Sensitivity of Ozone Production to Organic Nitrate Formation: Model results and comparisons to measurements

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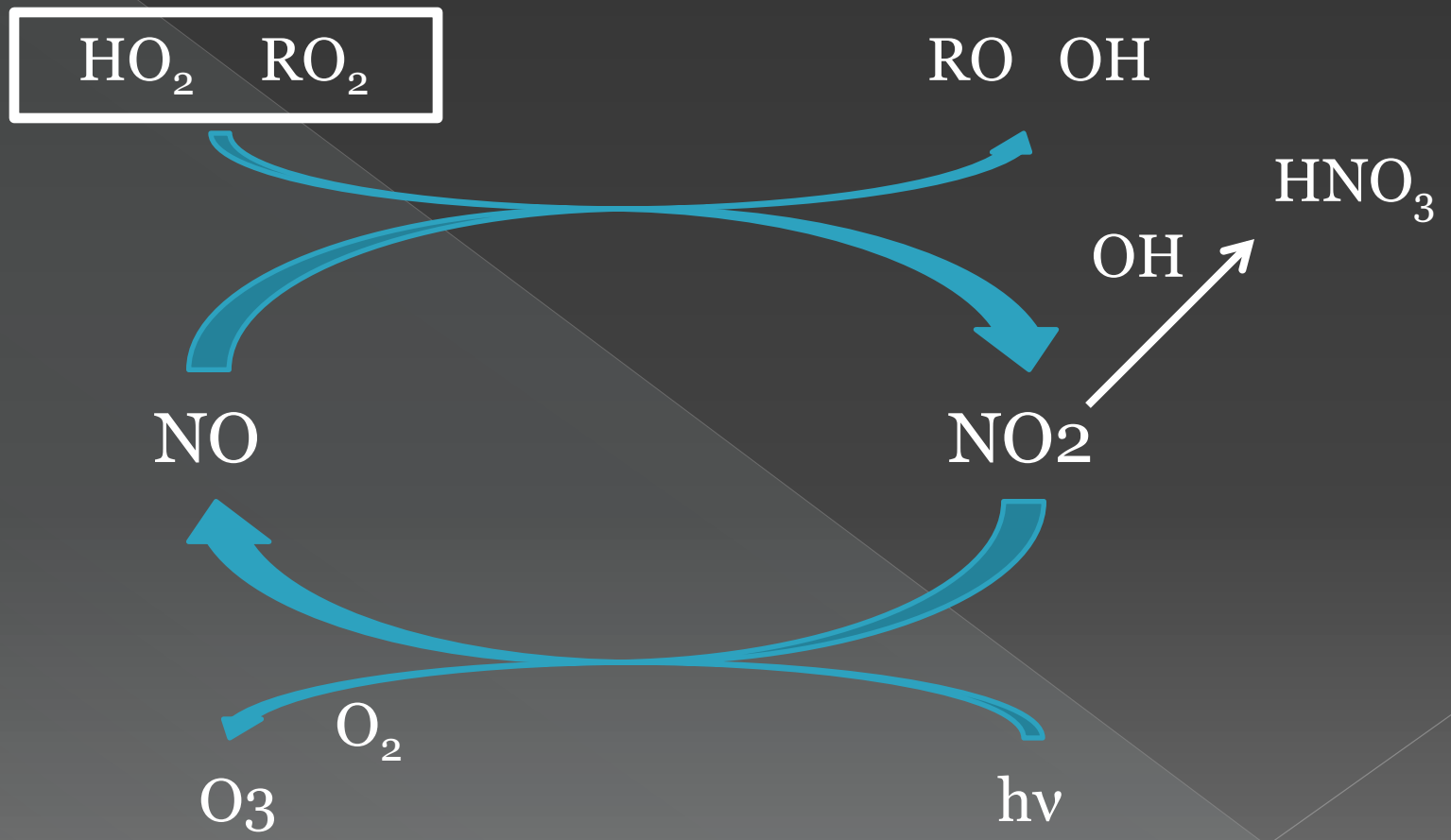
Standard view of Ozone Production

