Sensitivity Analysis of Ozone Formation and Transport for a Central California Air Pollution Episode

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Presented at the 2008 CCOS Technical Committee

Sacramento California
October 9, 2008

Outline

- New Sensitivity Code HDDM
- Applied to high ozone period with adverse meteorology
- Differences in 1-hr and 8-hr control strategies
- Changes in limiting reagents in time and space
- Importance of local versus upwind sources
- Effects of emissions timing
- Assess effects of uncertainties in emission inventories, reaction rate coefficients, and boundary conditions
- Future efforts

Team Members

- **Lawrence Berkeley National Laboratory:**
  Ling Jin, Shaheen Tonse, Daniel Cohan, Xiaoling Mao, Robert Harley, and Nancy Brown
- **Agencies supporting research:**
  - **Department of Energy (DOE)**
  - **California Energy Commission (CEC)**
  - **California Air Resources Board (CARB) through Central California Ozone Study (CCOS).**

The CMAQ+ HDDM Modeling System

- **A 3-D Eulerian photochemical airshed community model: .**

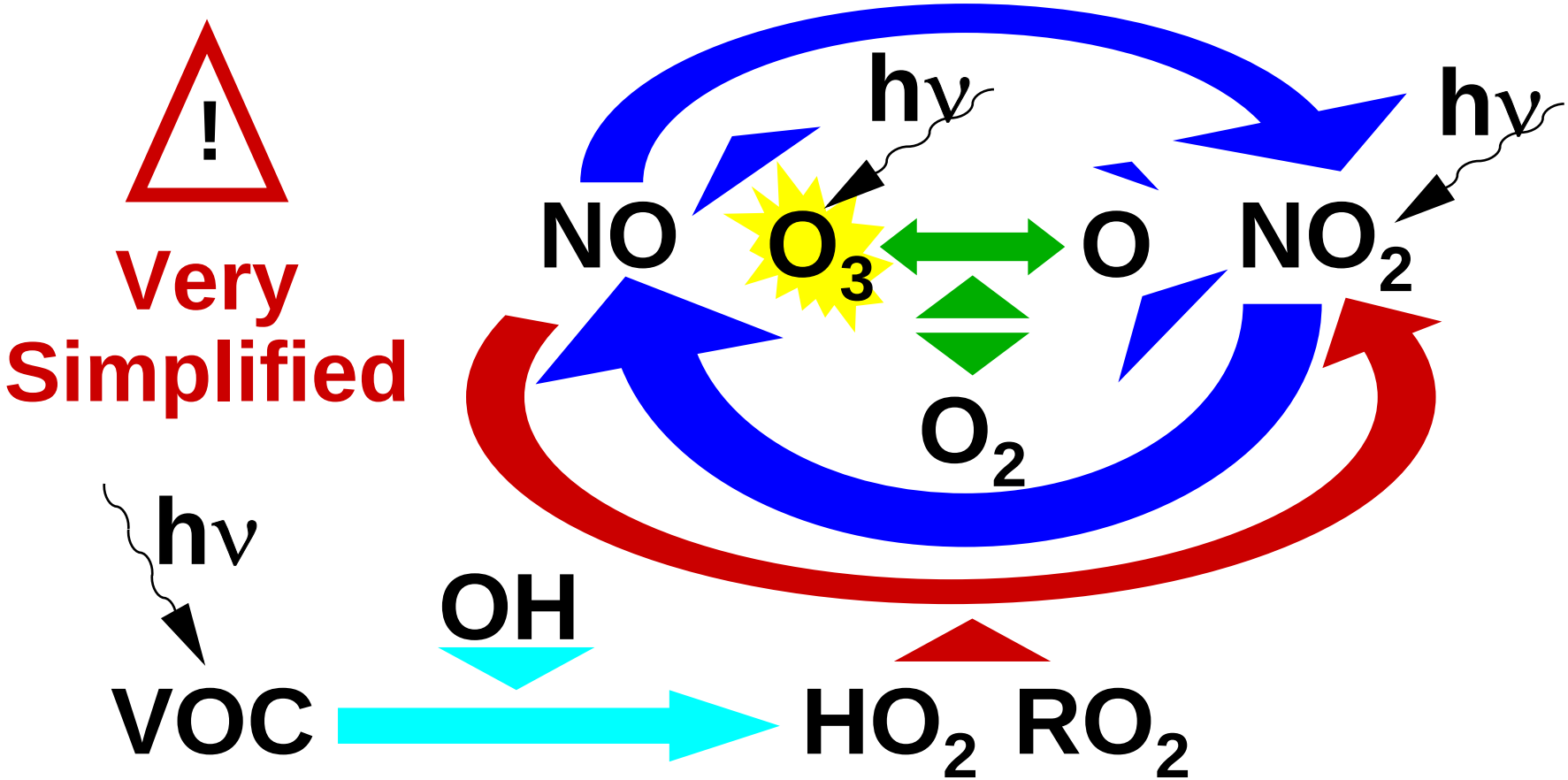
$$\frac{\partial C_i}{\partial t} = \text{advection} + \text{turbulent diffusion} + \text{reactions} + \text{emissions}$$

$$S_i^{(1)} = P_i \frac{\partial C}{\partial p_i} = \frac{\partial C}{\partial \varepsilon_i}$$

- **First and second order sensitivity equations are solved with parent equations with HDDM. Computationally intensive to evaluate first and second order coefficients. If we perturb Pi by 10%, it will cause a 0.10S_i change in C.**

Sensitivity study was performed for the July 29- August 2, 2000

Complexity of Tropospheric Ozone Production



- Non-linear response to emissions
- Spatial and temporal variability of response-limiting reagents depend on local VOC/NOx ratios

