Analysis of Weekday/Weekend Differences in Ambient Particulate Nitrate Concentrations and Formation in Southern California

Presentation Prepared for
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Particulate nitrate derives from NOx – highly nonlinear

- Chemical transformation - dependent on VOC and NOx concentrations:

  NO to NO2 to HNO3 (daytime and nighttime reactions)

- Chemical equilibrium - favors particulate nitrate at lower temperatures, higher RH - may be limited by NH3 (if low NH3 or high sulfate) :

  NH3(g) + HNO3(g) <-> NH4NO3(p)

- Coastal environments:

  NaCl(p) + HNO3(g) -> NaNO3(p)

DATABASES

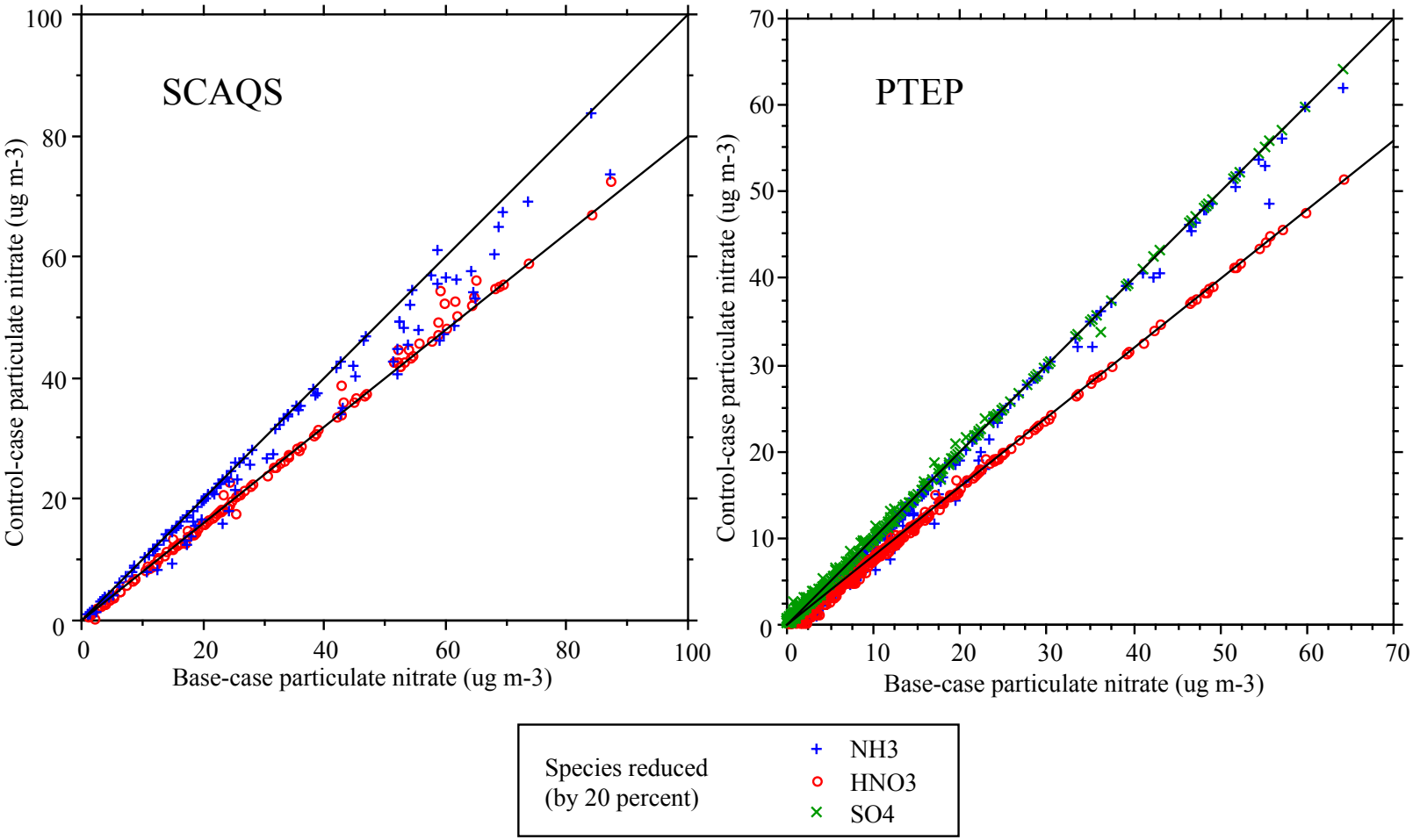
- Special studies: usually short-term but intensive measurements

  Carbon Species Methods Comparison Study (CSMCS) - 1986
  Southern California Air Quality Study (SCAQS) - 1987
  California Acid Deposition Monitoring Program (CADMP) – 1988-94
  PM10 Enhancement Program (PTEP) – 1995-96
  Southern California Ozone Study (SCOS) - 1997

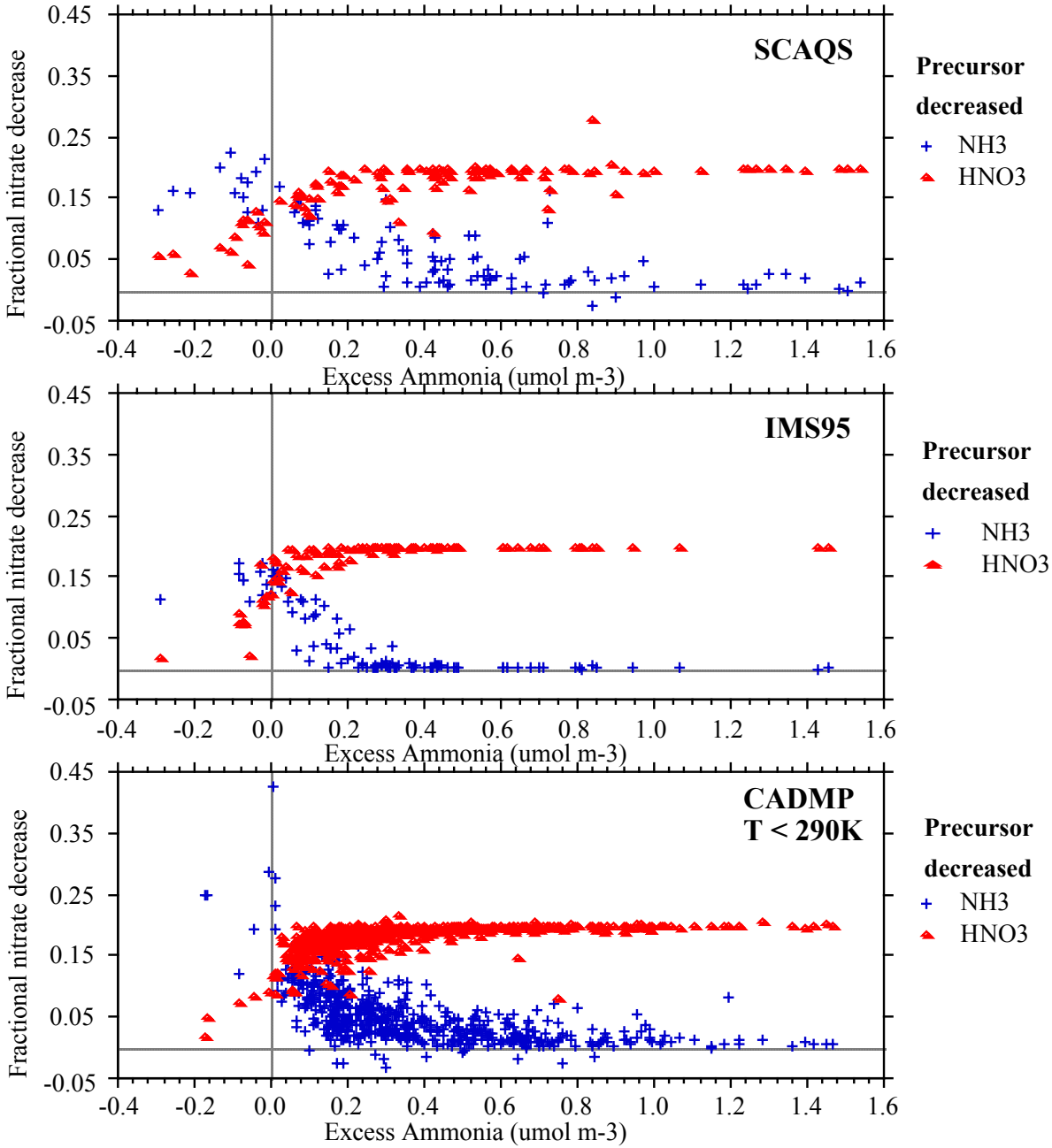
- Routine data: long term (statistical power), 1980-99 but data limitations

