

Understanding Relationships Between
Changes in Ambient Ozone and Precursor
Concentrations and
Changes in VOC and NO_x Emissions
from 1990 to 2004 in Central California

Eight Hypothesized Explanations of Ozone Trends
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Today's Topics

- I. Identify hypotheses to explain ozone trends
- II. Evaluate hypotheses
- III. Discuss relevance to policy questions
- IV. Get feedback

Key Question

- Substantial and statistically significant downward trends in NO_x, NMOC, CO.
- Generally downward trends in peak 8-hour ozone, but majority of sites less than 0.5 ppbv per year, only 7 of 42 statistically significant, and 10 sites have upward trends.
- Why hasn't peak ozone decreased as much in some areas as in others?

Hypothesis 1

Ozone precursor emissions did not decline.

Incorrect

1990 – 2004 AQ Trends Summary

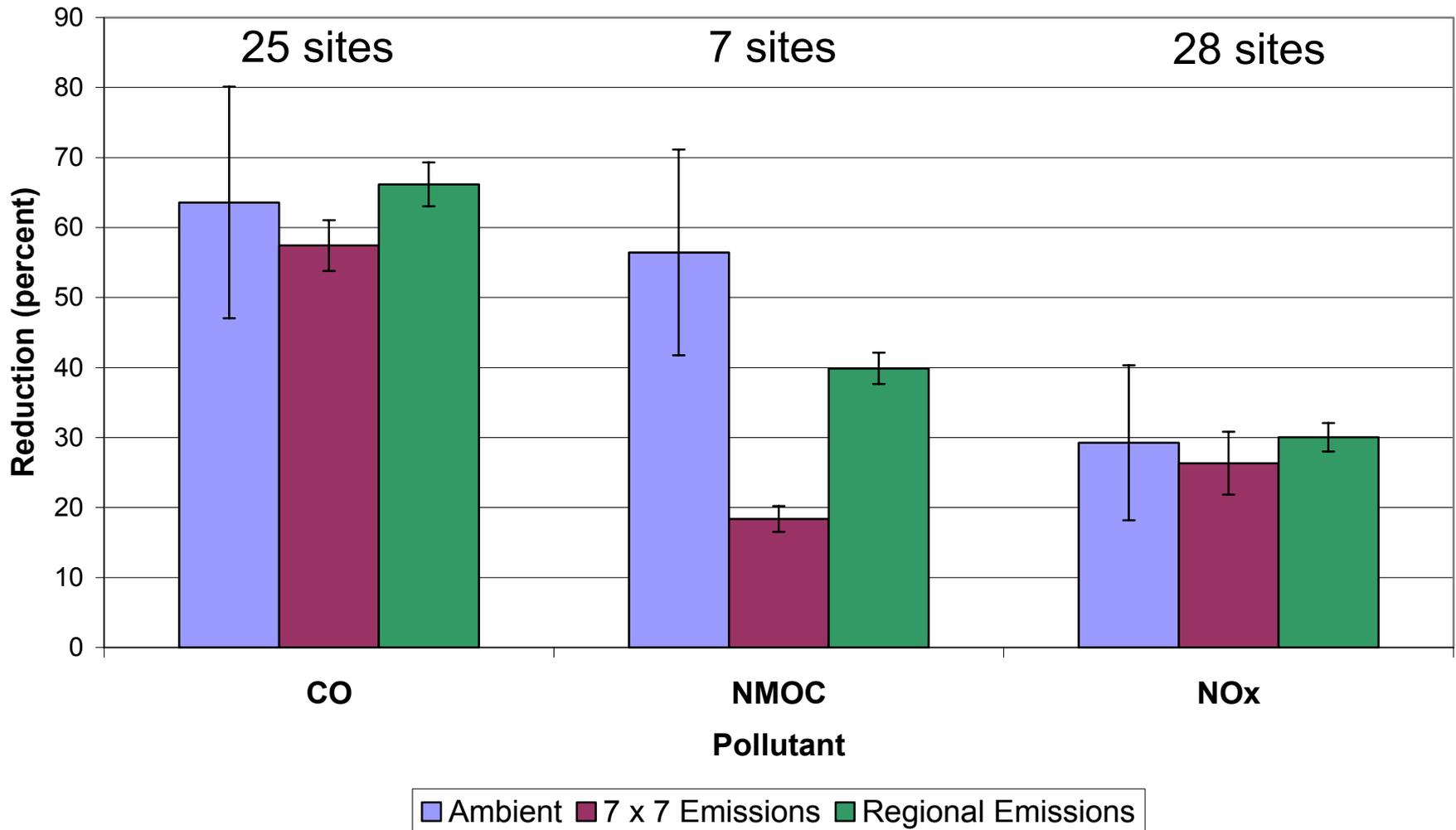
- No precursor trends significantly upward*
- NO_x sig* down at 22 of 28 sites**
- CO sig* down at 21 of 25 sites**
- NMOC sig* down at 6 of 7 sites***

* $p < 0.05$

** At least 10 years data. One or both metrics: morning (5 – 11 am) or midday (time of peak 8-hour ozone).

*** 7 - 10 years data, morning (5 – 8 am).

Average Reductions of Emissions and Ambient Concentrations, 1990 - 2004

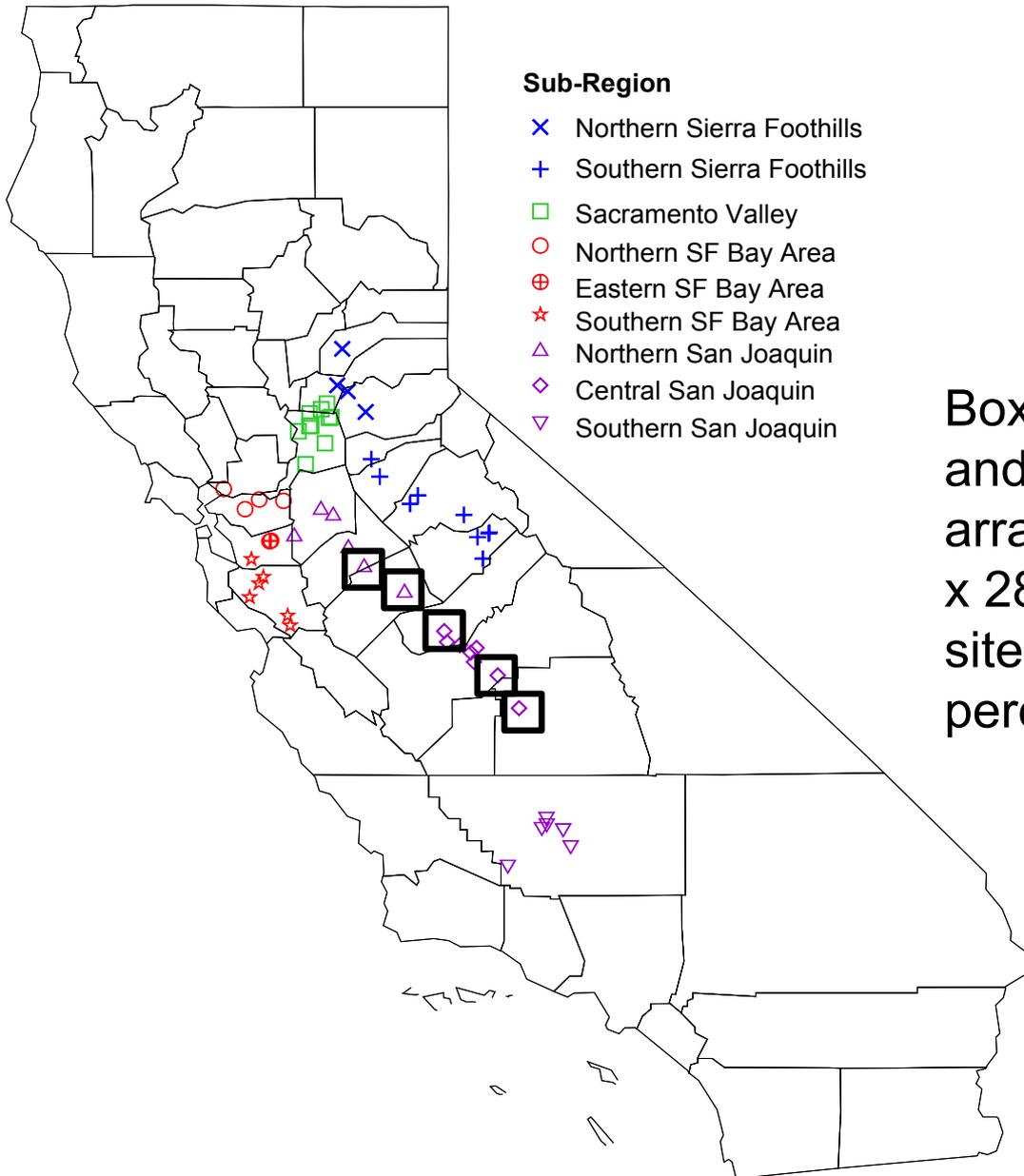


“7 x 7 Emissions” = in the 7x7 array of 4 km grid cells around a site

Hypothesis 2

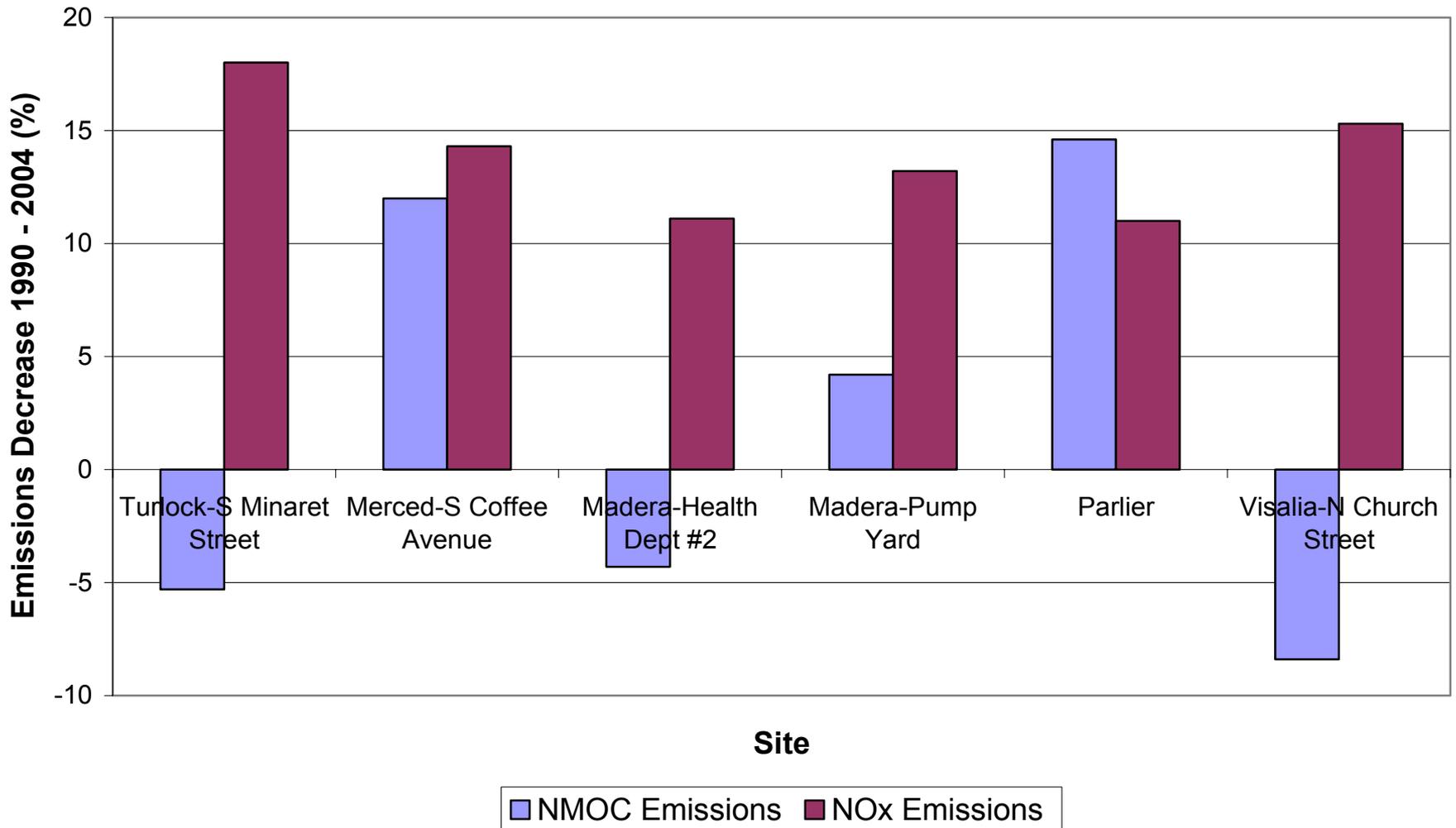
Ozone precursor emissions did not decline enough in some areas experiencing growth and development to produce a significant ozone response in those areas.

