

# Analysis of a Photochemical Reaction Mechanism Using the Adjoint Sensitivity Analysis Procedure

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# Acknowledgments

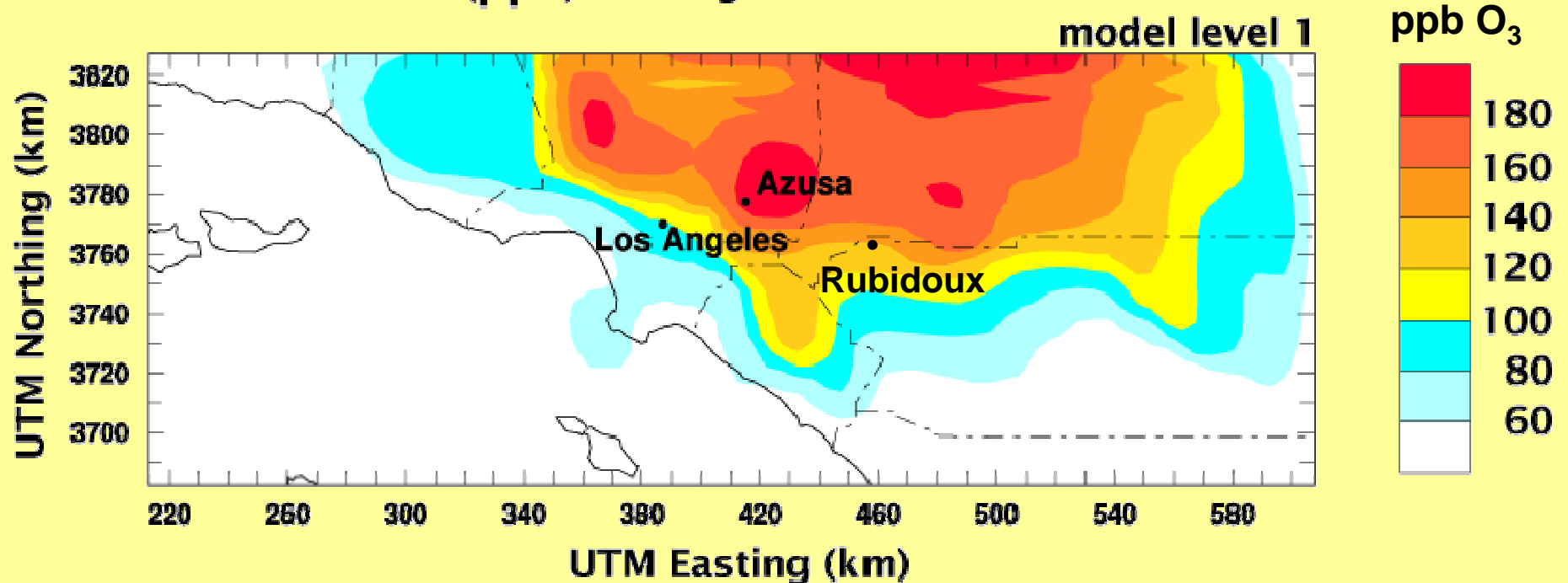
- Robert Harley, UCB
- Jana Milford, U. Colorado
- Dan Cacuci, UCB
- California Air Resources Board
- Bay Area Air Quality Management District

# Research Objectives

- Use sensitivity analysis to
  - Identify influential model inputs & parameters
  - Map source regions that affect air quality at specific receptors
- Investigate effects of emission changes on atmospheric chemistry in southern California

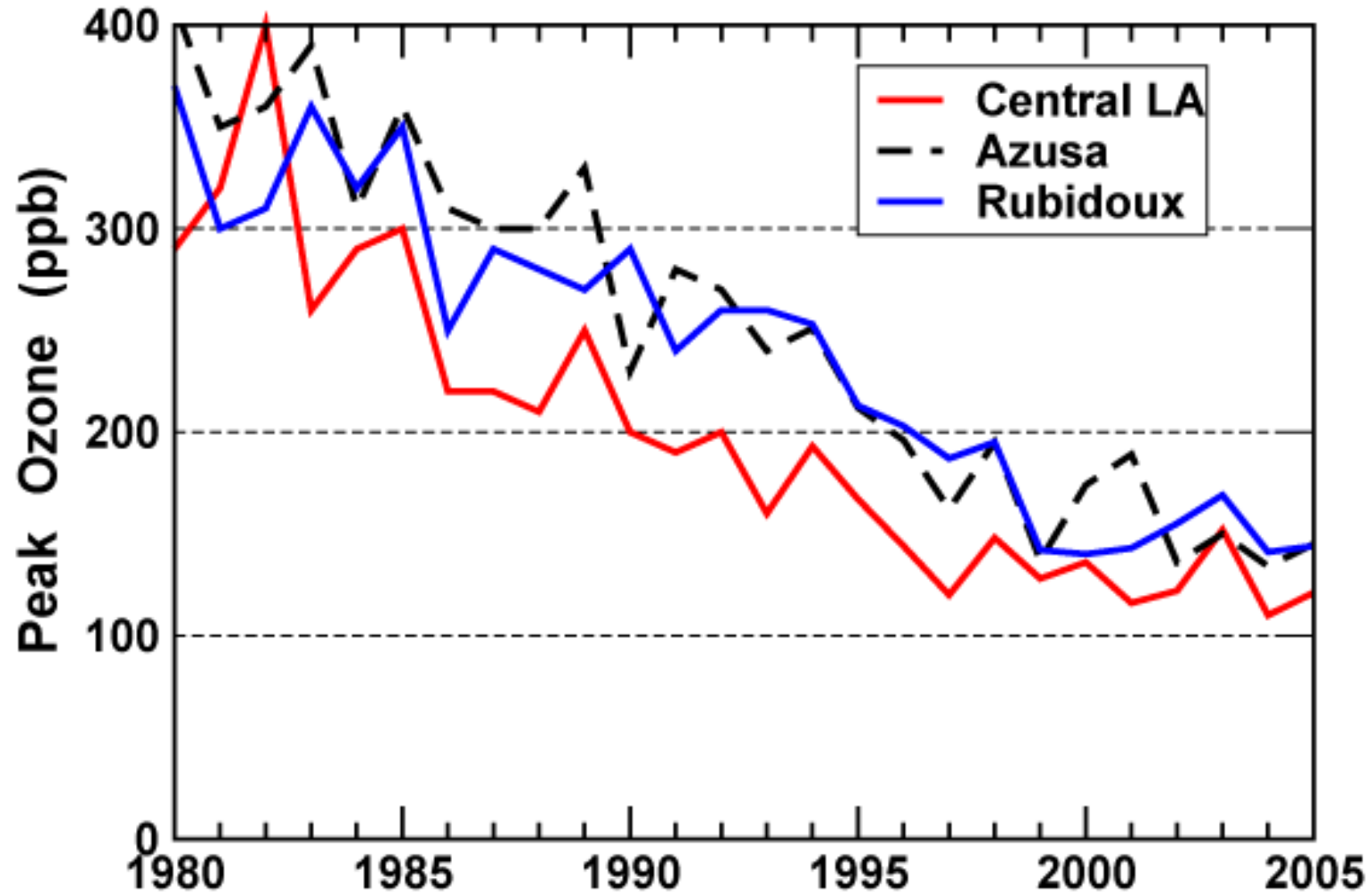
# Predicted O<sub>3</sub> in Southern California