  CO, NOx, O3,
  TSP, TSP nitrate and sulfate,
  PM10, PM10 nitrate and sulfate
  VOC data: limited, summer, 1994 - 99

Particulate nitrate formation is not usually NH3 limited in southern California



Particulate nitrate response calculated using a thermodynamic equilibrium model (SCAPE2)



Response of particulate nitrate to reductions of NH3 or HNO3 depends upon excess ammonia

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California data show excess ammonia at most times and places

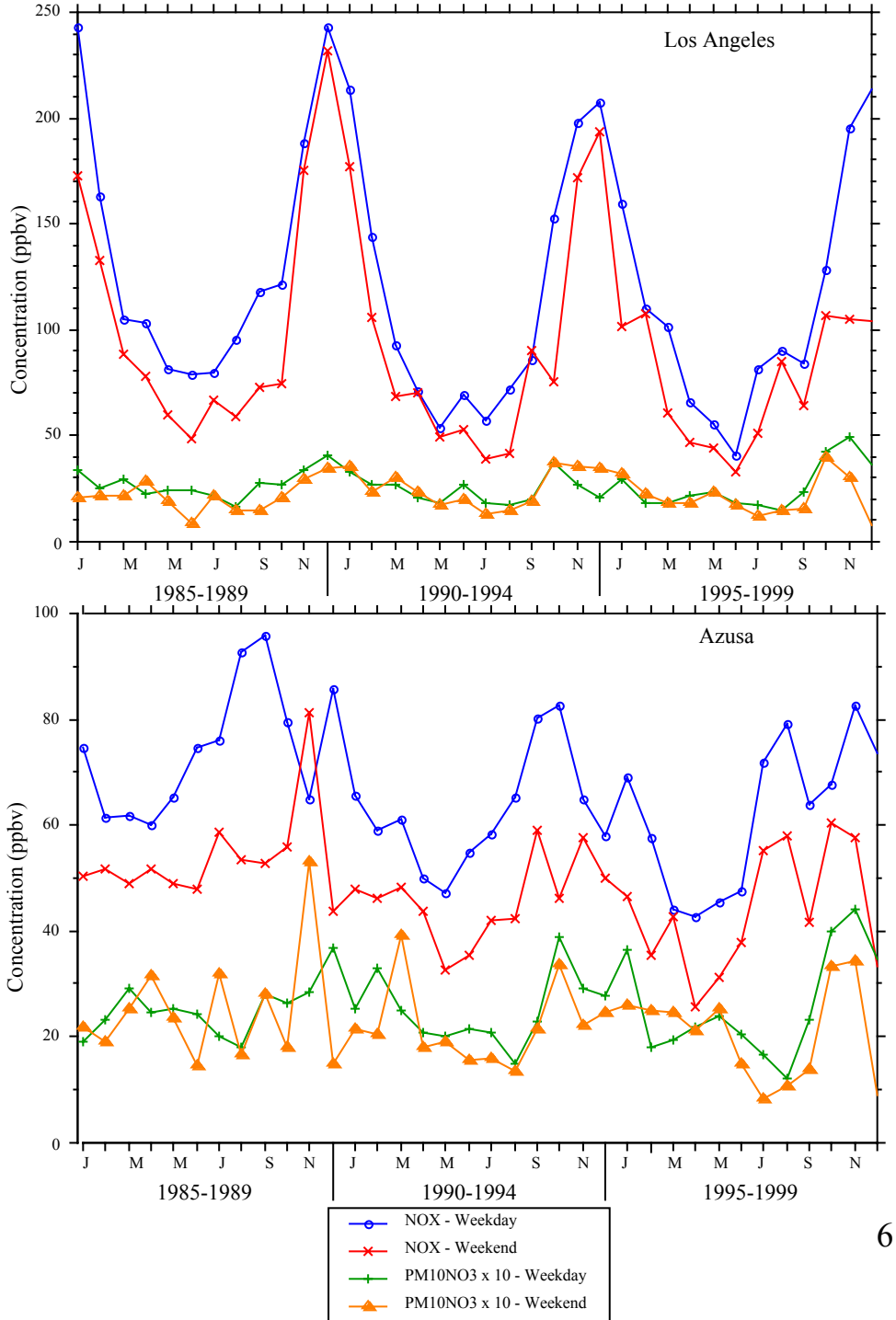
Particulate nitrate response calculated using SCAPE2

If PM nitrate formation is not NH3-limited, is another factor limiting?

