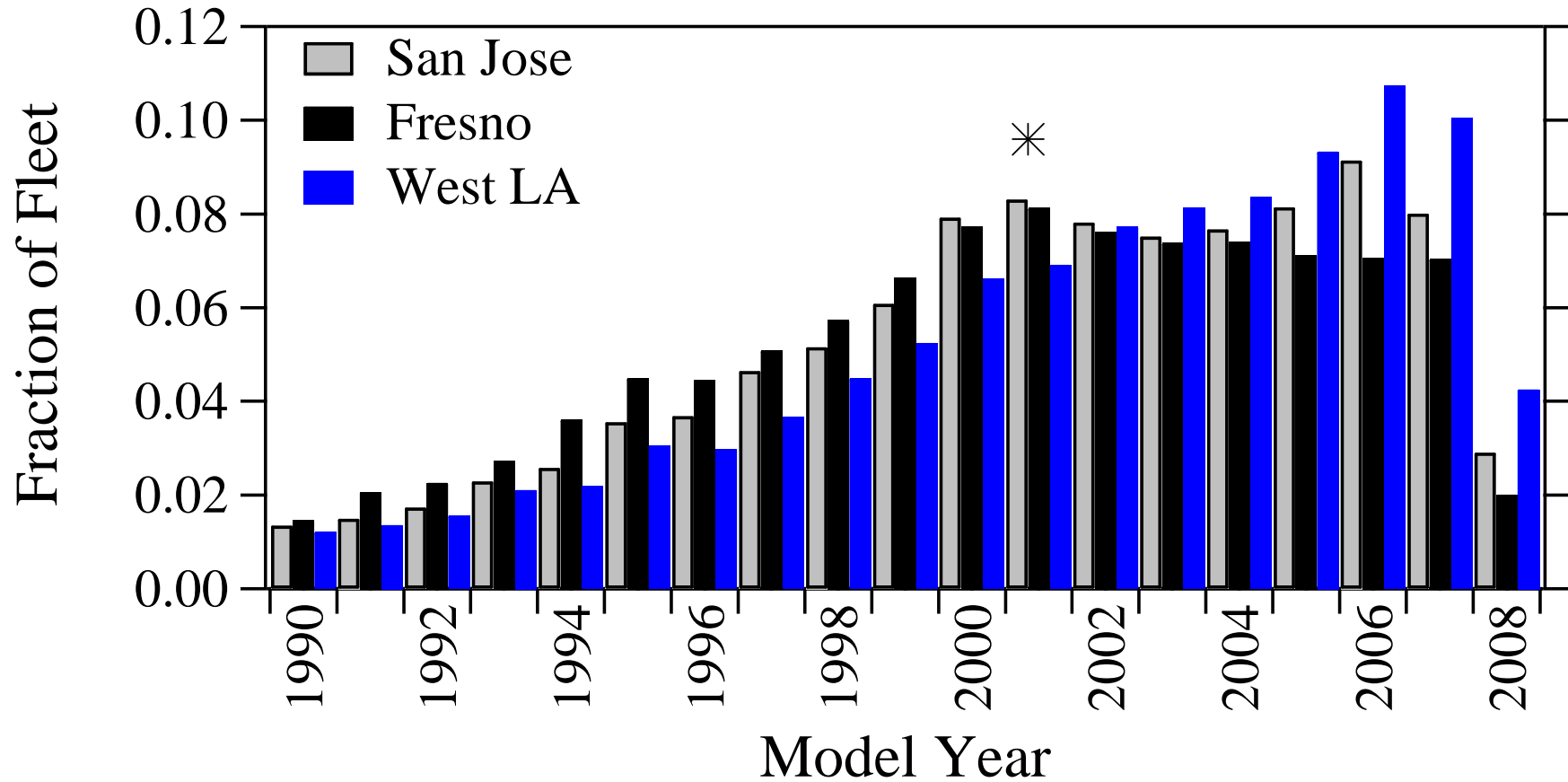
# Recessions and Fleet Fractions



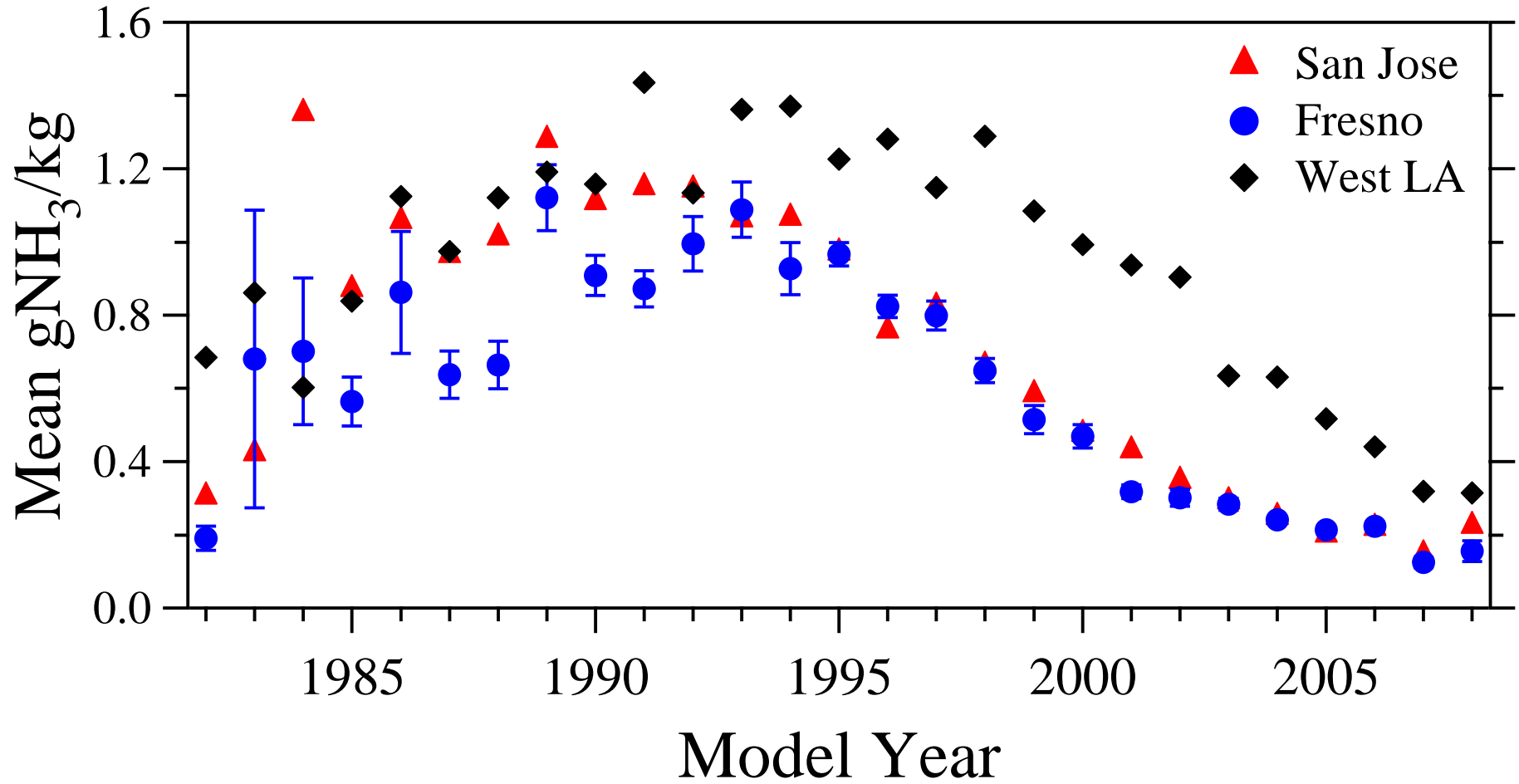
# Recessions and Fleet