Ozone (ppb) at 25 Jun 1987 1200 PST

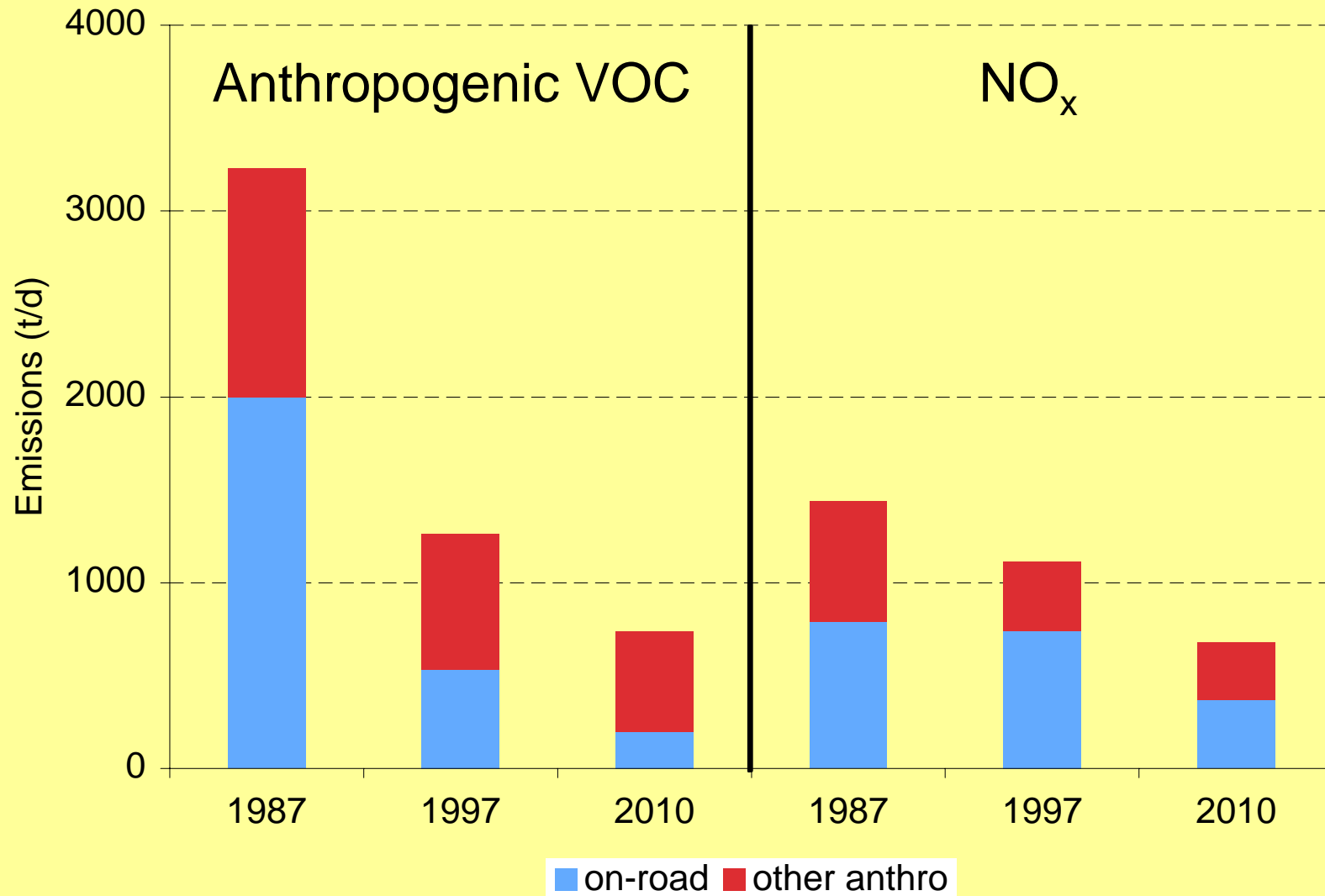


- 3-D Photochemical Model
- Augmented SAPRC99 chemical mechanism:  
100 species and 243 reactions