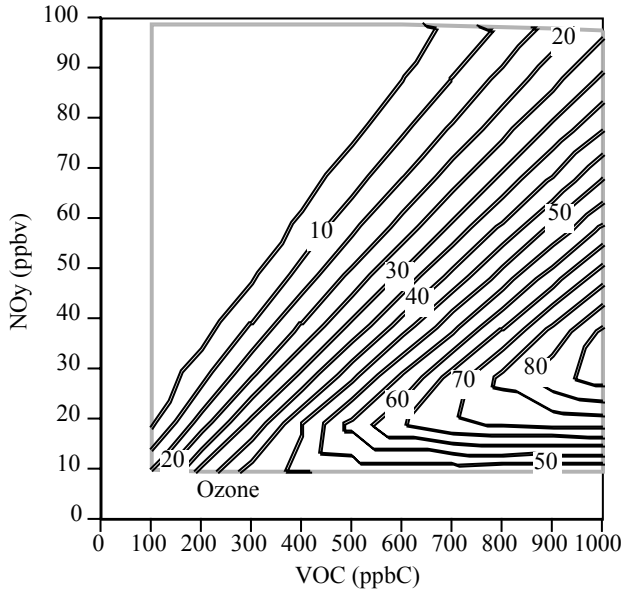
Yes – something is limiting, because PM nitrate is a small fraction of NOx

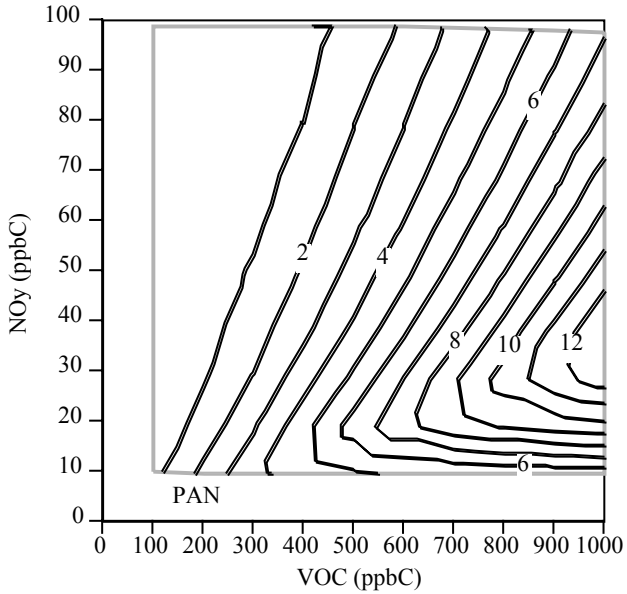
NOx reservoir is large

Note: PM nitrate scaled by 10X in plots

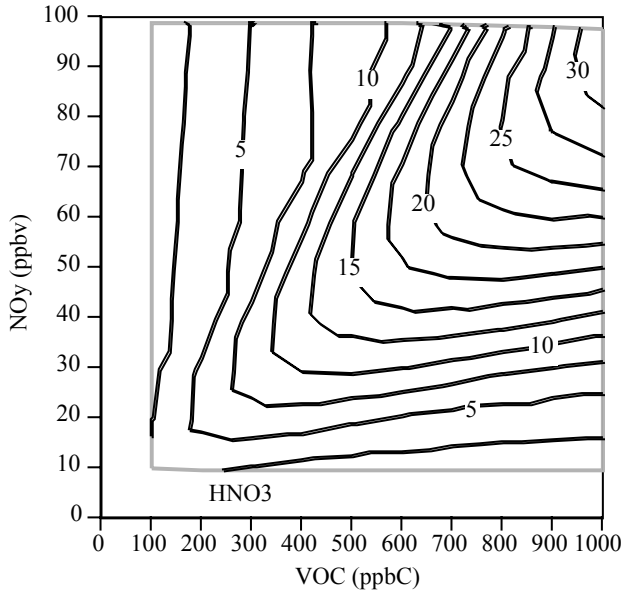


Gas-phase box-model simulations: 24-hour isopleths – ridgeline separates VOC and NOx sensitive regions



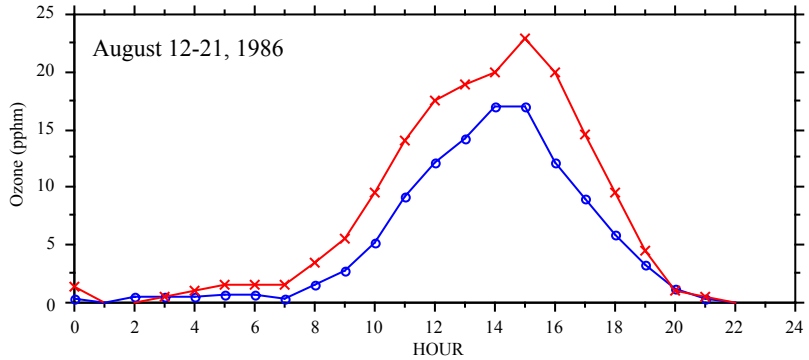


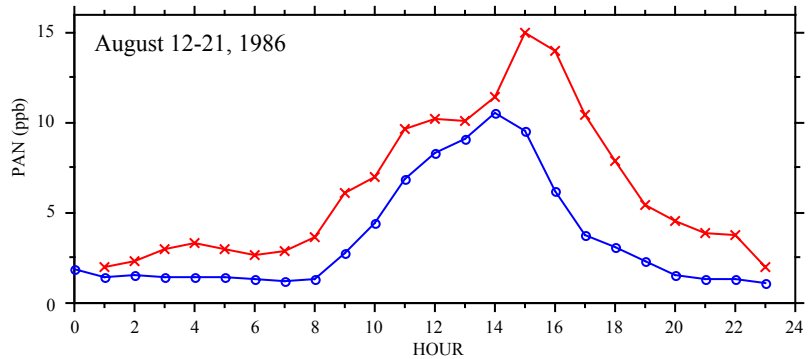
NO2 -> HNO3
may be NOx-
or radical-limited

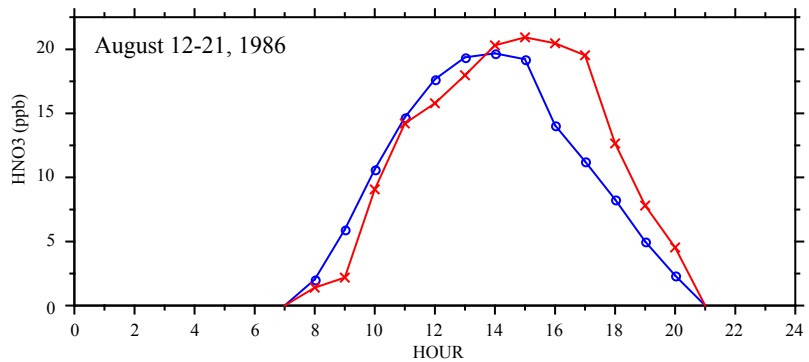


- HNO3 isopleths more L-shaped
- HNO3 less likely to increase than O3, PAN when NOx decreases
- HNO3 may not decrease when NOx decreases

Calculated using OZIPR with CALL mechanism (Lurmann et al., 1987) for December 21, 37N, clear sky conditions







CSMCS – 1986

FTIR PAN and HNO3

Citrus College (~2 mi east of Azusa)