Plausible



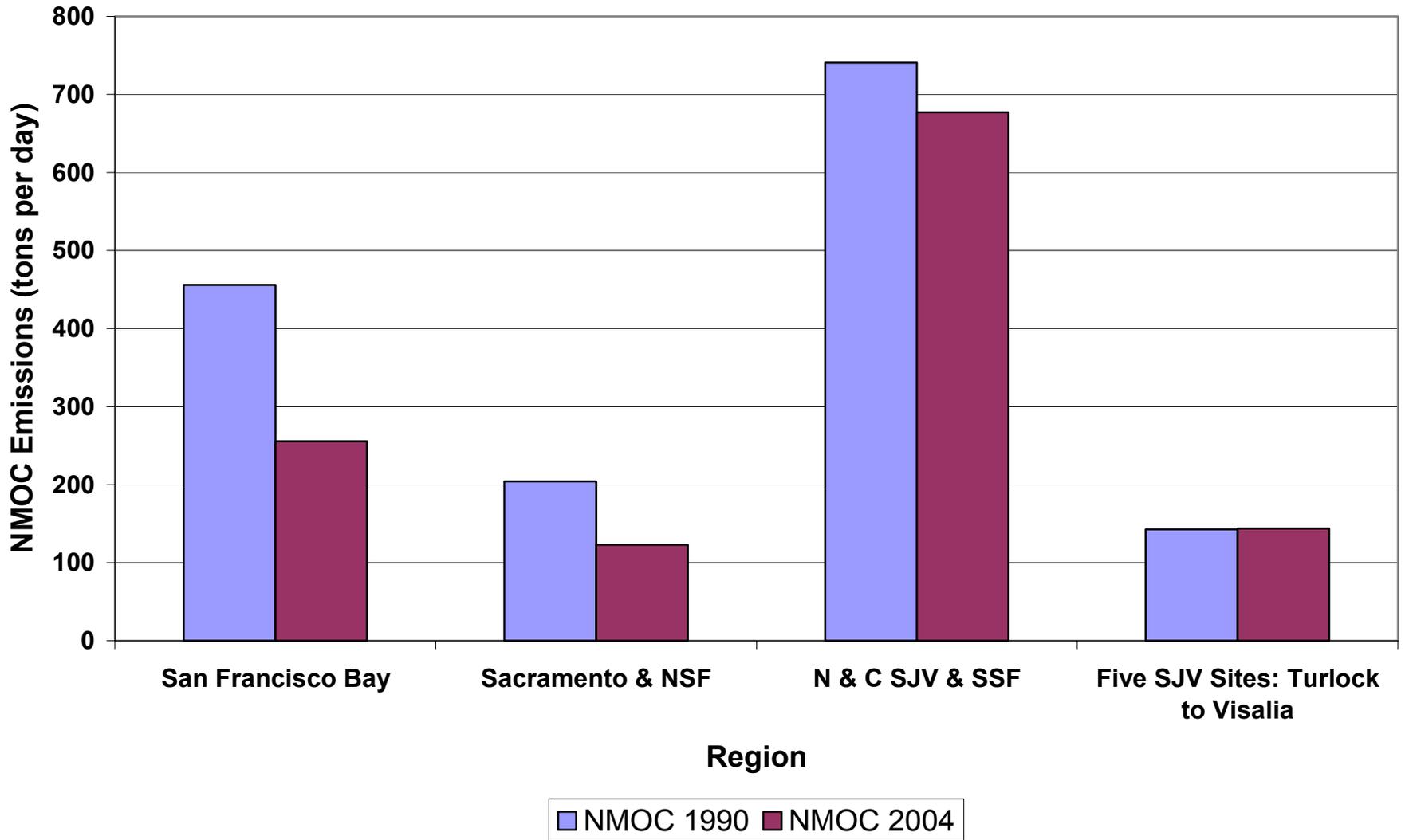
Boxes show where both NMOC and NO_x emissions in the 7x7 arrays of 4 km grid cells (28 km x 28 km) surrounding monitoring sites decreased by less than 20 percent from 1990 to 2004

Sites Where Local NMOC and NOx Emissions Decreased by Less Than 20 Percent From 1990 to 2004



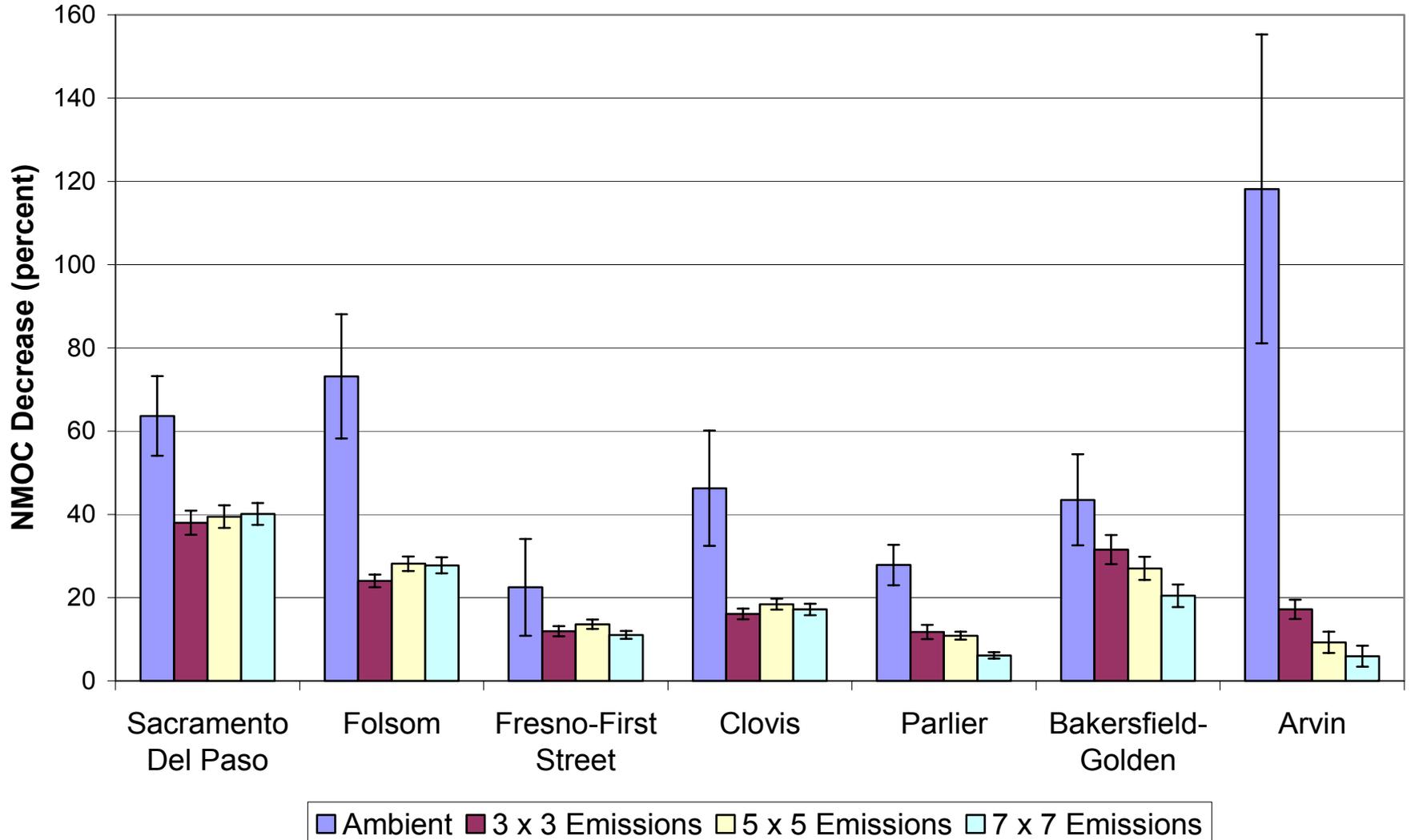
“Local” means in the 7x7 array of 4 km grid cells

Regional and Local Ozone-Season NMOC Emissions in 1990 and 2004



If local NMOC emissions unchanged, how much will ozone change? 10

NMOC Decrease (1994-2004)



Caveat: ambient NMOC decreases > inventory decreases

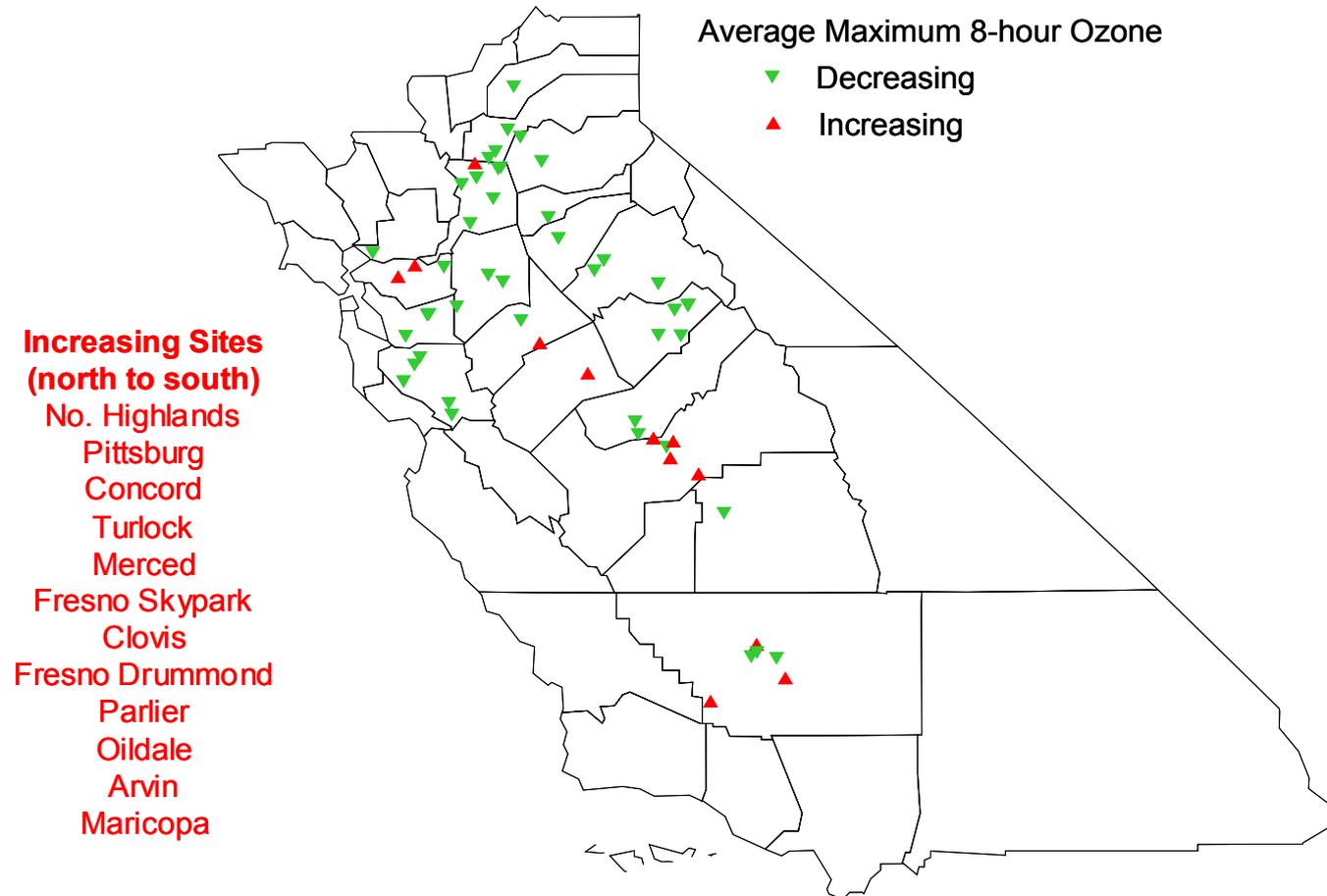
Hypothesis 3

Background* ozone concentrations increased.

* Background ozone means ozone formed outside the North American boundary layer.

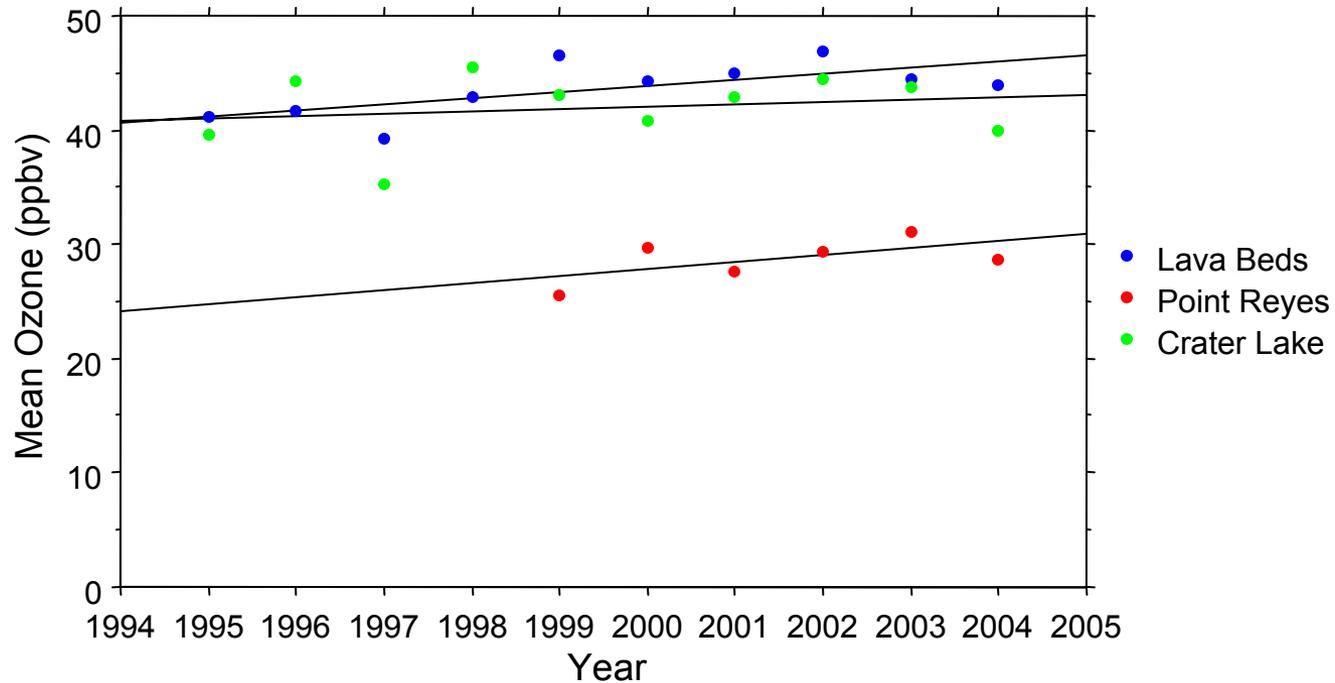
Implausible

Mean peak 8-hour ozone in 1990-94 and in 2000-04



Ozone increases occurred at scattered sites in separate subregions

National Park Service Passive Ozone Monitoring



Lava Beds = $-1011.904 + .528 * \text{Year}$; $R^2 = .438$
Point Reyes = $-1209.936 + .619 * \text{Year}$; $R^2 = .368$
Crater Lake = $-395.536 + .219 * \text{Year}$; $R^2 = .046$

