Overview of Ozone/VOC/NO_x Production and Transport in Northern/Central California

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Workshop on Passive Catalytic Oxidation of Air Pollution

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Overview

- Ozone: Sources, Sinks
- Two slides about modeling ozone
- Ozone chemistry - simplified picture
- Emissions of Ozone Precursors
- Sensitivity to Precursor Emissions
- Points of Relevance to Catalytic Oxidation

Ozone: Sources, Sinks (1)

- Secondary pollutant by photochemical reactions:

$$NO_x + VOC + sunlight \rightarrow O_3$$

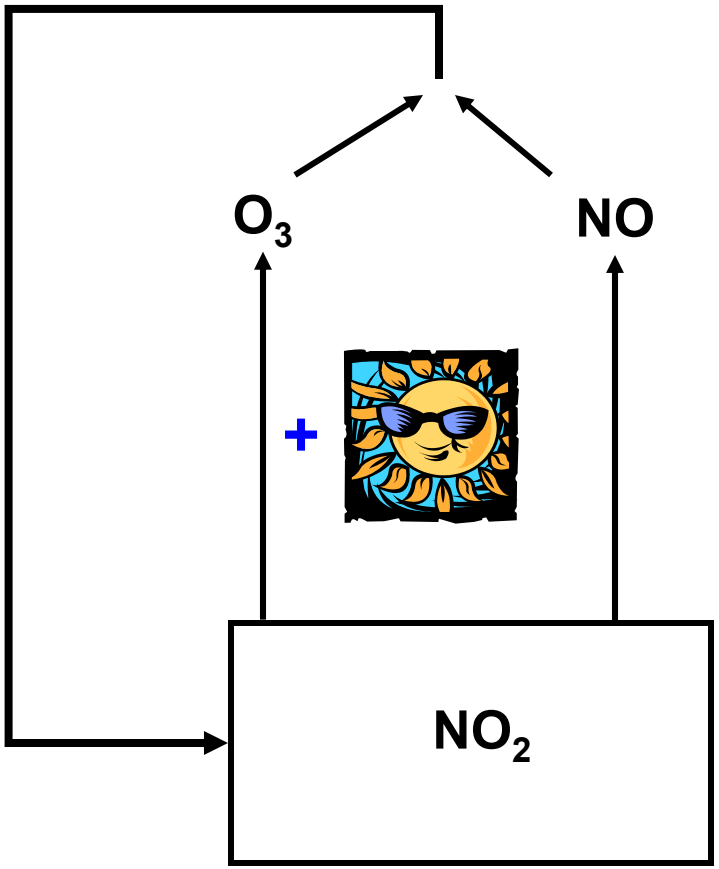
- Concentrations on a good day ~20-40 ppb
- A bad day: 120-150ppb (http://www.arb.ca.gov/aqd/aqinfo.htm)
- US EPA limit: Peak ozone ≥ 120ppb in any given hour or ozone ≥ 80ppb averaged in any 8-hour window

Ozone: Sources, Sinks (2)

- Human health
- Agricultural health

- Lifetime in atmosphere about 1 week, destroyed by photolyis:
  - $O_3 + h\nu \rightarrow O_1D$ followed by
  - $O_1d + H_2O \rightarrow 2\ OH$
- Also dry deposition to surface

