Reactivity Scales via 3-D Photochemical Modeling

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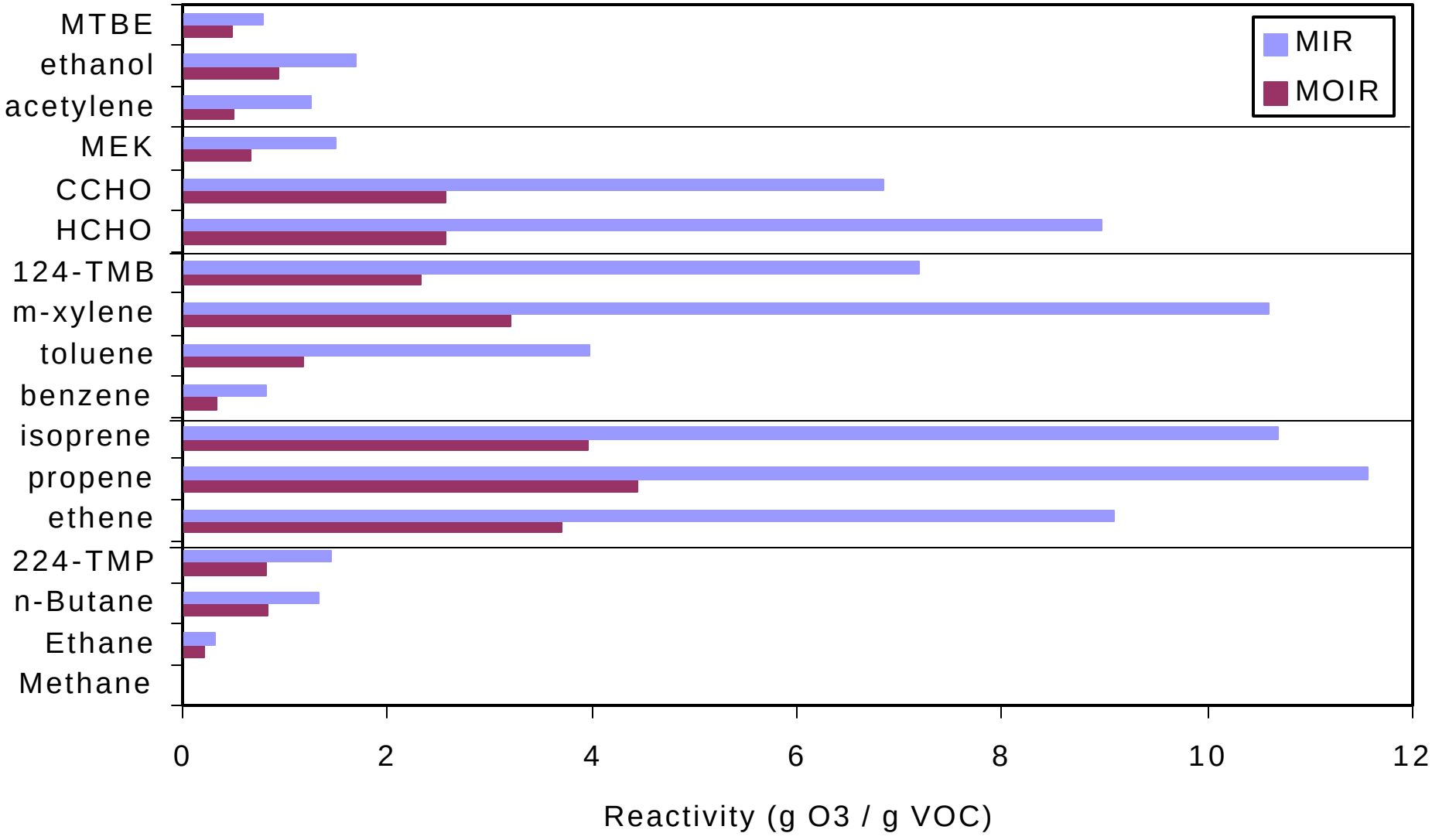
- Amir Hakami & Ted Russell (GA Tech)
- California Air Resources Board

Introduction

- California considers mass <u>and</u> reactivity of VOC in regulating some sources
- Relies on concept of maximum incremental reactivity (“MIR”), based on work of Carter with 0-D box model
- 3-D grid-based models provide more realistic representation of atmosphere

Incremental Reactivity Scales (Carter, 2000)



Objectives

- Use 3-D air quality models with online sensitivity analysis to assess reactivity of individual VOC
- Compare results from 3-D models to Carter's MIR scale
- Conduct formal uncertainty analysis

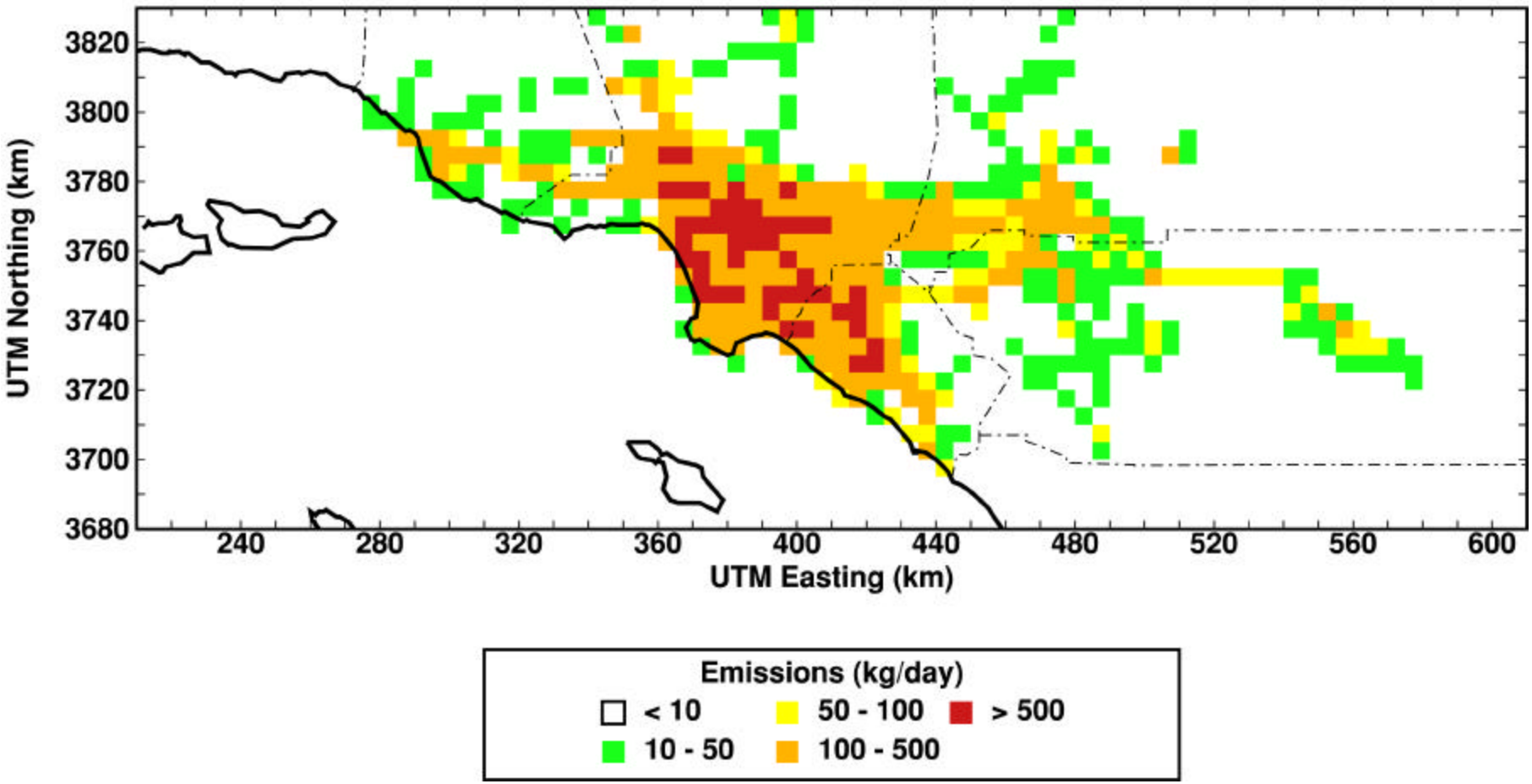
Approach

- SAPRC-99 mechanism with 30 individual VOC represented explicitly
- DDM-3D (Yang et al., 1997) used to calculate sensitivity of ozone to emissions of VOC
- Monte Carlo analysis to propagate input uncertainties through modeling system