# Observed O<sub>3</sub> Trends

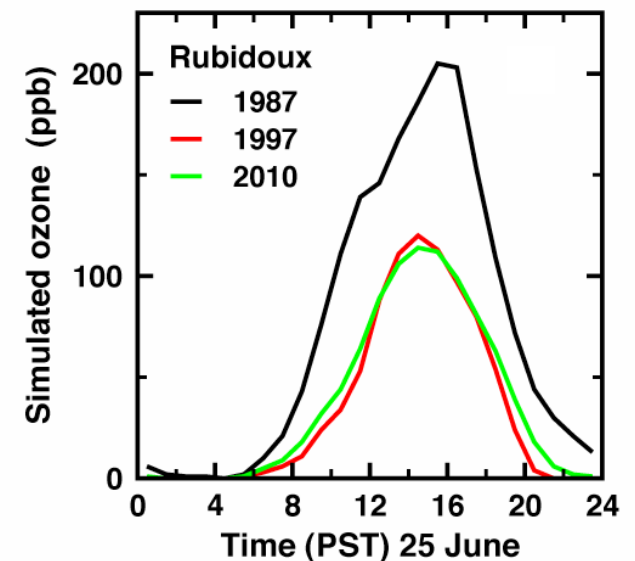
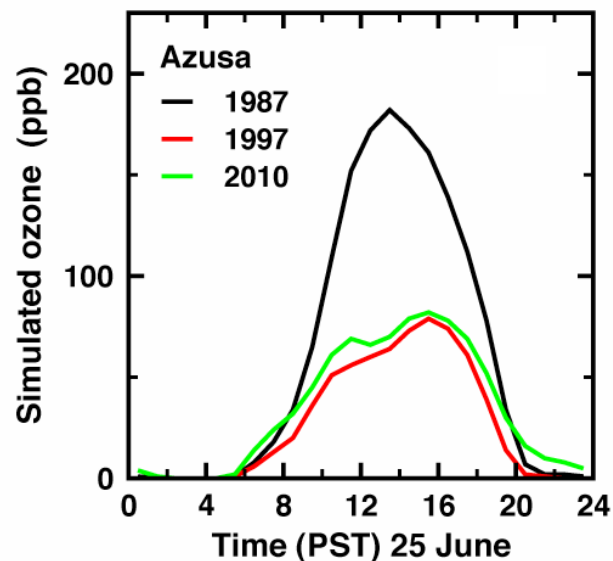
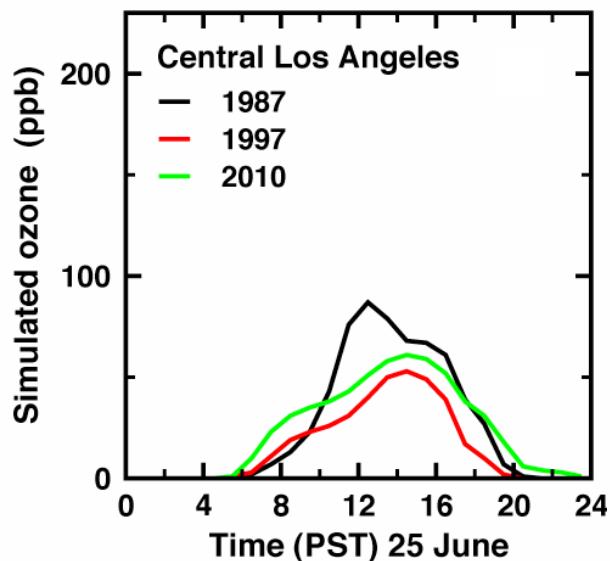


# Emission Scenarios



Sources: Harley et al. (*ES&T* 1997) for 1987; 2003 AQ Plan for 1997 & 2010

# Predicted O<sub>3</sub> Response to Emission Changes



- How do model sensitivities vary with changes in emissions?

# Sensitivity Analysis

- What is model sensitivity to input data?

$$S_{ij} = \frac{\partial C_i}{\partial \lambda_j}$$

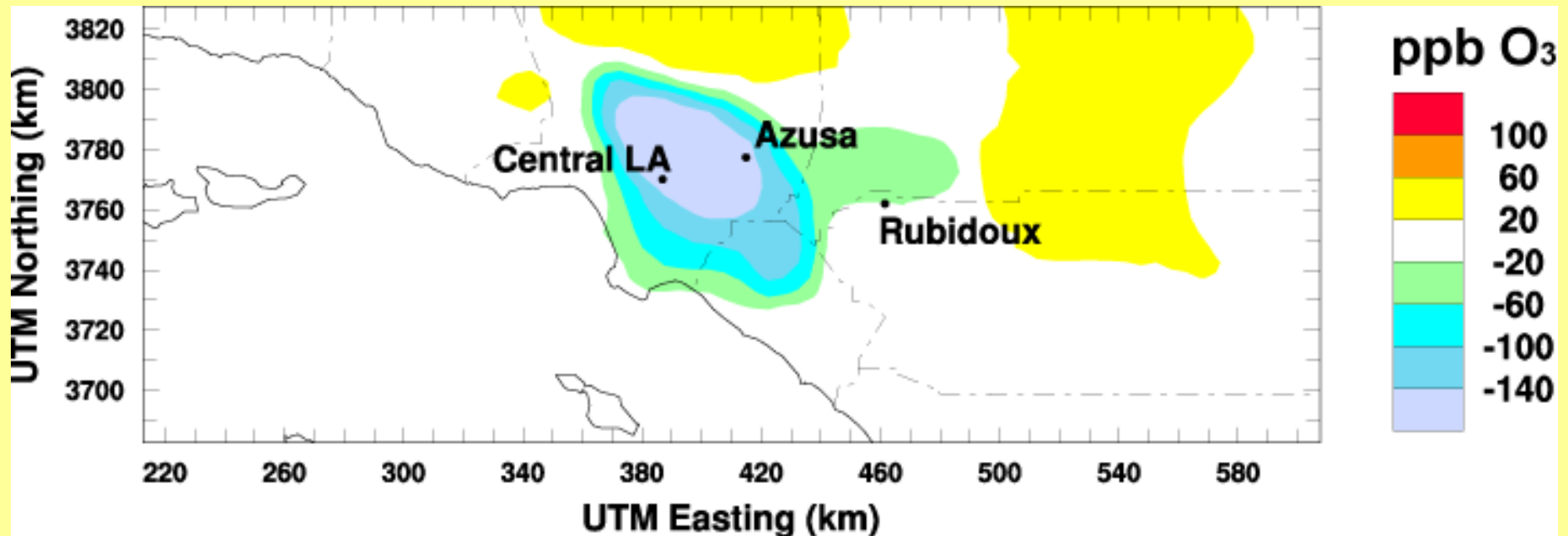
- Three emission scenarios (1987, 1997, 2010)
- Sensitivities to BCs, ICs, emissions, chemical rate coefficients, and deposition velocities
- Can be 100s to 1000s of sensitivities. How to calculate?