O_3 Production



$NO_2 + h\nu \rightarrow O + NO$

followed by

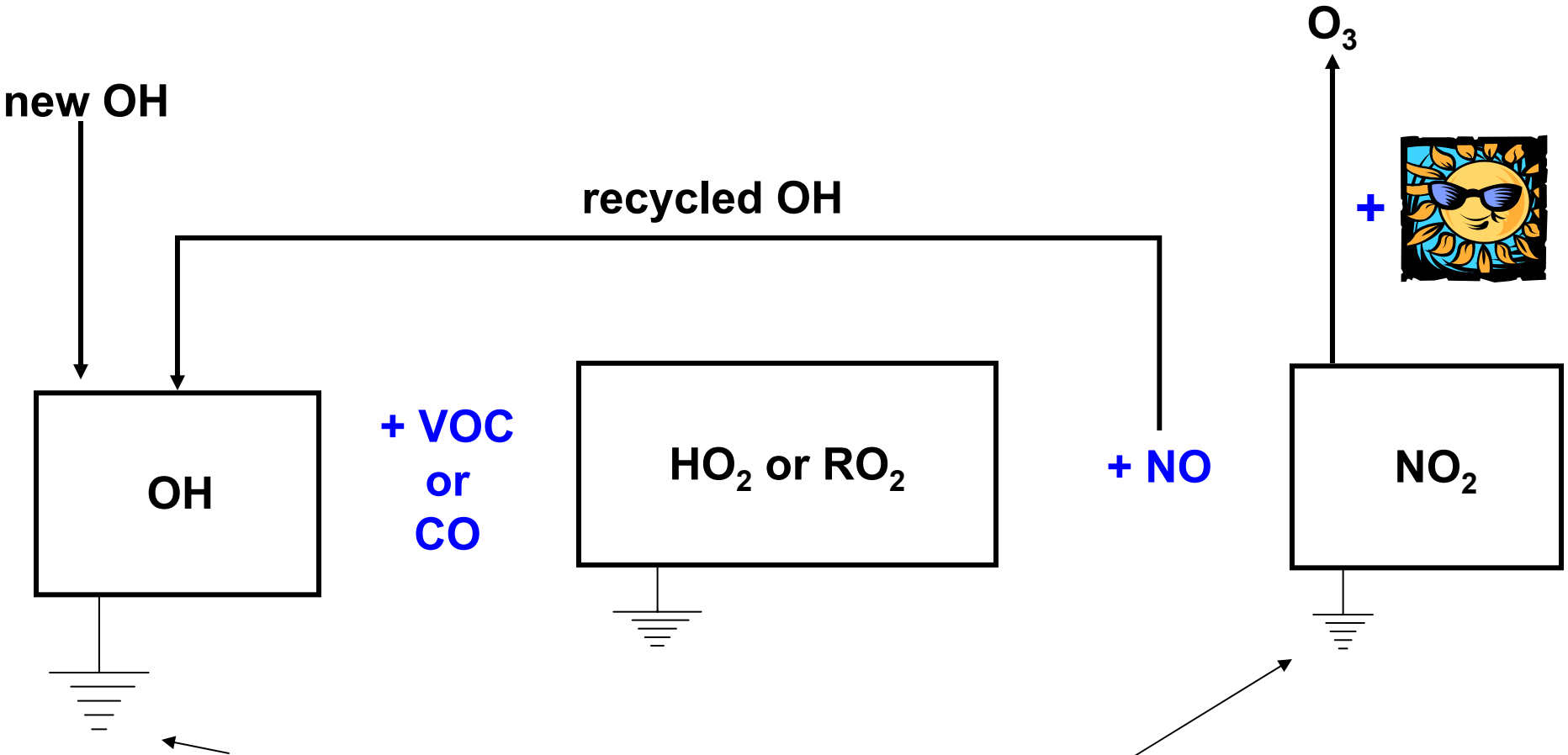
$O + O_2 \rightarrow O_3$

and

$O_3 + NO \rightarrow NO_2 + O_2$

…..should not see more than about 50ppb if this is all there is.

O_3 Production



Termination reaction $OH+NO_2 \rightarrow HNO_3$
(talk later)