Fractions



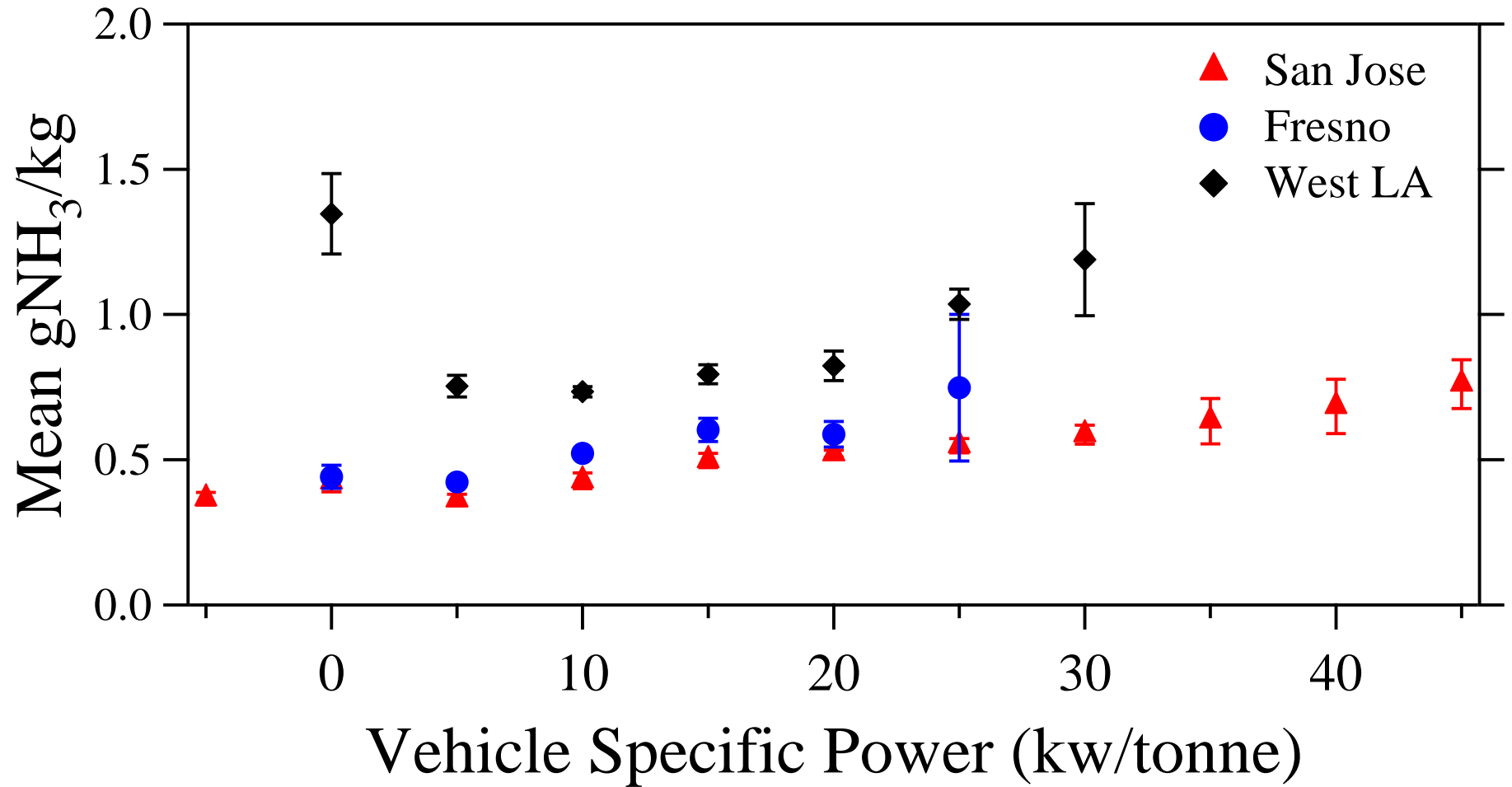
# Recessions and Fleet Fractions



# Ammonia Emissions by Model Year