# Calculating Sensitivities

- Brute-force method:
  - Rerun model, compute  $\Delta O_3 / \Delta \lambda$
- Decoupled, direct method (DDM):
  - Solve extra model equations to calculate sensitivity along with concentrations
  - Produce source-based sensitivity
- Adjoint sens. analysis procedure (ASAP):
  - Solve extra model equation similar to DDM
  - Solve backward in time
  - Produce receptor-based sensitivity

# Decoupled, Direct Method

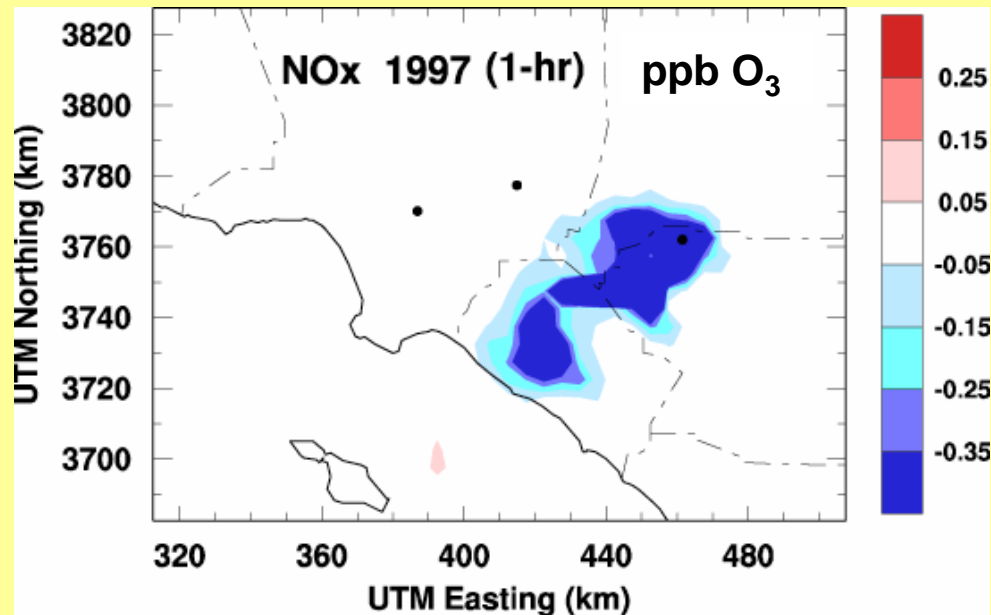
## O<sub>3</sub> Sensitivity to NO<sub>x</sub> Emissions



- Direct method efficiently computes sensitivities for:
- a few model inputs/parameters
  - many model responses (times, locations, species)