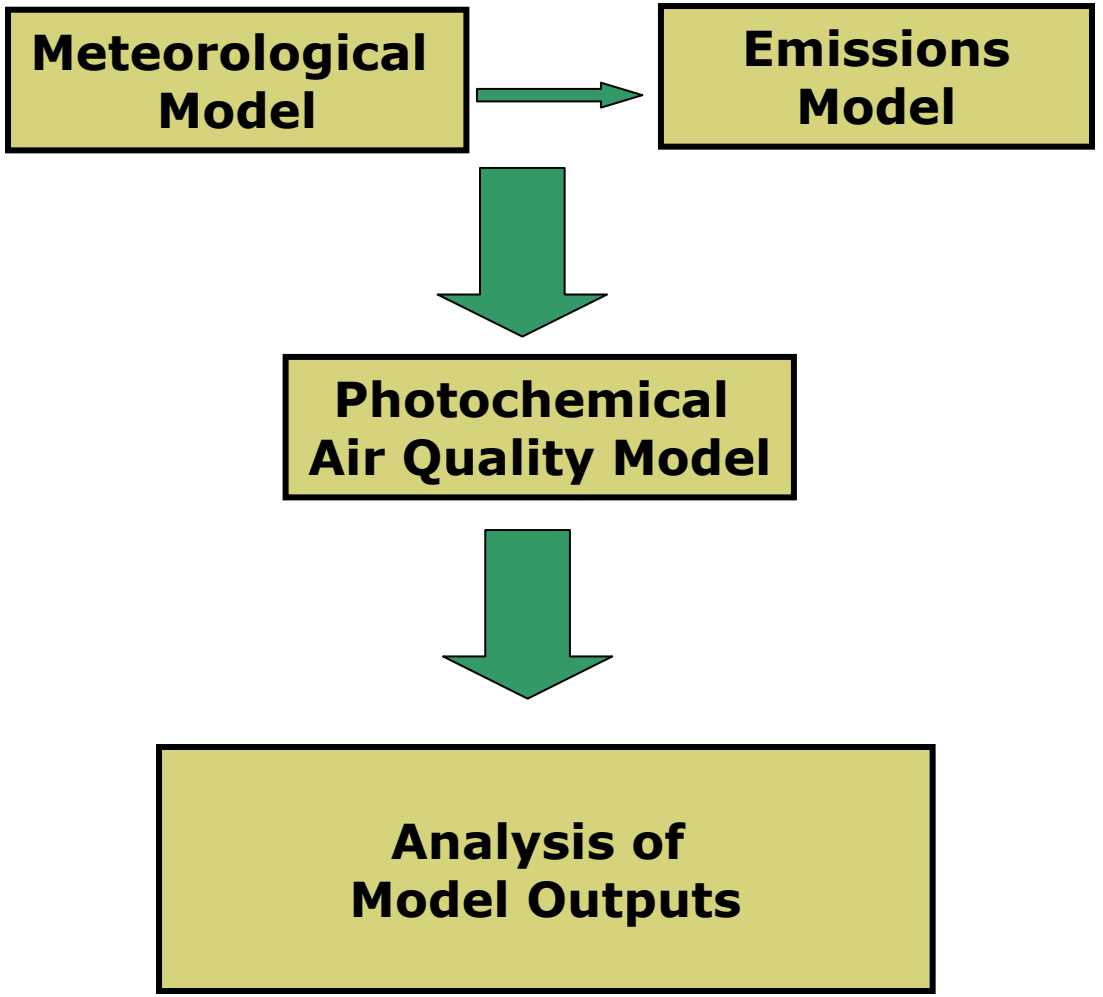
VOCs are key to conversion of NO to NO_2 without destruction of an O_3 molecule in the process

Modeling Approach

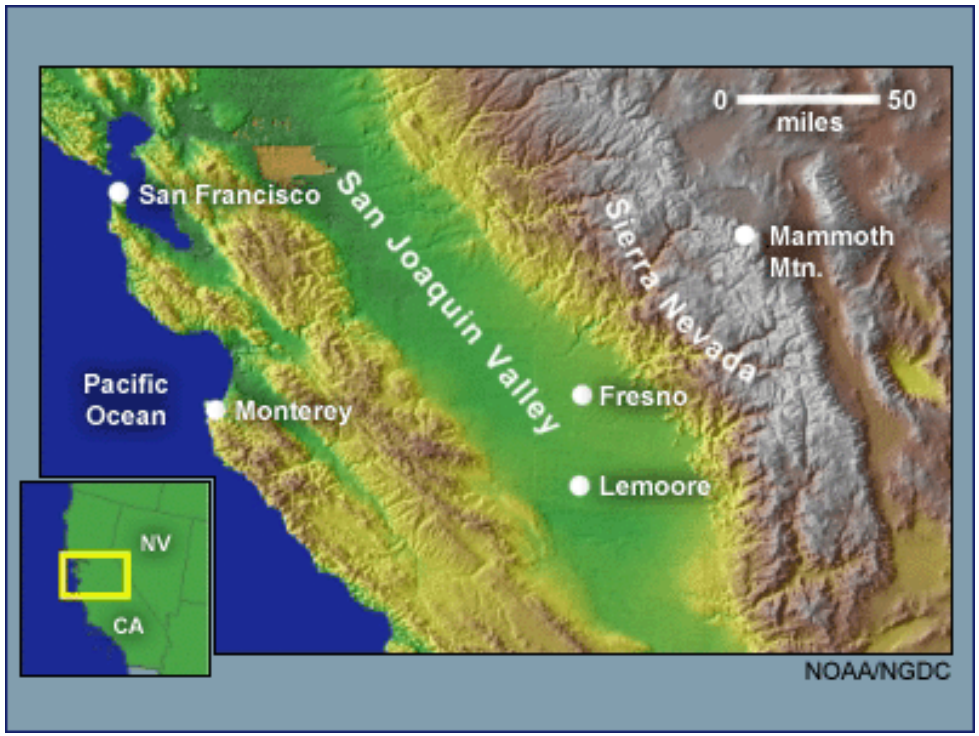
CMAQ Model: 3D advective/diffusive transport and photo-chemistry code