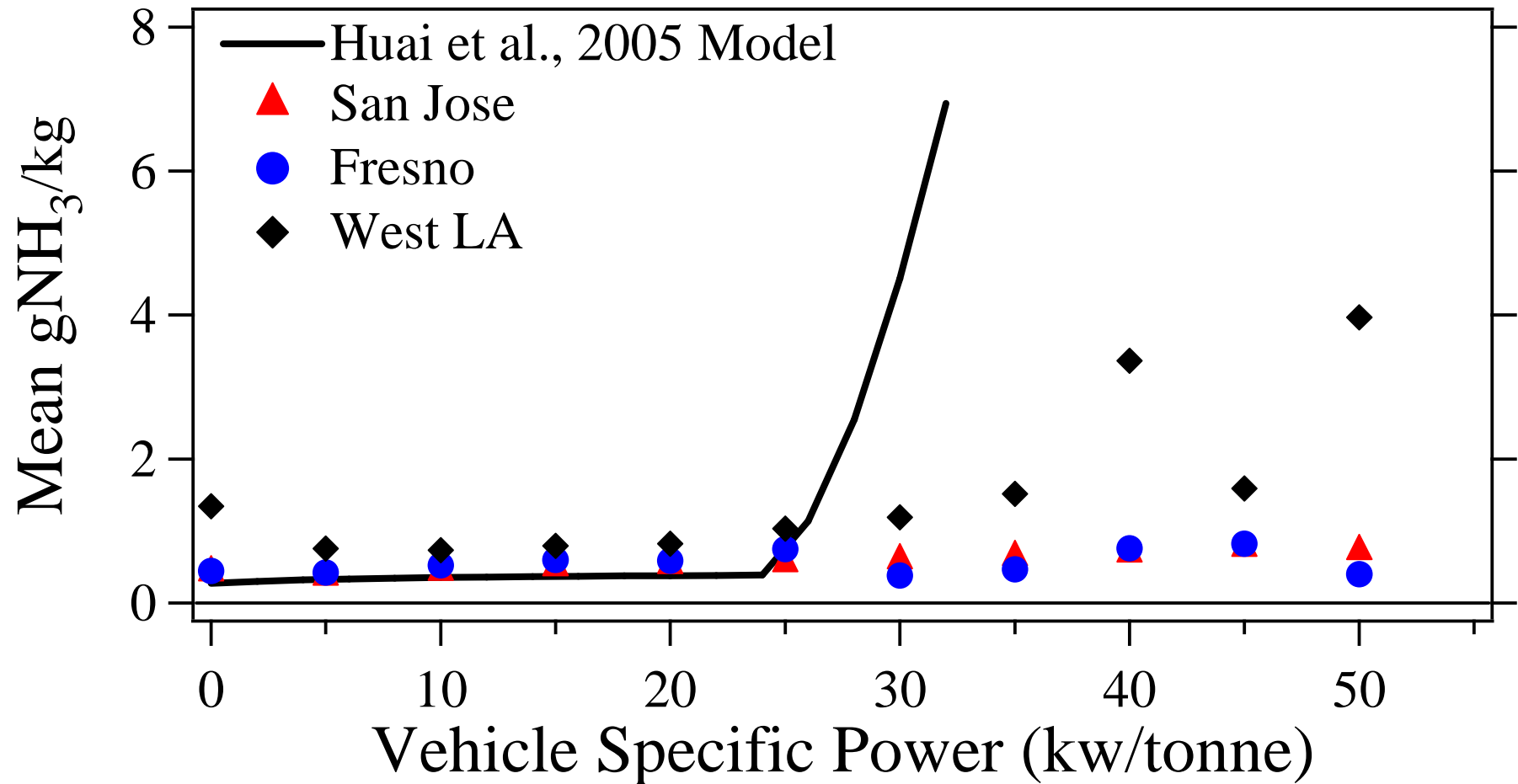


# VSP Dependence of Ammonia Emissions



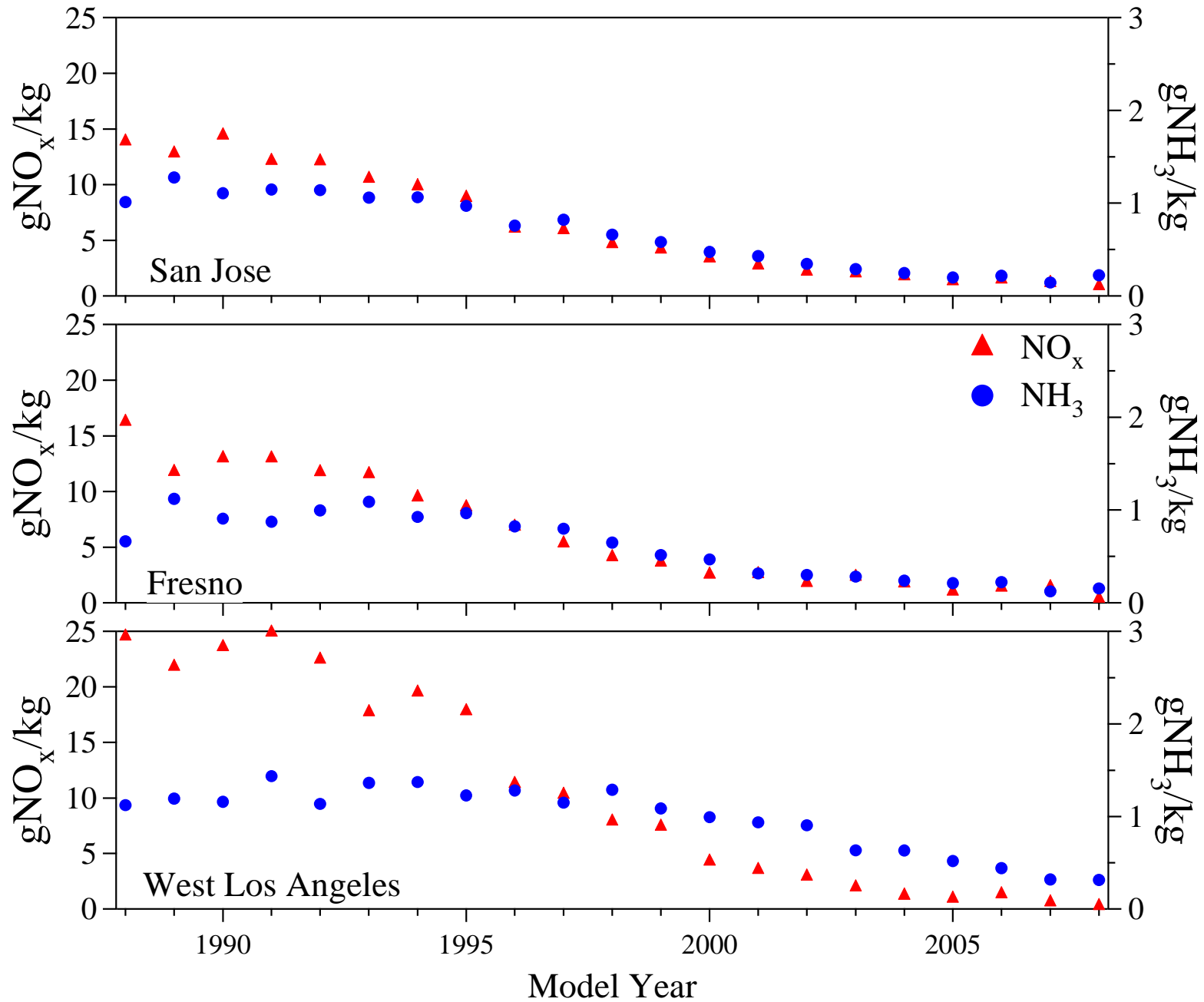


# Huai's Ammonia Model Comparison