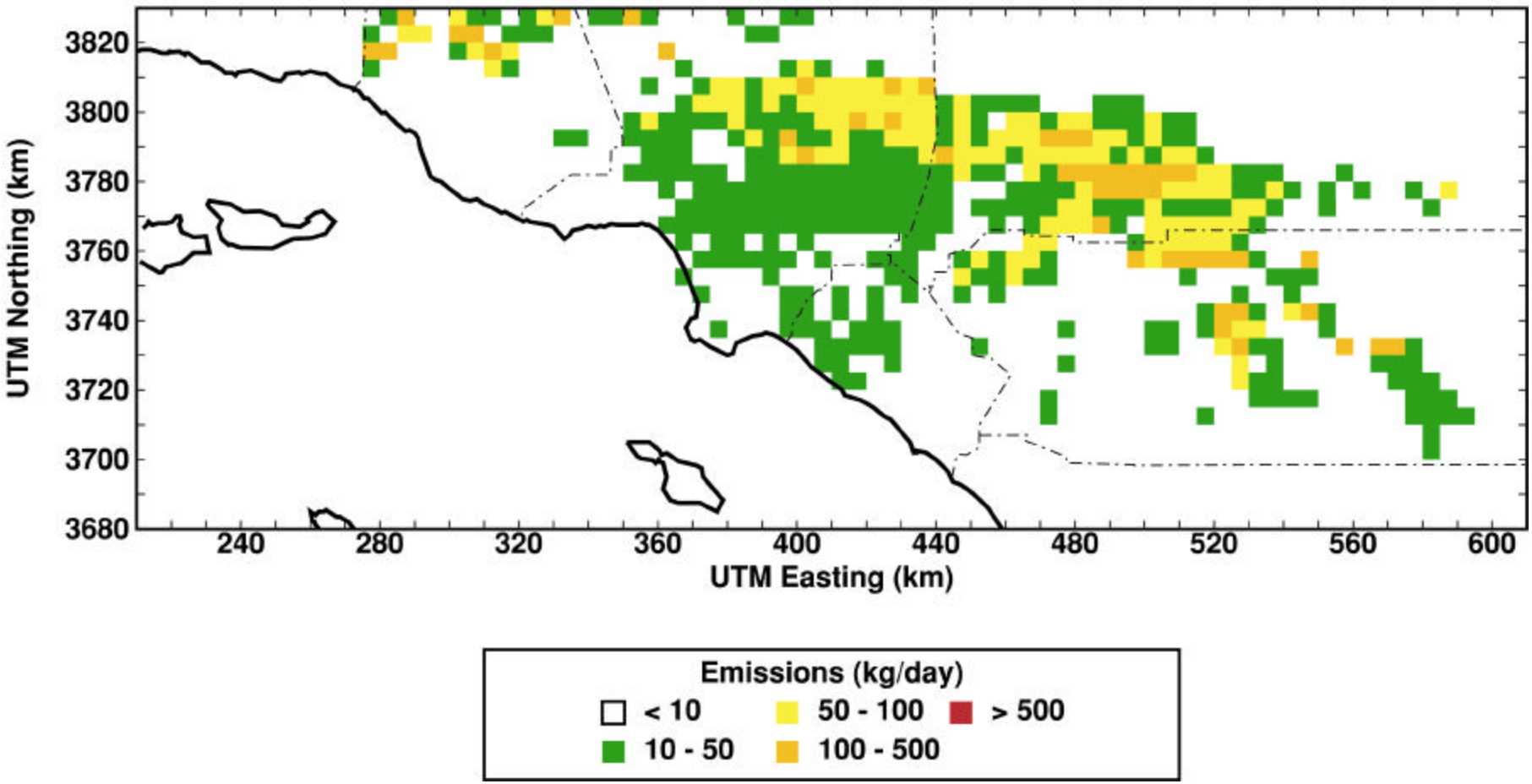
Model Application

- South Coast Air Basin
  - 24-25 June 1987 (SCAQS)
- Central California
  - 2-6 August 1990 (SJVAQS/AUSPEX)
- Use previously defined model inputs for meteorology and emissions