# Adjoint Sensitivity Analysis Procedure

Contributions to sensitivity of  $O_3$  peak at Rubidoux to  $e_{NOx}$

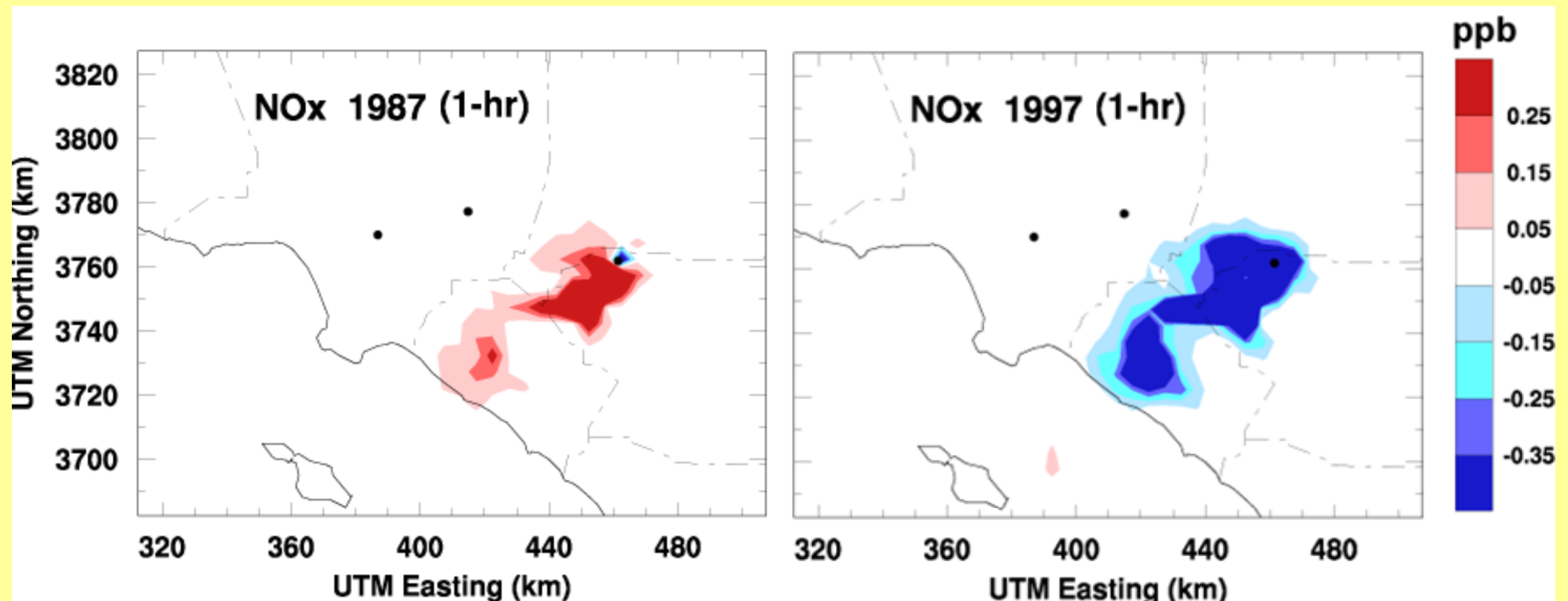


Adjoint method efficiently computes sensitivities for:

- many model inputs/parameters
- a few model responses

# Sensitivity Apportionment

Contributions to sensitivity of  $O_3$  peak at Rubidoux to  $e_{NOx}$

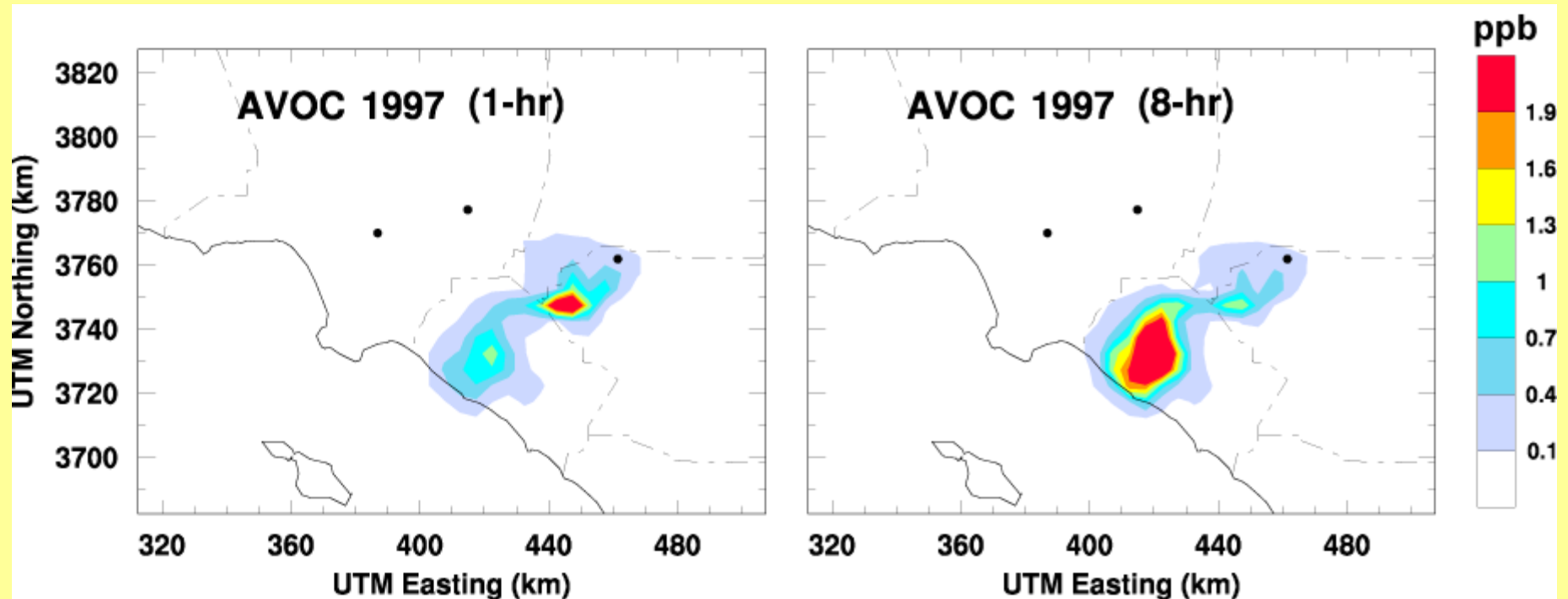


1987

1997

# Sensitivity Apportionment

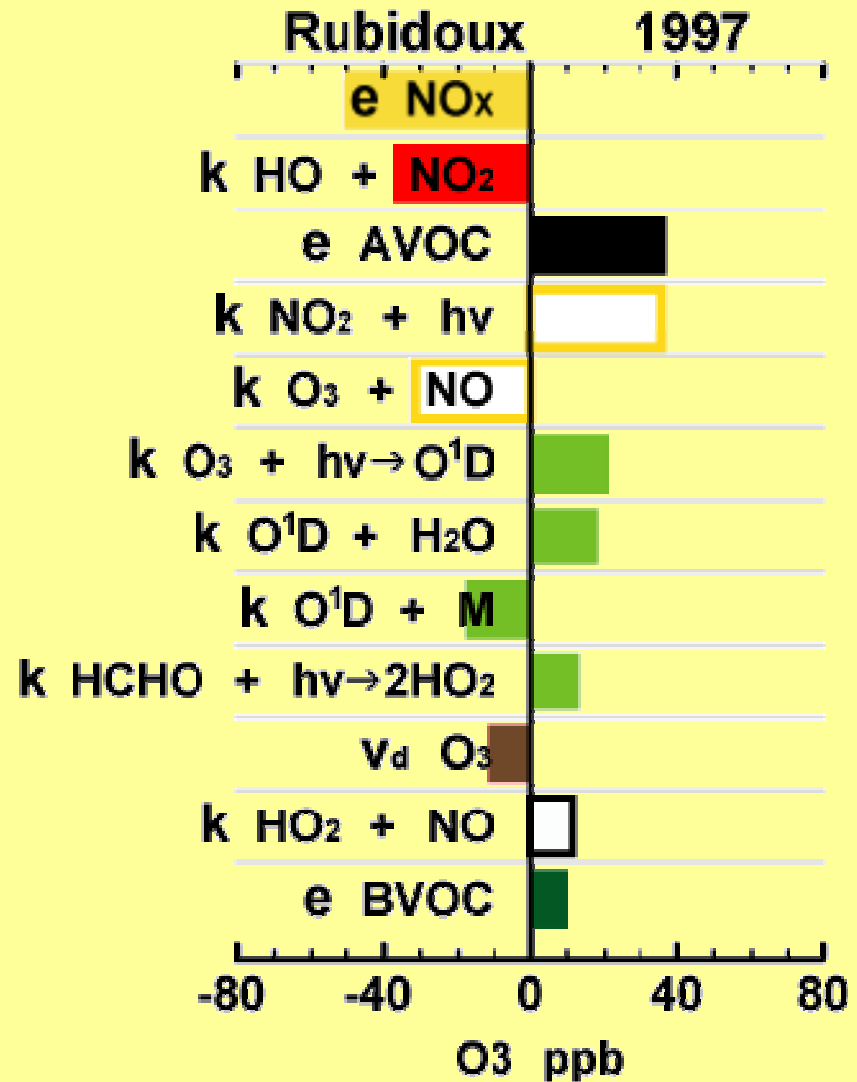
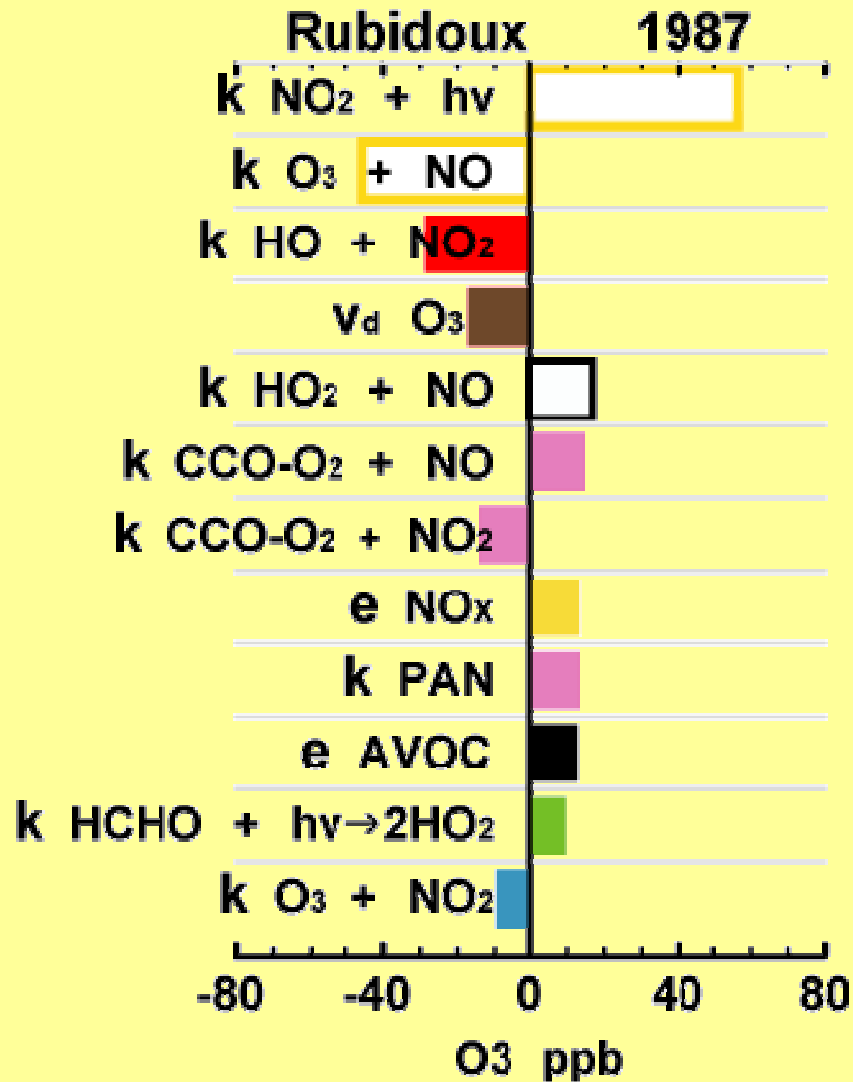
Contributions to sensitivity of  $O_3$  peak at Rubidoux to  $e_{AVOC}$