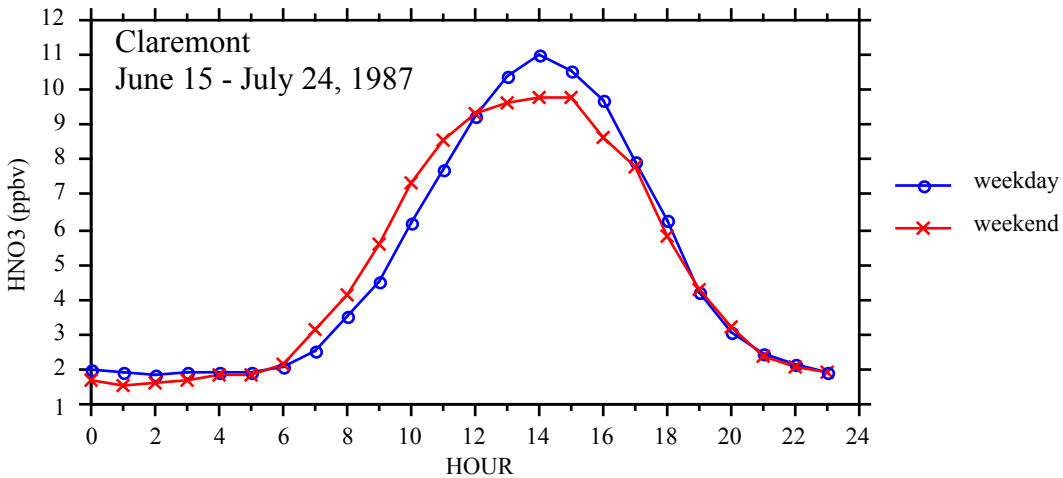
Elevated WE ozone and PAN

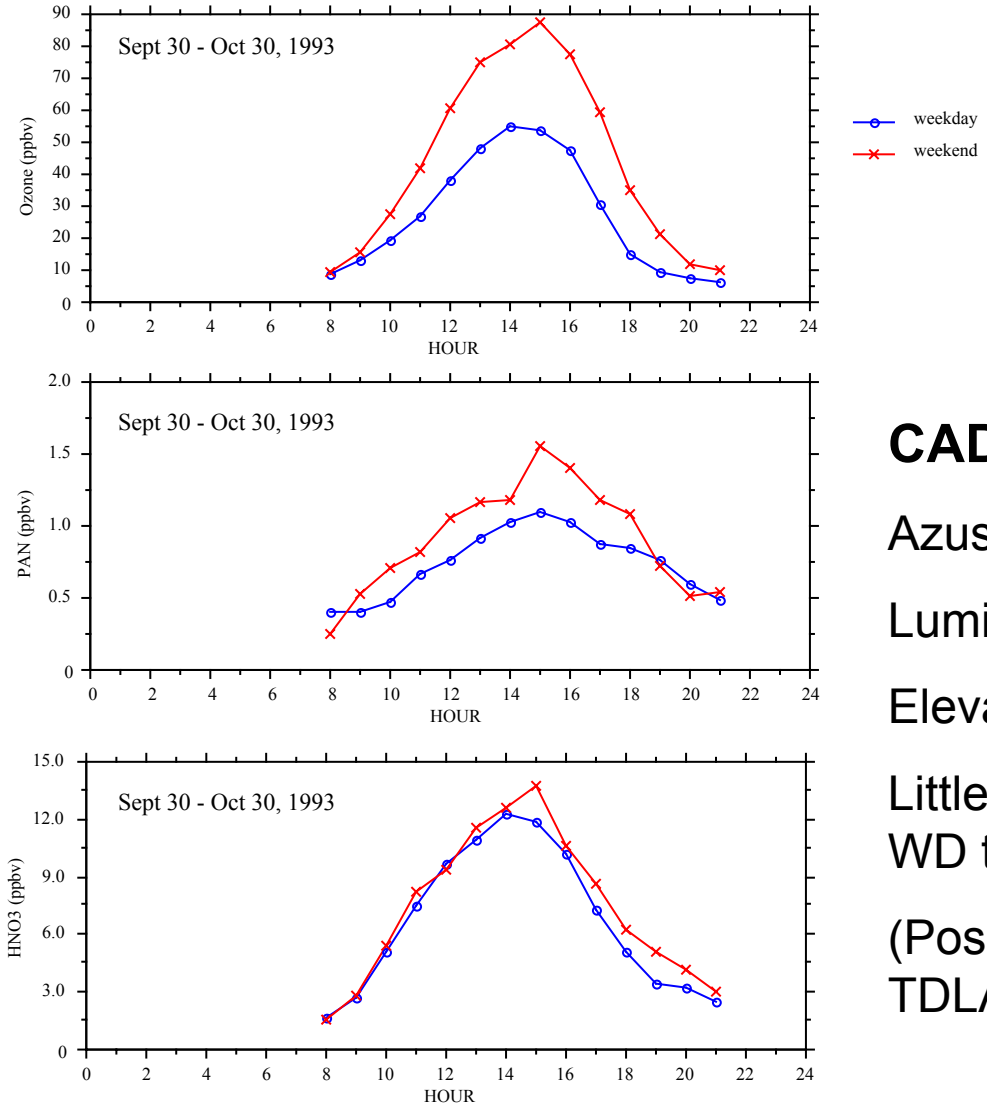
Hourly differences but little overall (24-hour) change in HNO3 from WD to WE