PROPENE EMISSIONS FOR 25 JUNE 1987



ISOPRENE EMISSIONS FOR 25 JUNE 1987



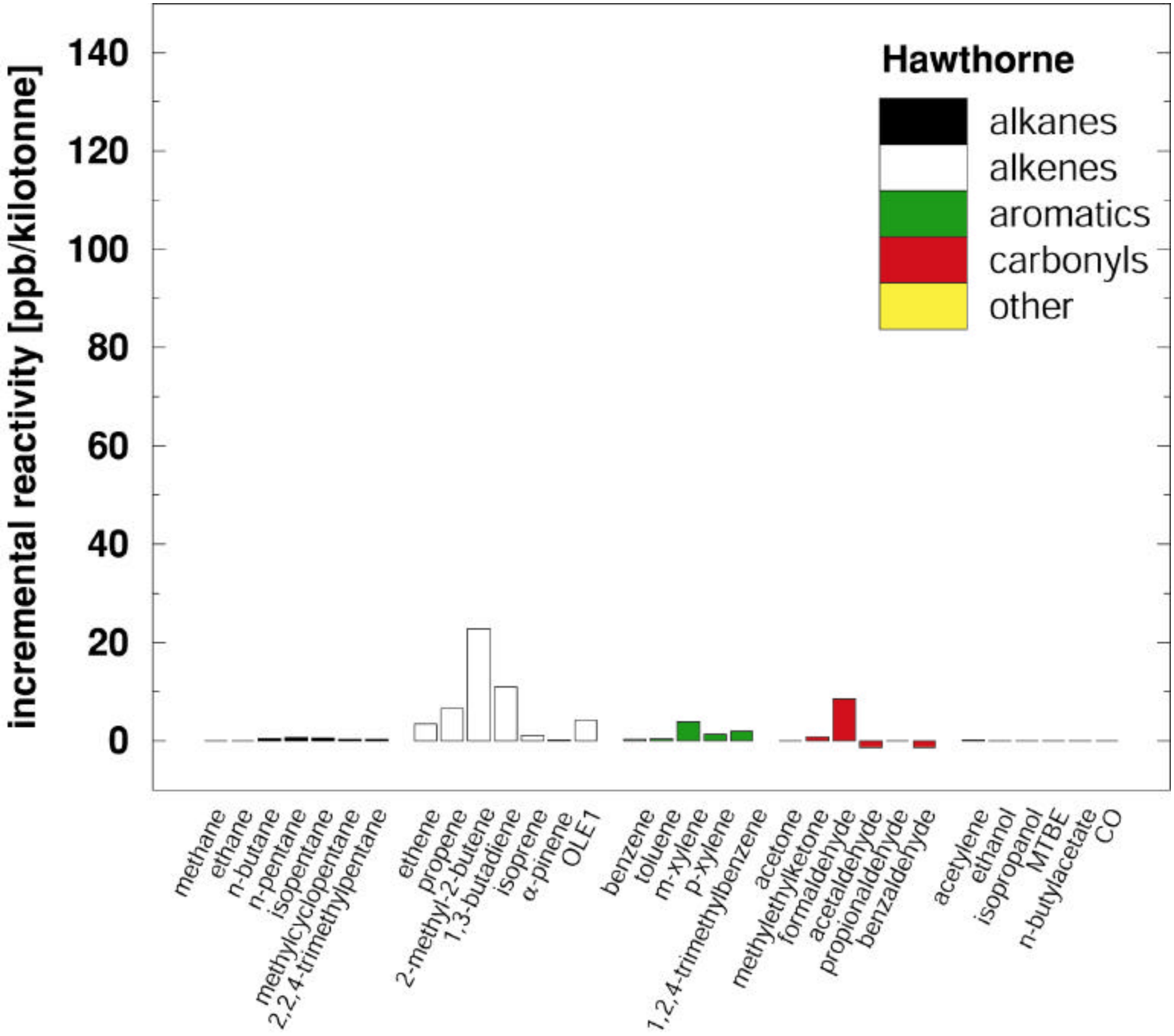
Calculating Reactivity

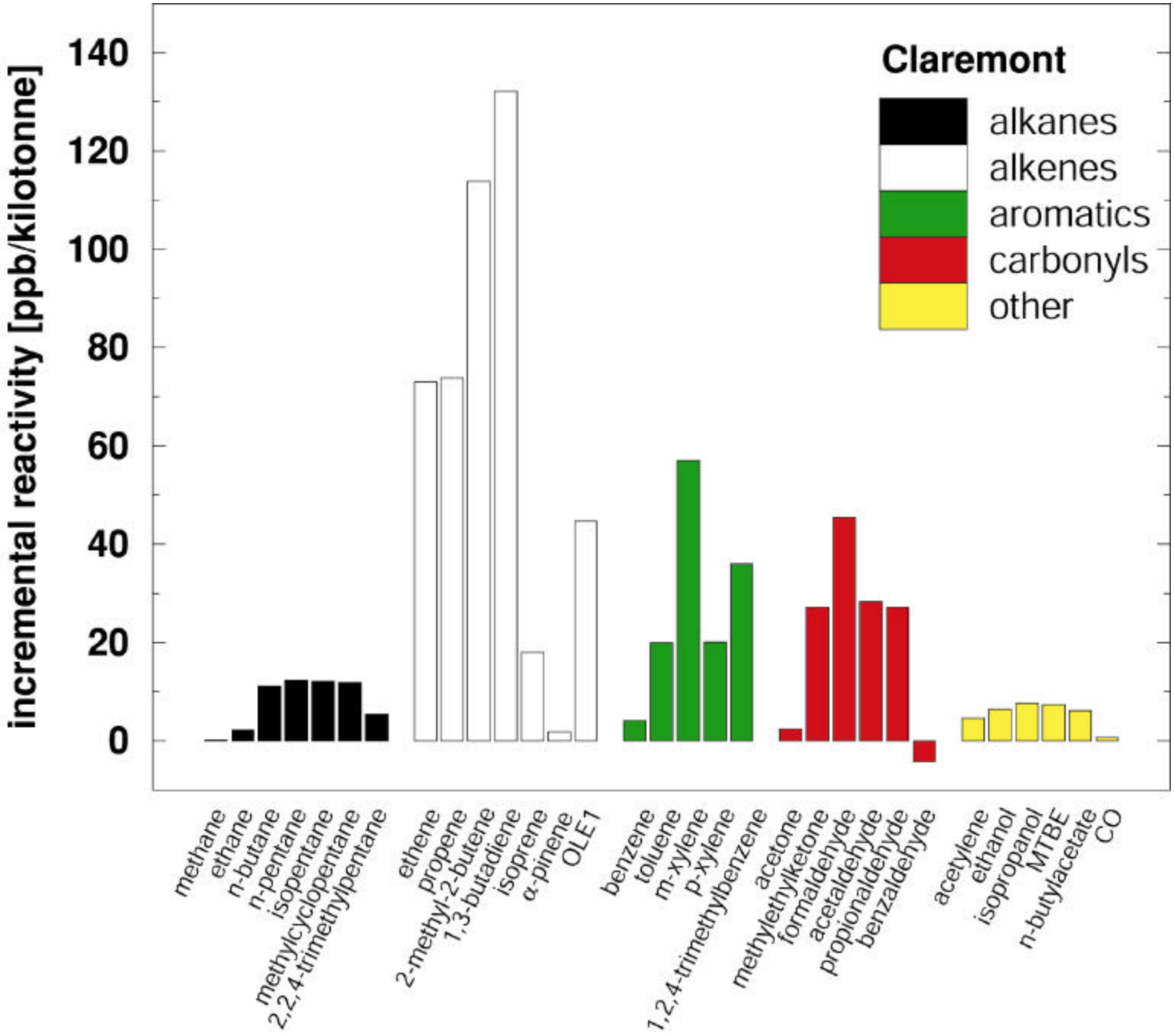
- Sensitivity Coefficient from DDM-3D:

$$s_{ij}^{*} = \frac{\partial[\mathrm{O}_3]}{\partial e_j} = E_j \frac{\partial[\mathrm{O}_3]}{\partial E_{\mathrm{j}}}$$

- Absolute Incremental Reactivity:

$$AIR_j = \frac{s_{ij}^{*}}{E_j MW_j}$$

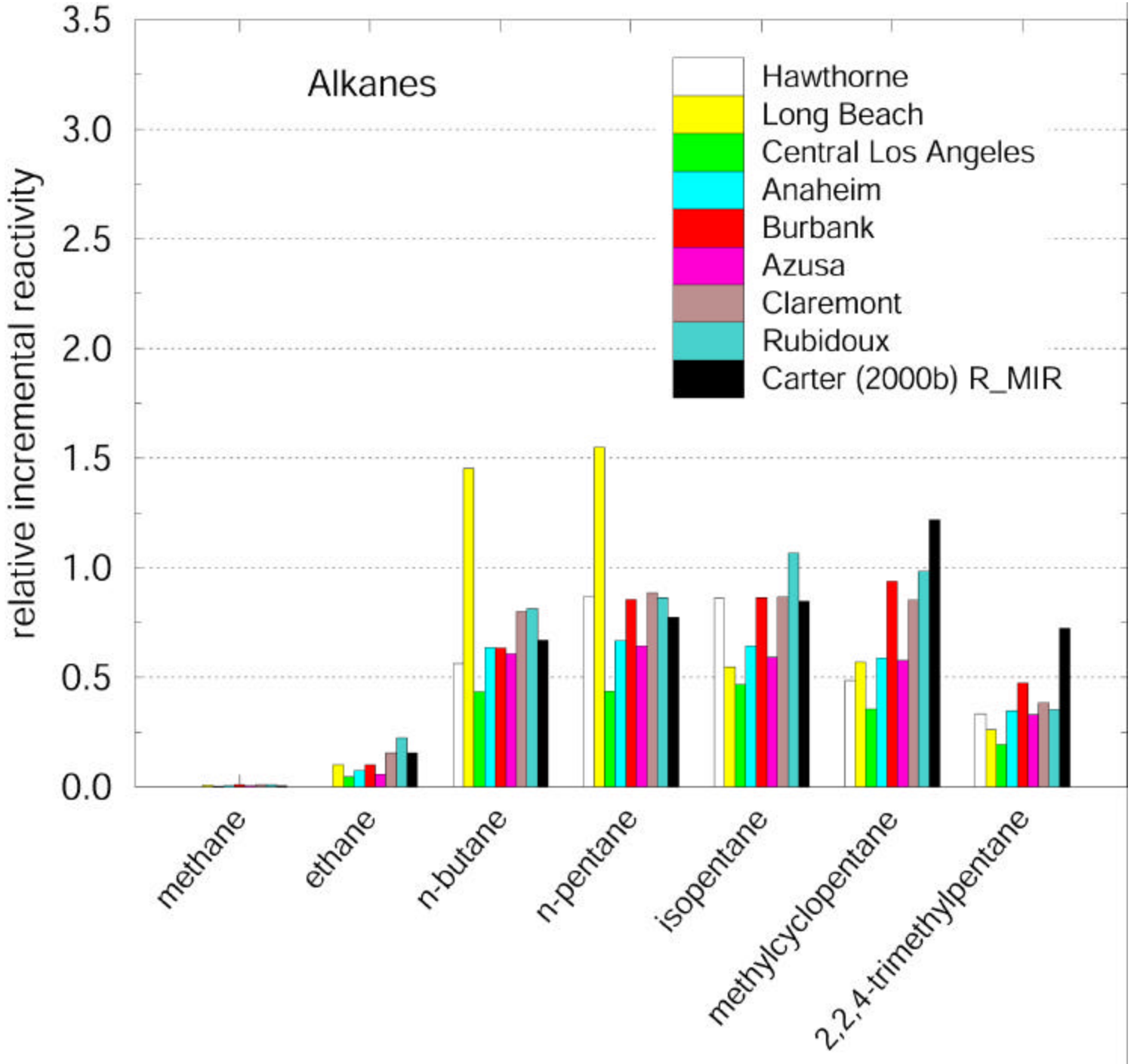

Hawthorne
alkanes
alkenes
aromatics
carbonyls
other
incremental reactivity [ppb/kilotonne]
140
120
100
80
60
40
20
0
methane
ethane
n-butane
n-pentane
isopentane
methylcyclopentane
2,2,4-trimethylpentane
ethene
propene
2-methyl-2-butene
1,3-butadiene
isoprene
α-pinene
OLE1
benzene
toluene
m-xylene
p-xylene
1,2,4-trimethylbenzene
acetone
methylethylketone
formaldehyde
acetaldehyde
propionaldehyde
benzaldehyde
acetylene
ethanol
isopropanol
MTBE
n-butylacetate
CO