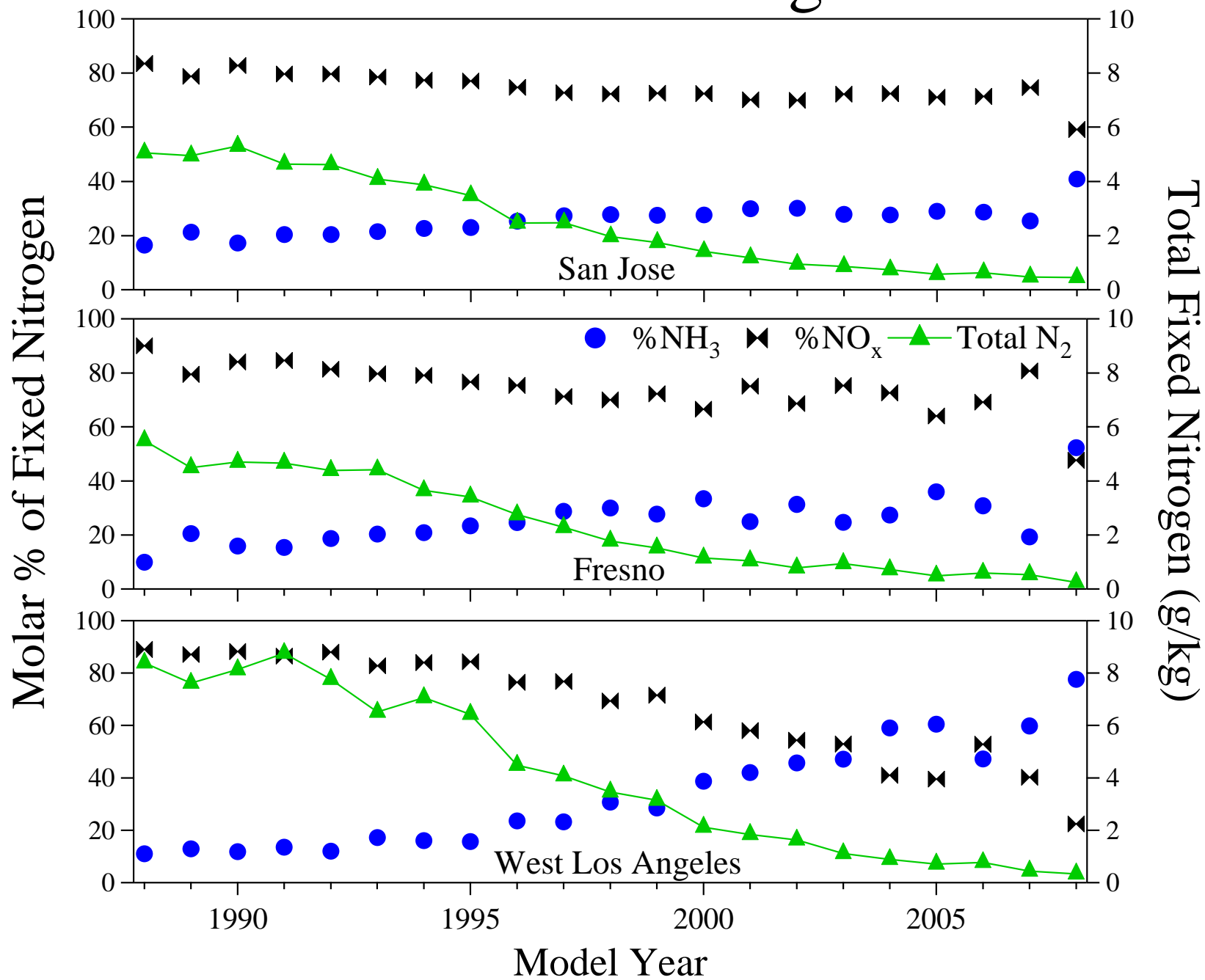


Note: West LA points at vsp's of 40, 45 and 50 have only 9, 9 and 3 vehicles.

# NO<sub>x</sub> and