SAPRC99 gas phase mechanism (72 lumped and individual species, 250 reactions)

Cells 4km to a side
96 cells east-west
117 cells north-south
27 vertical layers from up to 16km

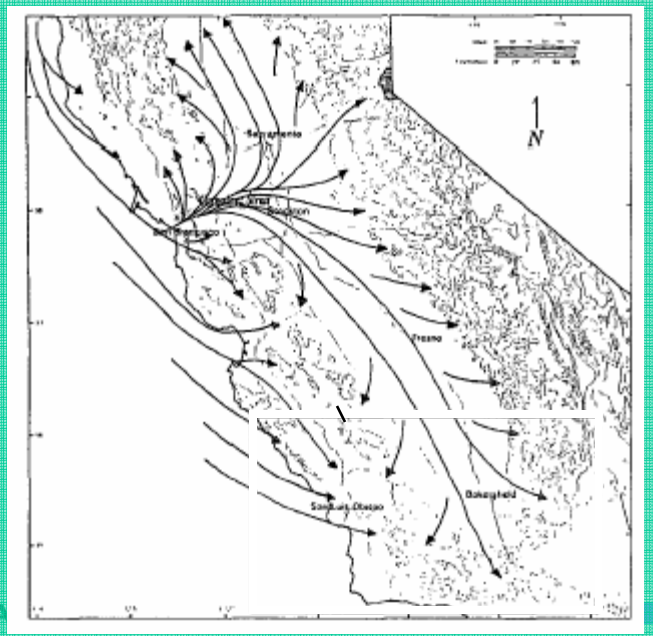


Geography of the Study Area



The SJV is surrounded by the Diablo and Coast Ranges on the west and the Sierra Nevada foothills on the east.

The predominant summer wind flow pattern



Niccum *et al.* 1995

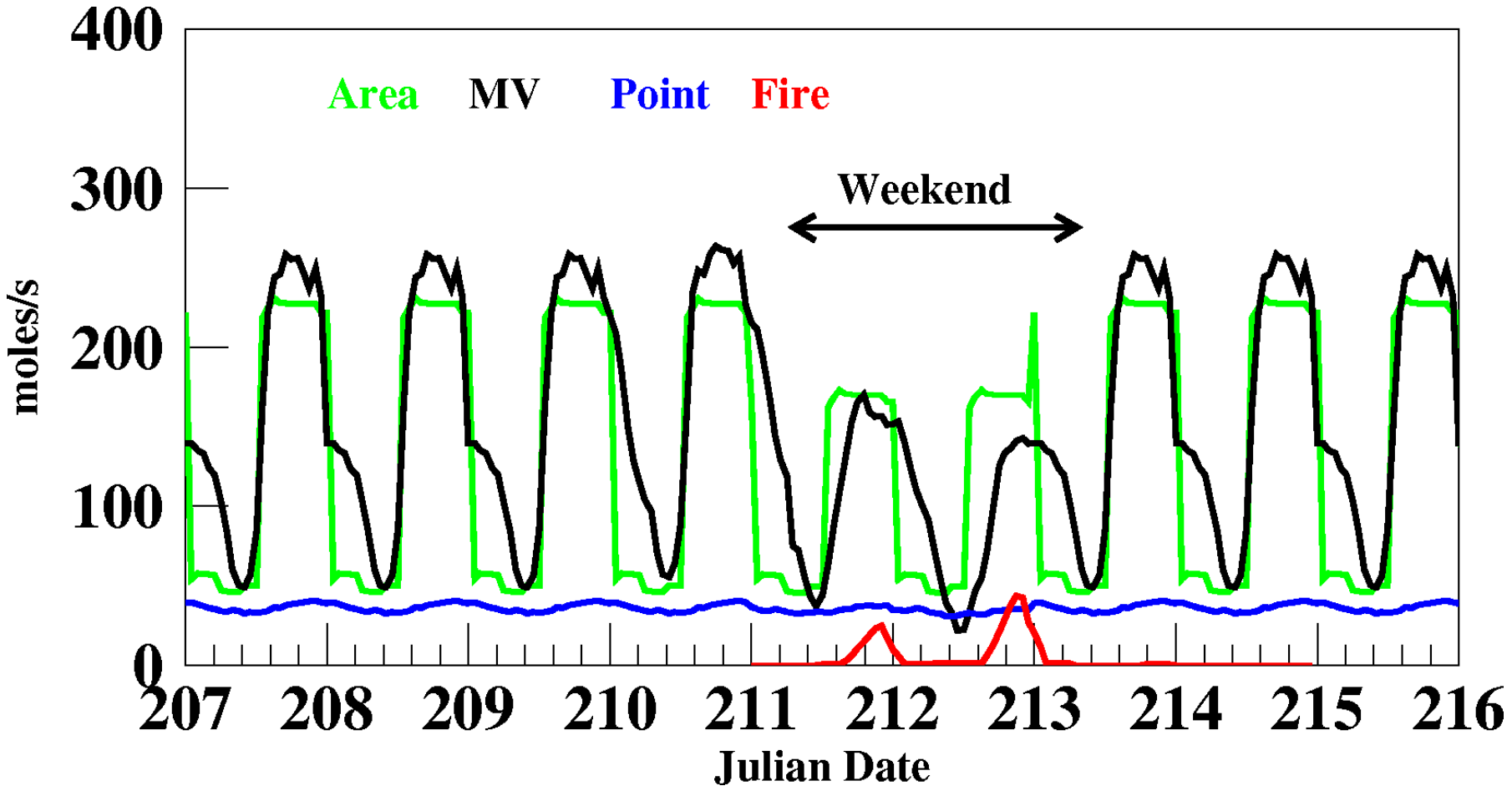
The mouth of the San Francisco Bay forms a gap in the coastal range that allow wind to blow pollutants into the valley from other regions.