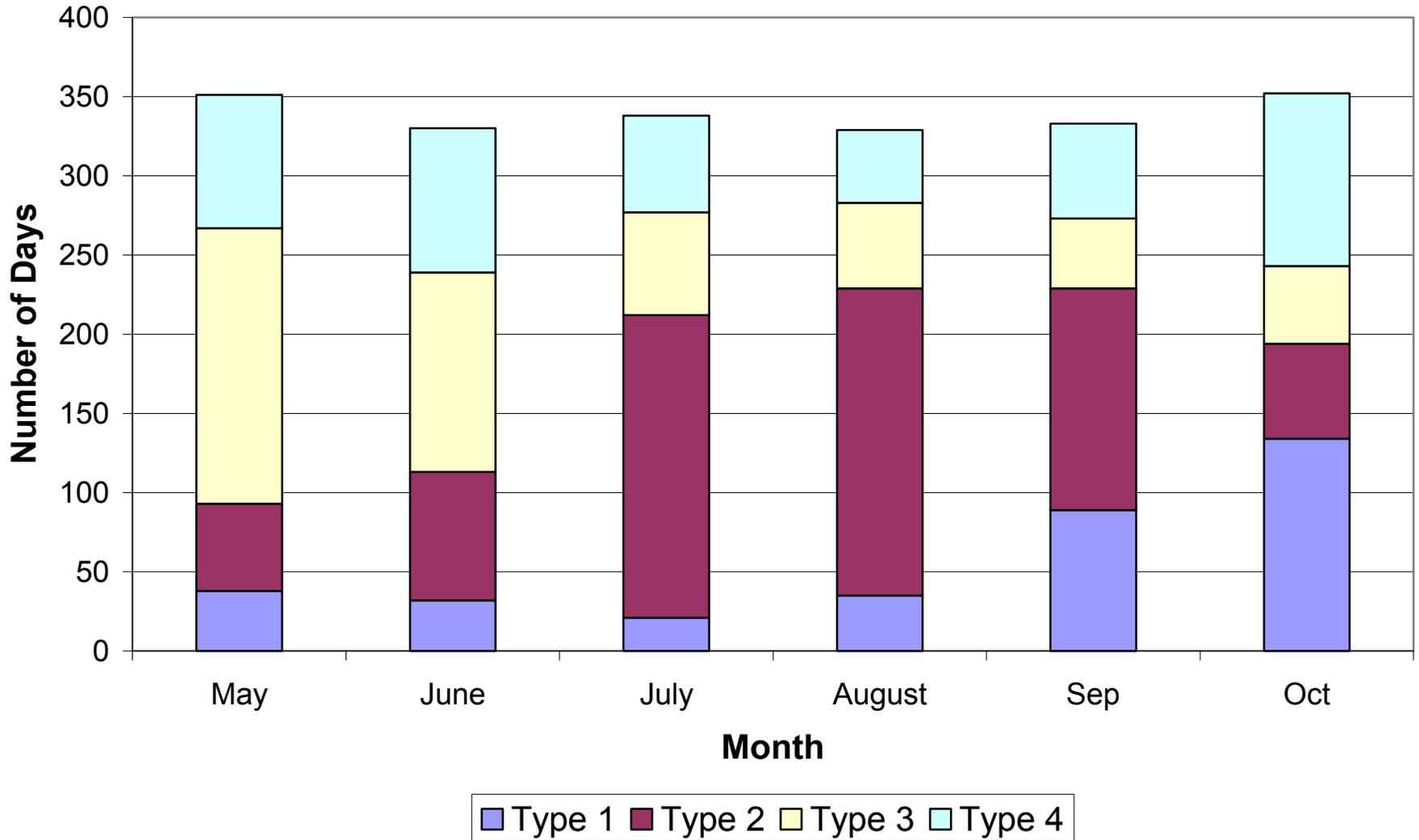
Possible upward trend in background ozone of ~0.5 ppbv per year
- if true, may make overall progress more difficult

Hypothesis 4

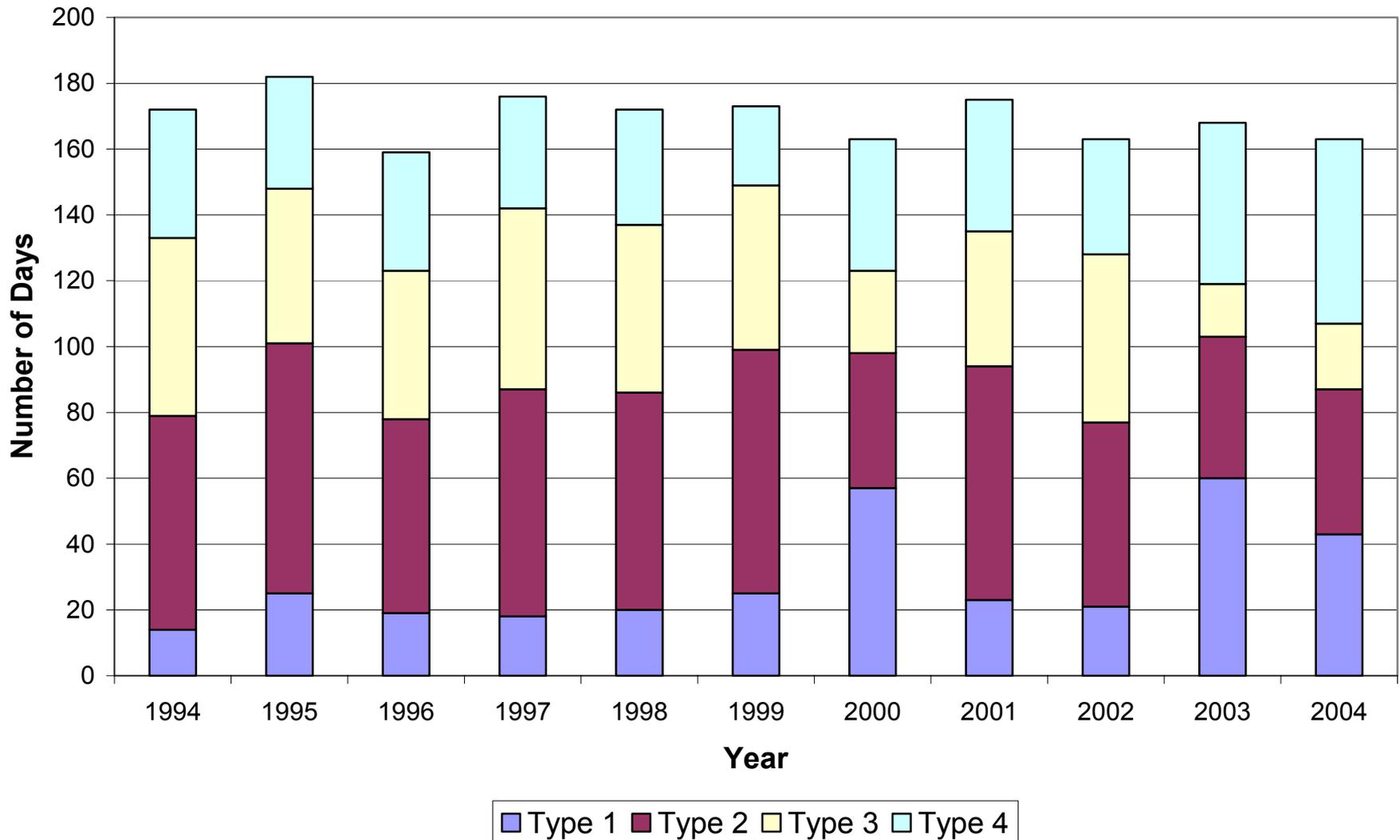
Ozone trends were masked by changes in meteorological conditions.

Implausible

Number of Days in Each Meteorological Type, By Month

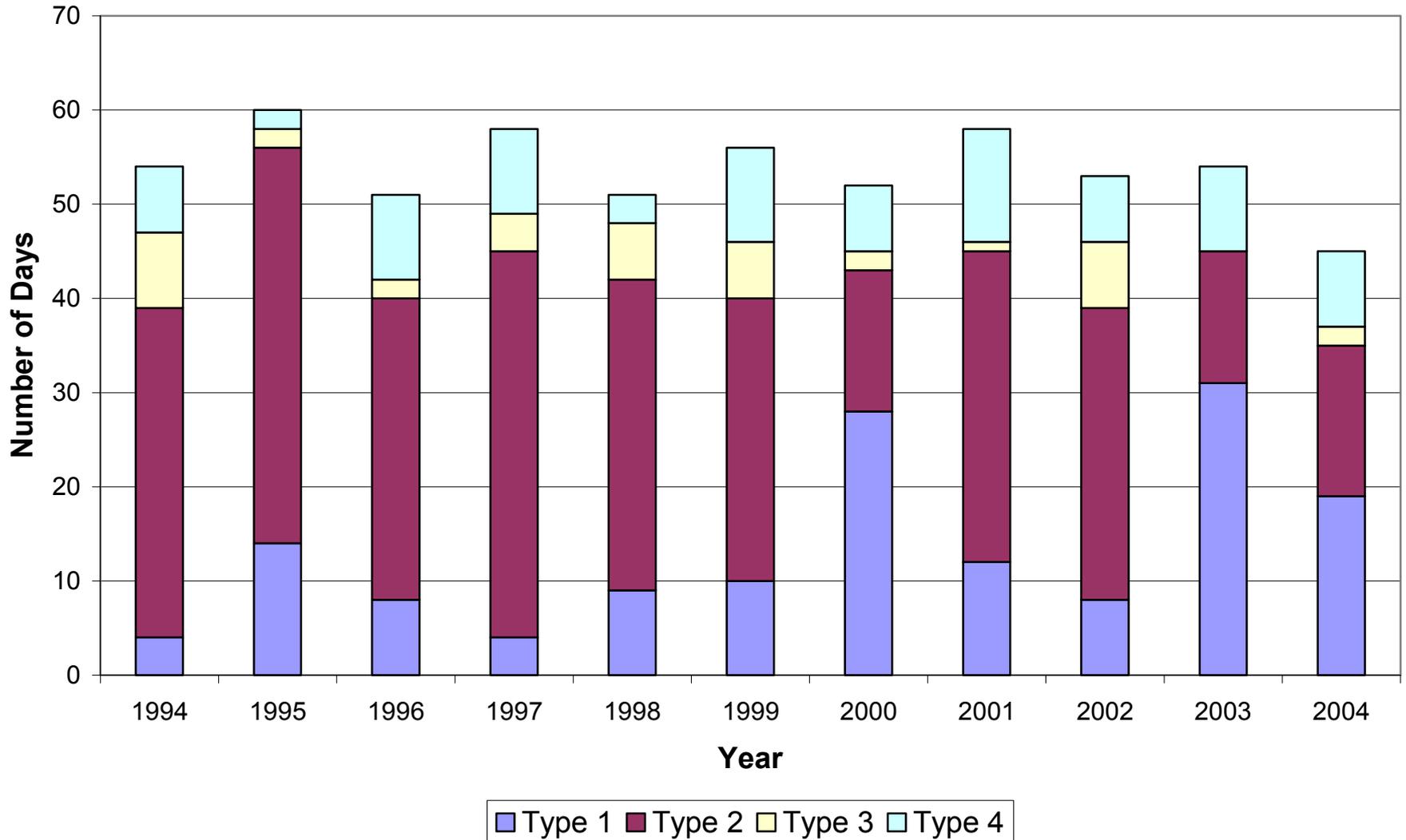


Frequency of Days In Each Meteorological Type (May - October)



