Title
Ozone Sensitivity to Emissions and Changes of Limiting Reagents

Authors
Brown, Nancy
Jin, Ling
Tonse, Shaheen
et al.

Publication Date
2006-12-01

2006 AGU FALL MEETING

Ozone Sensitivity to Emissions and Changes of Limiting Reagents

A21E-0867

Nancy Brown[1], Ling Jin[1], Shaheen Tonse[1], and Rob Harley[2]
1. Atmospheric Sciences Department, Lawrence Berkeley National Laboratory, Berkeley, CA 94720 U.S.A
2. Department of Civil and Environmental Engineering , University of California at Berkeley
Contact: njbrown@lbl.gov, 510-486-4241

BERKELEY LAB

Abstract

Regional control strategy options for reducing ozone change temporally and spatially in Central California where air pollution is particularly serious. The rate of ozone production is a complex function of the concentrations of volatile organic compounds (VOCs) and nitrogen oxides (NOx) as well as meteorological conditions. As a result, ozone formation exhibits a very non-linear dependence on its precursors. Determining the relative benefits of controlling NOx emissions or VOC emissions remains a challenging problem. Current practice of modeling 3 to 5 day episodes does not capture the changes in limiting reagents since they represent a limited sample of the diverse meteorology and human behavior that affect air pollution.

We are using CMAQ, the EPA's Community Multiscale Air Quality Model, to model a season of air quality in Central California for the summer of 2000 to illustrate some limitations of current practice. We have modeled a 15-day period and, in concert with the modeling, have also used the Decoupled Direct Method to compute ozone sensitivities to NOx and VOC emissions. Emissions have been disaggregated differently to extract mechanistic information regarding limiting reagents, and to explore issues of long range transport. We have computed ozone sensitivities to total NOx emissions and VOC emissions for the entire modeling domain, NOx emissions and VOC emissions from specific air basins, as well as emissions from specific air basins for specific time intervals. We demonstrate how the computed sensitivity coefficients of ozone to the various emission types may be used to demonstrate and understand limiting reagent changes throughout the modeling domain.

Introduction

- Geography and air quality in Central California: see poster A21E-0866
- San Joaquin Valley is divided into three sub-regions: north, middle, and south Selected sites (brown dots):
  - **North**: Modesto (M14), Pacheco Pass (PCP)
  - **Middle**: Parlier (PLR), Trimmer (KRV)
  - **South**: Bakersfield (BAC), Arvin (ARV)

Figure 1. Geography of central California

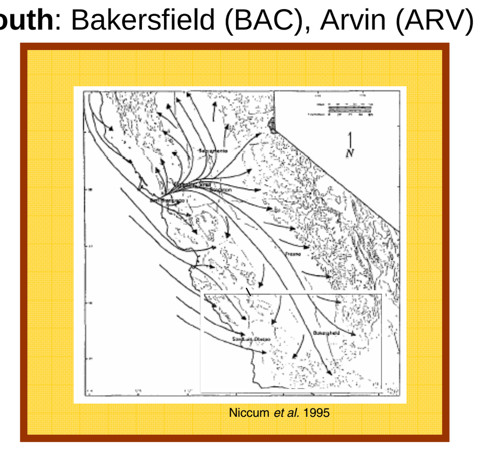

Figure 2. The predominant summer wind flow pattern

Definition of Limiting Reagent and Ozone Control Strategy

Semi-normalized ozone sensitivity coefficients (1) and (2)

- Sensitivity of hourly ozone is calculated by Decoupled Direct Method (DDM4.5). to:
  - Domain-wide emitted NOx or Anthropogenic VOC (AVOC)
  - Sub-regional emissions
  - Emissions at selected time intervals
- Sensitivity of eight-hour average ozone is calculated by moving average of hourly sensitivity