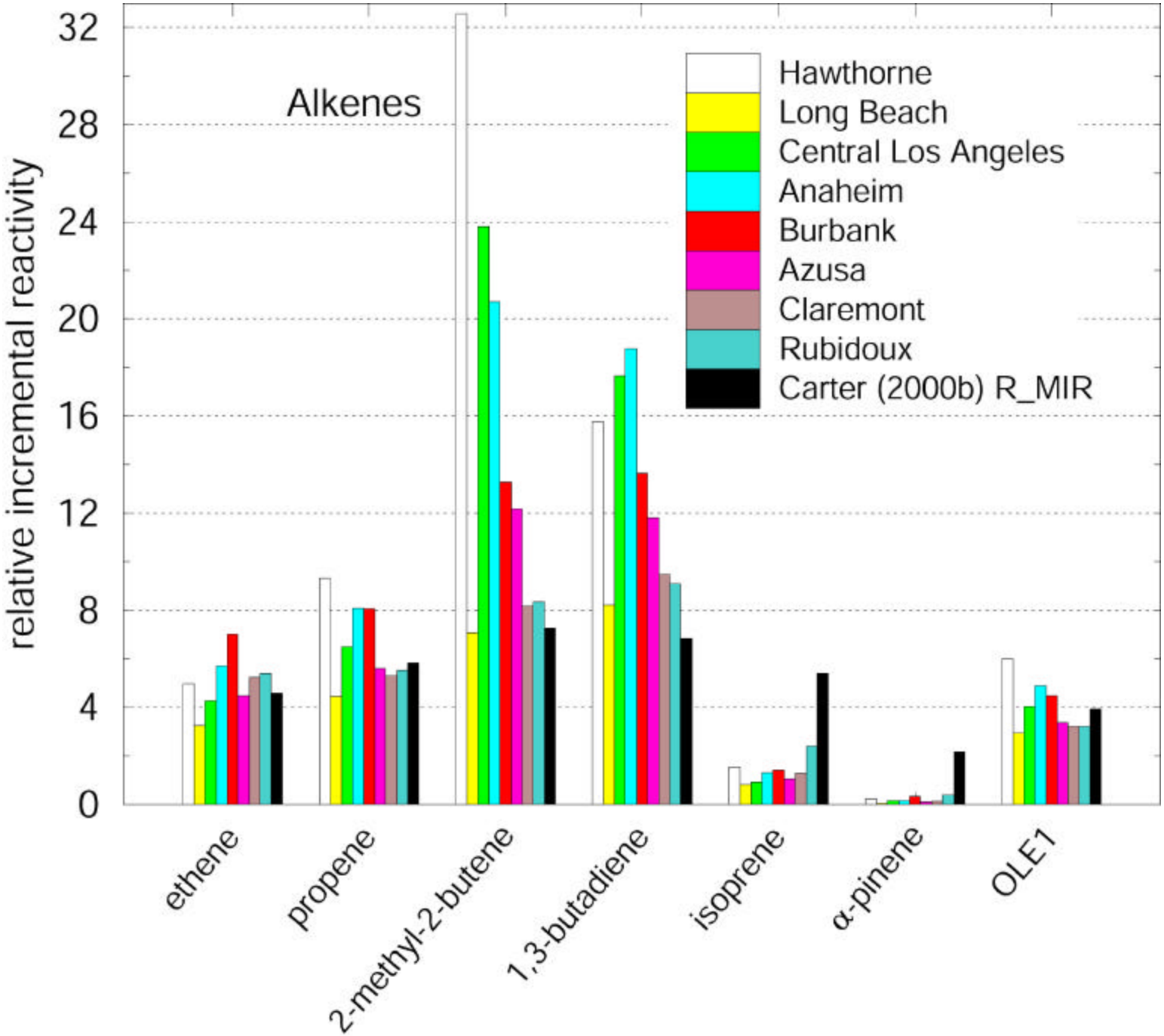

Claremont
alkanes
alkenes
aromatics
carbonyls
other
incremental reactivity [ppb/kilotonne]
0
20
40
60
80
100
120
140
methane
ethane
n-butane
n-pentane
isopentane
methylcyclopentane
2,2,4-trimethylpentane
ethene
propene
2-methyl-2-butene
1,3-butadiene
isoprene
α-pinene
OLE1
benzene
toluene
m-xylene
p-xylene
1,2,4-trimethylbenzene
acetone
methylethylketone
formaldehyde
acetaldehyde
propionaldehyde
benzaldehyde
acetylene
ethanol
isopropanol
MTBE
n-butylacetate
CO