Limiting Reagents—the Basis for Controls

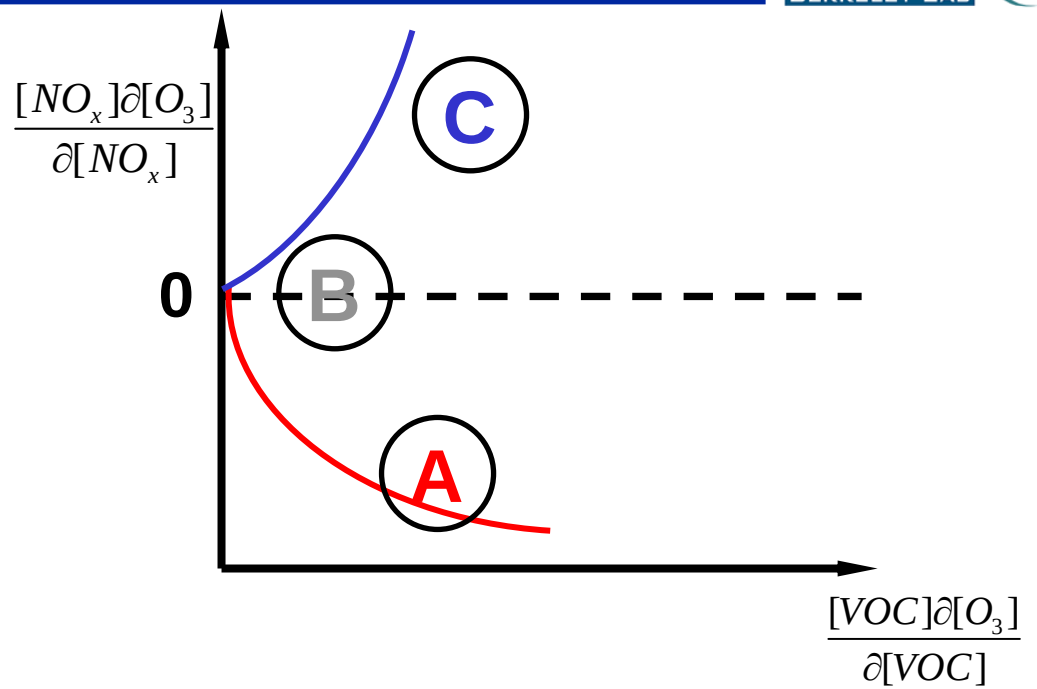
- Do our modeling results show evidence of the limiting reagent changing in time and space?
- How can we demonstrate this?

Sensitivity Analysis

- **Compute**

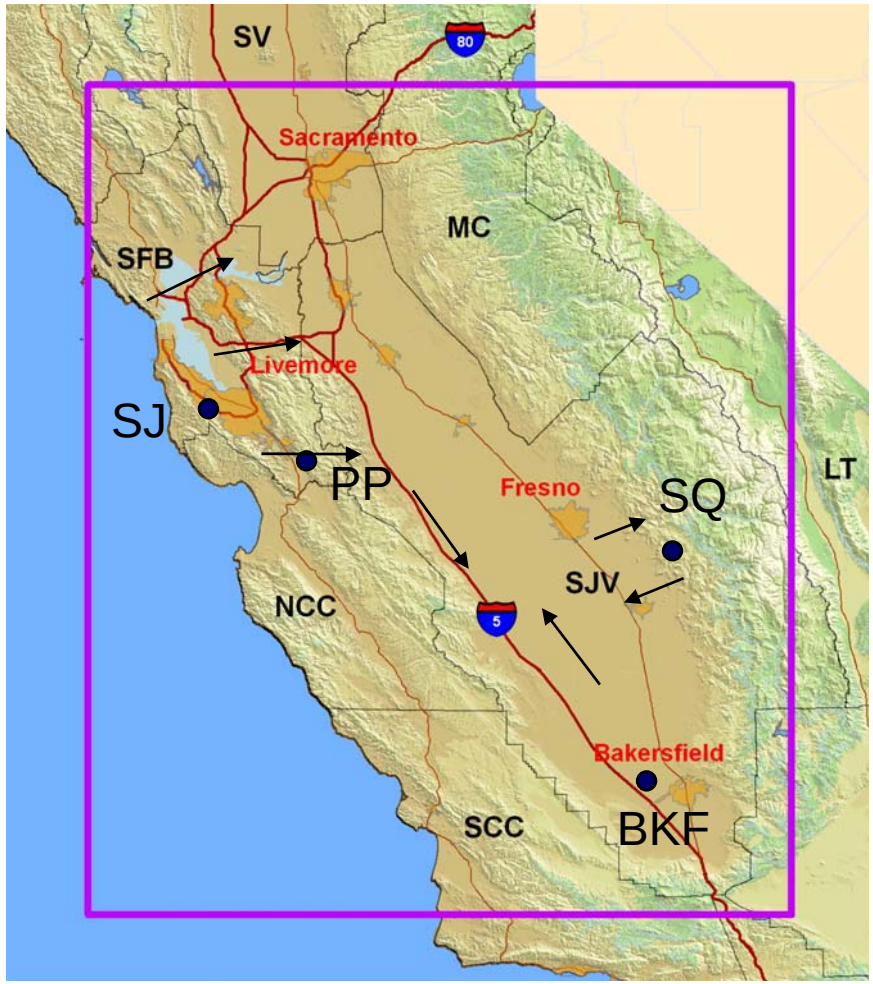
$$\frac{[NO_x]\partial[O_3]}{\partial[NO_x]} \quad (1)$$