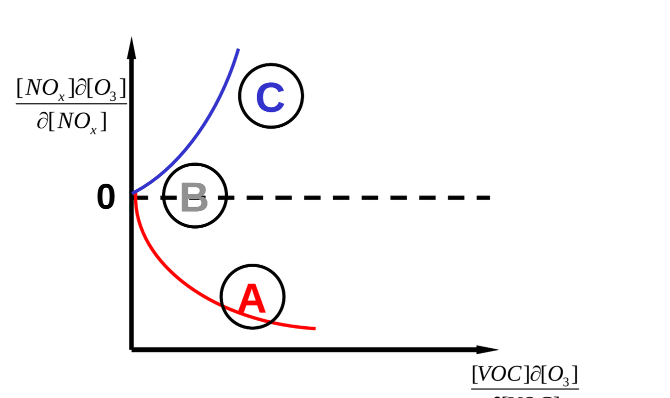

Figure 3. Scatter plot of seminormalized ozone sensitivity

$$\frac{[NO_x]\partial[O_3]}{\partial[NO_x]} \quad (1)$$

$$\frac{[VOC]\partial O_3}{\partial[VOC]} \quad (2)$$

Table 1. Limiting regime and control strategy

Case		Limiting Regime	Control Strategy	
(1) < 0		VOC sensitive	Reduce VOC's NO_x disbenefit	A
(1) >0	(1) ~(2)	Transition Region	Not effective	B
	(1)>>(2)	NO_x Sensitive	Reduce NO_x	C

Ozone Sensitivity to Domain-wide Emissions

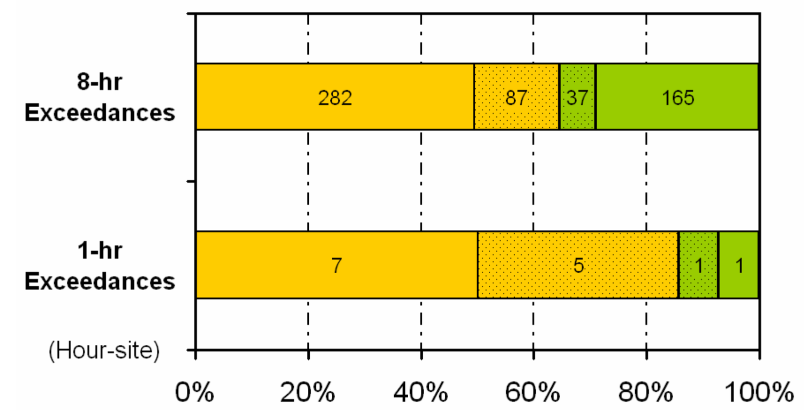

Figure 4. Summary of 1-hr and 8-hr exceedances in SJV
Episode: Jul 29 ~ Aug 2, 2000
Non-episode: Jul24 ~ 28, and Aug 3 ~ 7
Weekend: indicated by dotted pattern.

- More site-hours exceed 8 hour average standard (84 ppb) than 1 hour standard (120 ppb). In general, sites that violate 1-hour standard also violate 8-hour standard.
- Reduced emissions (mostly NOx) on weekend can cause increased ozone levels at VOC controlled sites ("weekend effect"). We see that weekend effect contributes more to the 1-hour violations than to the 8-hour averages in both episode and non-episode (Fig.4).
- There is a greater fraction (Fig.4) of non-episode hour-sites in exceedance of the 8-hour standard than the 1-hour standard.
- Control strategies would not be significantly different for episodes and non-episodes for this 15-day period.

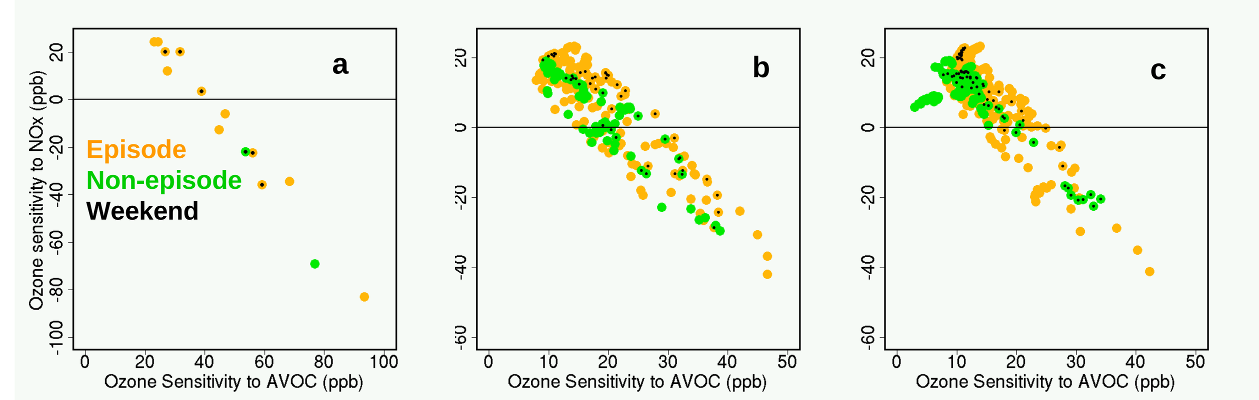

Figure 5. Ozone sensitivity scatter plots. (**a**) 1 hr ozone sensitivity for 1 hour exceedances
(**b**) 8 hr average ozone sensitivity for 8 hour exceedances at sites also exceeding 1 hour standard (**old standard also**)
(**c**) 8 hr average ozone sensitivity for 8 hour exceedances at sites that do not exceed 1 hour standard (**new standard only**)