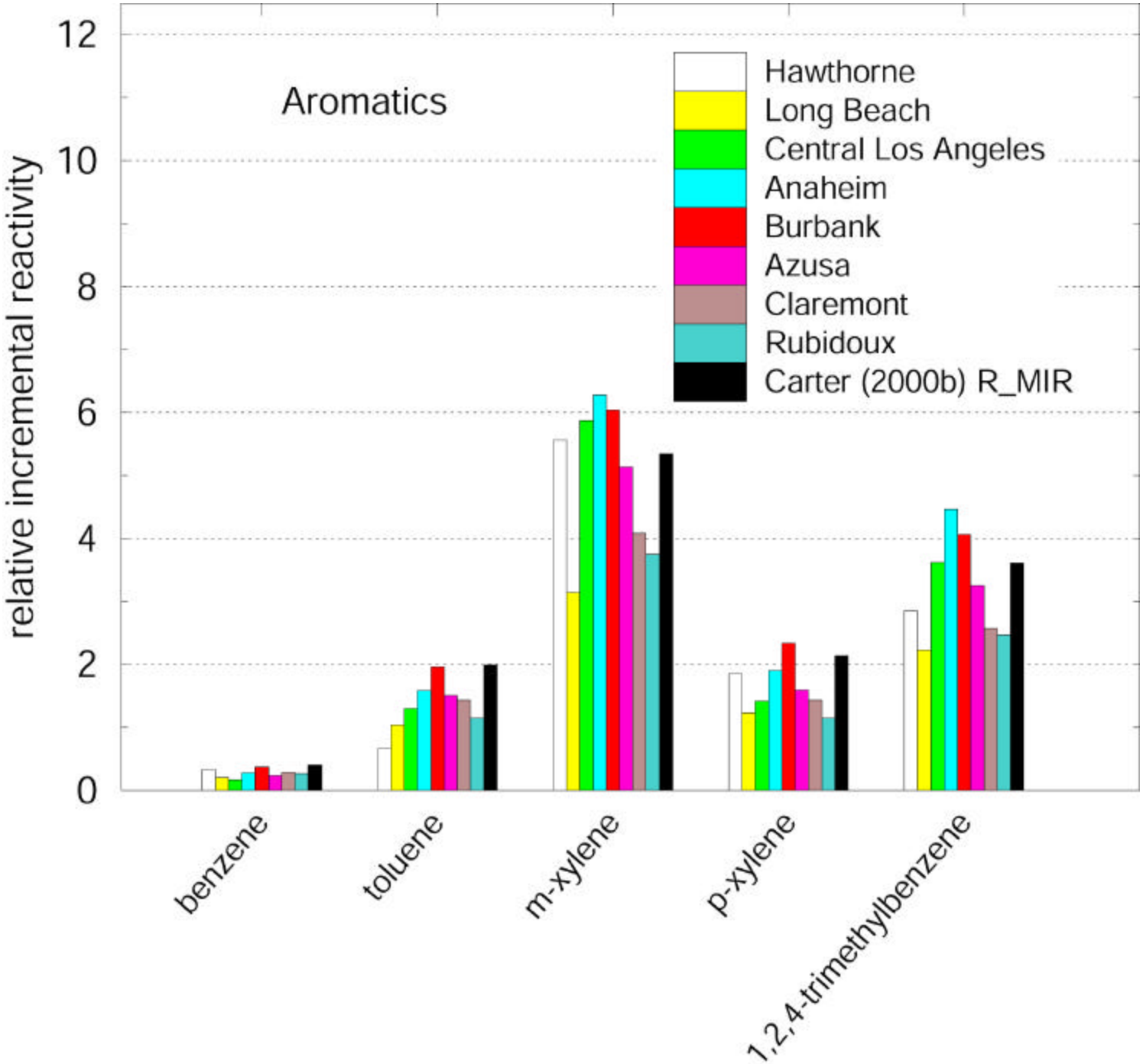
Relative Reactivity

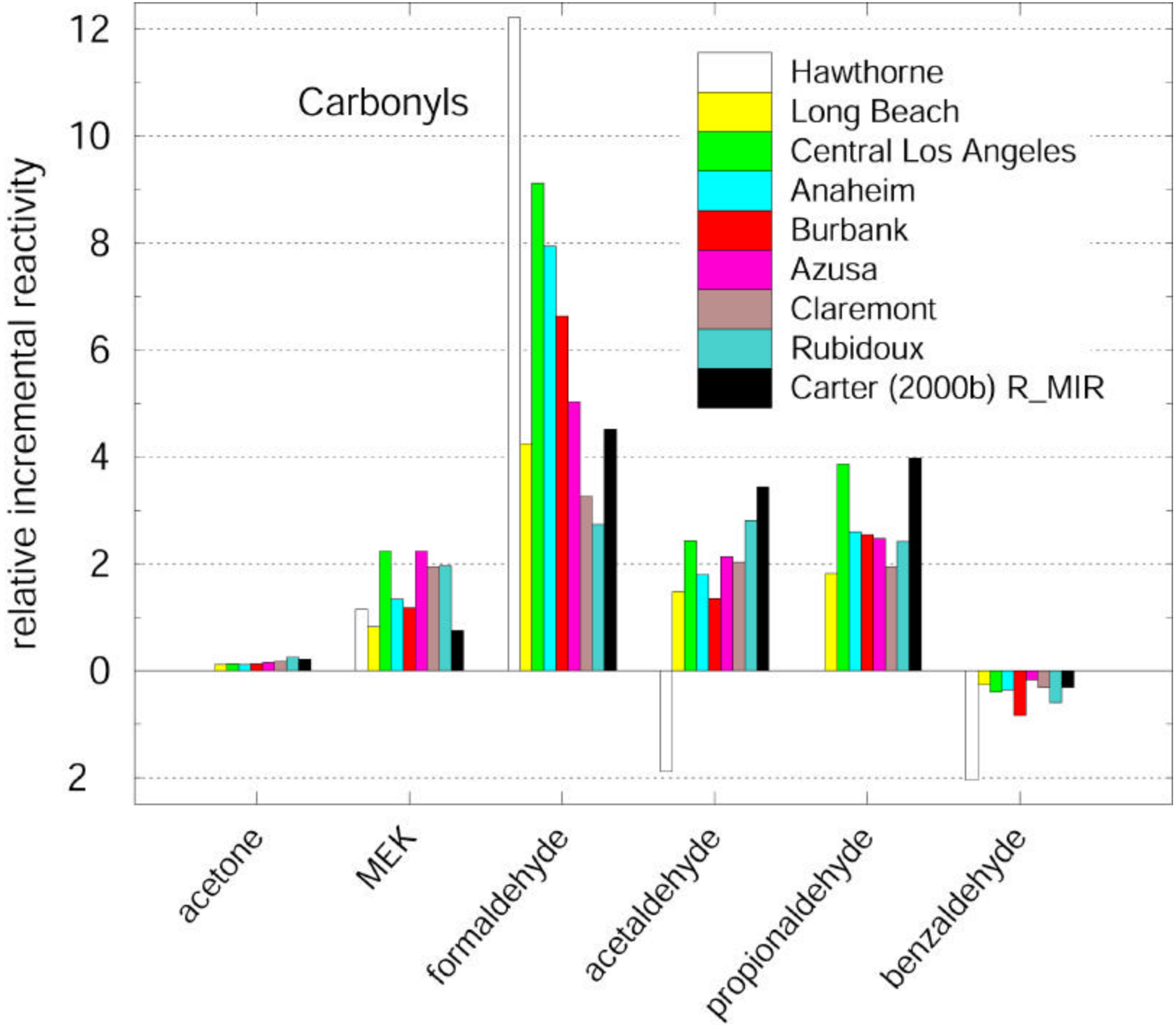
- AIR from 3-D model varies by location
  - Coastal/mid-basin sites not affected by increases in downwind emissions
- Define relative incremental reactivity:

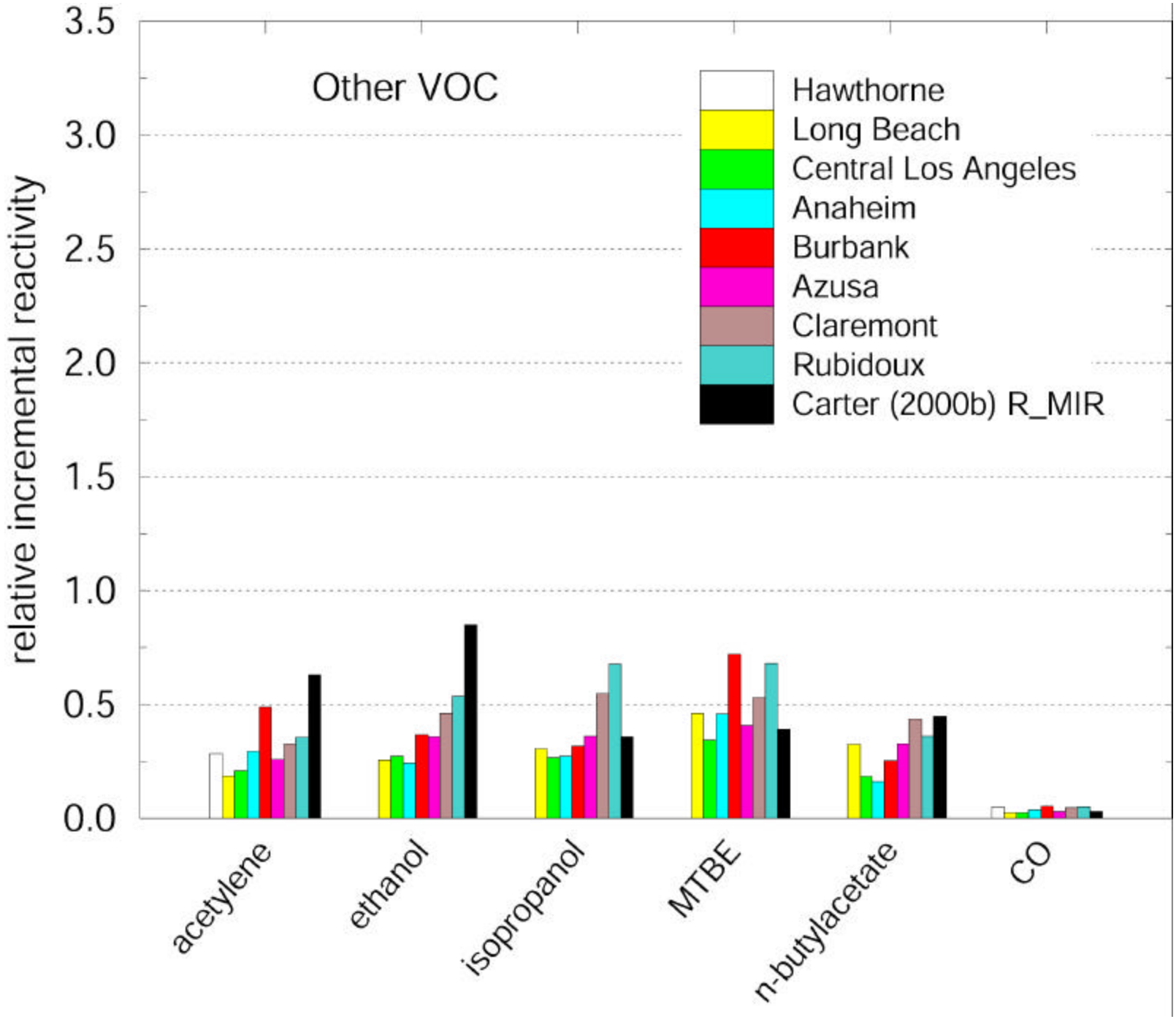
$$RIR_j = \frac{AIR_j}{\sum_k w_k AIR_k}$$