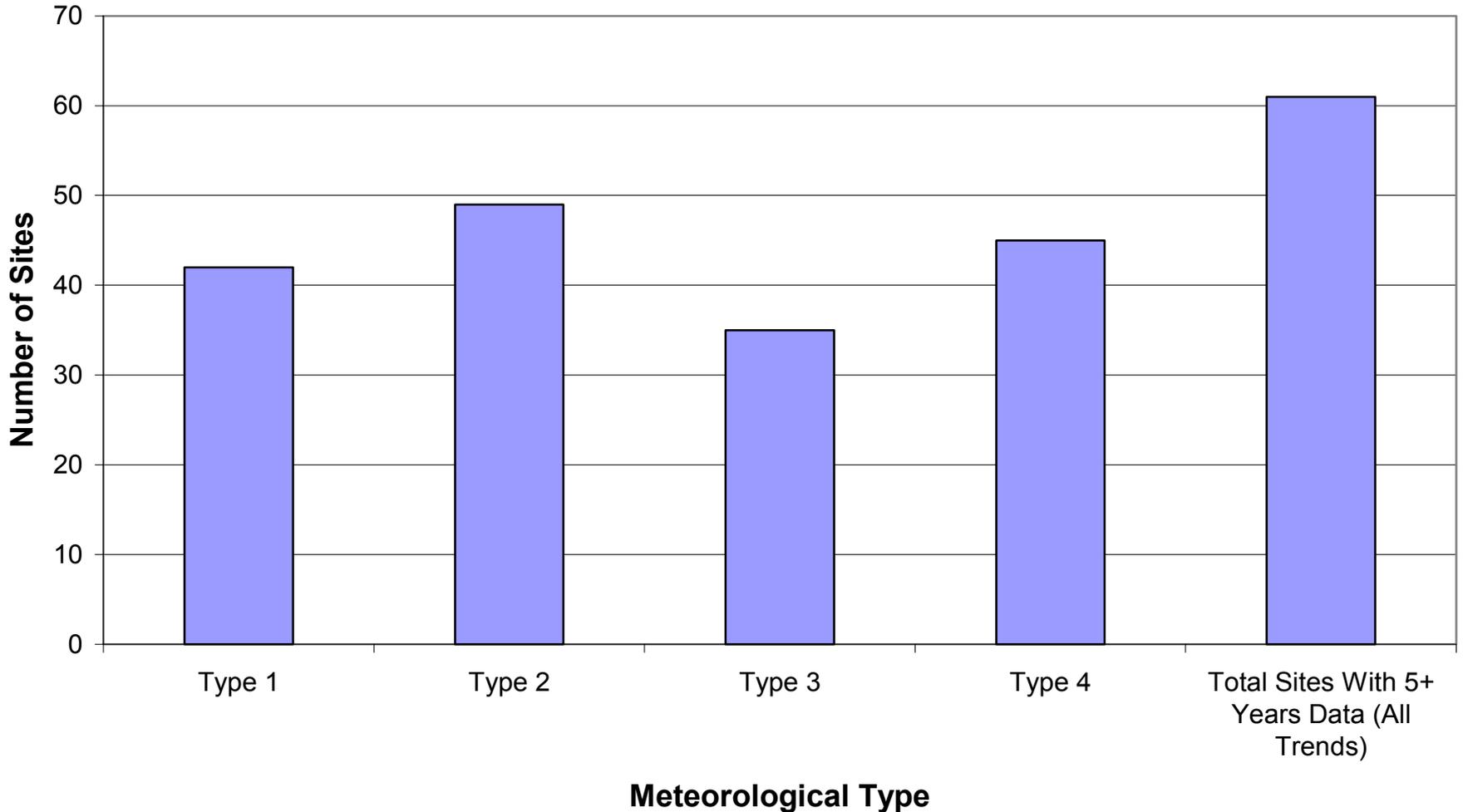
Year-to-year variations occurred in frequency of met types

Central San Joaquin High-Ozone Days By Meteorological Type



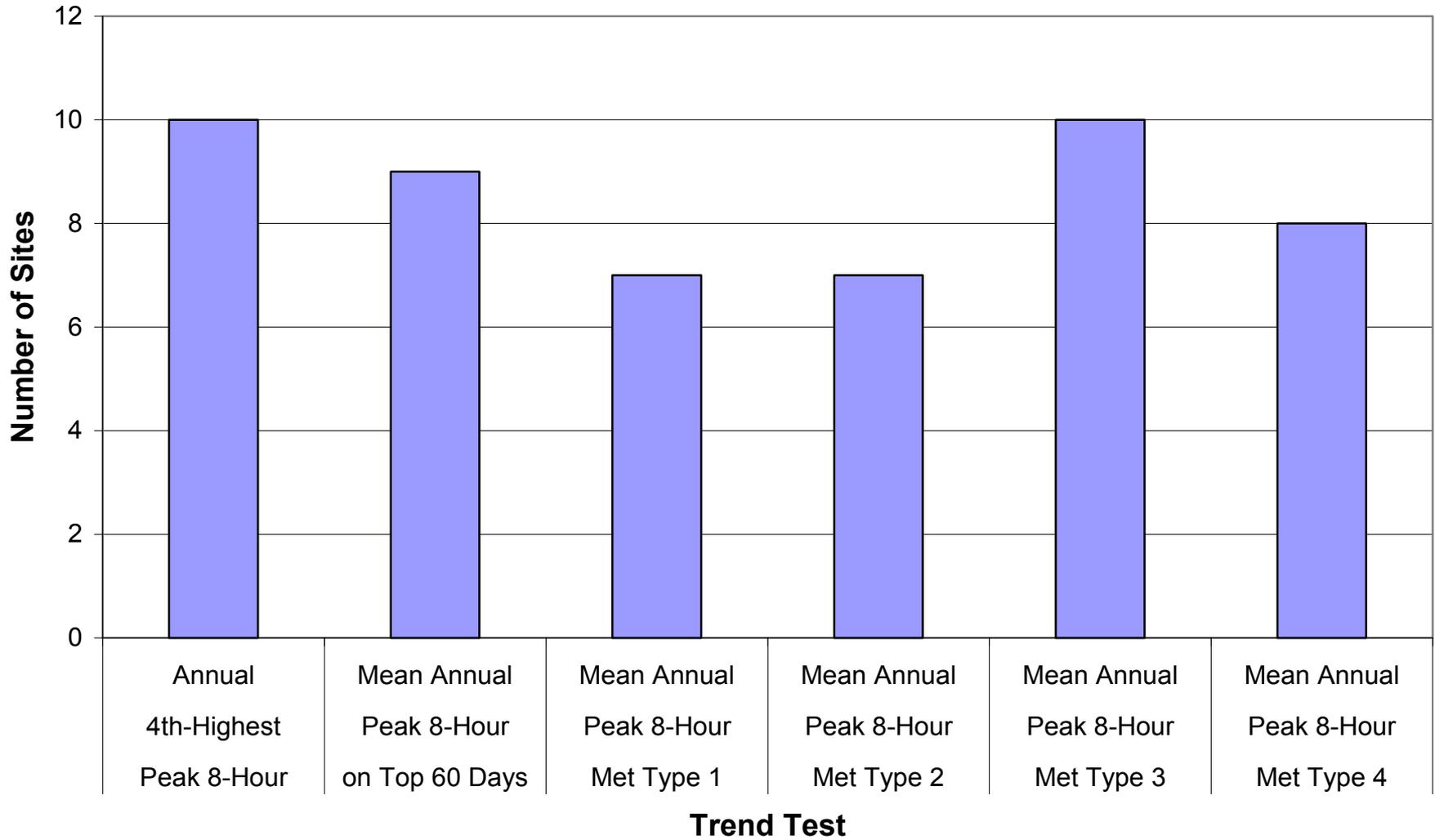
.... And the distributions of high-ozone days varied

Number of Sites With Downward Ozone Trends, 1994-2004, by Meteorological Type



.... But downward ozone trends did not depend upon met type

Number of Sites With Upward Trends



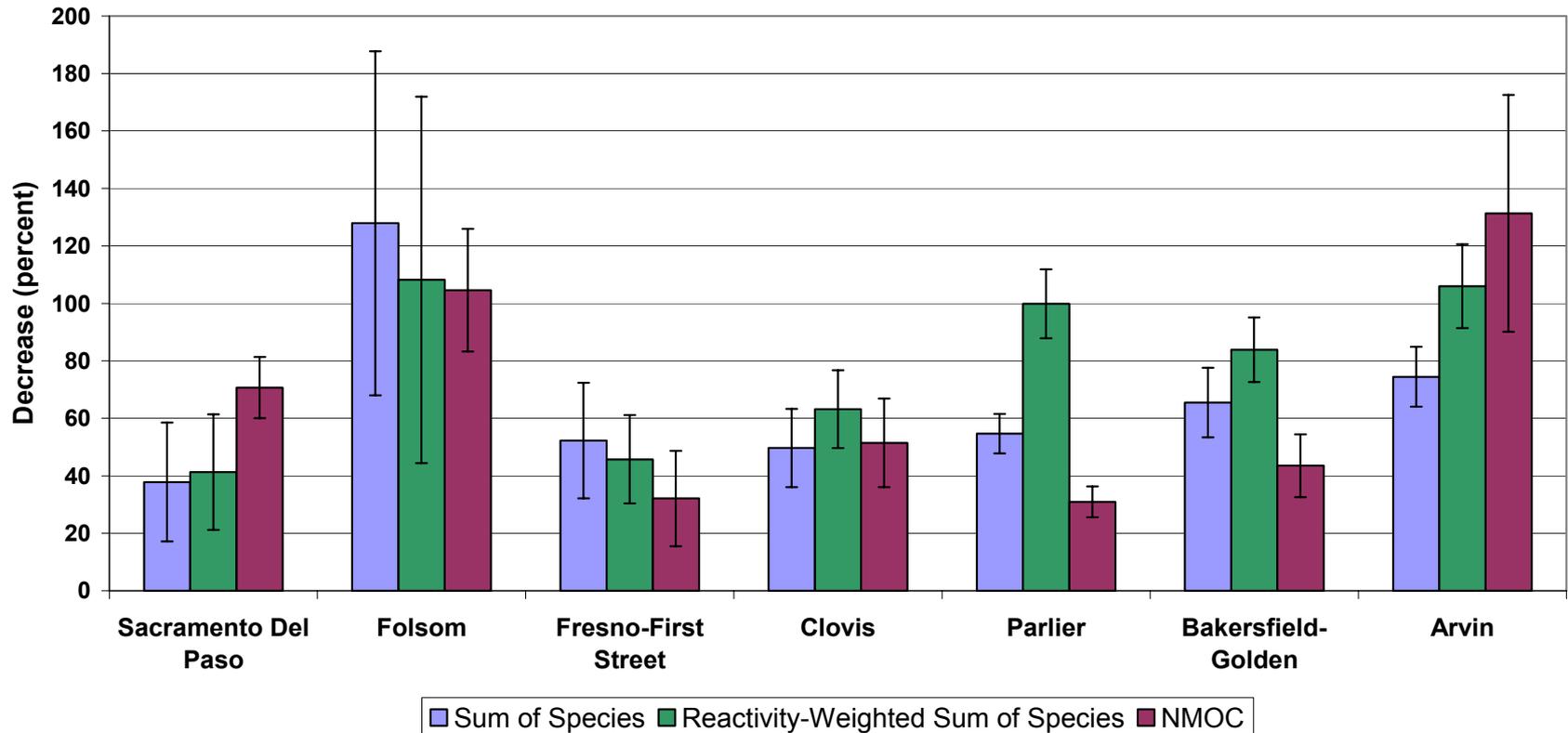
.... And upward ozone trends were consistent across met types