SCAQS – 1987

TDLAS HNO3 at Claremont

Hourly differences but little overall (24-hour) change in HNO3 from WD to WE





CADMP Evaluation – 1993

Azusa

Luminol PAN and TDLAS HNO3

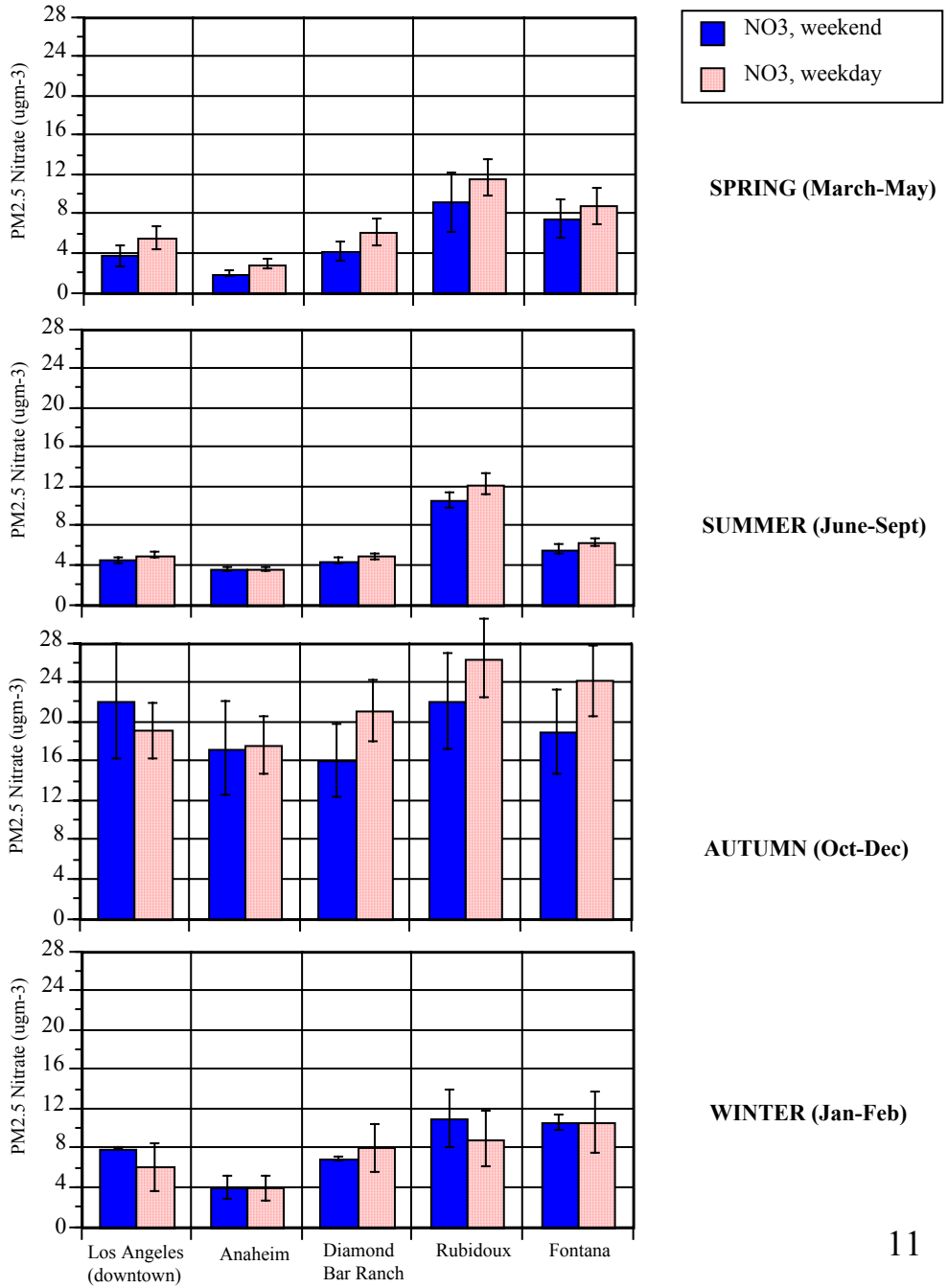
Elevated WE ozone and PAN

Little overall change in HNO3 from WD to WE

(Possible spectral interferences with TDLAS HNO3?)

If there are no significant WD/WE HNO3 differences, will WD/WE nitrate levels differ?

PTEP data show no significant differences between seasonal mean WD and WE PM2.5 nitrate concentrations



CADMP DATA

Data characteristics

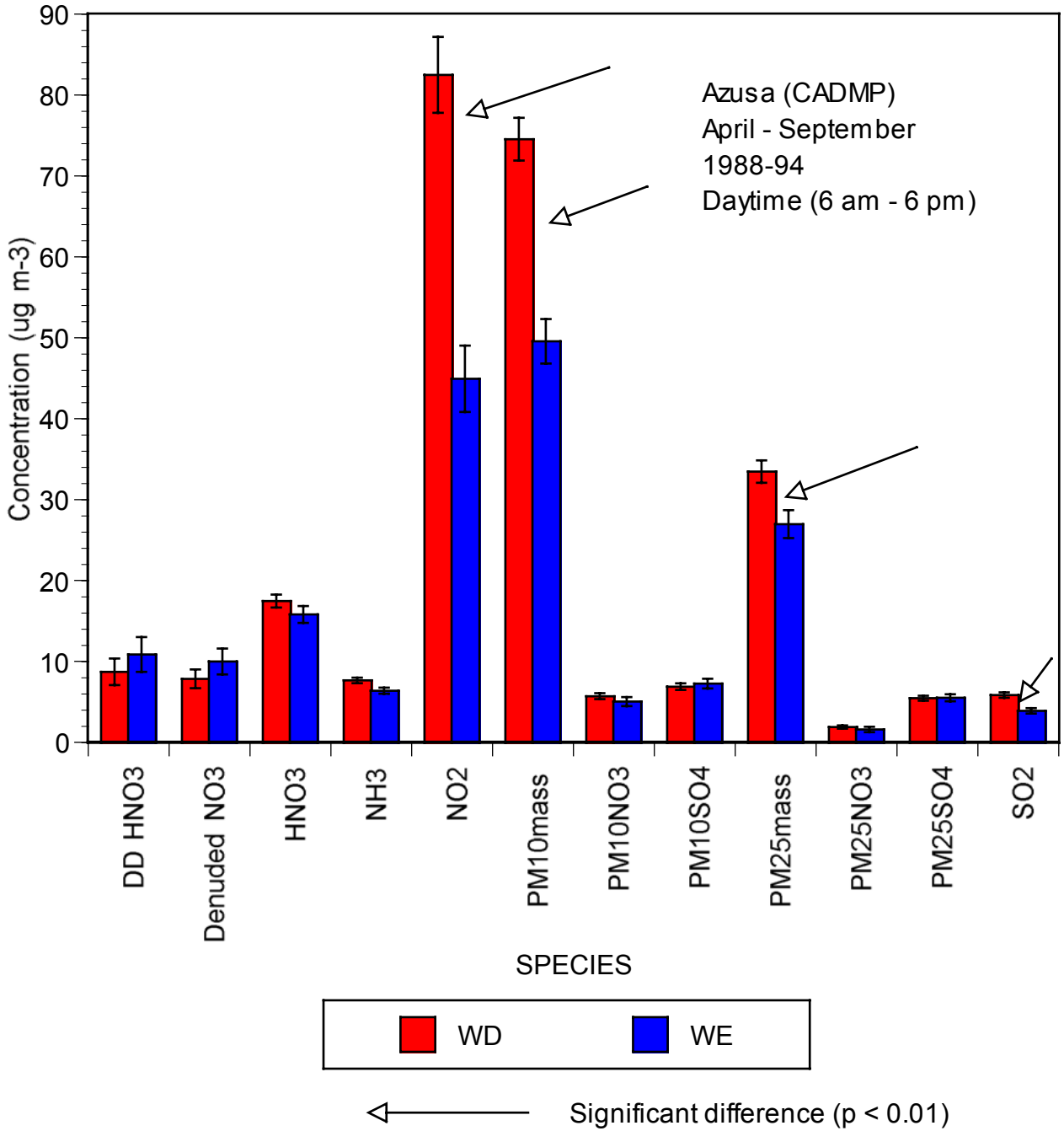
Sites: Azusa, Los Angeles, Long Beach
Period: September 1988 – September 1994
Sample collection: Once per 6 days
Time resolution: 12 hours (6 am – 6 pm or 6 pm – 6 am)
Size fraction: PM10 and PM2.5
Gas-phase: SO2, NO2, NH3, HNO3
Redundancy: HNO3 denuder system and nondenuded
Data analysis: split by season (Oct-Mar or Apr-Sep) and day/night