NH<sub>3</sub> Emission Trends



# Total Fixed Nitrogen



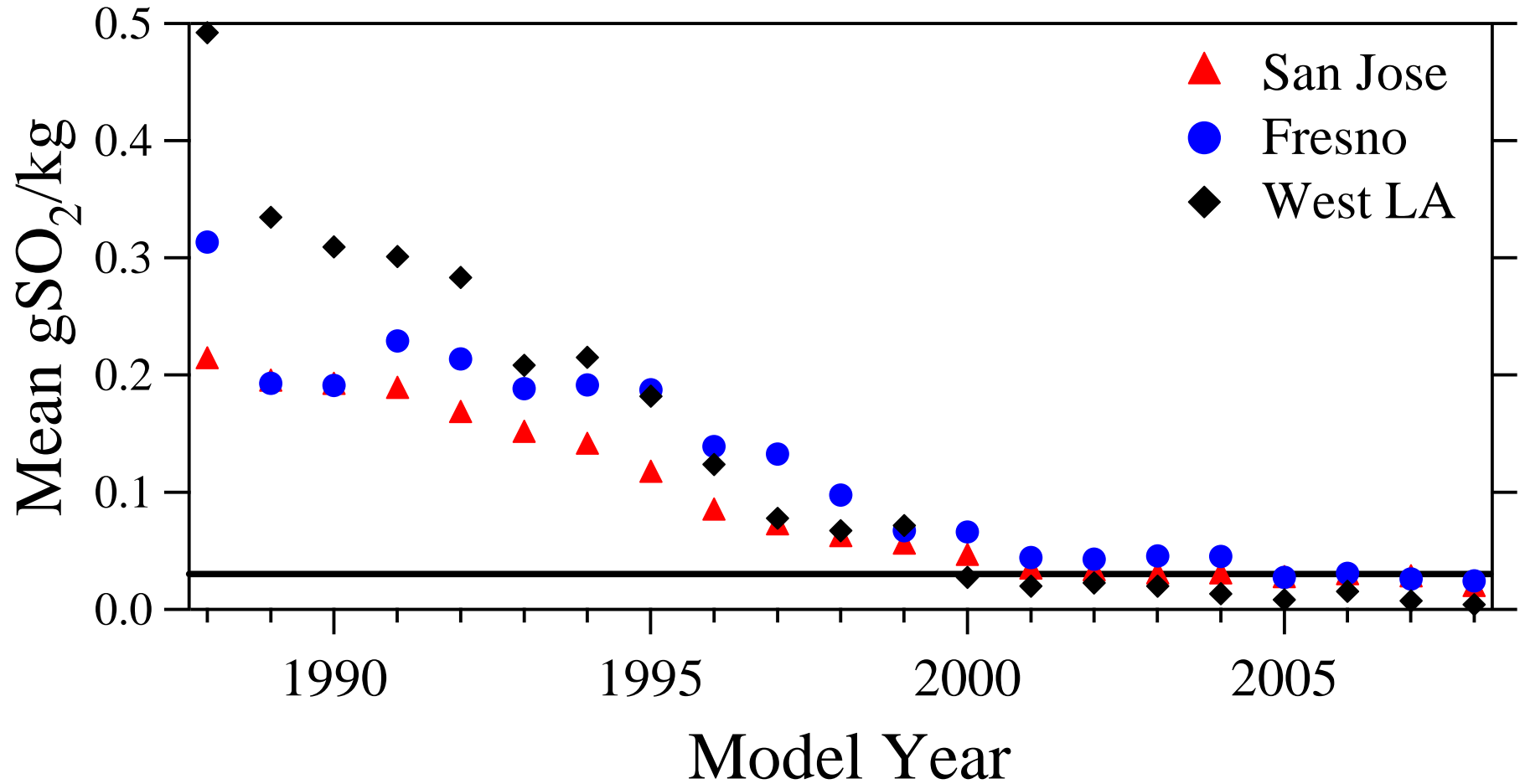
# 2007 National Ammonia Inventory Comparison