Hypothesis 5

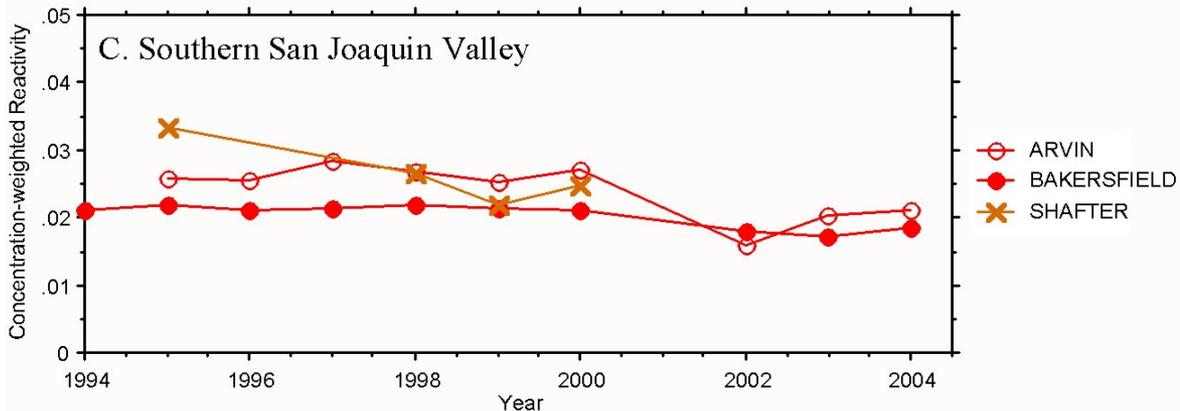
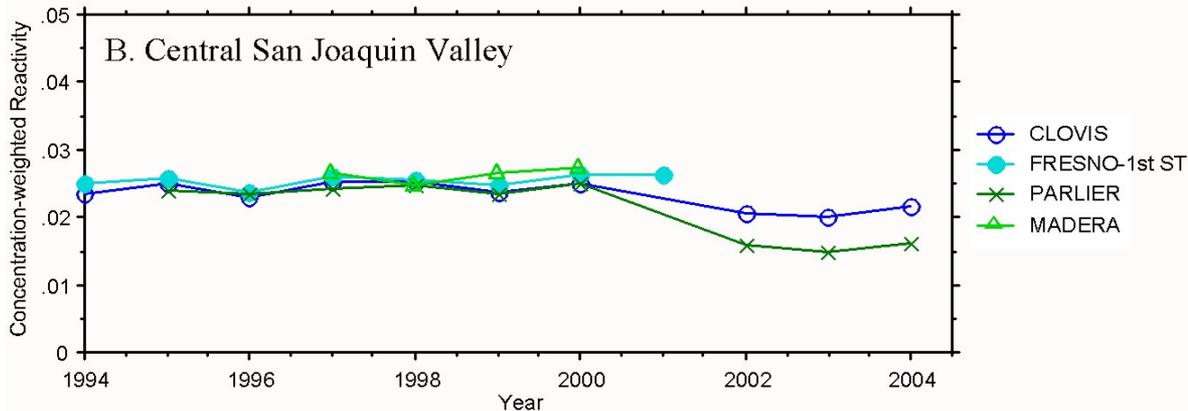
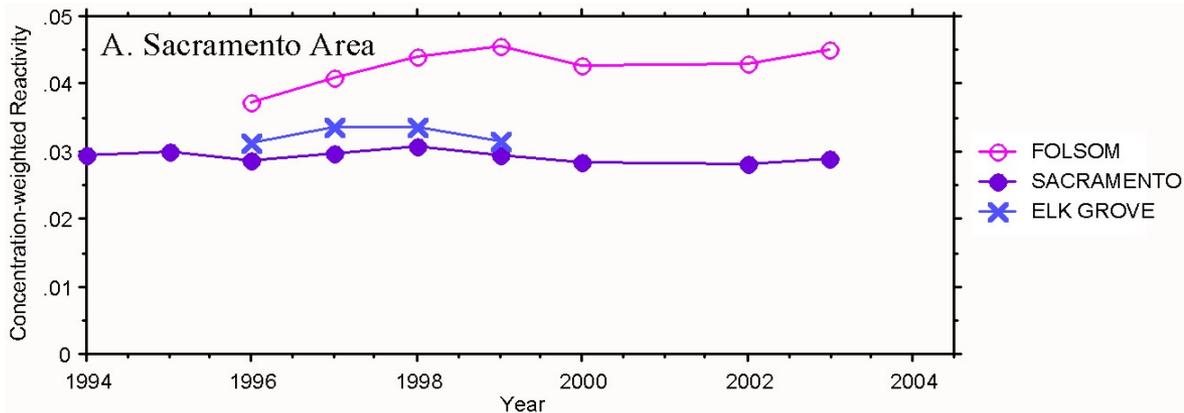
Decreases in VOC emissions and reactivity slowed the rate of ozone formation but did not reduce the ultimate amount of ozone formed. Therefore, reductions of peak ozone occurred in urban cores and at near-downwind sites, but not at far downwind locations.

Plausible

Sum of Species, Reactivity-Weighted Sum of Species, and Total NMOC Decreases (1994-2004)



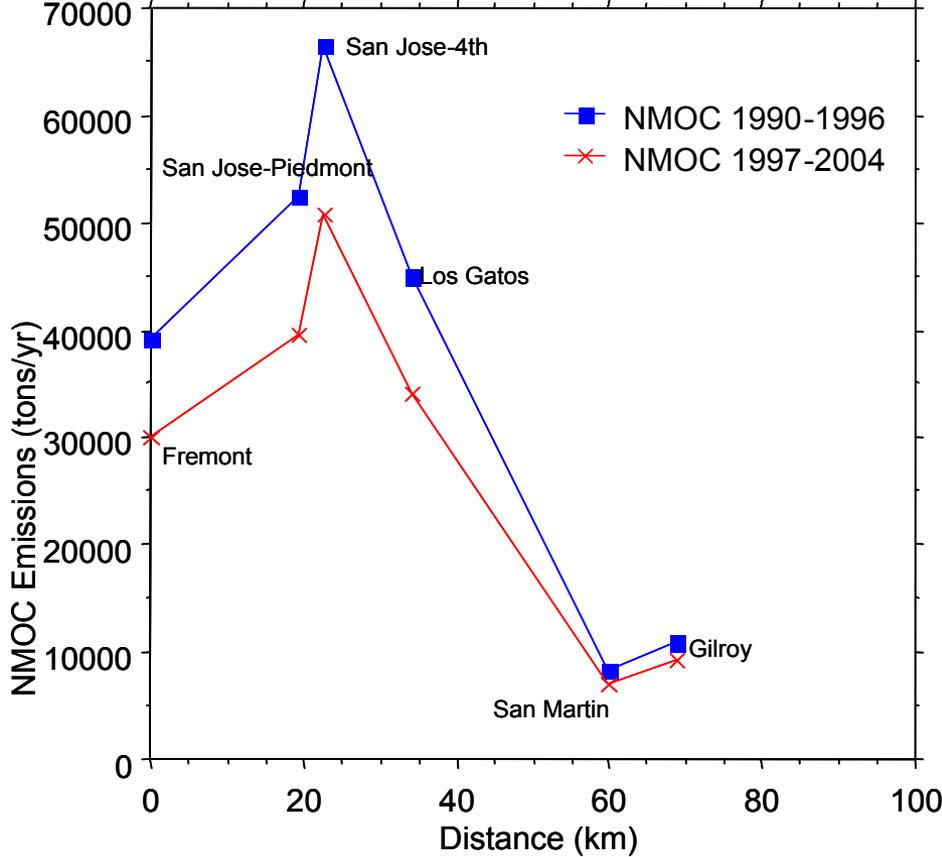
Measurements show ~30 – 120% decreases in ambient NMOC concentrations



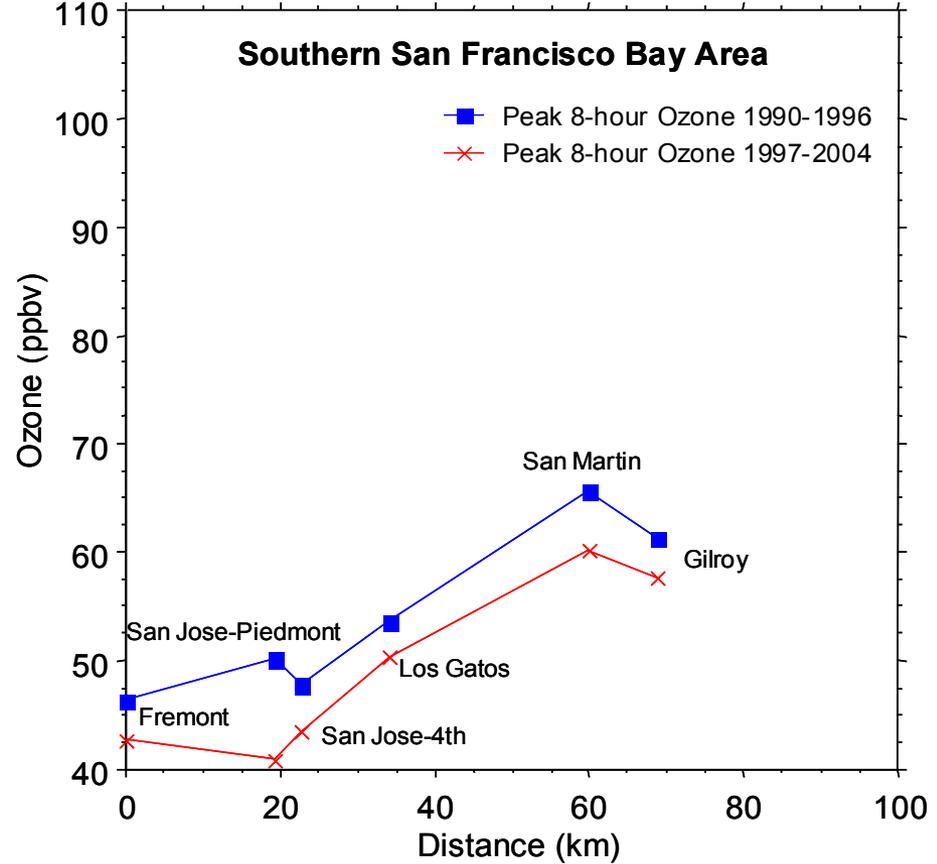
Average reactivity* shows some declines (but mass decrease is larger and more important)

* k_{OH} weighted by mean annual concentrations (units are $\text{ppbC}^{-1} \text{sec}^{-1}$)

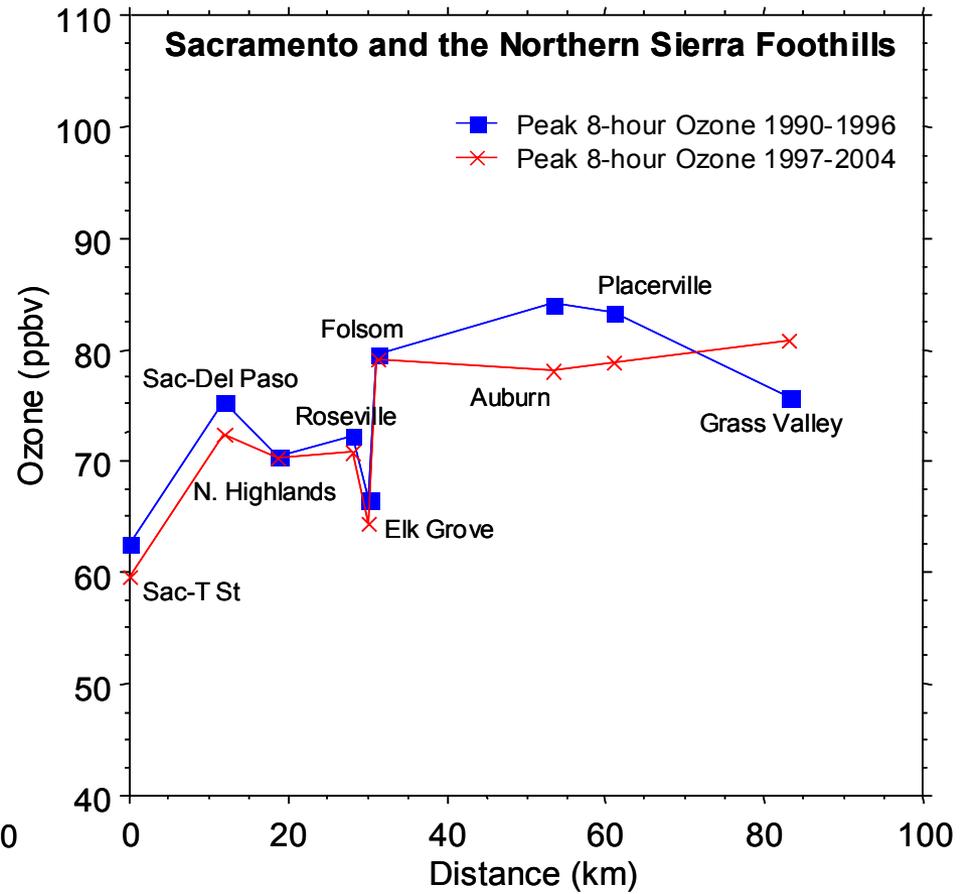
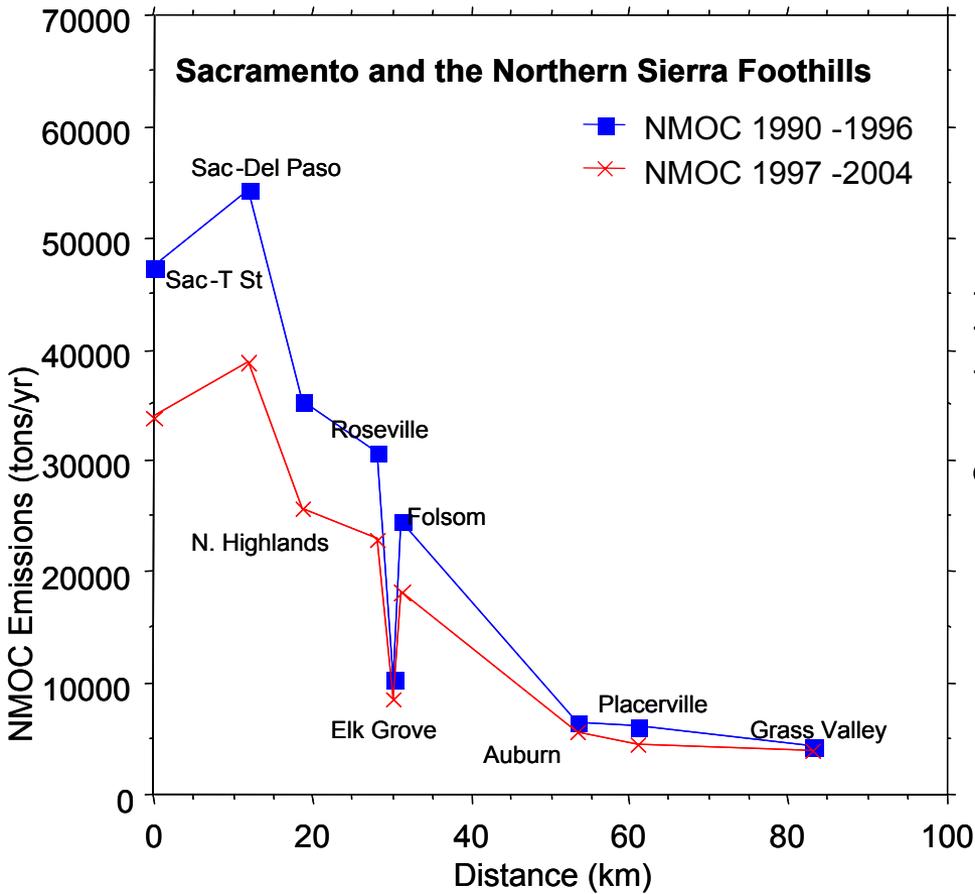
Southern San Francisco Bay Area