- San Francisco Bay Area (SFB) is about 100% VOC controlled for both 1-hour and 8-hour average exceedances. Picture in the valley (SJV) is quite different. VOC control dominates 1-hour exceedances, while for 8-hour exceedances, the strategy shifts toward controlling NOx
- In Figure 5 and 6, 8-hr exceedances are further divided into two cases: old standard also (**b**), and new standard only (**c**). Although all the 8-hour exceedances shift toward NOx limited regime, NOx control is more important for the new standard only exceedances (~90% in blue for c).

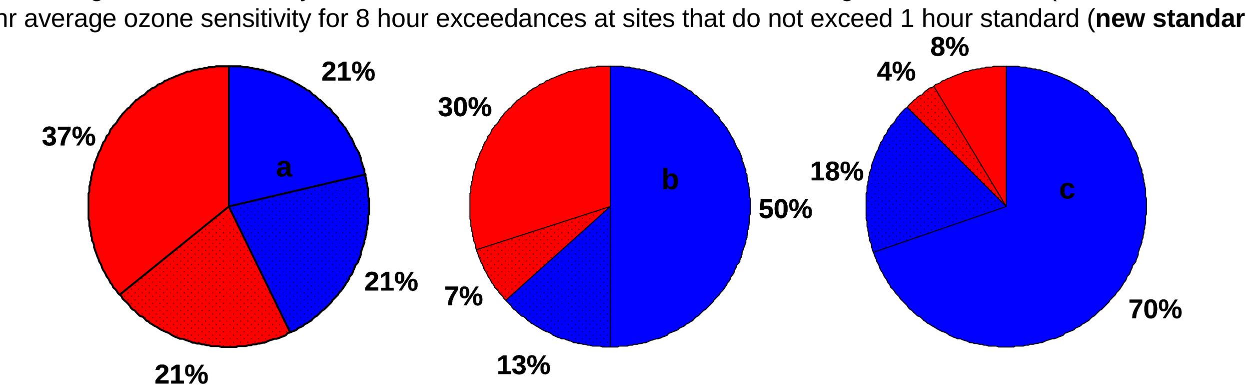

Figure 6. Limiting reagents for cases (**a**), (**b**), and (**c**) defined in **Figure 5**. **Weekend**: indicated by dotted pattern.
NOx control (or in transition regime): ozone sensitivity to NOx > 0. **VOC control**: ozone sensitivity to NOx <0.

The dominant wind direction is from the SFB to the SJV. Combining the SJV sites into one scatter plot may mask the spatial site to site differences in control strategies. Considering the distance of sites in the SJV from the SFB, we divided SJV into three parts: North, Middle and South (see Figures 1 and 7).

Dominant limiting reagents for the 8-hour average exceedances are determined for individual sites in the SJV and plotted on the map in a color coded fashion. NOx control dominates for all the downwind rural sites (at coastal ranges, or foothill of sierras, e.g. PCP, KRV, and ARV),. More variations in limiting reagent are seen for the urban sites. The Northern part of the SJV (closest to SFB emission sources) is primarily in a VOC-limited regime. The middle part exhibits both regimes, part of the time VOC control is more effective, and part of the time , NOx control is more effective, e.g., PLR. The southern part is far downwind and is in a NOx limited regime, e.g., BAC.