| City              | Mean<br>gNH <sub>3</sub> /kg | National*<br>NH <sub>3</sub> Short Tons |
|-------------------|------------------------------|---|
| San Jose / Fresno | 0.49                         | 210,000                                 |
| West LA           | 0.79                         | 330,000                                 |

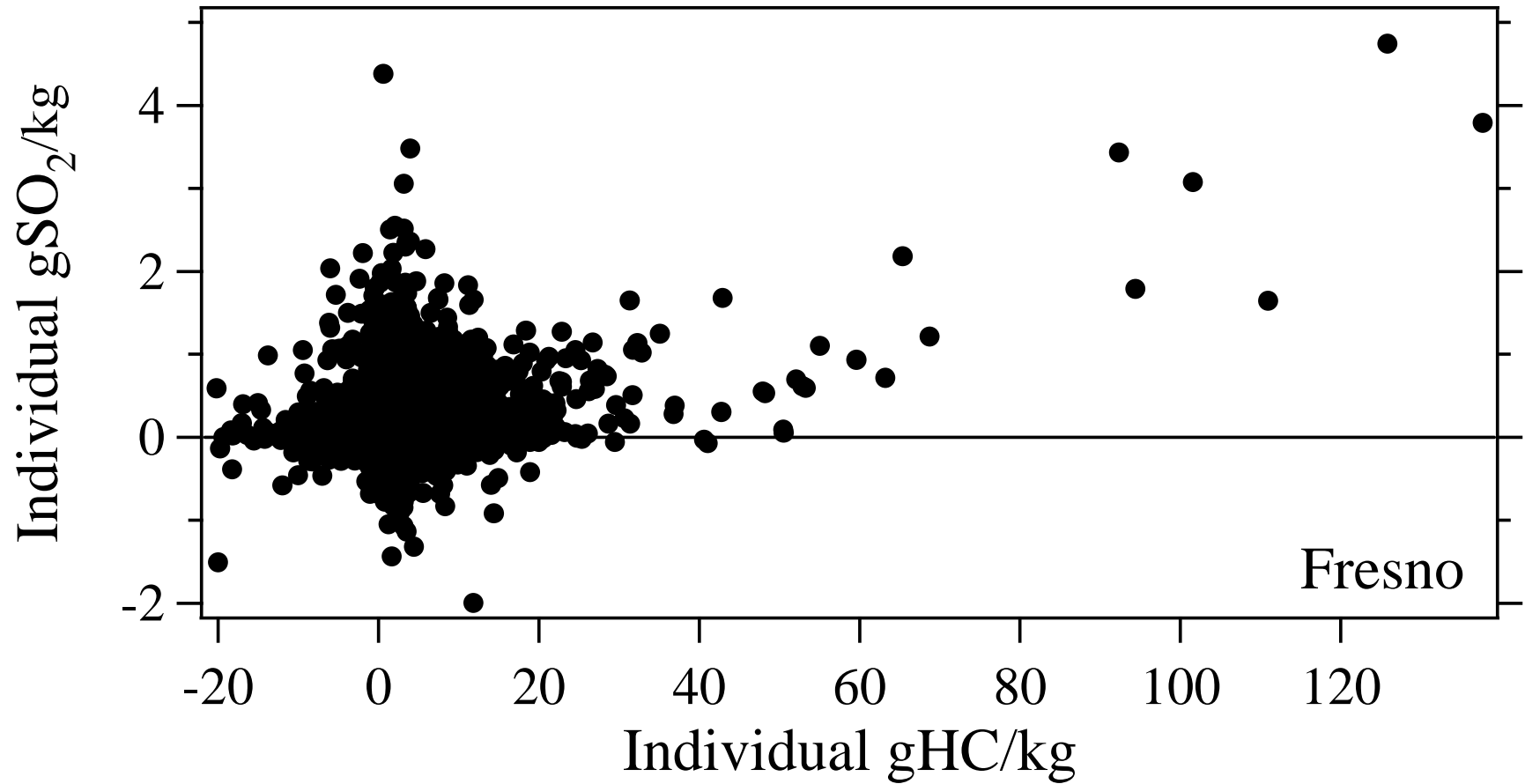
The US EPA 2007 Estimate is 307,000 short tons.