Southern San Francisco Bay Area



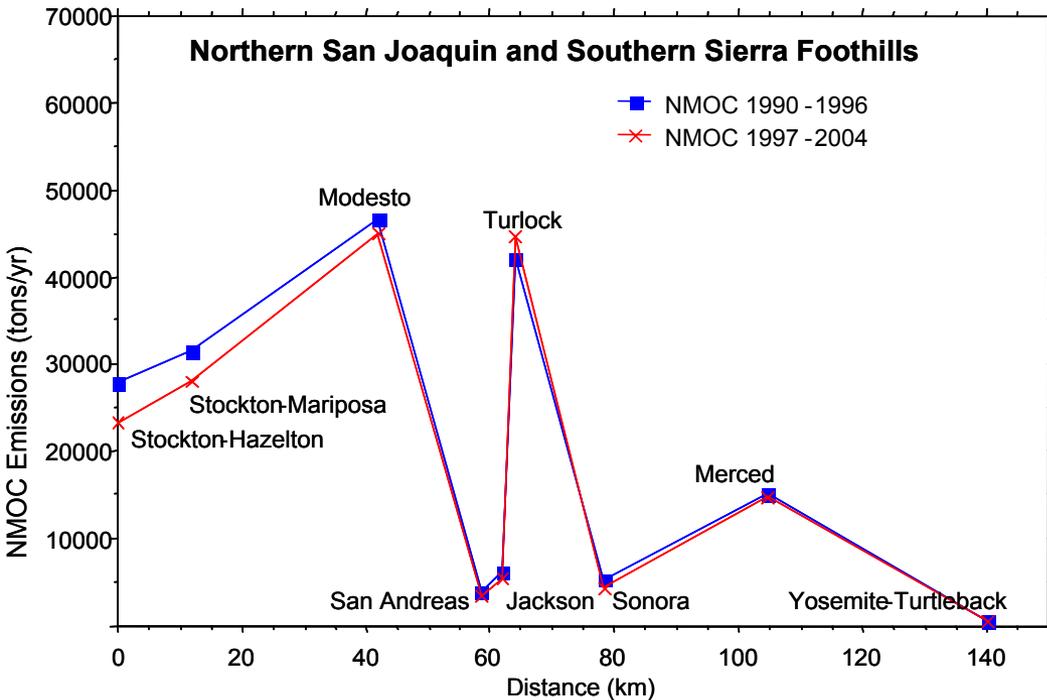
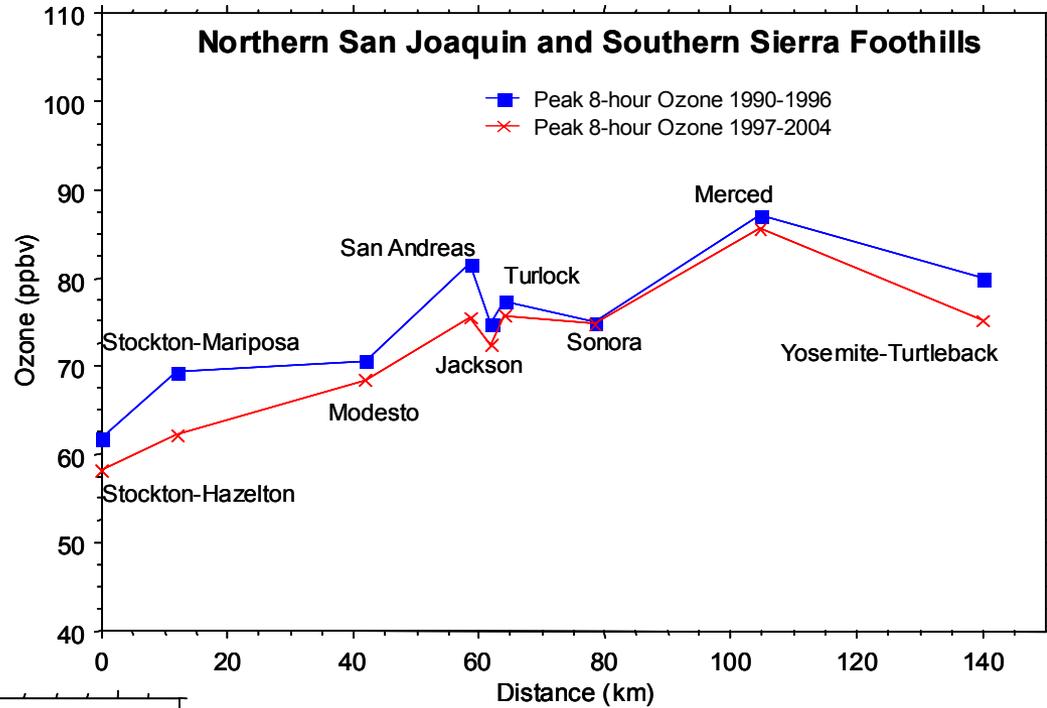
In S Bay area, ozone declined at both urban and downwind sites



In Sacramento, ozone declines varied among sites.

Ozone →

NMOC Emissions ↓



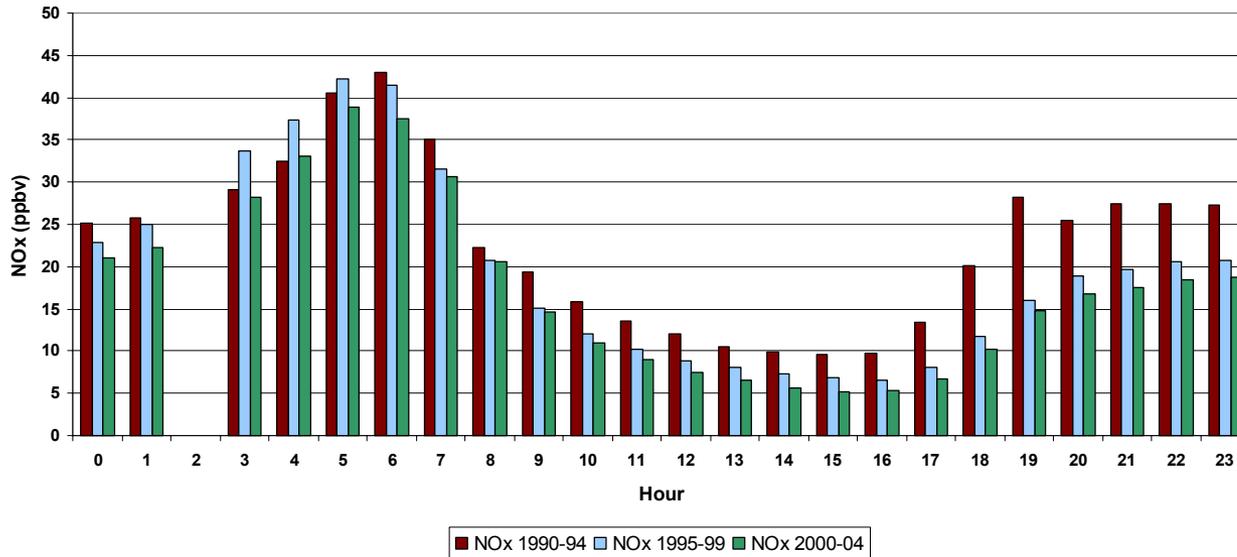
NMOC emissions did not decline in some parts of the N SJV and SSF. This makes it difficult to assess the argument that NMOC-control was not effective at the far downwind sites.

Hypothesis 6

Decreases in NO_x emissions and concentrations resulted in less titration of ozone. Therefore, ozone concentrations increased in NO_x-rich areas, but peak ozone declined in NO_x-limited areas.

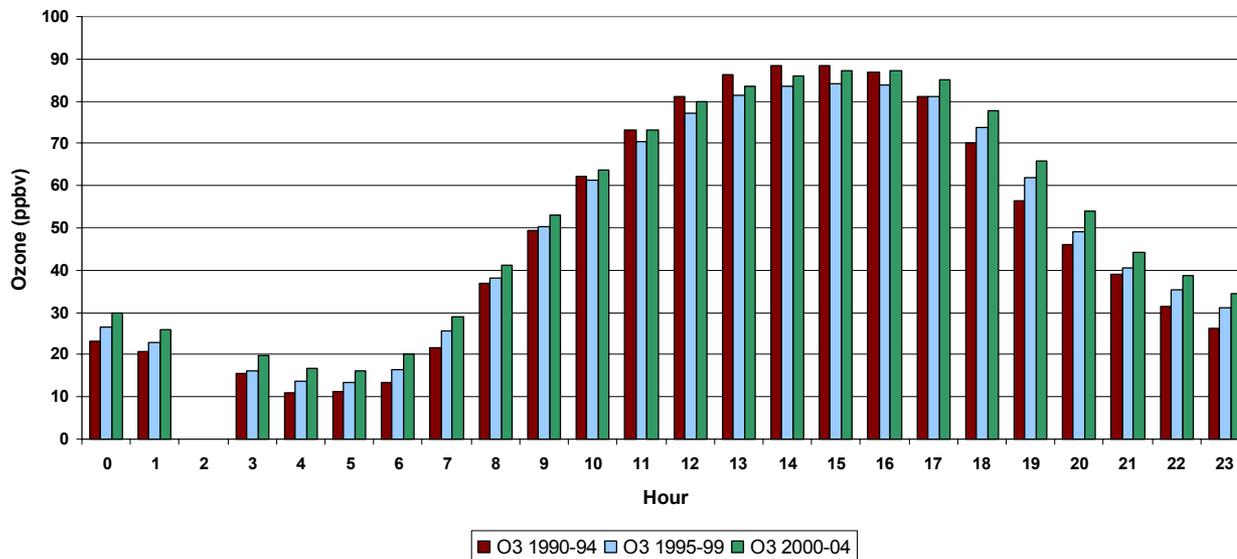
Plausible

Mean Hourly NOx at Merced



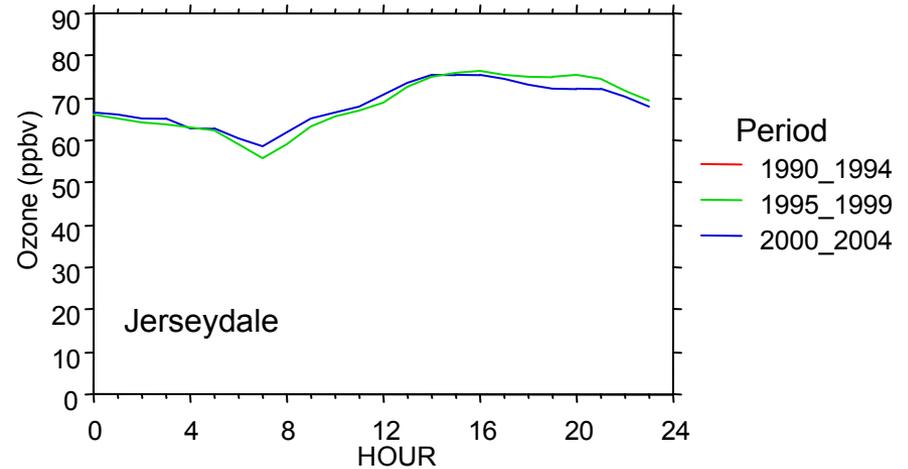
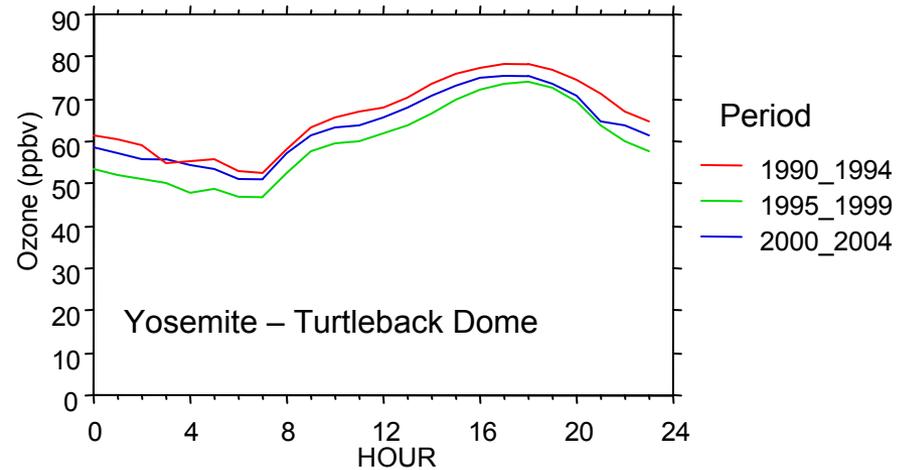
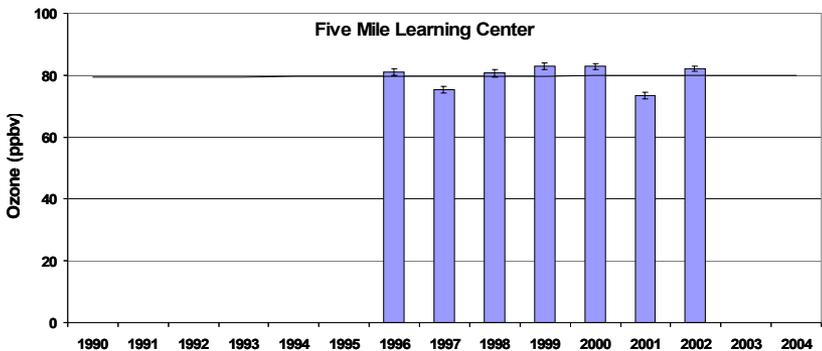
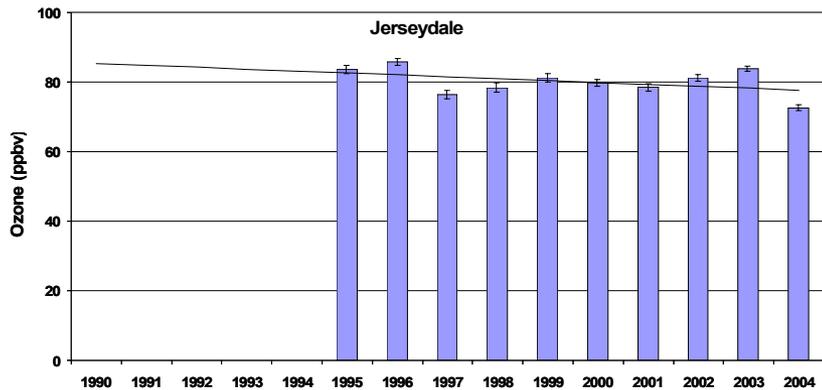
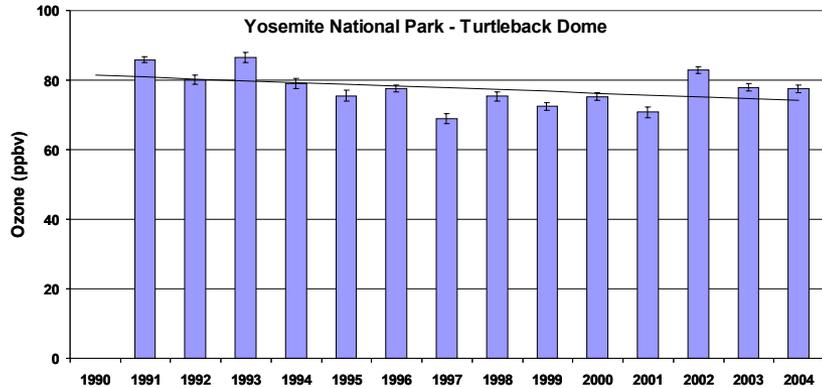
Ozone increases at night can be linked to lower NOx