Alkanes
Hawthorne
Long Beach
Central Los Angeles
Anaheim
Burbank
Azusa
Claremont
Rubidoux
Carter (2000b) R_MIR
relative incremental reactivity
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
methane
ethane
n-butane
n-pentane
isopentane
methylcyclopentane
2,2,4-trimethylpentane


Alkenes
relative incremental reactivity
0
4
8
12
16
20
24
28
32
Hawthorne
Long Beach
Central Los Angeles
Anaheim
Burbank
Azusa
Claremont
Rubidoux
Carter (2000b) R_MIR
ethene
propene
2-methyl-2-butene
1,3-butadiene
isoprene
α-pinene
OLE1

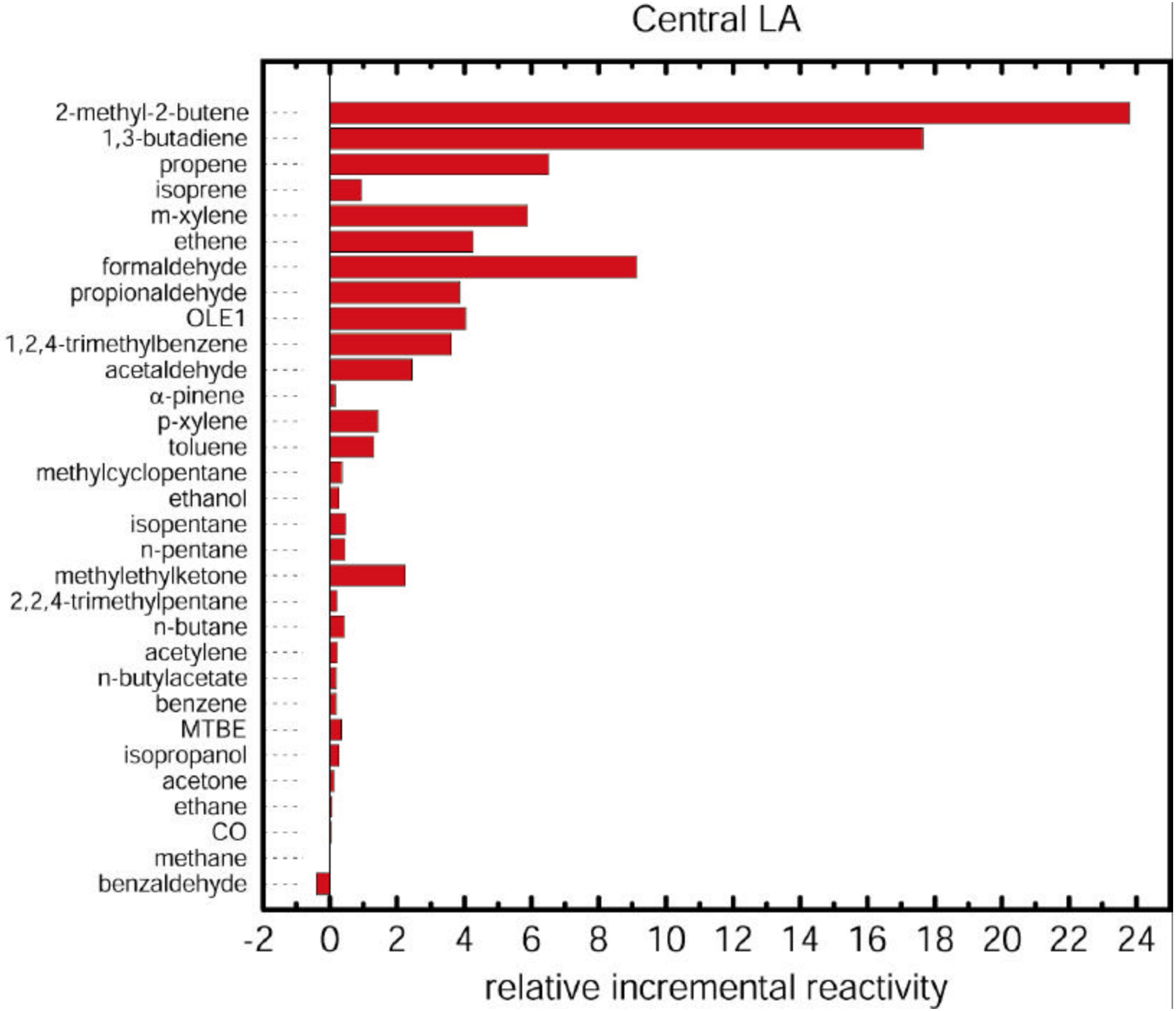

Aromatics
Hawthorne
Long Beach
Central Los Angeles
Anaheim
Burbank
Azusa
Claremont
Rubidoux
Carter (2000b) R_MIR
relative incremental reactivity
0
2
4
6
8
10
12
benzene
toluene
m-xylene
p-xylene
1,2,4-trimethylbenzene