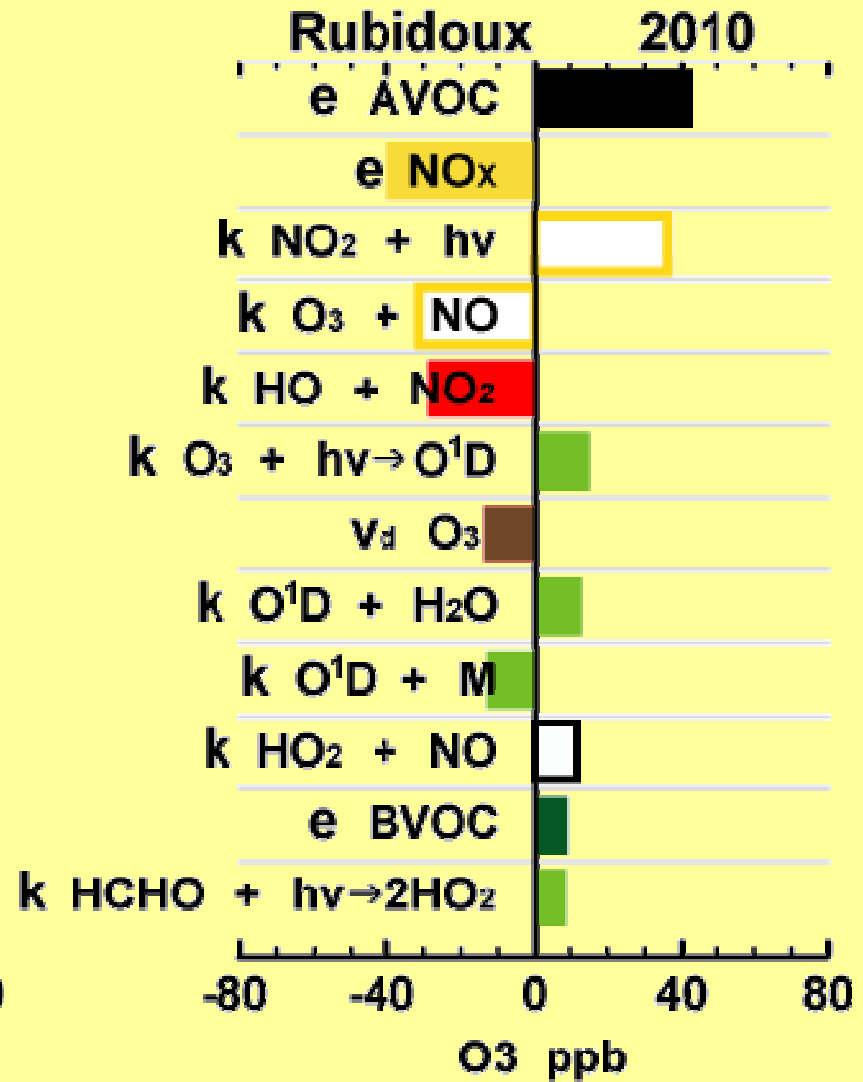
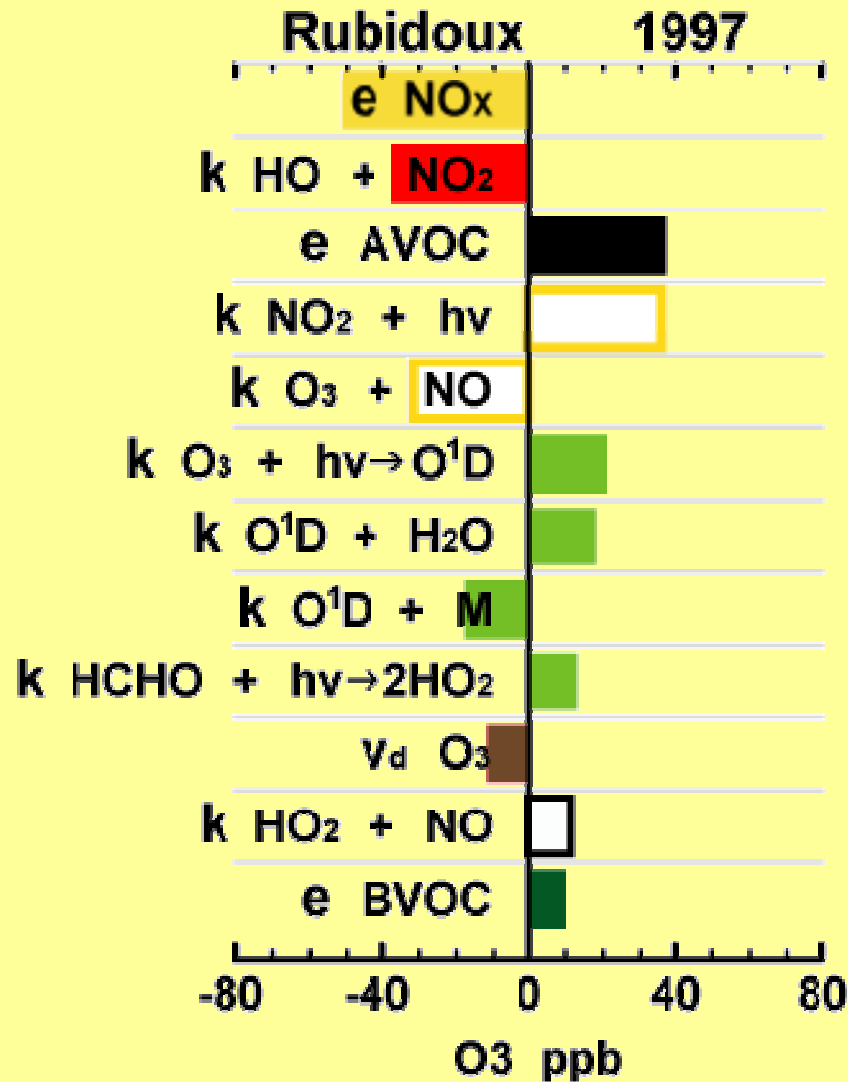
1-hour peak  $O_3$