Mean Hourly Ozone at Merced



... But effects on peak ozone are difficult to interpret

Mean Peak 8-Hour Ozone



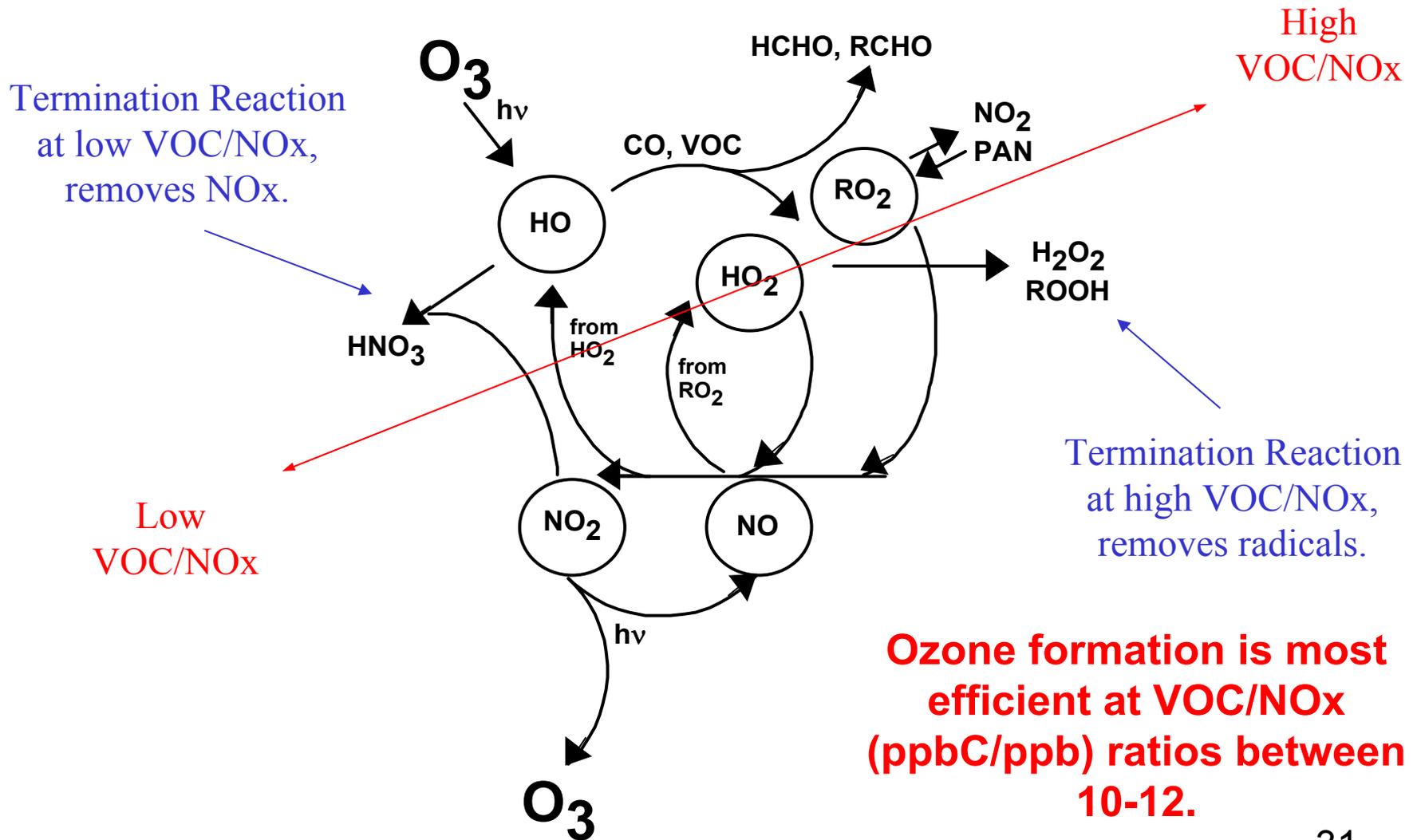
Mid-elevation Sierra Nevada sites show peak ozone improvements compared to early 1990s (but less change since the mid-1990s)

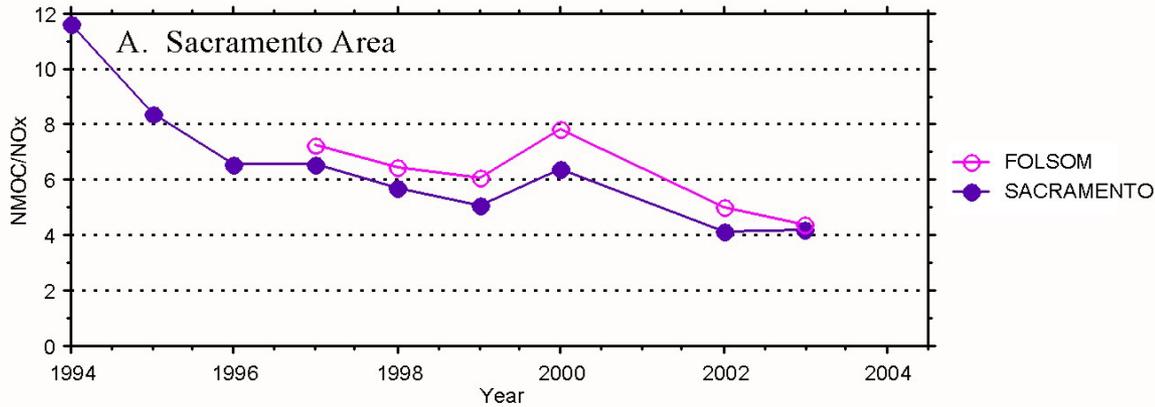
Hypothesis 7

Greater or lesser decreases of VOC emissions compared to NO_x emissions resulted in changes in VOC/NO_x ratios, which led to changes in the efficiency of ozone production per unit of precursor mass.

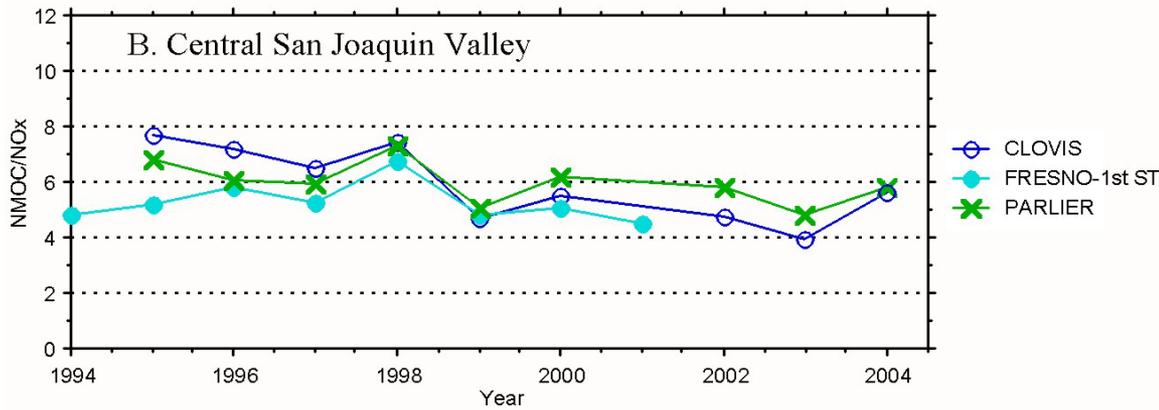
Plausible

Significance of VOC/NO_x Ratios in Ozone Formation

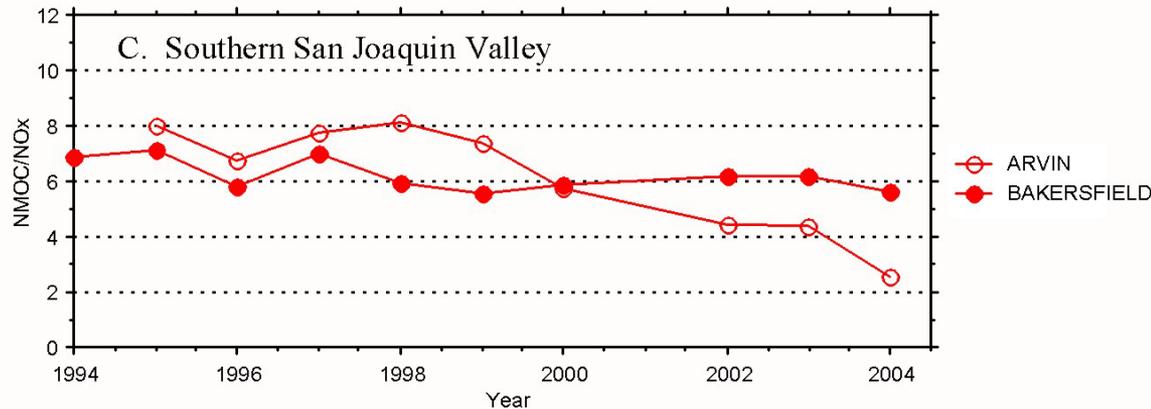




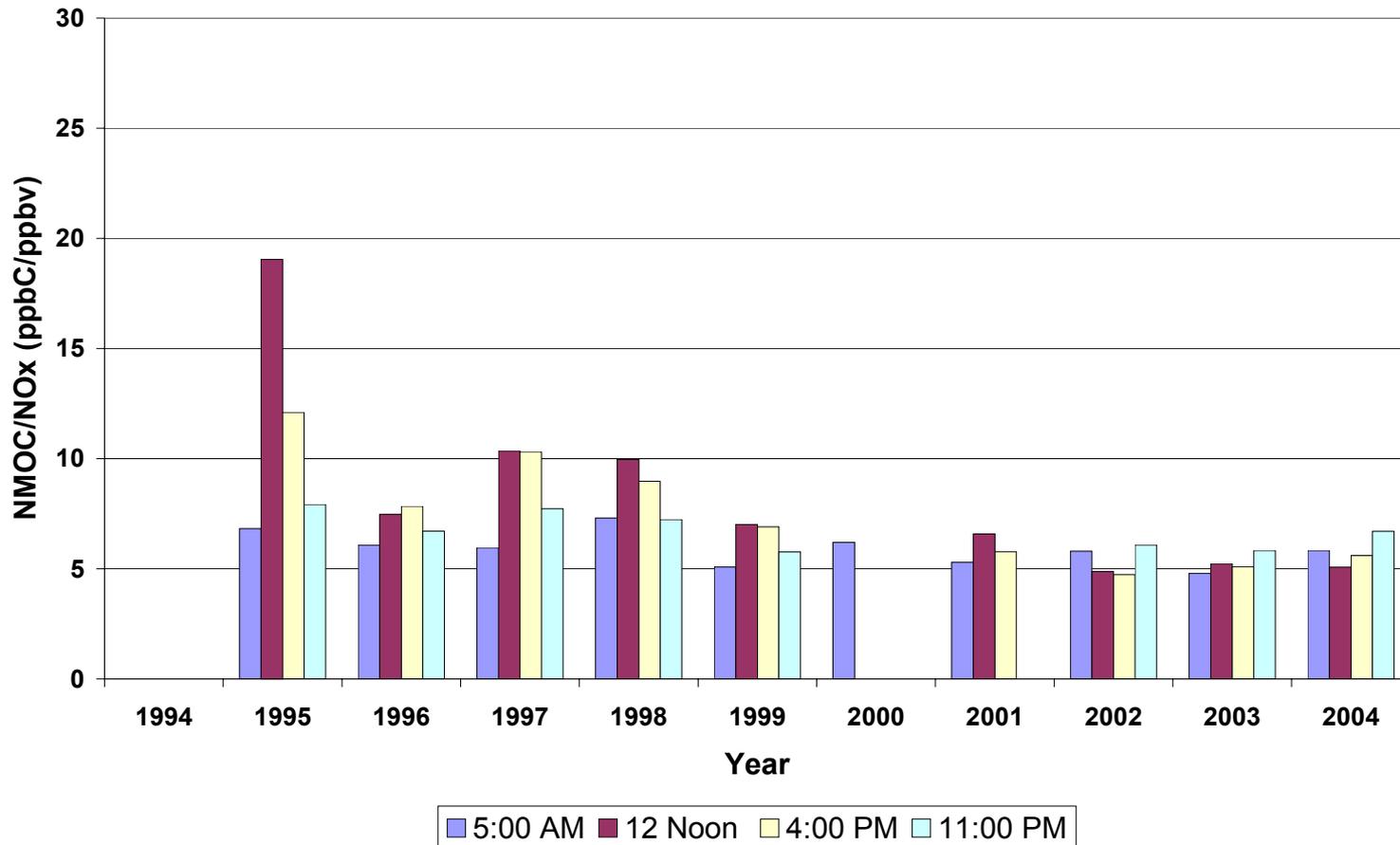
Morning (5 – 8 a.m.)
 NMOC/NOx ratios
 declined over time