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

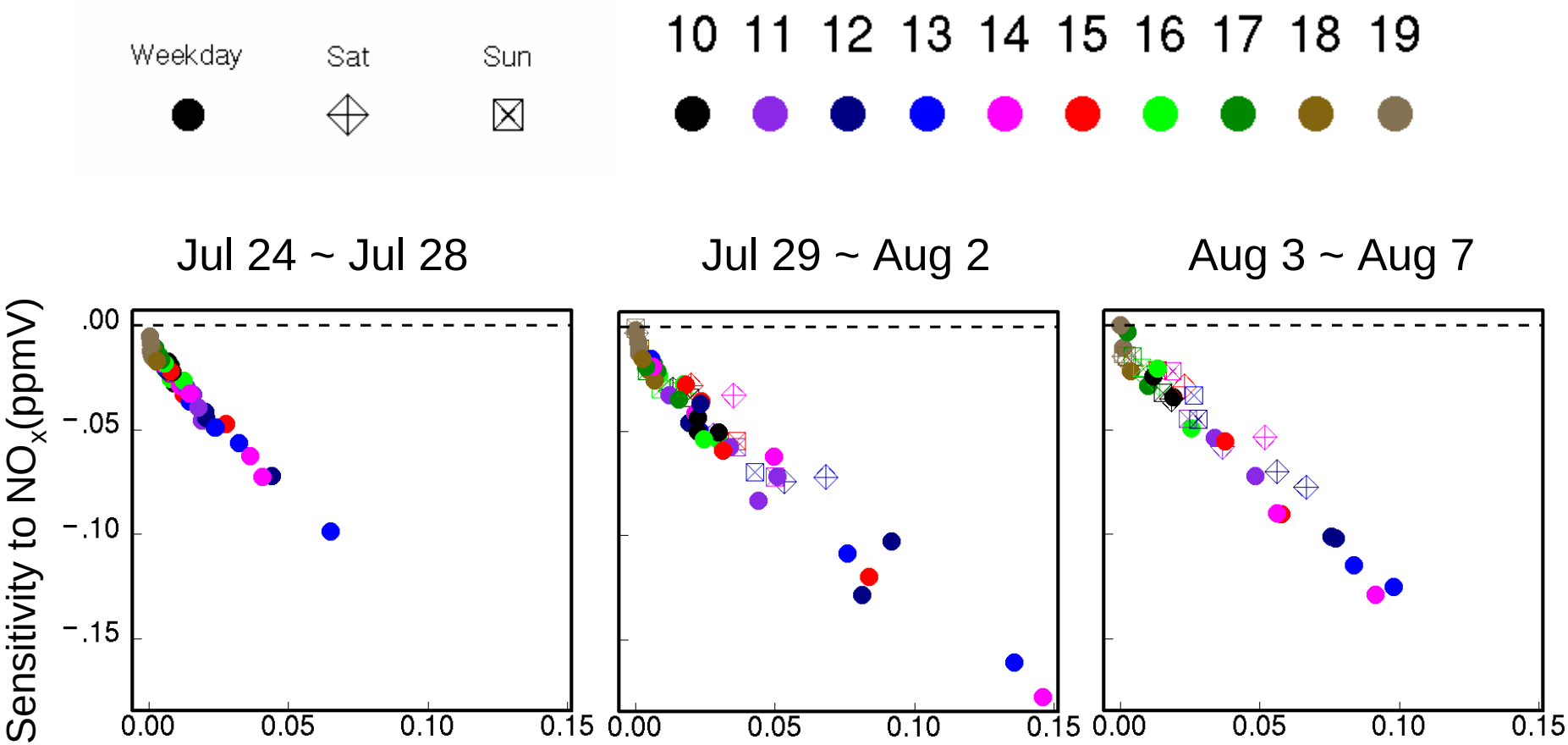


Case		Limiting Regime	Control Strategy	
(1) < 0		**VOC sensitive**	**Reduce VOC's NO_x disbenefit**	A
(1) >0	**(1) ~(2)**	**Transition Region**	**Not effective**	B
	(1)>>(2)	**NO_x Sensitive**	**Reduce NO_x**	C