Results

All sites – significant ($p < 0.01$) daytime decrease of NO2 from WD to WE
- no significant change in HNO3 or particulate nitrate
– few significant differences at night

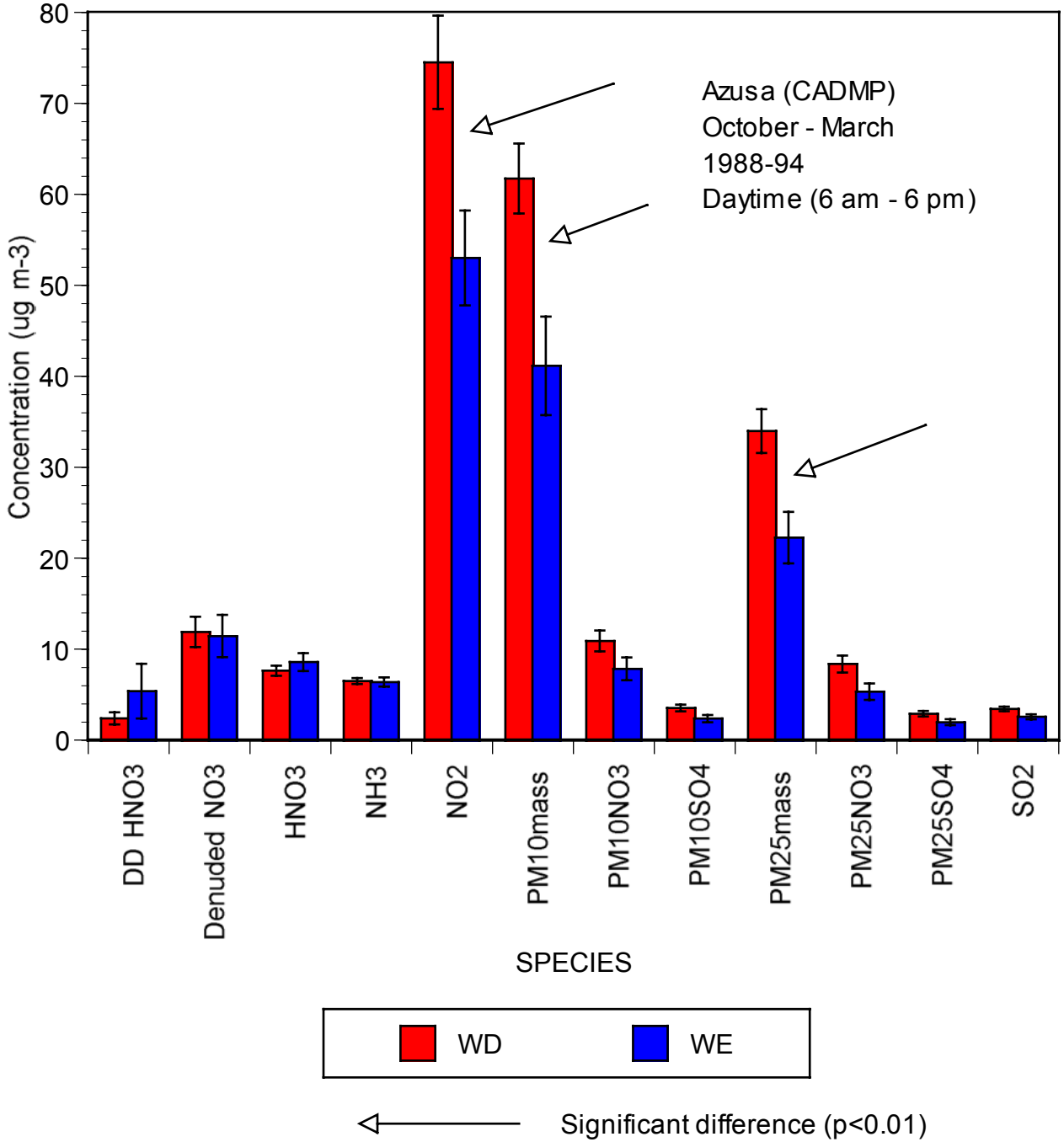
Azusa - statistically significant ($p < 0.01$) decreases of NO2, PM10, PM2.5

Significant WE decreases of NO2, PM10 mass, PM2.5 mass – but not PM nitrate



Dry season
Day

Significant WE decreases of NO2, PM10 mass, PM2.5 mass – but not PM nitrate



Wet season
Day

ROUTINE DATA

Data characteristics

Sites: South Coast, South Central Coast, Mojave Desert
Period: 1980 – 1999
Sample collection: Once per 6 days
Time resolution: 24hours (midnight - midnight)
Gas phase: match CO, NOx, O3 to 24-hour PM time resolution on PM days
Size fraction: PM10 and TSP
Data analysis: split by season (Oct-Mar or Apr-Sep)
10+ years data at 70% completeness (21 days/season/year)
15 CO, 17 NOx, 25 O3, 9 PM10, 26 TSP sites

Results

Sparse data, high variability. Seasonality and time trends.

Significant ($p < 0.01$) decreases of CO, NOx, PM10, TSP from WD to WE
Significant ($p < 0.01$) increases of ozone from WD to WE
Nonsignificant and variable changes of PM and TSP nitrate