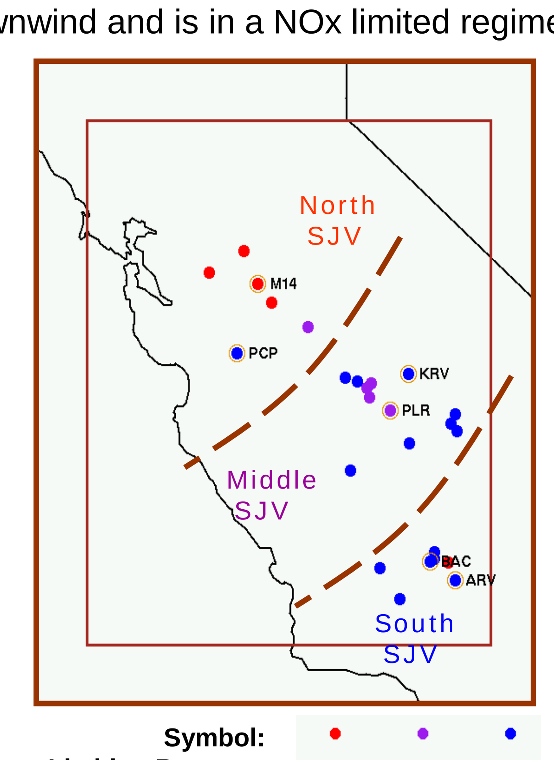

Figure 7. Dominant control strategy at individual violating sites in SJV.

Selected: Sensitivity scatter plots at selected sites (one near emission source, one in downwind rural area) for each part of SJV are shown in Figure 8.