Emission Inventory

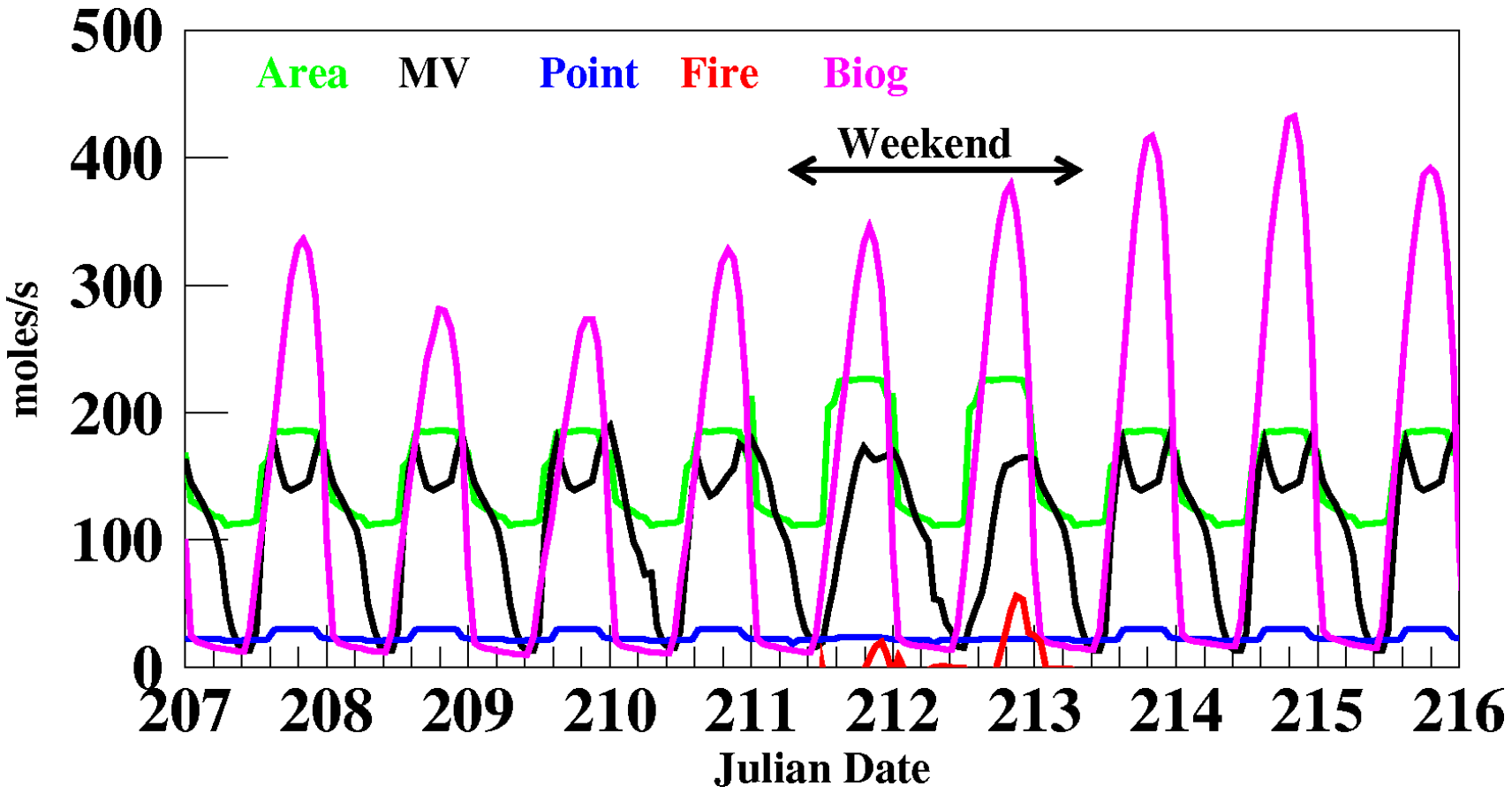
- **Mobile** (automobiles, diesel trucks)
- **Point** (cement, power plants, industry)
- **Area** (residential, off road vehicles, business)
- **Biogenic** (trees, agriculture)
- **Forest Fires**