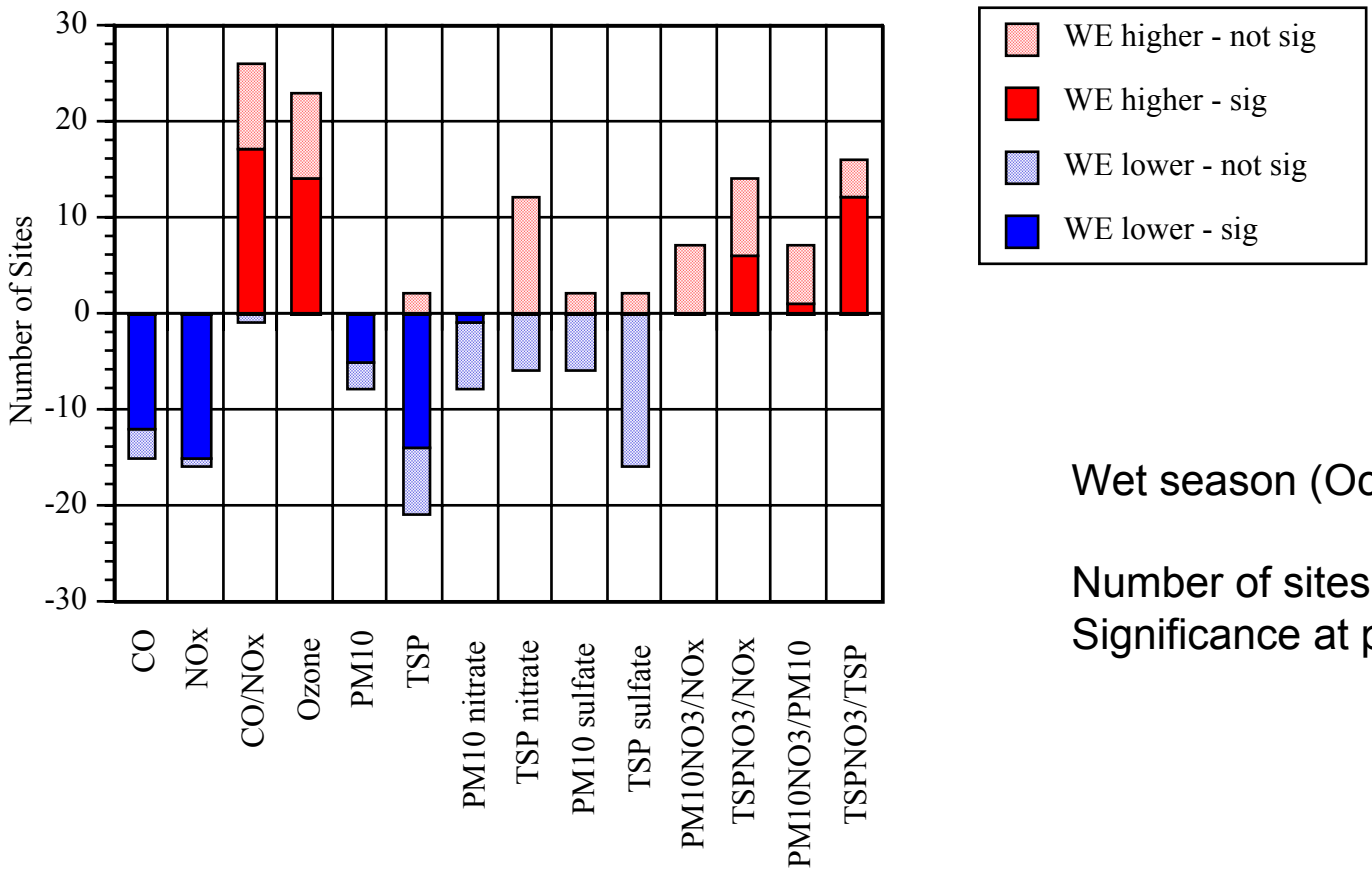
Statistical test for differences in 24-hour mean WD and WE concentrations – t-tests by site, stratified by year – show:

> Significantly lower WE CO, NOx, PM10, TSP

> Significantly higher WE ozone and CO/NOx

> No significant change in nitrate – mixed higher & lower

> Increases in ratios of nitrate/NOx or nitrate/mass



Wet season (Oct-Mar)

Number of sites
Significance at $p < 0.01$

WE NMOC concentrations tend to be lower than weekday NMOC concentrations

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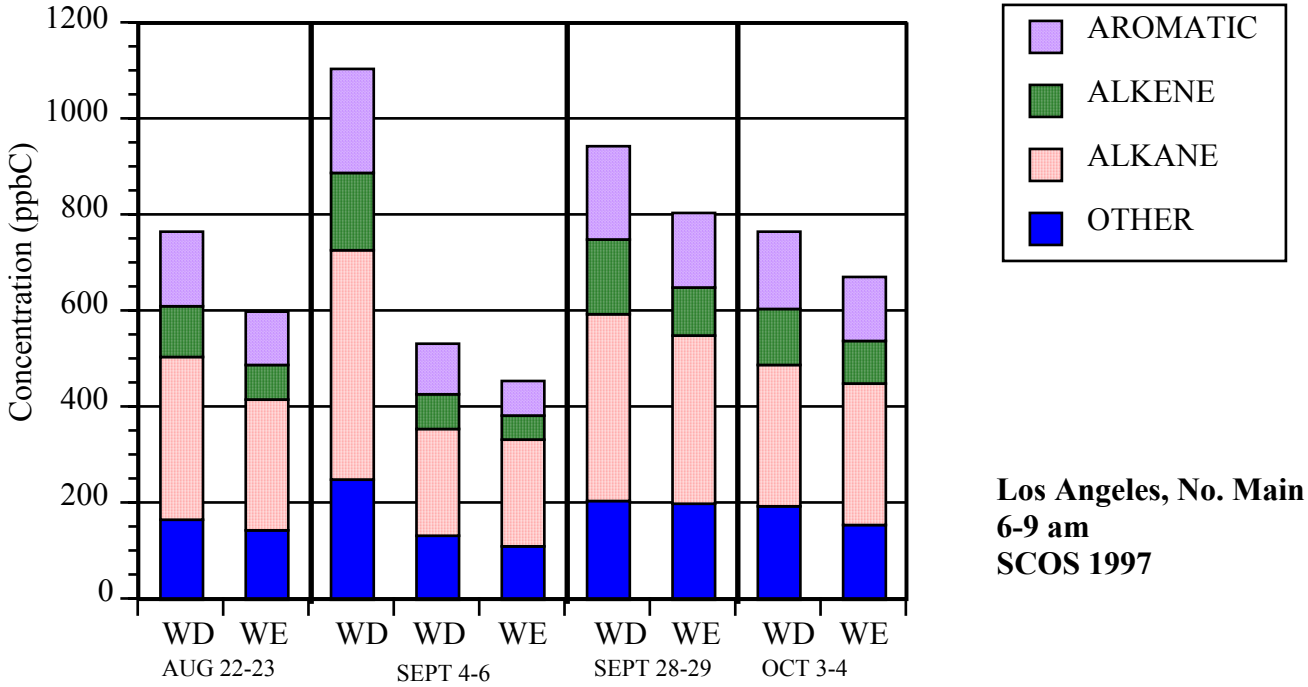
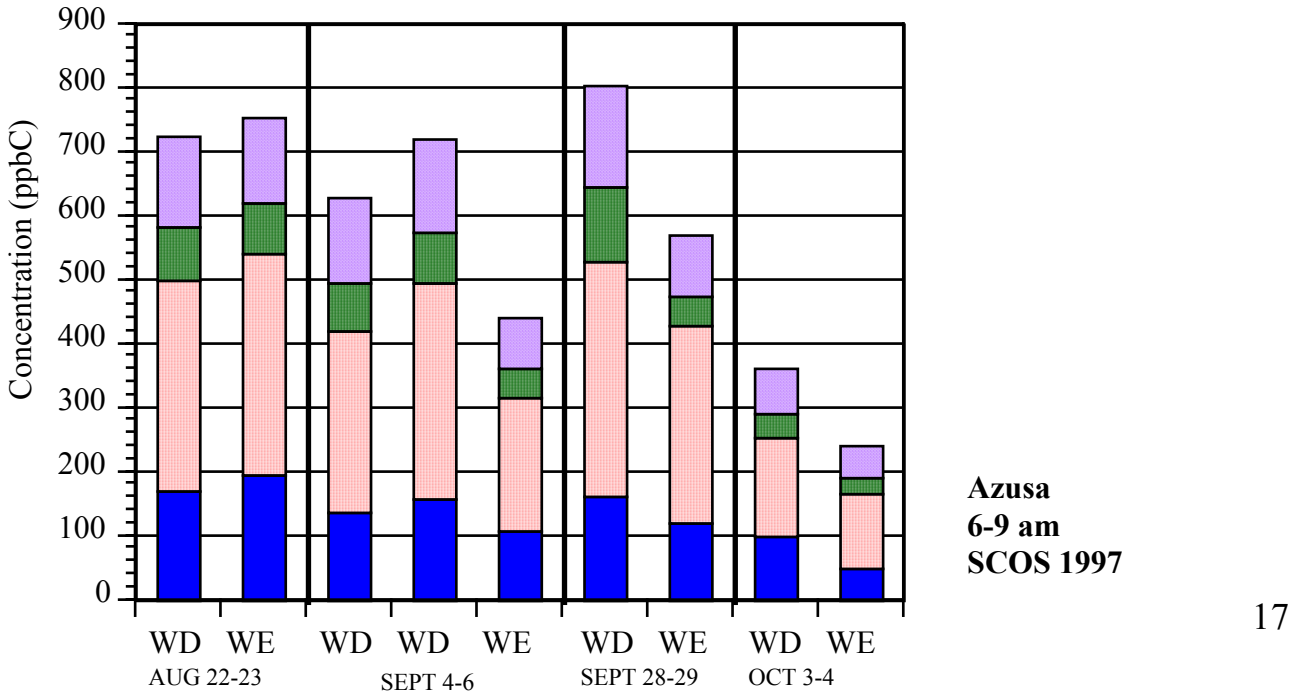
Differences are not statistically significant