8-hour peak  $O_3$

# O<sub>3</sub> Sensitivity (Ranked)



# O<sub>3</sub> Sensitivity (Ranked)

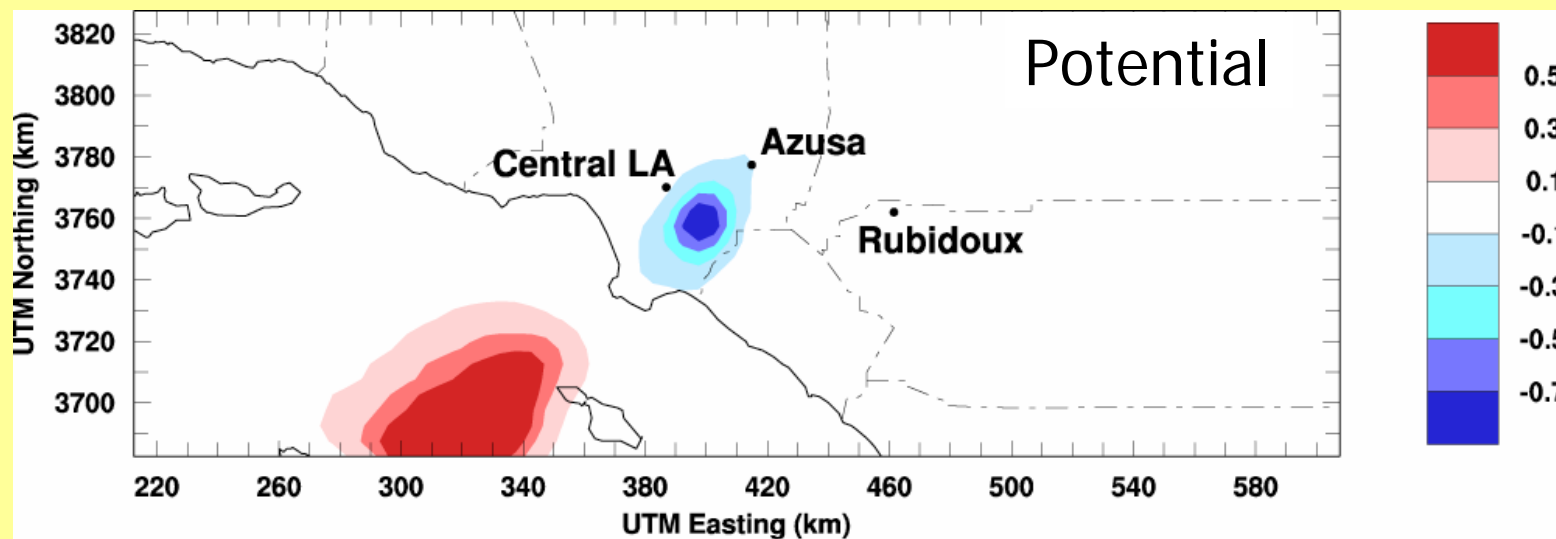
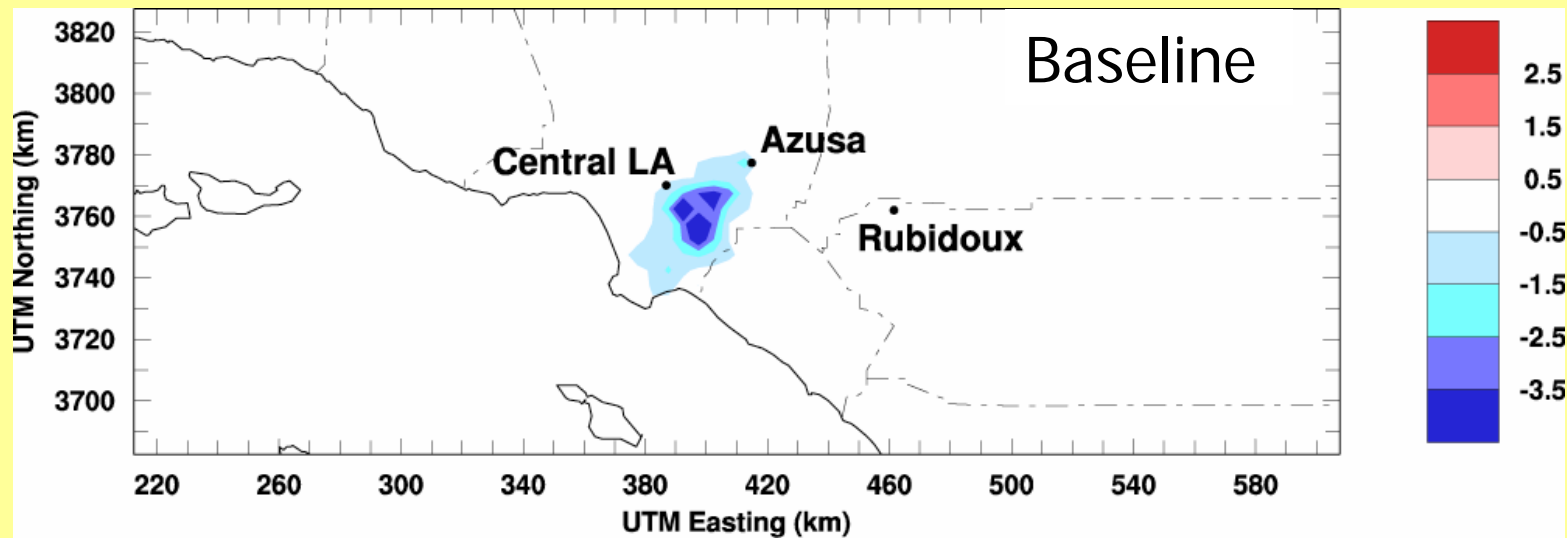


# Potential Sensitivity

- Previous results show effects of multiplicative scaling of parameters  $\lambda_j$ 
  - Perturbation is proportional to existing parameter
  - Produces “baseline” sensitivity
- Can also calculate sensitivity to additive perturbations to  $\lambda_j$ 
  - Perturbation is constant in space & time
  - Produces “potential” sensitivity
  - Example: effects of adding emissions where  $e = 0$  in base case?

# Baseline vs. Potential Sensitivity

Sensitivity of peak  $O_3$  at Azusa to  $e_{NOx}$



# Summary

- Used adjoint method to study  $O_3$  sensitivity to ~900 parameters (BC, IC,  $e$ ,  $k$ ,  $v_d$ )
- Southern California  $O_3$  most sensitive to
  - $e$  (AVOC &  $NO_x$ )
  - $J_{NO_2}$ ,  $k_{O_3+NO}$ ,  $k_{OH+NO_2}$
- Mapped source regions that do (or could) influence specific air quality measures
- Control of  $NO_x$  and VOC precursors
  - shifts the sensitivities of  $O_3$  production
  - alters the contribution of source regions