(Emission ratios
 average about 30%
 lower than ambient
 ratios)



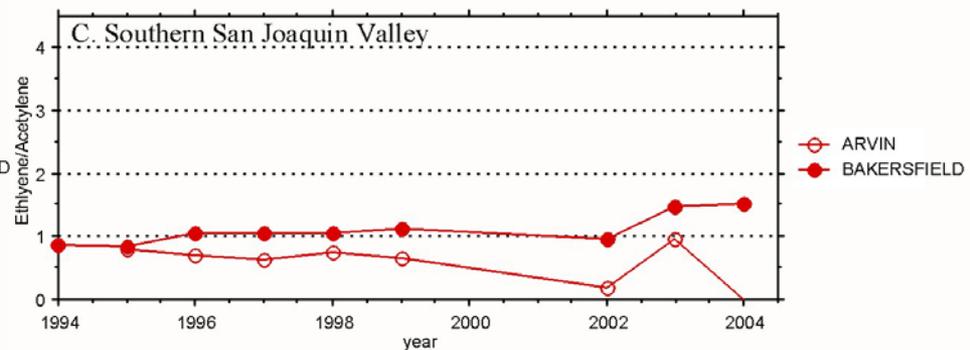
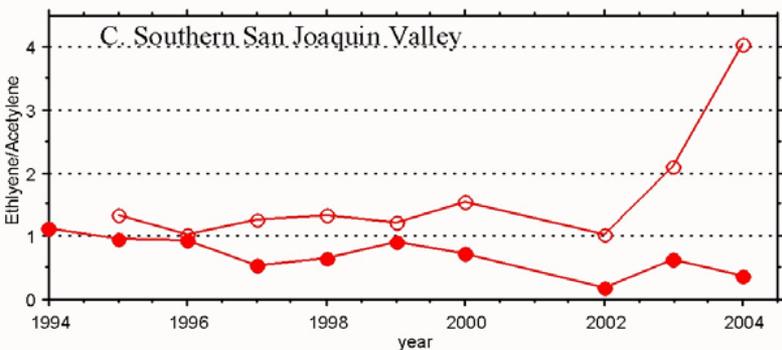
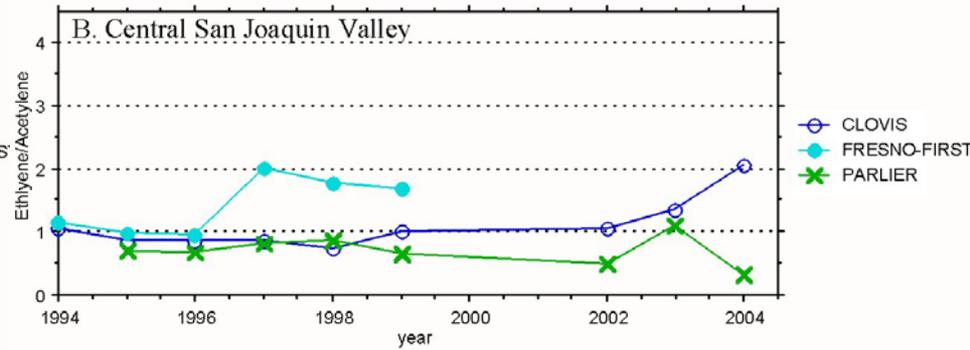
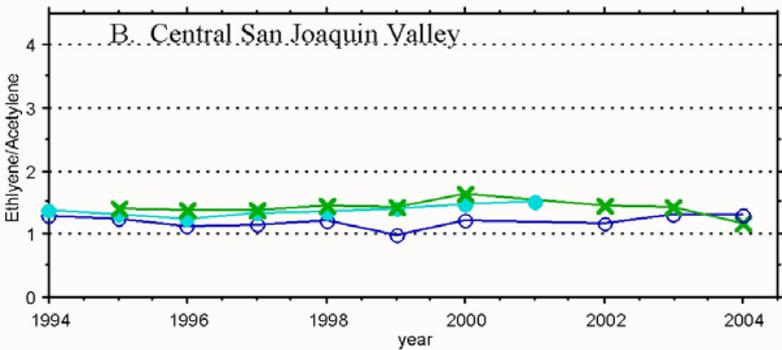
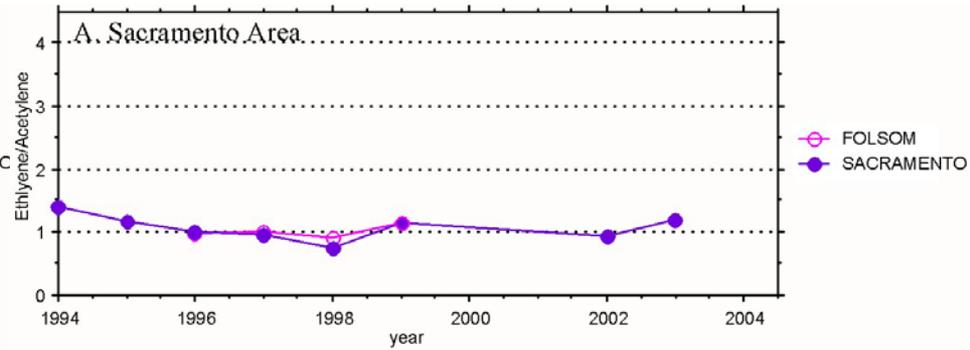
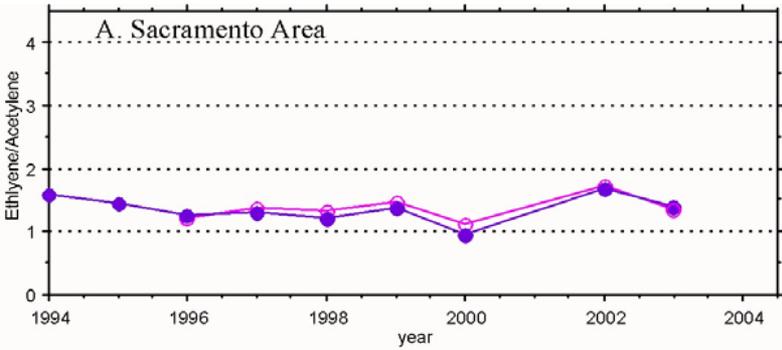
NMOC/NOx - Parlier



Differences between morning and afternoon NMOC/NOx ratios declined

5 – 8 a.m

12 Noon – 2 p.m.



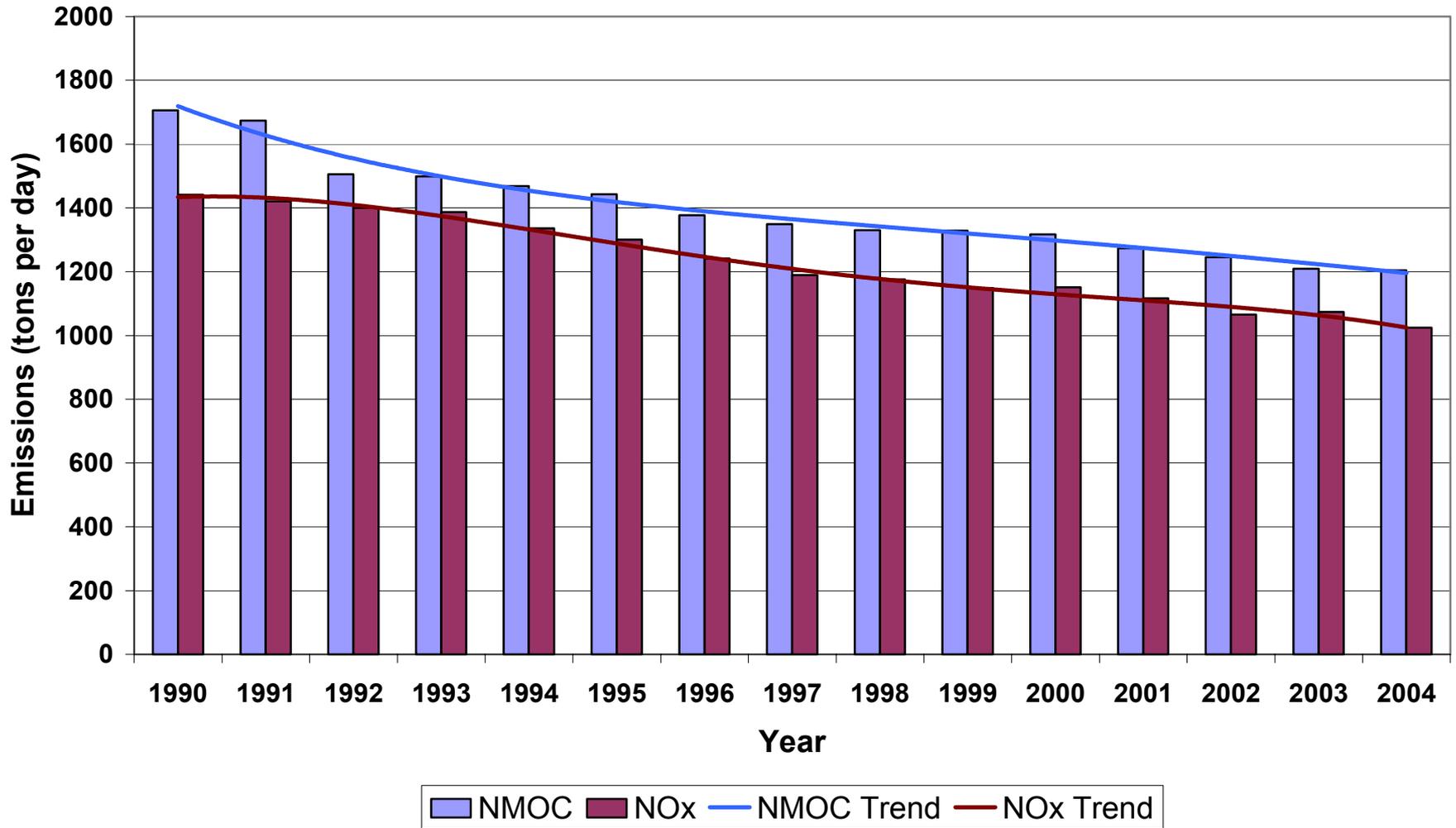
Other ratios suggest changes in air mass ages or aging

Hypothesis 8

The validity of hypotheses 5, 6, and 7 varied during the trend period, with hypothesis 5 (VOC reductions) having greater relevance early and hypotheses 6 (NO_x reductions) and 7 (VOC/NO_x ratios) increasing in importance toward the end.

Plausible

Ozone-Season Emission Trends Nineteen Counties in CCOS Domain



Somewhat larger NMOC declines from early to mid '90s

Plausible Hypotheses

H2: Emissions did not decline enough in some areas to affect ozone concentrations

- Applicable in portions of N SJV & C SJV
- NMOC emissions in affected area are ~20 percent of N & C SJV total

Plausible Hypotheses (continued)

H5: VOC emission reductions were effective in urban centers and near-downwind areas but not far downwind

- Ambient NMOC reductions are evident, but spatial patterns of ozone more complex than hypothesis
- Difficult to infer causal link to ozone

Plausible Hypotheses (continued)

H6: NO_x emission reductions increased ozone in NO_x-rich areas but reduced peak ozone at NO_x-limited sites

- Higher ozone during non-peak hours is probably related to decreased NO
- Effects of NO_x reductions on peak ozone are unclear

Plausible Hypotheses (continued)

H7: Changes in VOC/NO_x made ozone production more (or less) efficient

- Declines in NMOC/NO_x ratios occurred in measurements and the inventory
- Differences between afternoon and morning NMOC/NO_x ratios declined - may indicate that air mass ages and aging changed

Plausible Hypotheses (continued)

H8: H5, H6, and H7 are all applicable, but differed in importance at different times

- Consistent with data but difficult to demonstrate

Preliminary Implications

- Observed ozone trends reflect emission changes and atmospheric chemistry
- Ongoing emission reductions needed – including local reductions in some areas
- NMOC emissions: some areas became more NMOC-sensitive. NMOC mass changes have probably been more important than reductions of reactivity