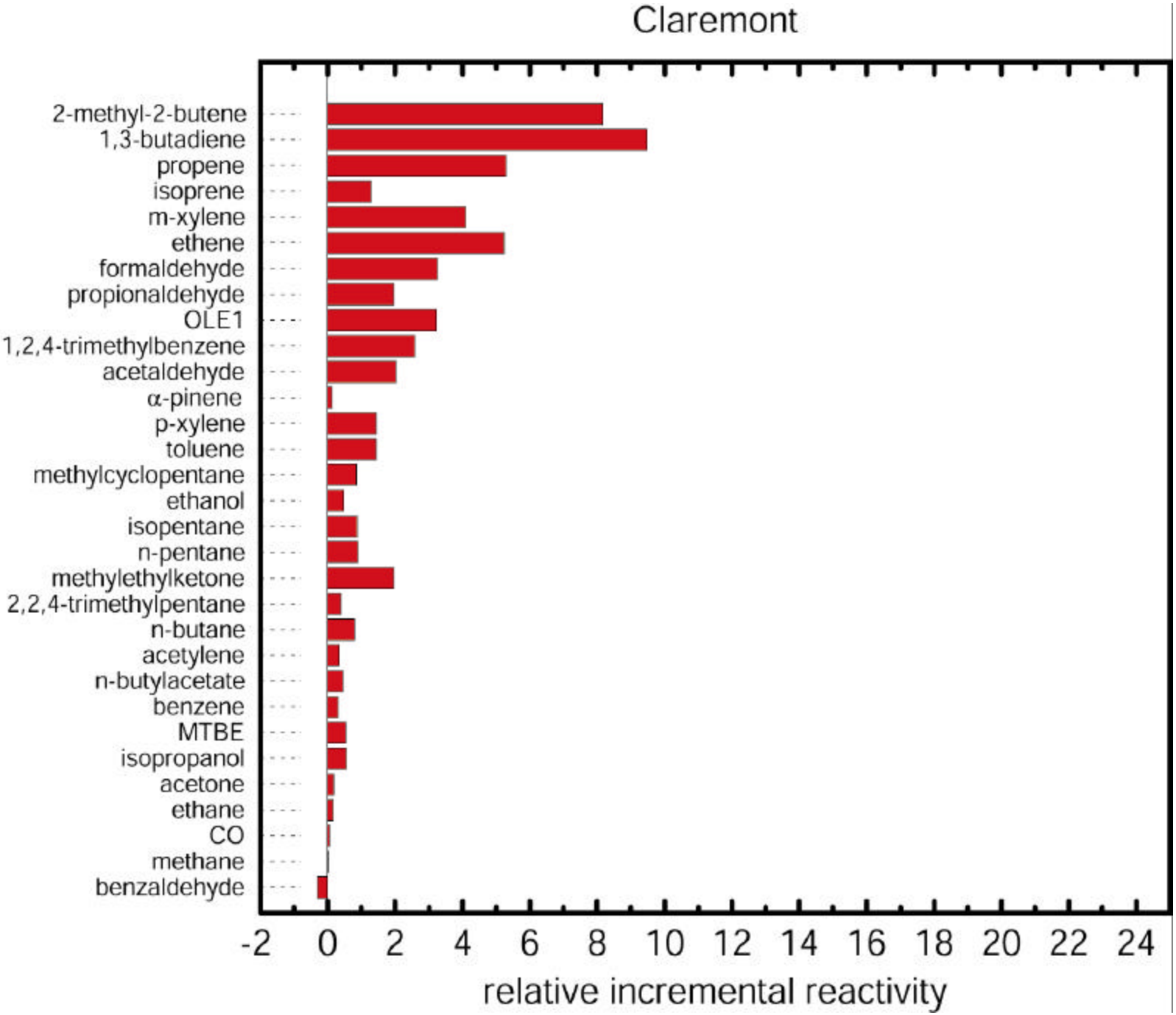

Carbonyls
relative incremental reactivity
12
10
8
6
4
2
0
2
Hawthorne
Long Beach
Central Los Angeles
Anaheim
Burbank
Azusa
Claremont
Rubidoux
Carter (2000b) R_MIR
acetone
MEK
formaldehyde
acetaldehyde
propionaldehyde
benzaldehyde


Other VOC
Hawthorne
Long Beach
Central Los Angeles
Anaheim
Burbank
Azusa
Claremont
Rubidoux
Carter (2000b) R_MIR
relative incremental reactivity
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
acetylene
ethanol
isopropanol
MTBE
n-butylacetate
CO

Reactivity Rankings

- Sort compounds from highest to lowest based on Carter MIR
- Plot RIR from 3-D modeling for each compound
- Expect RIR to decrease monotonically

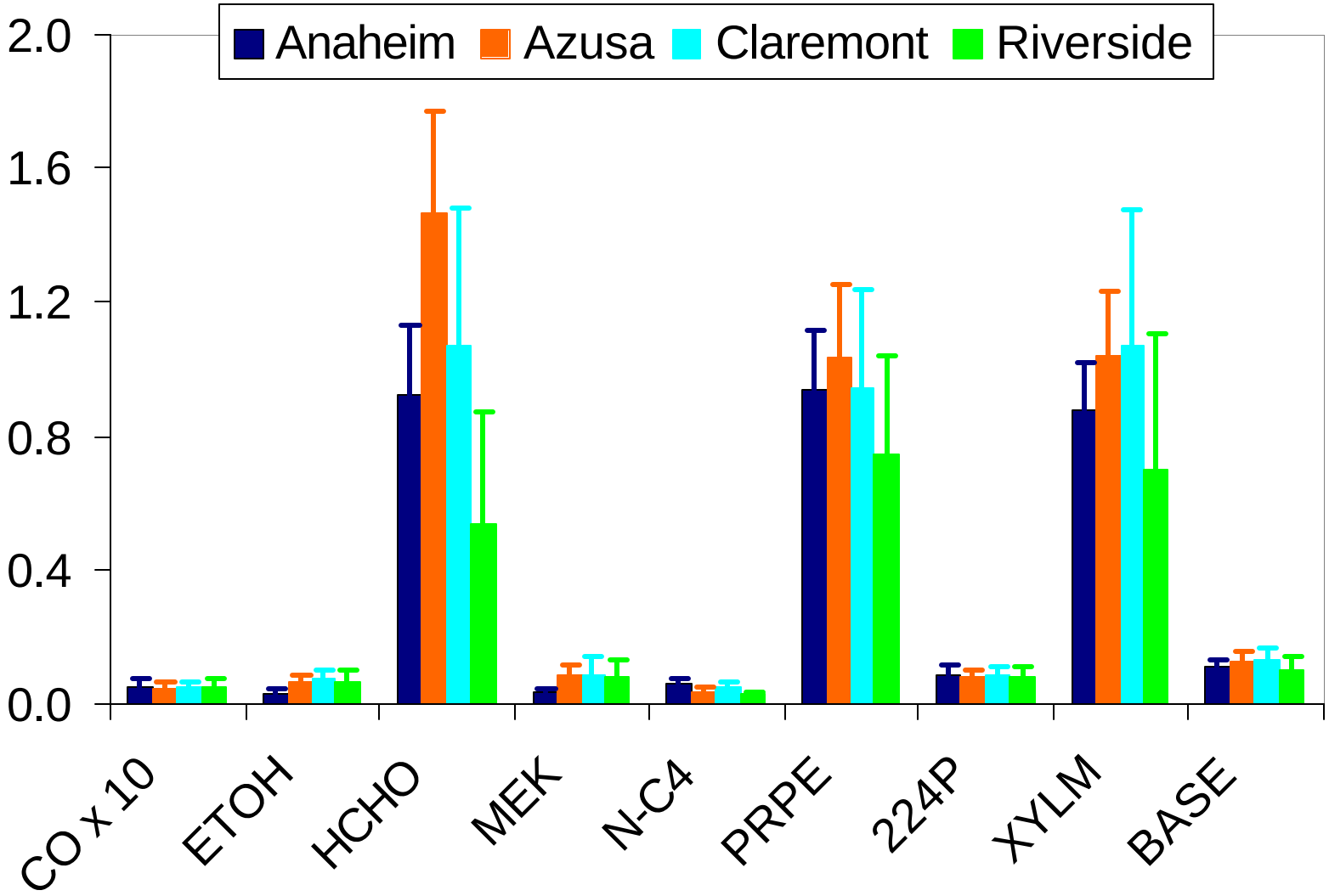

Central LA
2-methyl-2-butene
1,3-butadiene
propene
isoprene
m-xylene
ethene
formaldehyde
propionaldehyde
OLE1
1,2,4-trimethylbenzene
acetaldehyde
α-pinene
p-xylene
toluene
methylcyclopentane
ethanol
isopentane
n-pentane
methylethylketone
2,2,4-trimethylpentane
n-butane
acetylene
n-butylacetate
benzene
MTBE
isopropanol
acetone
ethane
CO
methane
benzaldehyde
-2
0
2
4
6
8
10
12
14
16
18
20
22
24
relative incremental reactivity


Claremont
2-methyl-2-butene
1,3-butadiene
propene
isoprene
m-xylene
ethene
formaldehyde
propionaldehyde
OLE1
1,2,4-trimethylbenzene
acetaldehyde
α-pinene
p-xylene
toluene
methylcyclopentane
ethanol
isopentane
n-pentane
methylethylketone
2,2,4-trimethylpentane
n-butane
acetylene
n-butylacetate
benzene
MTBE
isopropanol
acetone
ethane
CO
methane
benzaldehyde
-2
0
2
4
6
8
10
12
14
16
18
20
22
24
relative incremental reactivity

Uncertainty Analysis

- Treat 33 input parameters as uncertain:
  - Chemical rate coefficients
  - Oxidation product yields
  - Emissions of CO, VOC & NO_x
  - Deposition velocities for O_3 and NO_2
- Use trajectory model and Monte Carlo/LHS to get output uncertainties