Relationship Between Sites

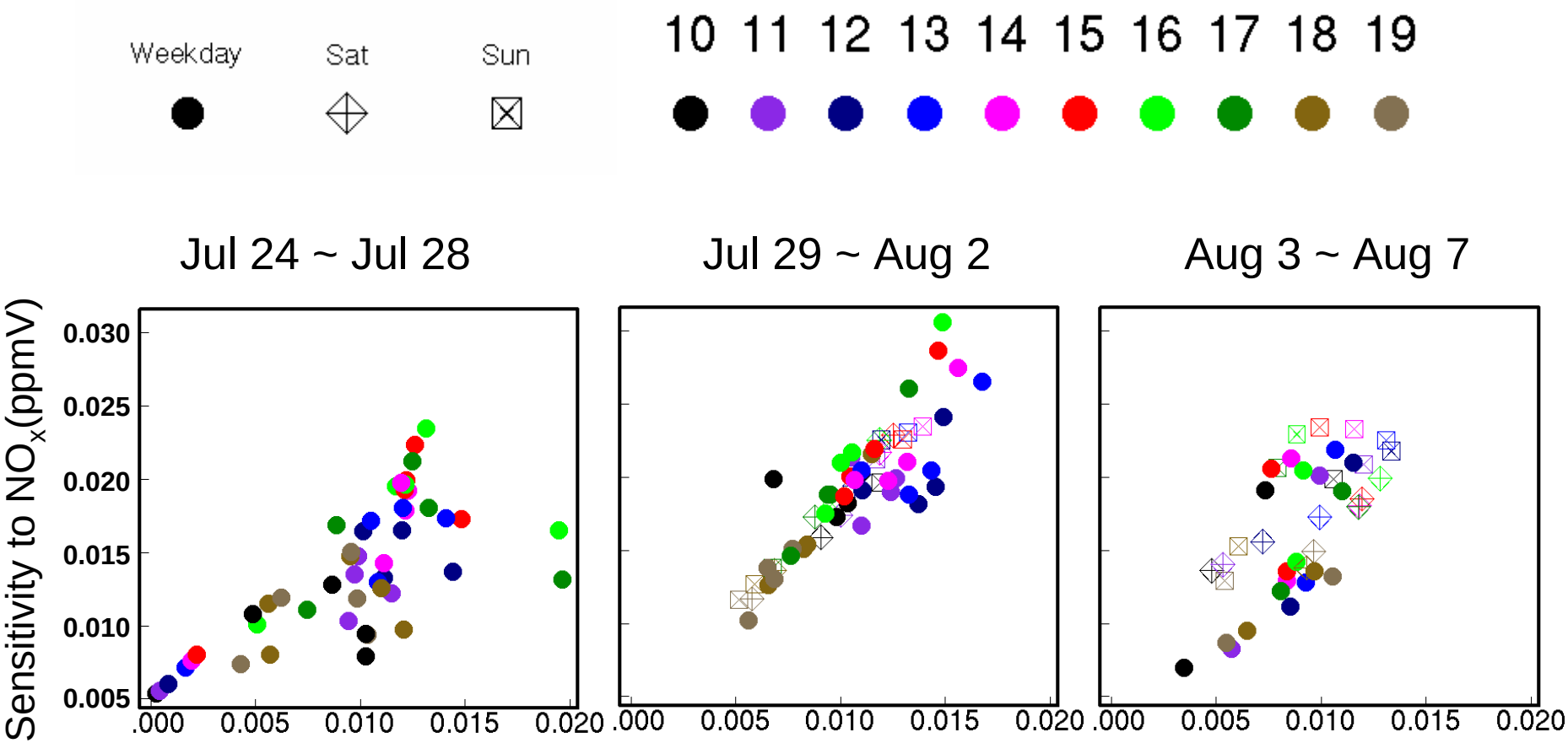


Sensitivity Scatter Plot San Jose in San Francisco Bay Area 10 am to 7 pm



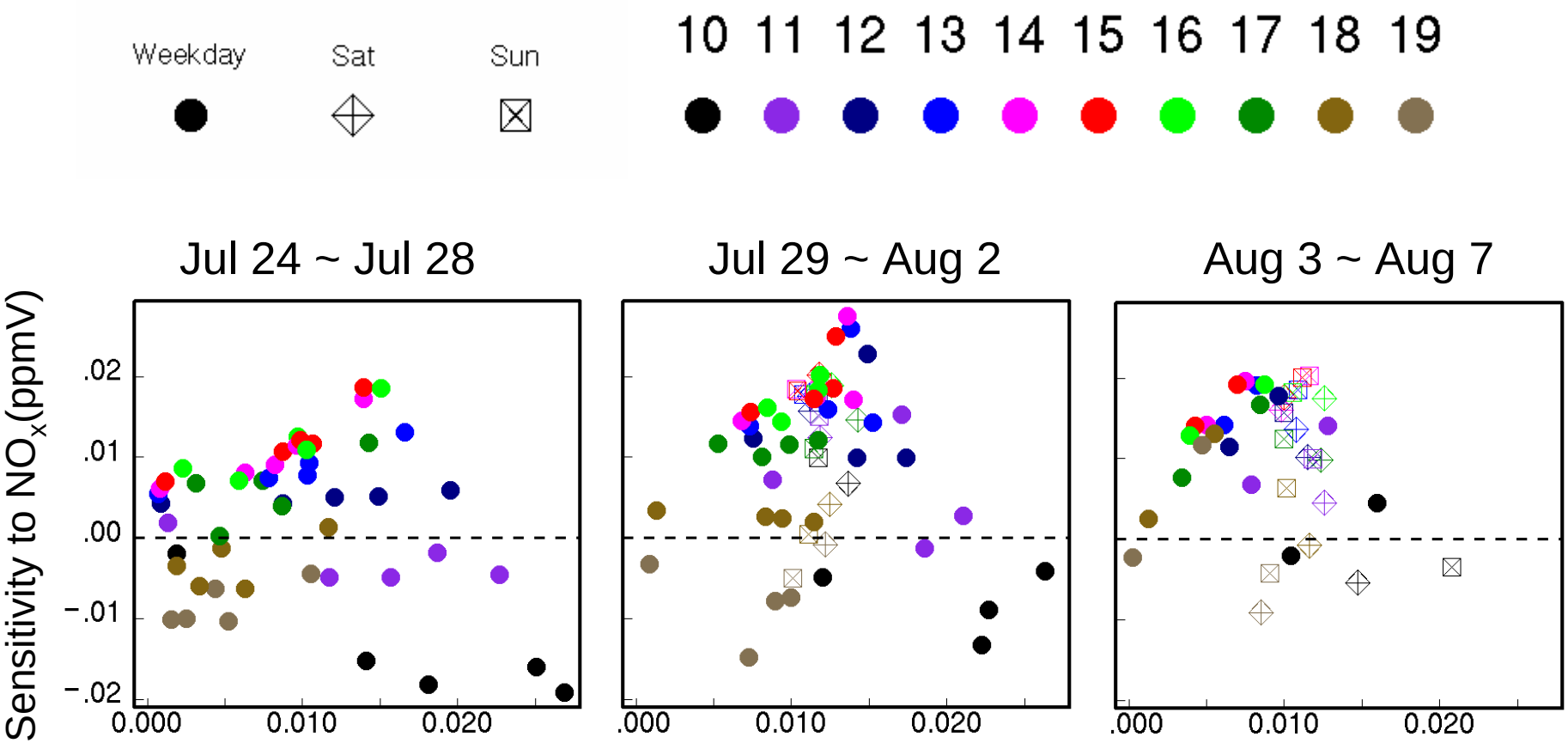
Semi-normalized ozone sensitivity to VOC (ppmV)

Sensitivity Scatter Plot Sequoia in SJV 10 am to 7 pm



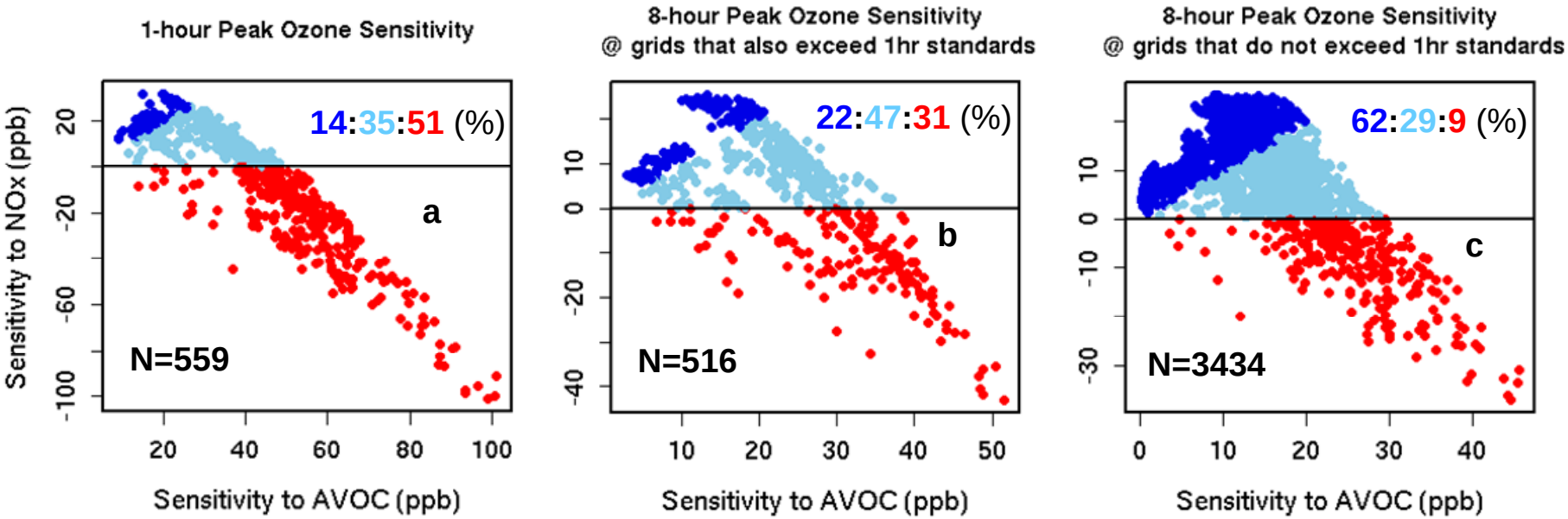
Semi-normalized ozone sensitivity to VOC (ppmV)

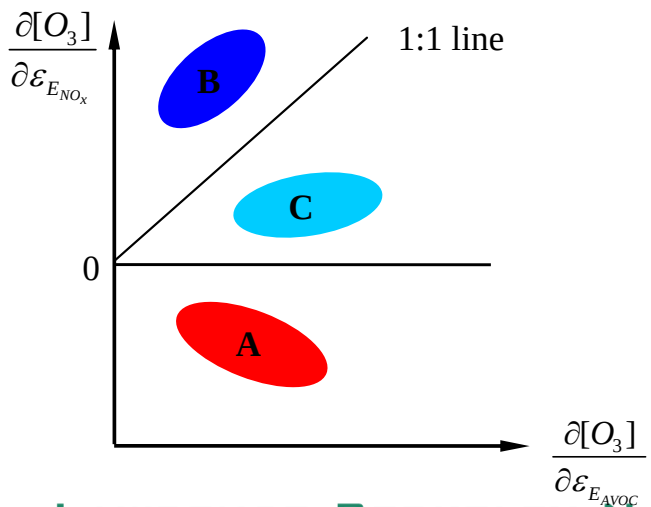
Sensitivity Scatter Plot Bakersfield in SJV 10 am to 7 pm