\*Assumes 378,000,000 gal/day of gasoline and a density of 6.073 lbs/gallon and NH<sub>3</sub> emissions are negligible from cold start gasoline and all diesel vehicles.

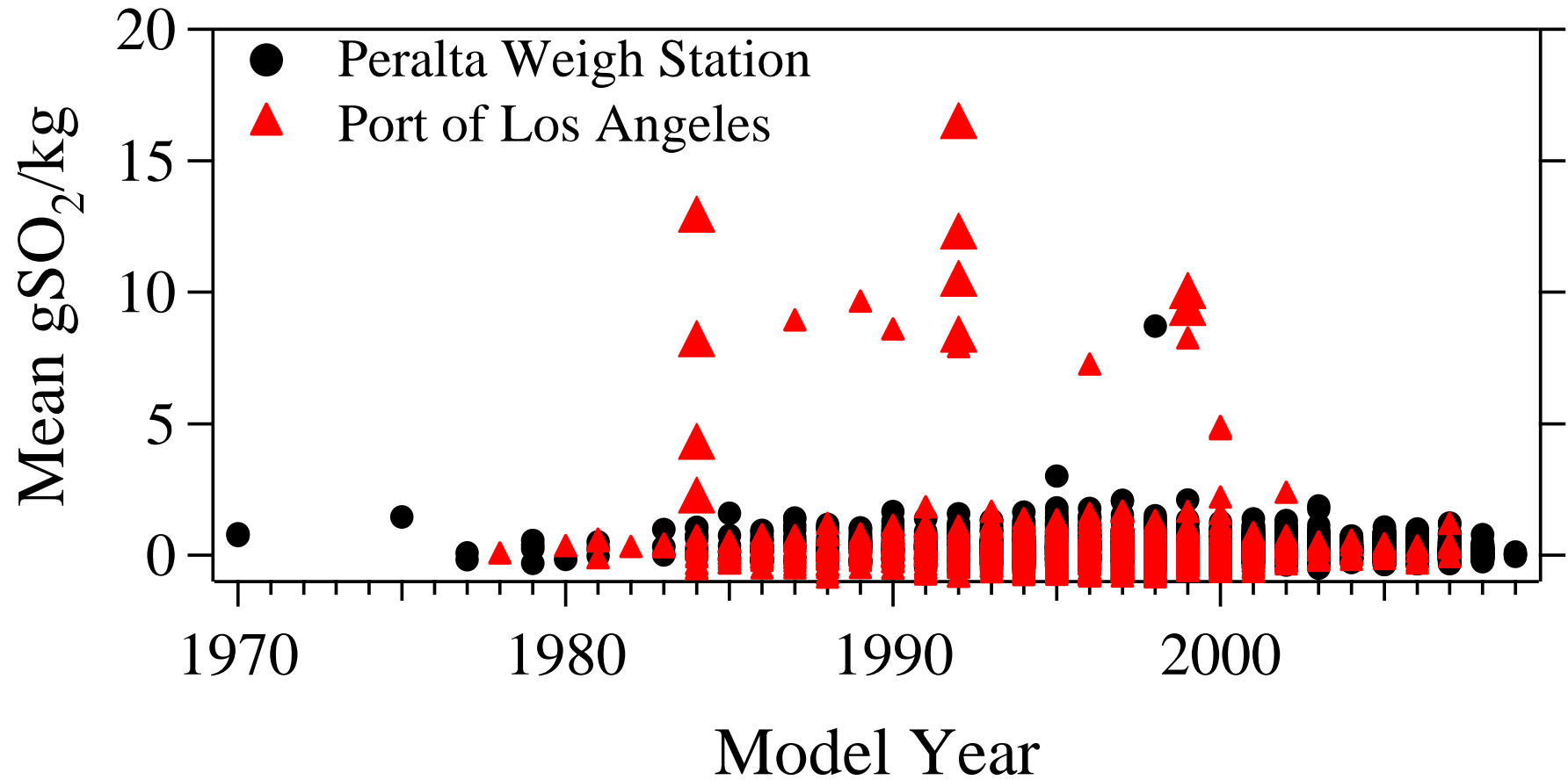
# Sulfur Dioxide Emission by Model Year



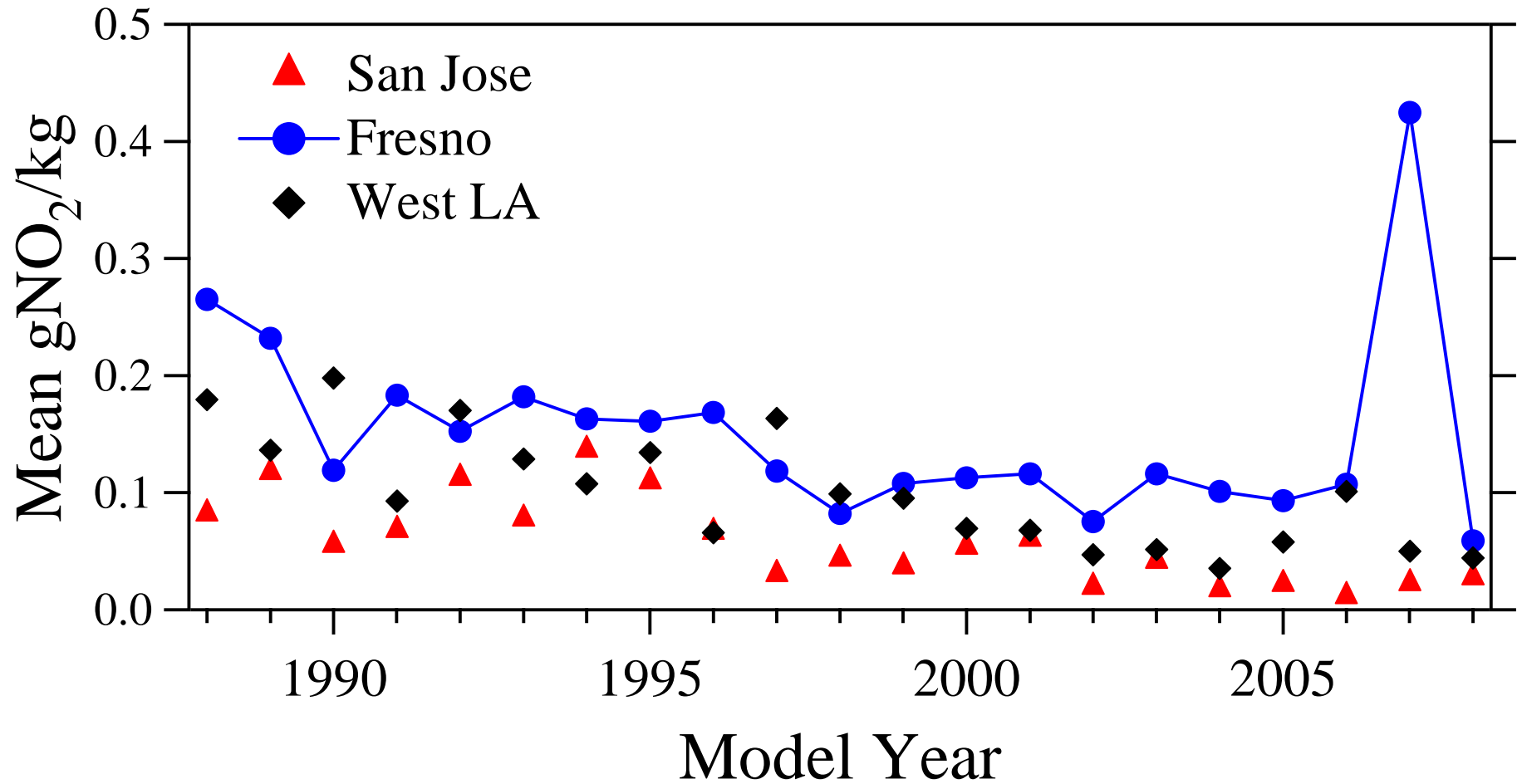
# Hydrocarbon Interference



# 2008 HDDV Measurements



# Nitrogen Dioxide Emissions by Model Year





# Fresno 2007 Model Year Fleet Comparison

| Group            | Samples | Mean<br>%IR<br>Opacity      | Mean<br>gNH <sub>3</sub> /kg | Mean g/kg<br>NO/NO <sub>2</sub> /NO <sub>x</sub> | Mass Ratio<br>NO <sub>2</sub> /NO <sub>x</sub> |
|------------------|---------|-----------------------------|------------------------------|--|--|
| Sprinters        | 57      | <b>0.6</b><br>± <b>0.2</b>  | 0.02<br>± 0.01               | 2.1 ± 0.2<br>4.9 ± 0.6<br><b>8.0 ± 0.8</b>       | 0.61   |
| Other<br>Diesels | 22      | <b>1.2</b><br>± <b>0.7</b>  | 0.02<br>± 0.01               | 12.1 ± 0.9<br>1.4 ± 0.4<br><b>19.9 ± 1.2</b>     | 0.07   |
| Non-<br>Diesels  | 792     | <b>0.4</b><br>± <b>0.04</b> | 0.14<br>± 0.02               | 0.22 ± 0.08<br>0.08 ± 0.01<br><b>0.42 ± 0.12</b> | 0.19   |

# Conclusions

- Similar reductions in regulated emissions since 1999 were found at the San Jose and West LA sites.
- New vehicles emit large percentages of their reactive nitrogen as ammonia (up to 80% at the West LA site). Largest ammonia emissions occur in ~15 year old vehicles and is heavily influenced by driving mode.
- Sulfur dioxide emissions show an unexpected model year dependence for older vehicles, likely due to a hydrocarbon interference.
- Nitrogen dioxide emissions are usually less than 5% of the total  $\text{NO}_x$ , except for a group of diesel powered ambulances observed in Fresno.

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