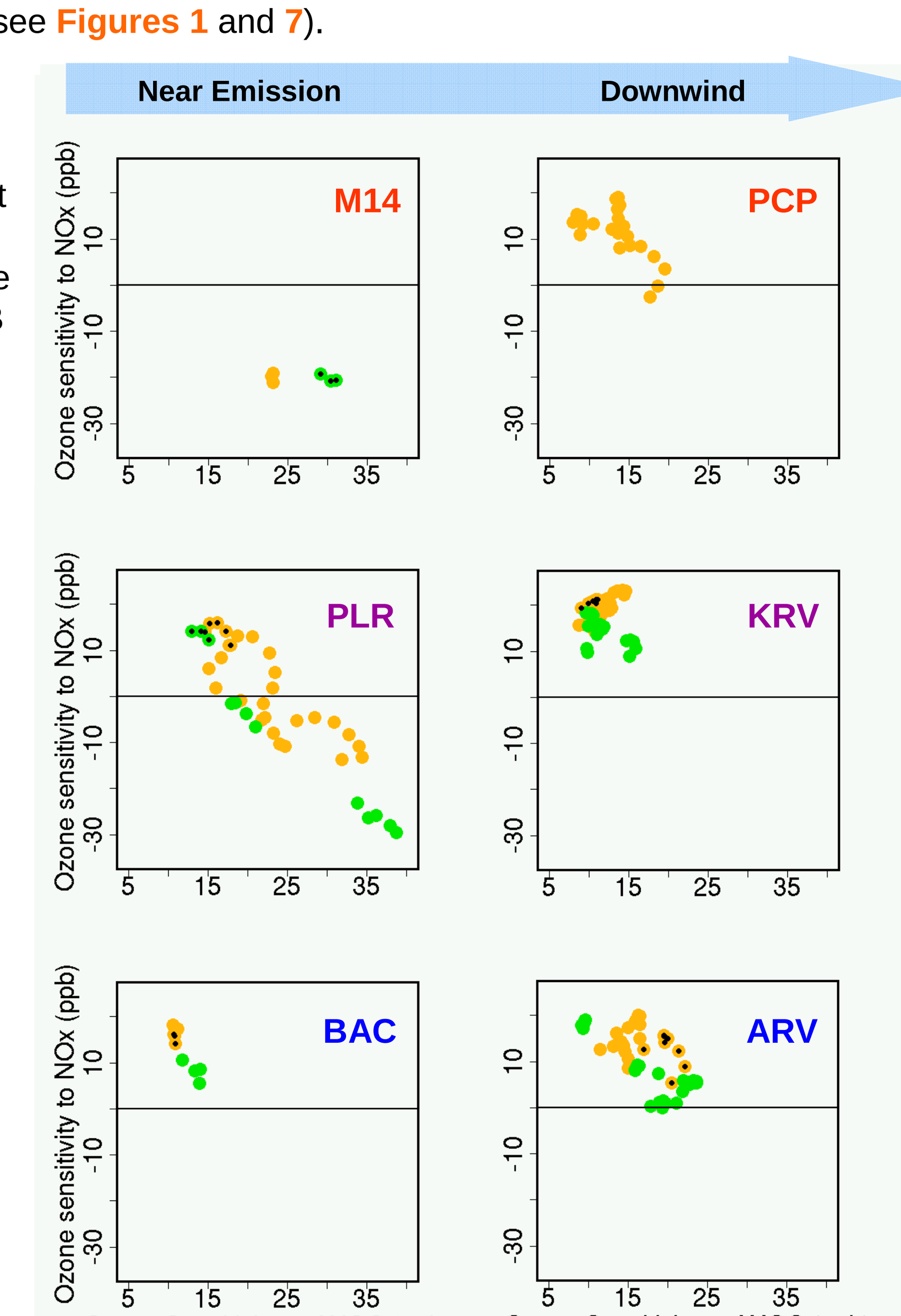

Figure 8. Ozone sensitivity scatter plots for the entire 15-day period at selected sites in North, Middle and South SJV.

Inter- and Within-basin Transport

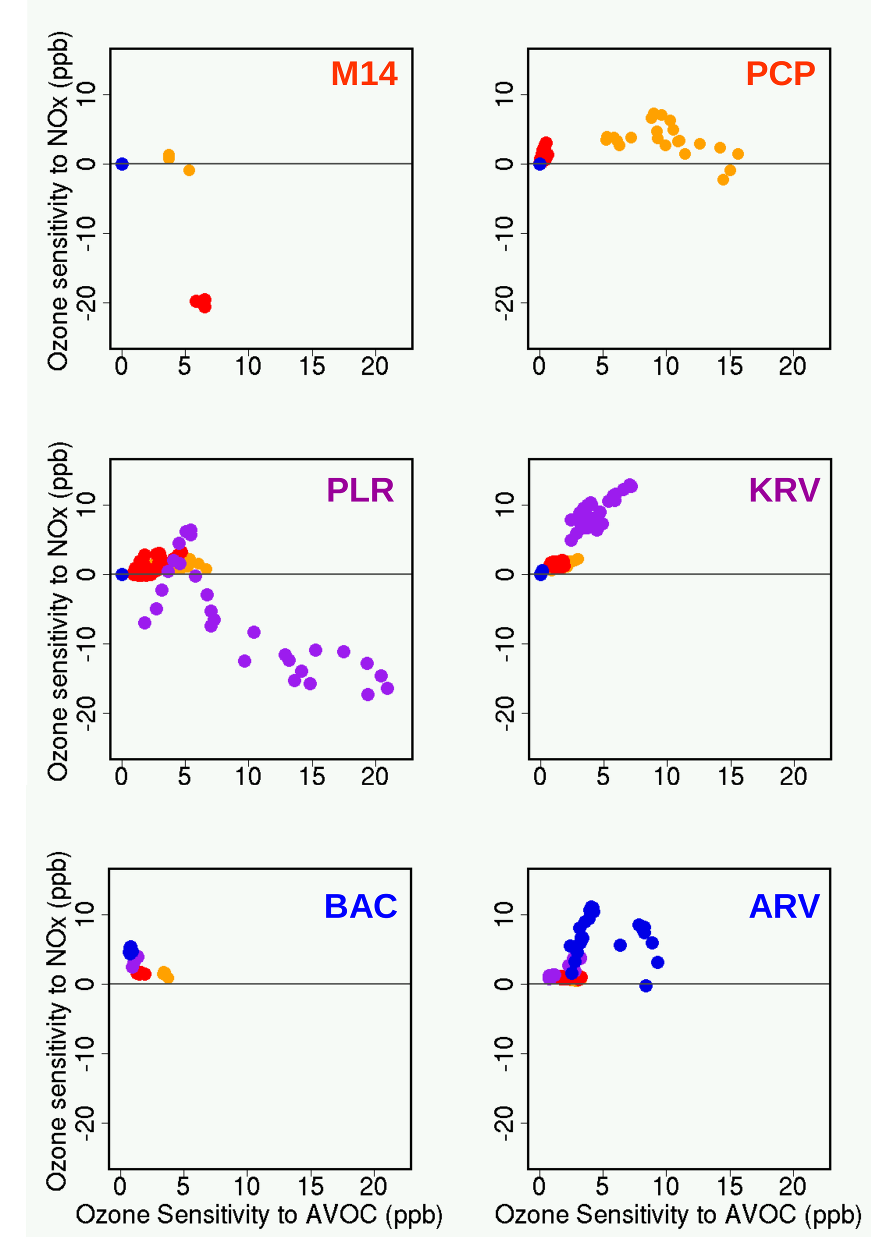

Figure 9. Ozone sensitivity to emissions from different source regions for the 5-day ozone episode.
Sensitivity to emissions from SFB, North SJV, Middle SJV, and South SJV

Ozone sensitivity during the episode to emissions from SFB, and three parts of SJV (north, middle, and south), respectively is calculated. At individual SJV sites, ozone sensitivity to SFB emissions indicates the effect of inter-basin transport of pollutants (ozone or its precursors), while sensitivity to the three parts of SJV indicates the importance of with-in basin transport.