Semi-normalized ozone sensitivity to VOC (ppmV)

Ozone control options for peak ozone exceedances during 5-day episode





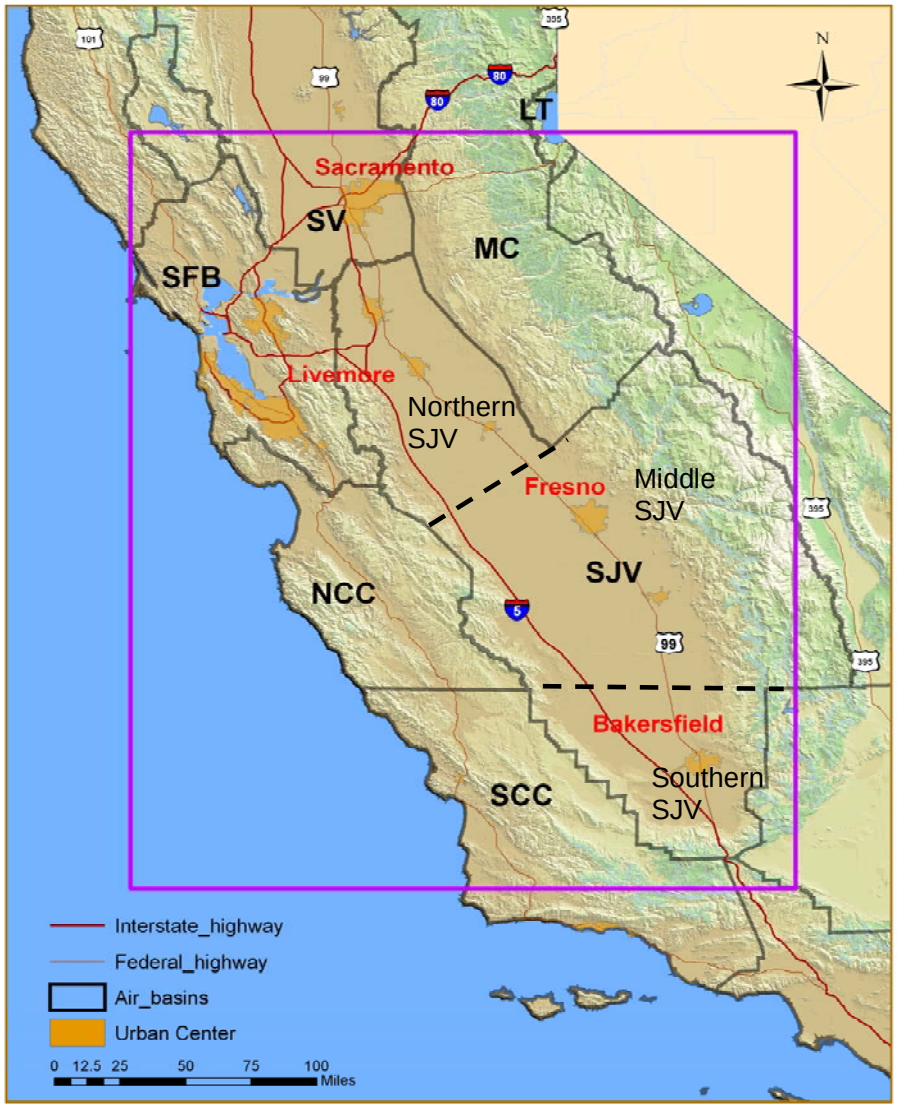
Definition of Ozone control options

A: , VOC control,

B: , NO_x control,

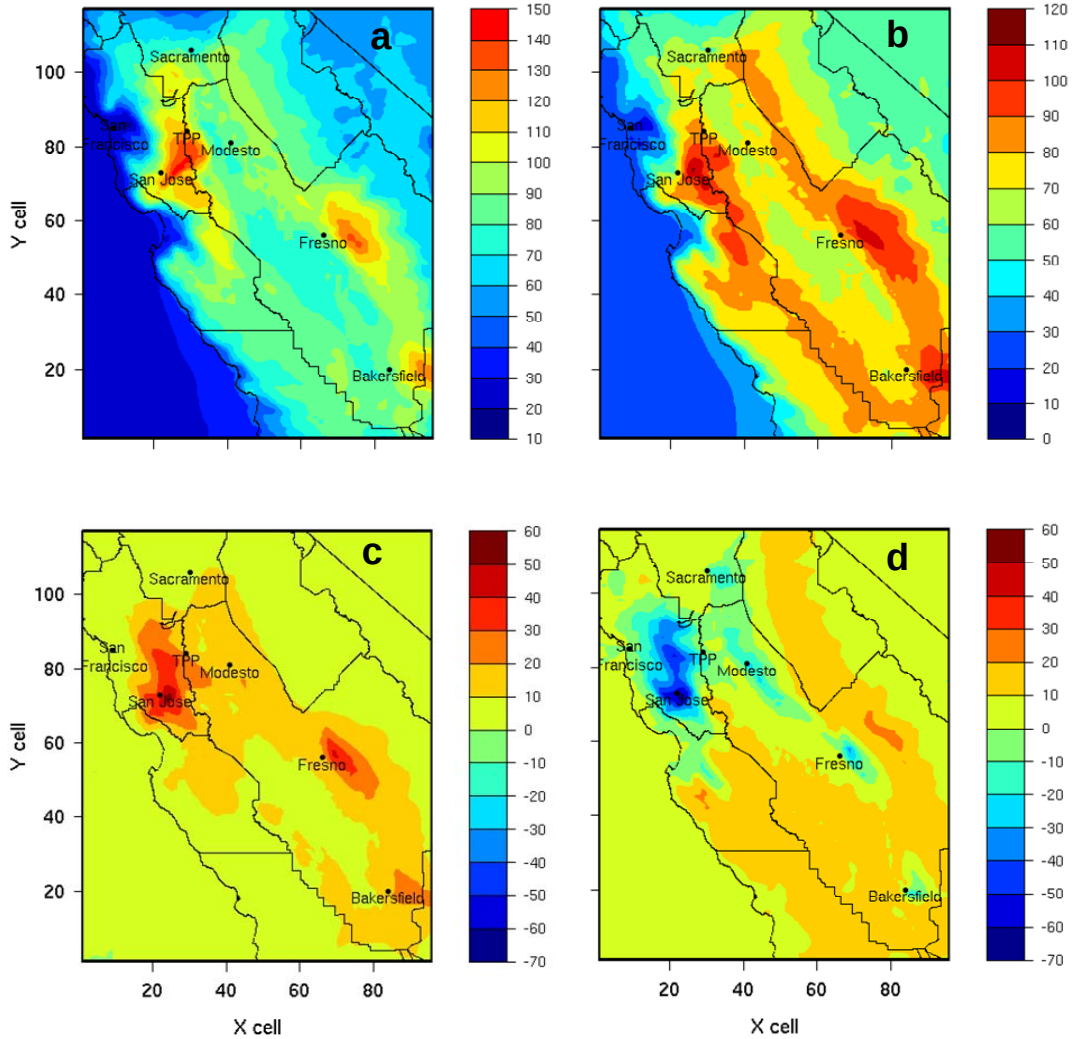
C: , Transition.