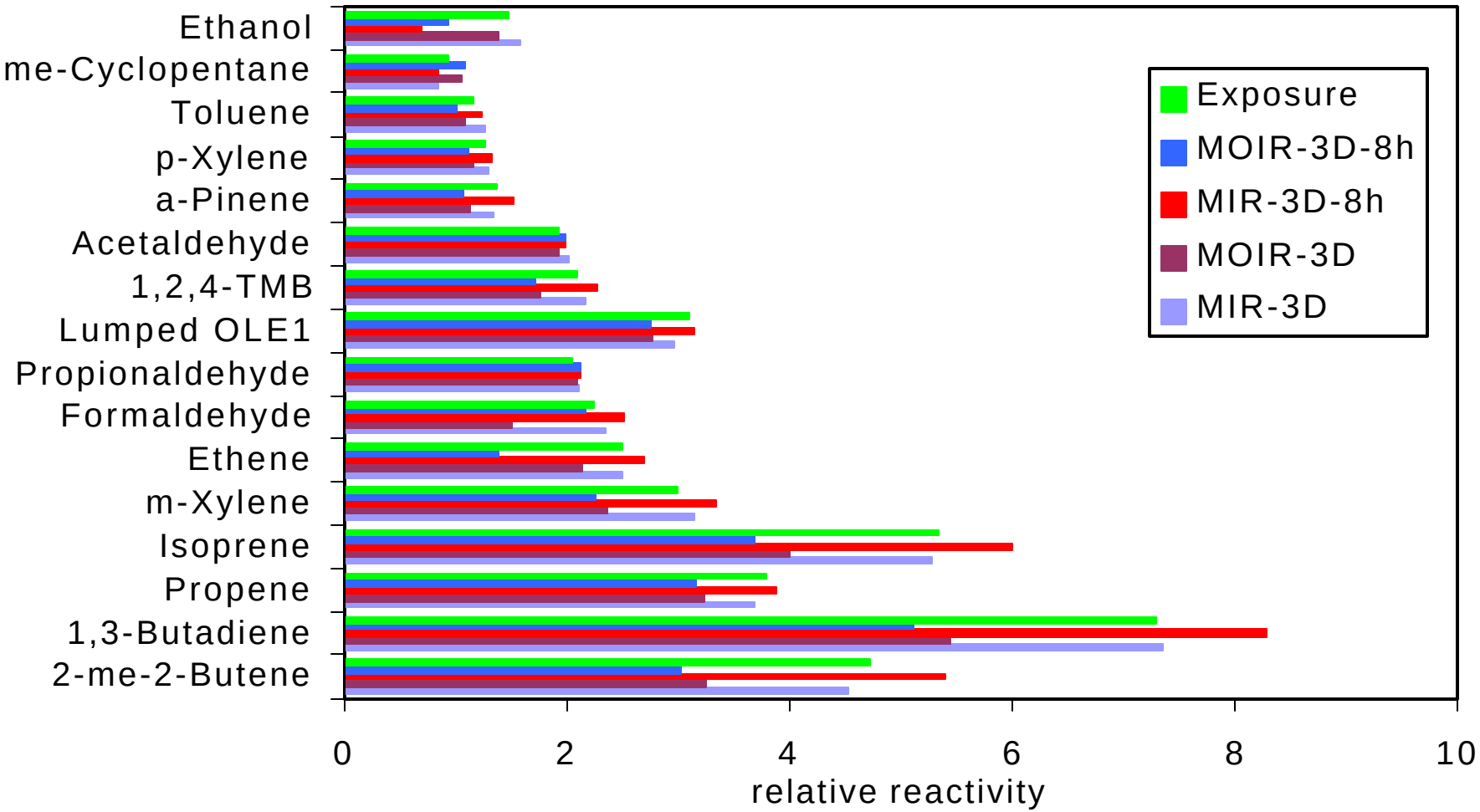
Absolute Incremental Reactivities



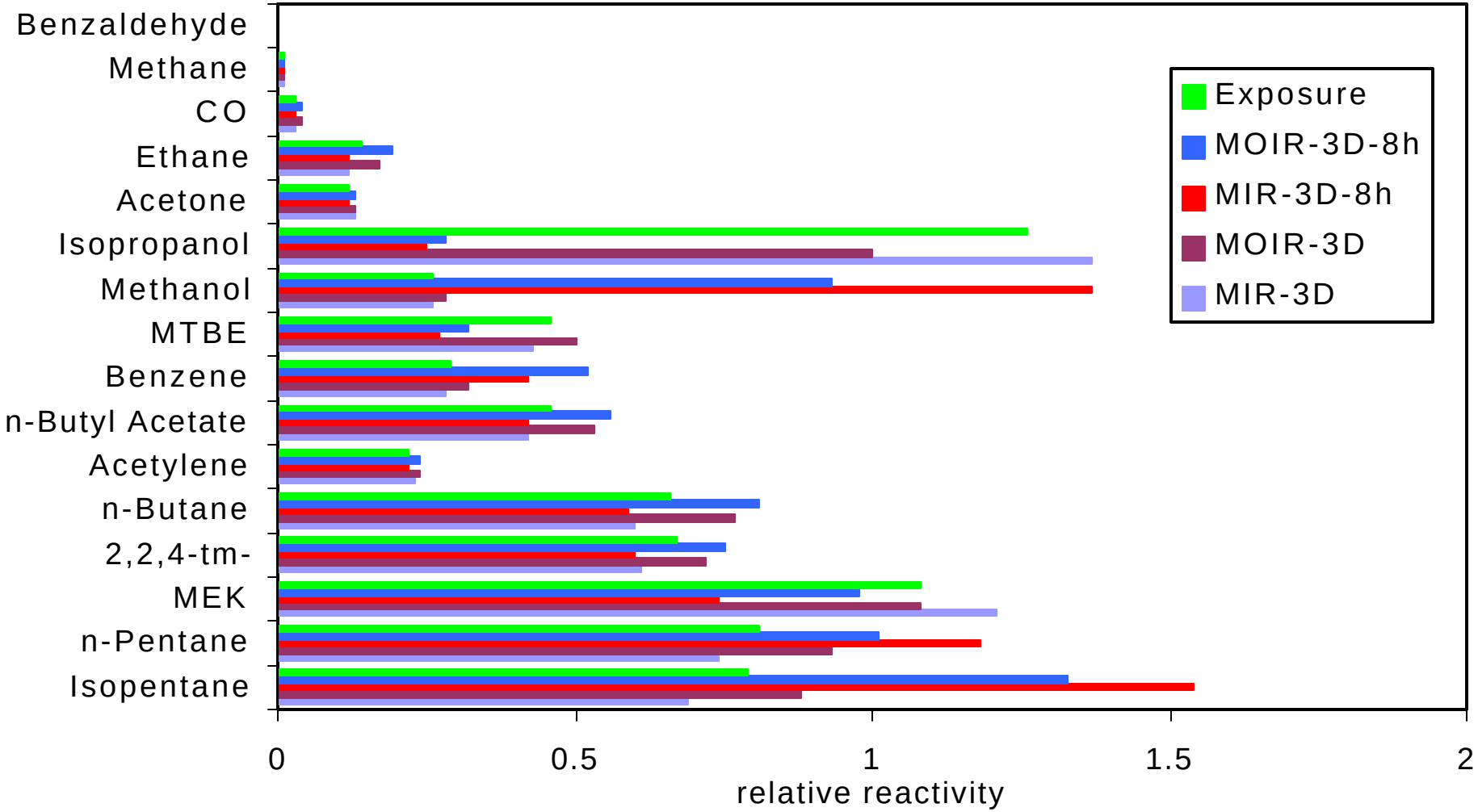
Central California

- Used different 3-D model (MAQSIP)
- Considered many reactivity metrics:
  - 1 hr vs. 8 hr ozone
  - MIR vs. MOIR conditions
  - Population exposure
- Long modeling period (2-6 Aug 1990) for larger region incl. Bay Area & SJV

Comparison of 3-D Metrics



Comparison of 3-D Metrics



Summary

- Reactivity more robust on relative rather than absolute basis
  - less site-to-site variability
  - typical RIR uncertainty 20-35%
- Reactivity metrics derived from 3-D modeling similar to Carter MIR scale
- Spatial distribution of emissions can be important (lg. point sources, biogenics)

Summary (continued)

- HO_x radical initiators (esp. C_4-C_5 alkenes and HCHO) have variable RIR
- Acetaldehyde shows negative reactivity at upwind boundaries because PAN formation competes with NO_2 photolysis
- RIR increases downwind for some low-reactivity compounds