NOx emissions by category

(next 3 figures from Phase 1 report)



VOC emissions by category

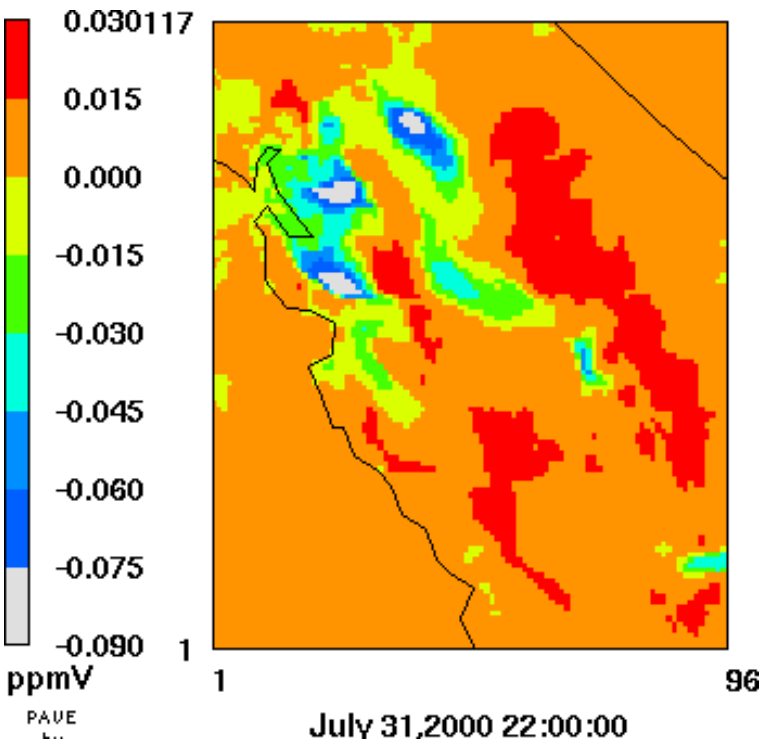


How does Ozone change w.r.t. Precursors:

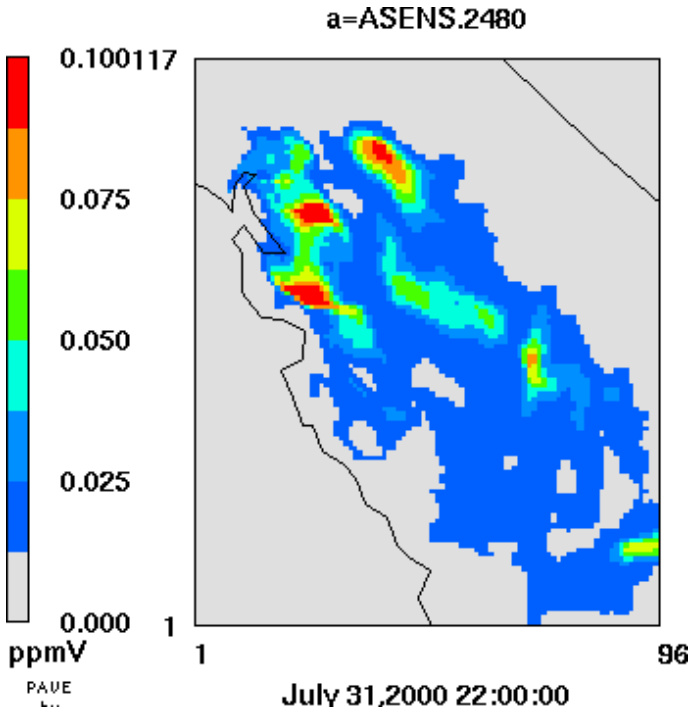
Sensitivity Analysis with CMAQ Decoupled Direct Method

Sensitivities w.r.t. emissions

dO_3 /d(NO_x): Sometimes negative, sometimes positive.



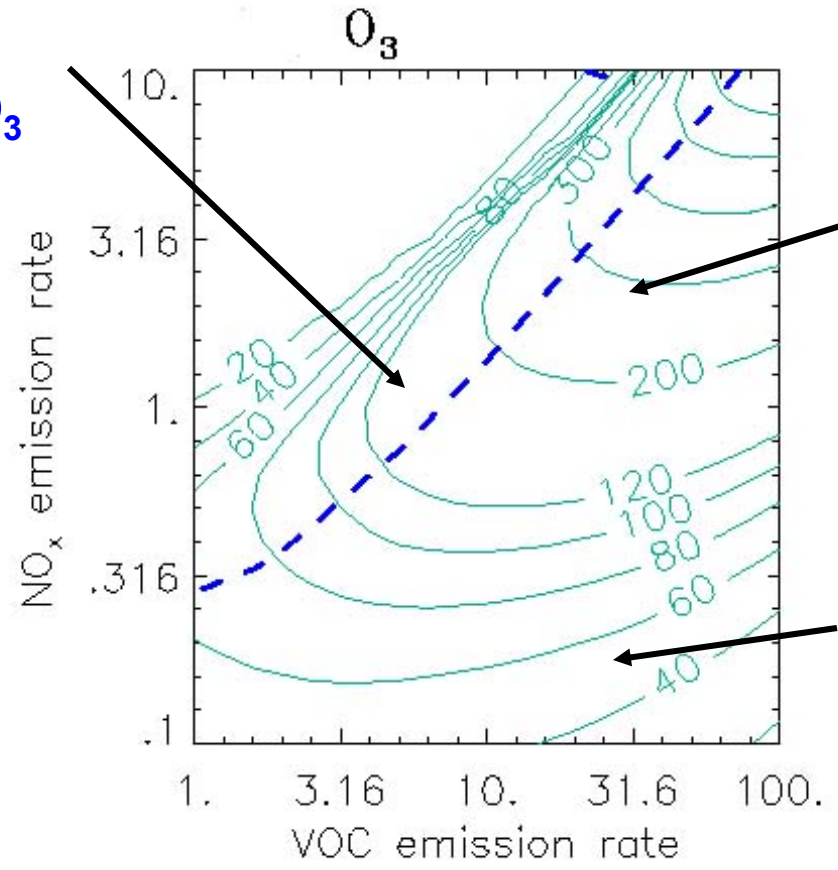
dO_3/d(VOC): Always positive



Ozone Isopleth Plot (Googled)

Urban area

$OH+NO_2 \rightarrow HNO_3$



Houston, TX: autos + petrochemical industry

Forested area

Points of Relevance to Catalytic Oxidation

Main benefit of reducing VOC and NO_x concentrations is to reduce ozone. (California does not violate air quality standards for VOC and NO_x

Most NOx emissions are in the from of NO. NO2 is 5-10%

NO oxidation: If only to NO_2 then there will be an increase in ozone

Careful about reducing NOx if an increase in ozone will result

VOC oxidation: During ozone production a primary VOC is successively oxidized in steps, producing intermediate compounds (aldehydes, ketones) in the process