Regions of the SJV



Weekday average simulation results

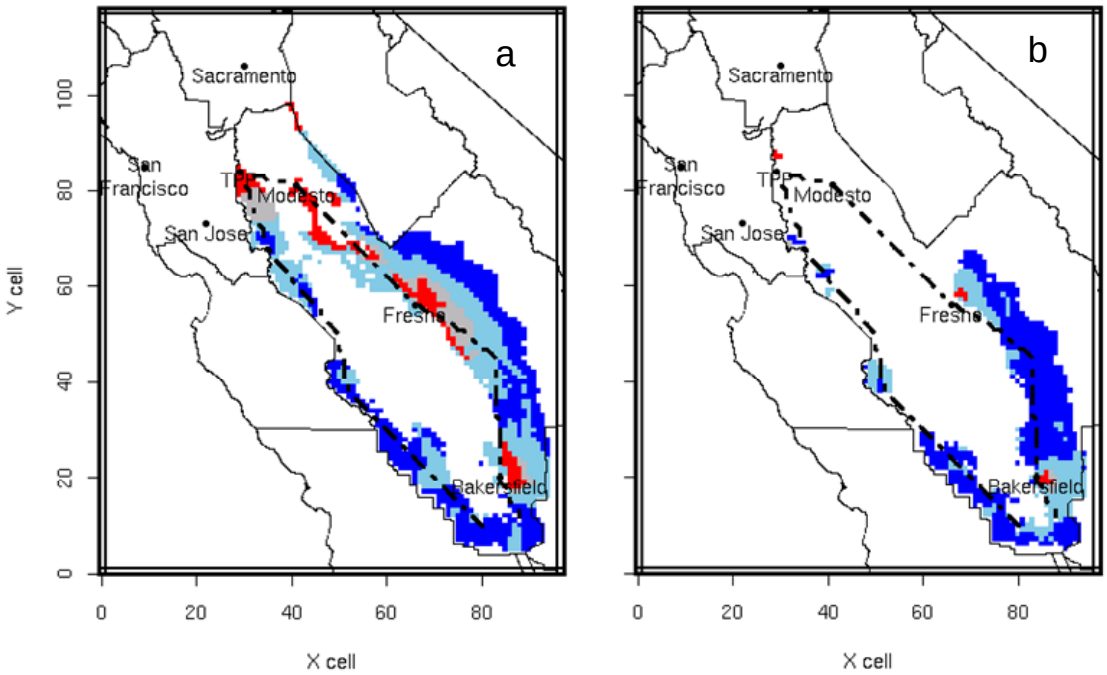
a. 1-hr peak ozone concentrations
b. 8-hr average peak ozone concentrations
c. 8-hr average peak ozone sensitivity to domain wide AVOC emissions,
d. 8-hr average peak ozone sensitivity to domain wide NOx emissions.



Mapping ozone sensitivity options

8-hr peak ozone exceedances in the SJV

Red - Locations always in "VOC control"
Light Blue - NOx control always beneficial
Darker Blue - always in "NOx control" option are coded in blue
Grey - a mixed regime (changes signs) in grey