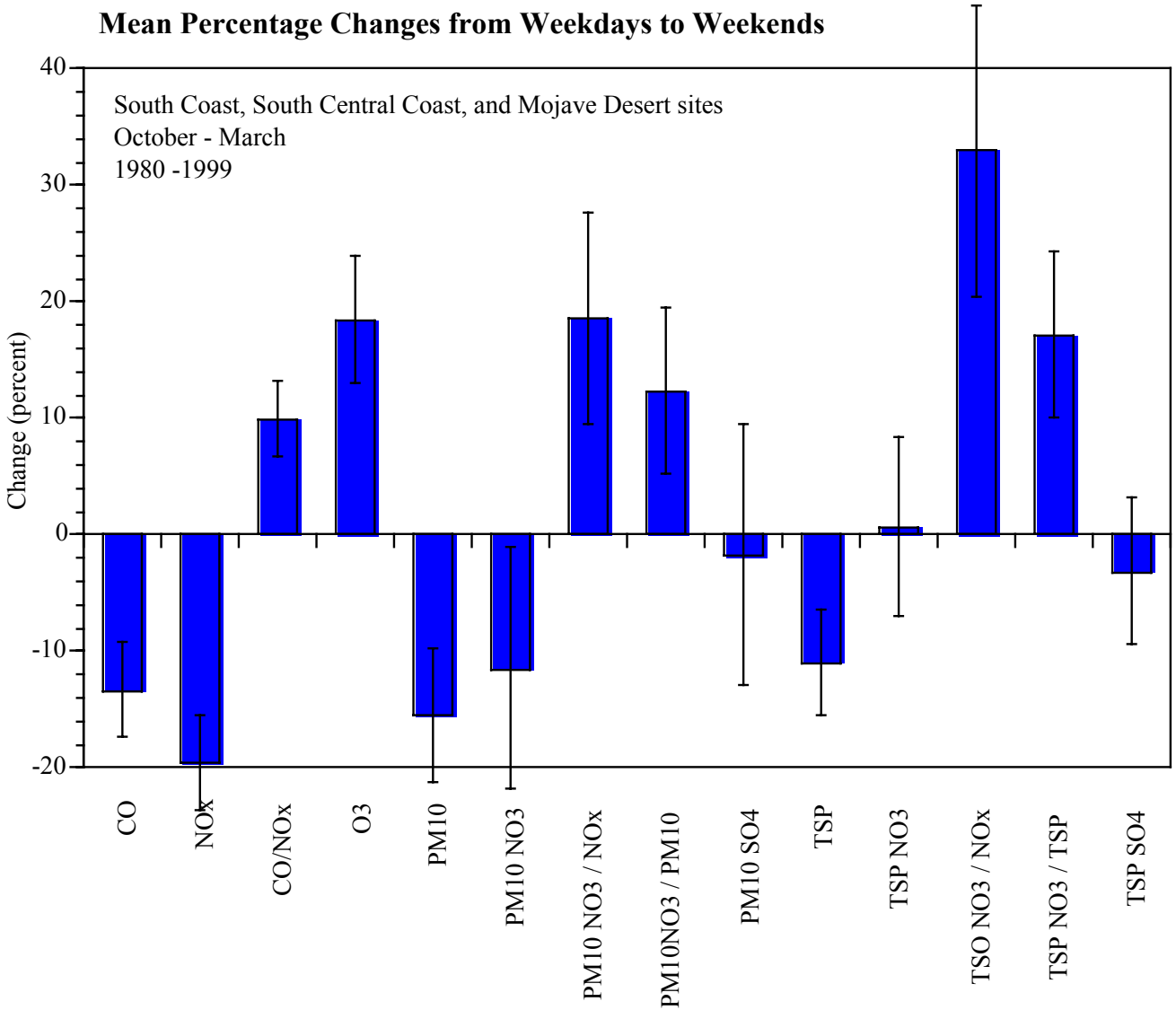


Los Angeles, No. Main
6-9 am
SCOS 1997



Azusa
6-9 am
SCOS 1997

Mean WD-WE PM10 nitrate decrease ~ half NOx decrease
No TSP nitrate decrease



Graph shows averages of sites' percent changes

Error bars are averages of sites' 1 SE

CONCLUSION

> Particulate nitrate formation is not usually NH3 limited in southern California

> Mean particulate nitrate and HNO3 levels are low relative to NOx

> WE particulate nitrate levels not responsive to lower emissions:

Significantly lower WE NO2, NOx, CO, PM10 mass, TSP mass

Lower WE NMOC – not statistically significant

Significantly higher 24-hour WE ozone

Variable and nonsignificant WD-WE changes in 12-24 hour nitrate, HNO3

> Downward trends in particulate nitrate over time (other studies)

> Does particulate nitrate reduction depend on lowering VOC emissions?