We selected the same SJV sites to show spatial variations in the relative importance of interbasin vs. within basin transport of pollutants.

- Ozone is most sensitive to the closest emission sources (mostly local sources), which largely determine the overall control strategy.
- Sensitivities to upwind emission sources are generally smaller, and are indicative of a NOx limited or transition regime.

Table 2 shows that NOx emitted in the SFB only affects the northern part of SJV. Ozone in the valley is most sensitive to locally emitted NOx. VOCs emitted in the SFB area, however, have an effect throughout the valley.

Color legend: < 10%; 10 ~ 20%; 20 ~ 40%; 40 ~ 60%; 60 ~ 80%; >= 80%

Table 2. Contributions to the magnitude of ozone sensitivity to emissions

To NOx:

Receptor Sites		Inter-basin Transport: SFB	Within-basin Transport: SJV North	SJV Middle	SJV South
North SJV	PCP	78	22	0	0
	M14	5	95	0	0
Middle SJV	PLR	12	13	76	0
	KRV	12	12	75	1
South SJV	BAC	12	14	31	43
	ARV	7	9	22	62

To AVOC:

Receptor Sites		Inter-basin Transport: SFB	Within-basin Transport: SJV North	SJV Middle	SJV South
North SJV	PCP	97	3	0	0
	M14	40	60	0	0
Middle SJV	PLR	22	15	63	0
	KRV	25	17	57	1
South SJV	BAC	50	22	16	11
	ARV	23	18	18	42

To explain the different effects of AVOC and NOx emissions from the SFB area on ozone formation in the downwind areas, we calculated sensitivity of NOx and AVOC to SFB emissions.

- Emissions from the SFB area affect domain wide VOC budgets more than NOx budgets.
- The influence of afternoon emissions from the SFB area persists for longer time periods (>20hr) than morning emissions (~10hr).
- NOx sensitivity is reduced to nearly zero before ozone peaks (~1-3pm), while VOCs remain sensitive to the afternoon emissions from the SFB of the previous day.

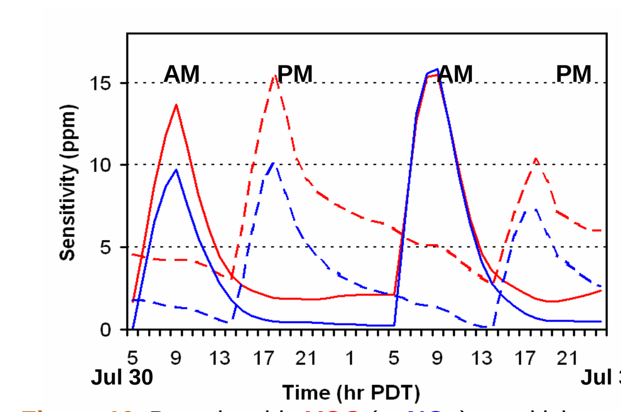

Figure 10. Domain-wide VOC (or NOx) sensitivity to AVOC (or NOx) emitted in the SFB area.
Solid line: sensitivity to morning emissions (6am -10am)
Dashed line: sensitivity to afternoon emissions (3pm – 7pm)

Conclusions

- In contrast to the SFB area, where ozone is limited by VOC concentrations, limiting reagents in the SJ valley shift from being primarily VOCs toward NOx, especially for sites out of compliance with the 8-hr standard that did not exceed the 1-hour standard.
- Spatially, limiting precursors change throughout the valley, with VOC dominating the northern part, and NOx dominating the southern part. Urban sites in the middle part (near Fresno) do not have consistent limiting reagents.
- Closest (mostly localized) emission sources affect local ozone formation most, and this is especially true for NOx emissions. Afternoon emissions of AVOC from the SFB area have long range effects on the ozone formed in the valley as a result of increasing the VOC budgets in downwind areas.

Acknowledgement

This work is supported by the U.S. Department of Energy, California Energy Commission and the California Air Resources Board.