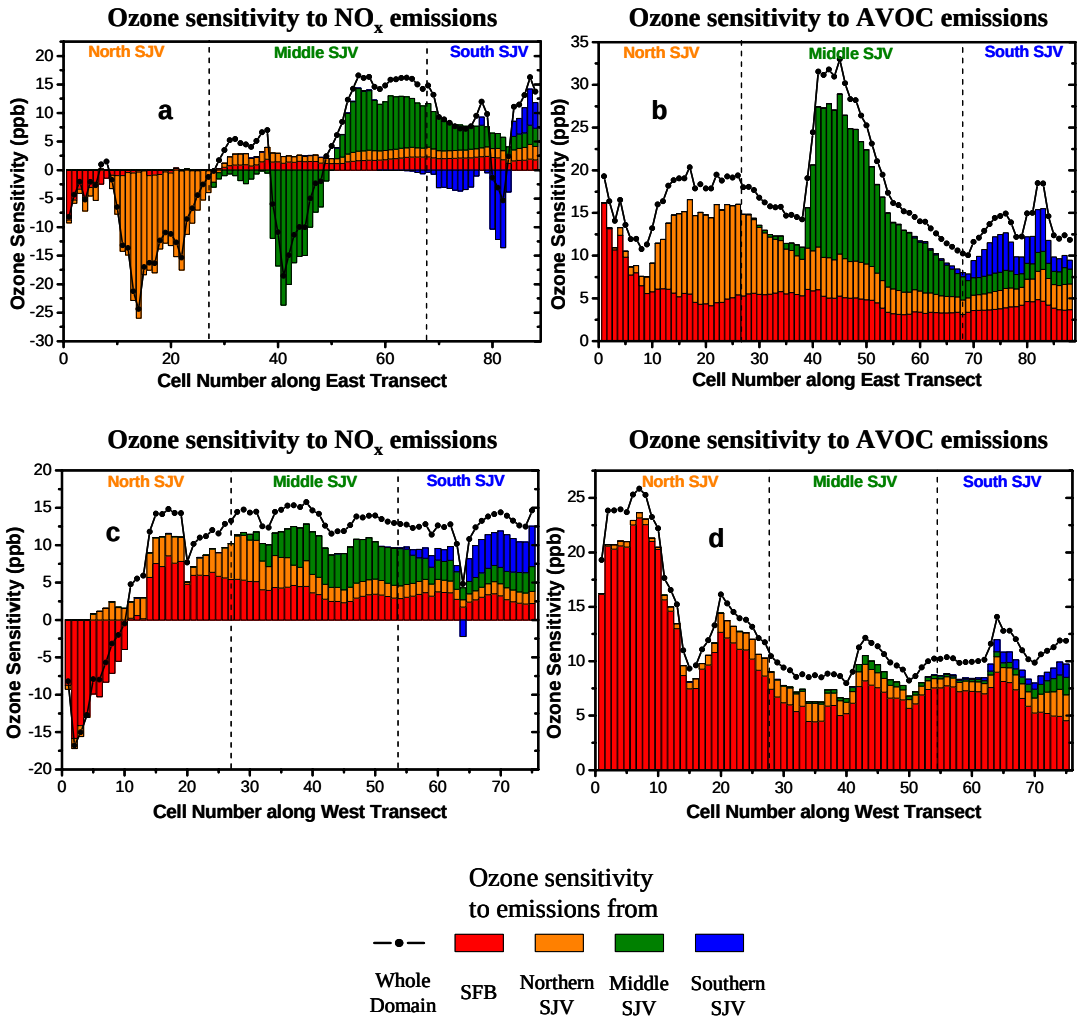


Weekdays Weekends

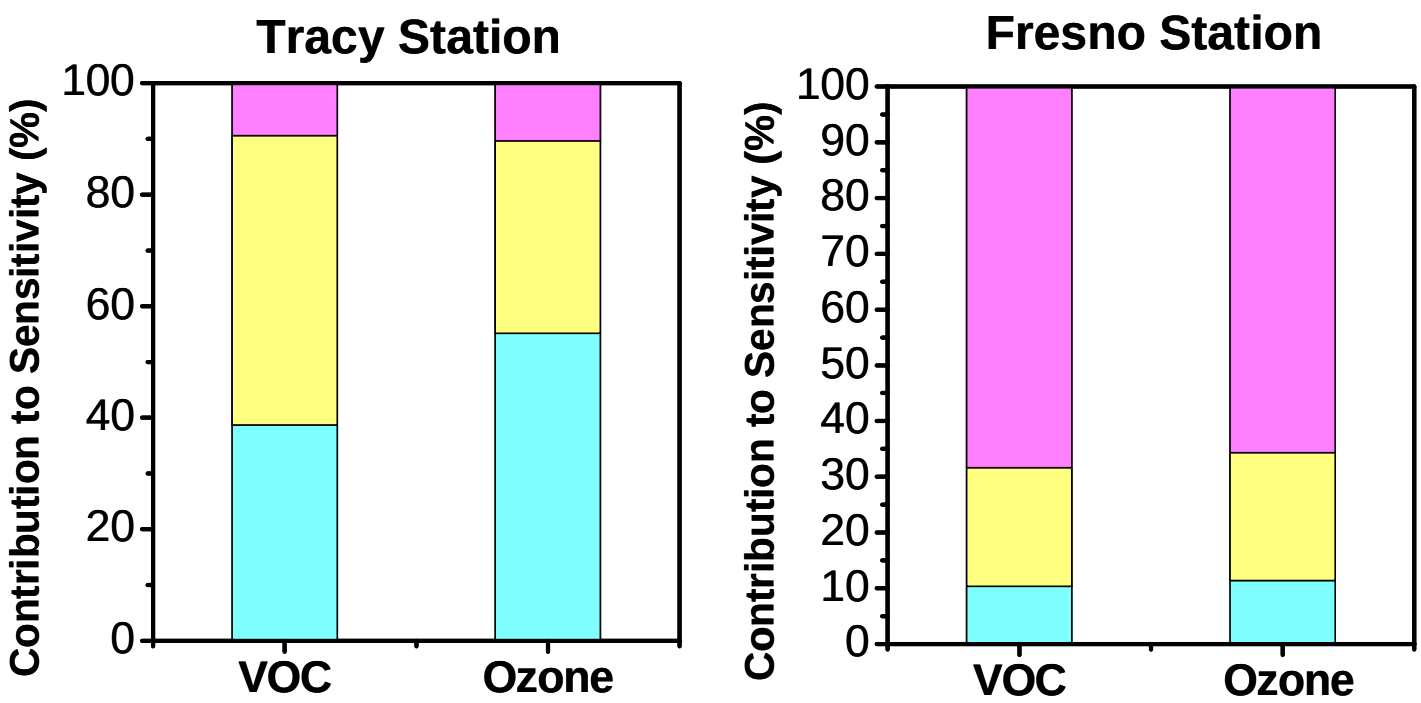
Weekday average 8-hr peak ozone sensitivity

Decomposition of contributions from subregions with respect to:

a. NOx emissions along the east transect;
b. AVOC emissions along the east transect;
c. NOx emissions along the west transect;
d. AVOC emissions along the west transect.



Ozone control options for peak ozone exceedances during 5-day episode

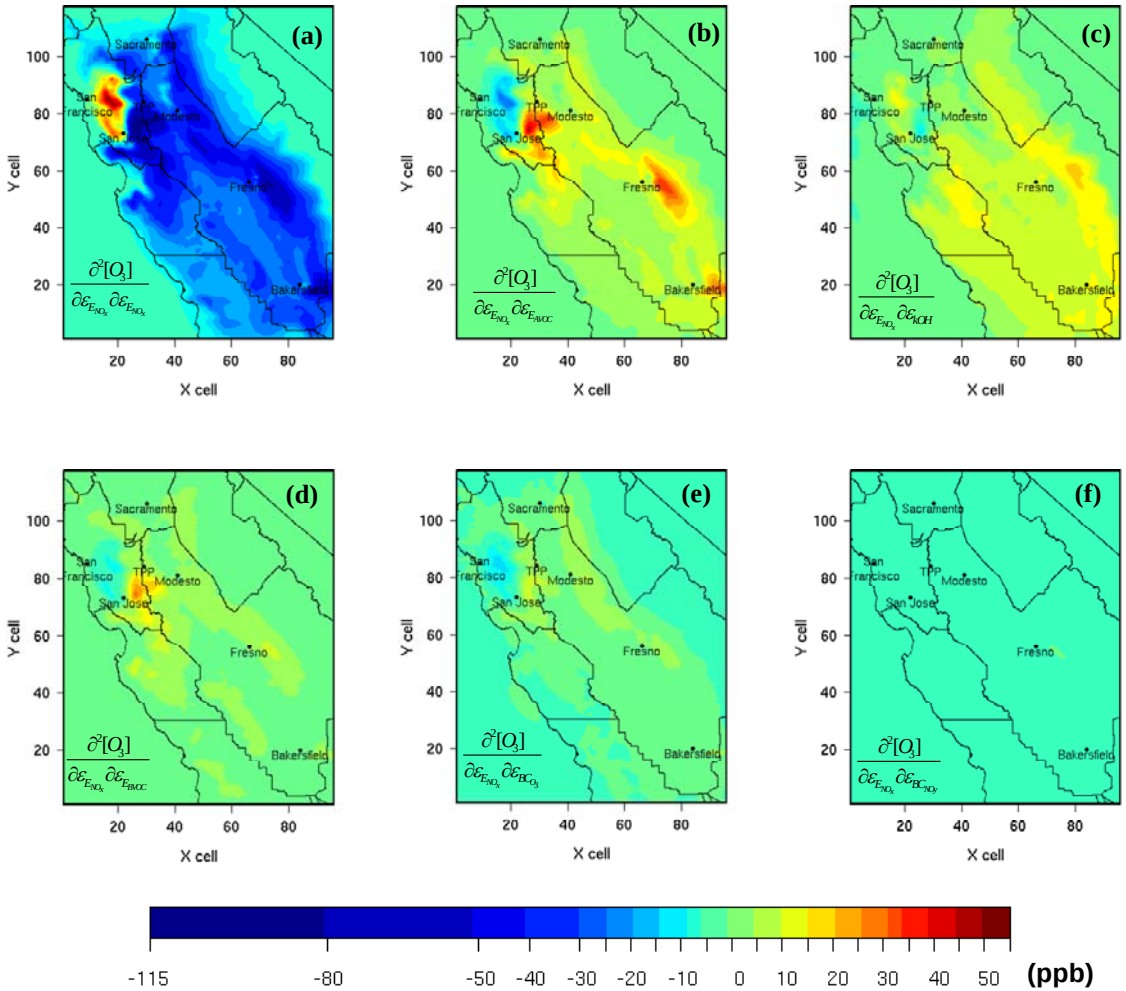


Contributions to (or) from SFB AVOC emitted in the morning (cyan), in the afternoon (yellow), and in the evening (magenta). Results are show at two locations each covering 20 km by 20 km.

Second-order sensitivities of 8-hr peak ozone

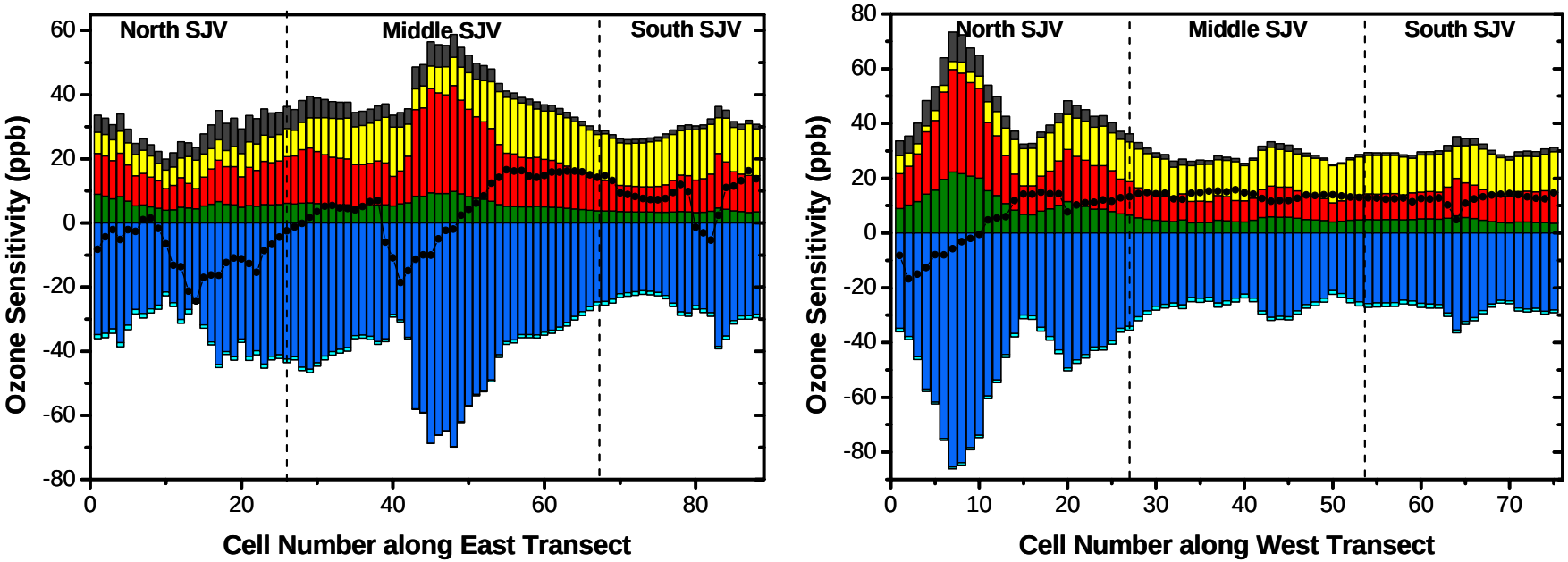
These are sensitivities of "average peak ozone sensitivity with respect to NOx emissions" to

a. NOx emissions
b. AVOC emissions
c. OH+NO_2 rate coefficient
d. BVOC emissions
e. O3 inflow boundary condition
f. NOy inflow boundary condition



Weekday average of second-order sensitivity coefficients

8-hr peak ozone along eastern and western transects.



$$\frac{\partial[O_3]}{\partial\varepsilon_{E_{NO_x}}}$$

$$\frac{\partial^2[O_3]}{\partial\varepsilon_{E_{NO_x}}\partial\varepsilon_{BC_{O_3}}}$$ BC:O_3

$$\frac{\partial^2[O_3]}{\partial\varepsilon_{E_{NO_x}}\partial\varepsilon_{BC_{NO_y}}}$$ BC:NO_x

$$\frac{\partial^2[O_3]}{\partial\varepsilon_{E_{NO_x}}\partial\varepsilon_{kOH}}$$ kOH

$$\frac{\partial^2[O_3]}{\partial\varepsilon_{E_{NO_x}}\partial\varepsilon_{E_{NO_x}}}$$ E:NOx

$$\frac{\partial^2[O_3]}{\partial\varepsilon_{E_{NO_x}}\partial\varepsilon_{E_{AVOC}}}$$ E:AVOC

$$\frac{\partial^2[O_3]}{\partial\varepsilon_{E_{NO_x}}\partial\varepsilon_{E_{BVOC}}}$$ E:BVOC

Future Research

- **Extend the sensitivity studies to other periods that have interesting ozone producing characteristics:**
  - **Weekdays versus weekends**
  - **Different meteorologies**

Conclusions

- **Developed a new code for sensitivity analysis that includes chemical rate sensitivities and the computation of second-order coefficients.**
- **Developed a formal sensitivity analysis approach that is useful for characterizing :**
  - **the change of limiting reagents in time and space**
  - **Intra- and inter-basin transport**
  - **how sensitivities change due to uncertainties in important parameters**

- **Provided a brief overview of future directions.**

Conclusions (con'td)

- Eastern transect: Local emissions dominate ozone response
- Western transect (WT): Bay area emissions influence locations further downwind.
- WT: Bay area NOx emissions influence ozone response in the northern SJV and Bay area AVOC emissions influence ozone throughout the SJV
- Emission timing is important
- Uncertainties in NOx, AVOCs, and k_{OH+NO2} are most influential on NOx sensitivities.