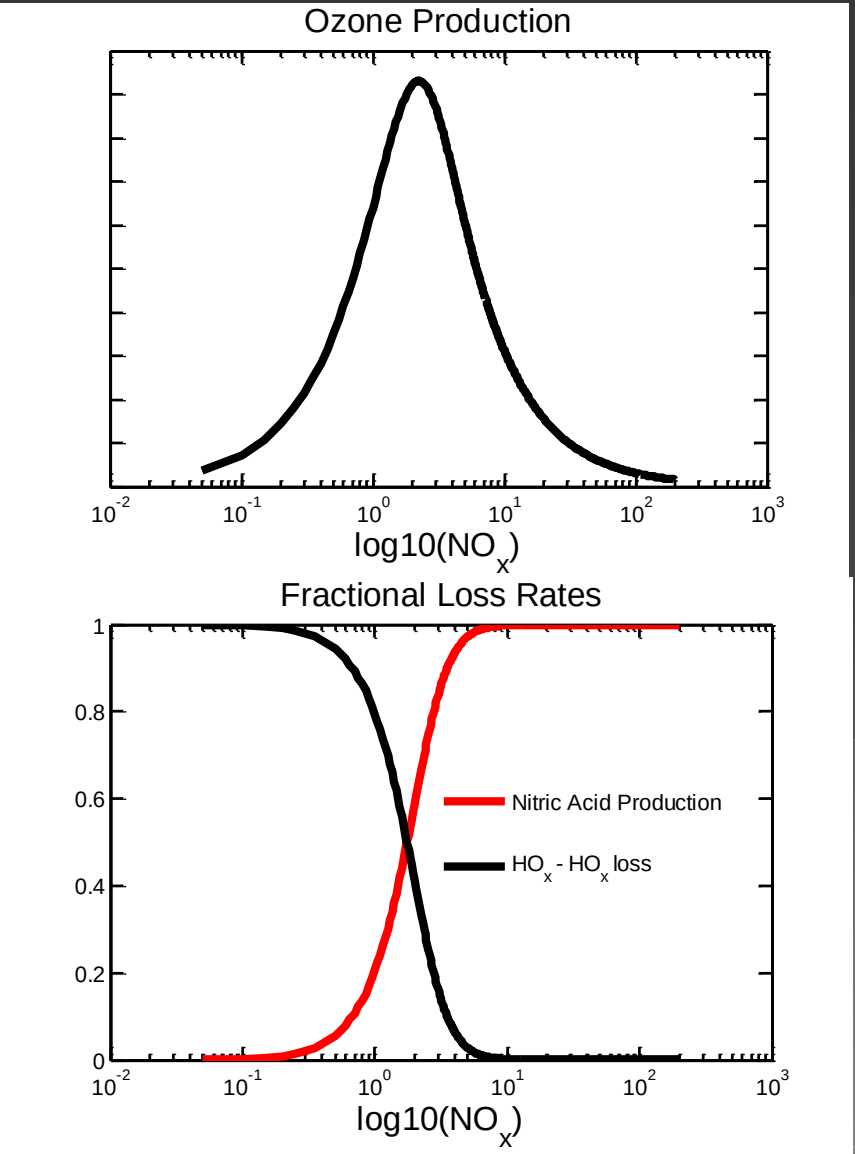


Standard View of Ozone Production

NO_x Limited

Termination Reactions

$HO_2 + HO_2$
$RO_2 + HO_2$
$RO_2 + RO_2$

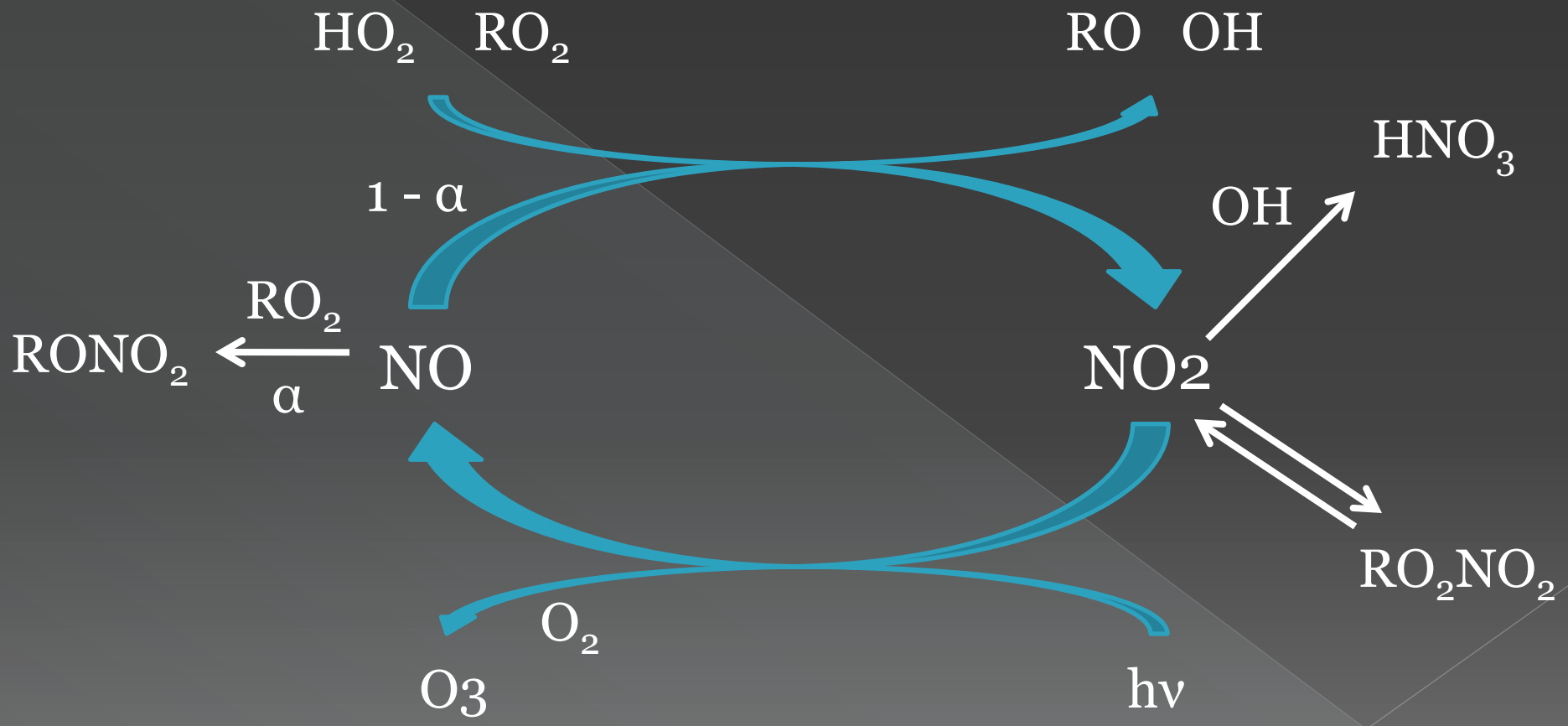


VOC Limited

Termination Reactions

$NO_2 + OH$

Termination reactions that couple HO_x and NO_x



Organic nitrate formation varies drastically by location

	ANs v. Ox slope	Implied Branching Ratio
Houston	41	4.65
Granite Bay	34	5.56
Mexico City	26	7.14
Los Angeles	24	7.69
Eastern U.S.	59	3.28
Blodgett Forest	80	2.44
Mid-Pacific	250	0.79

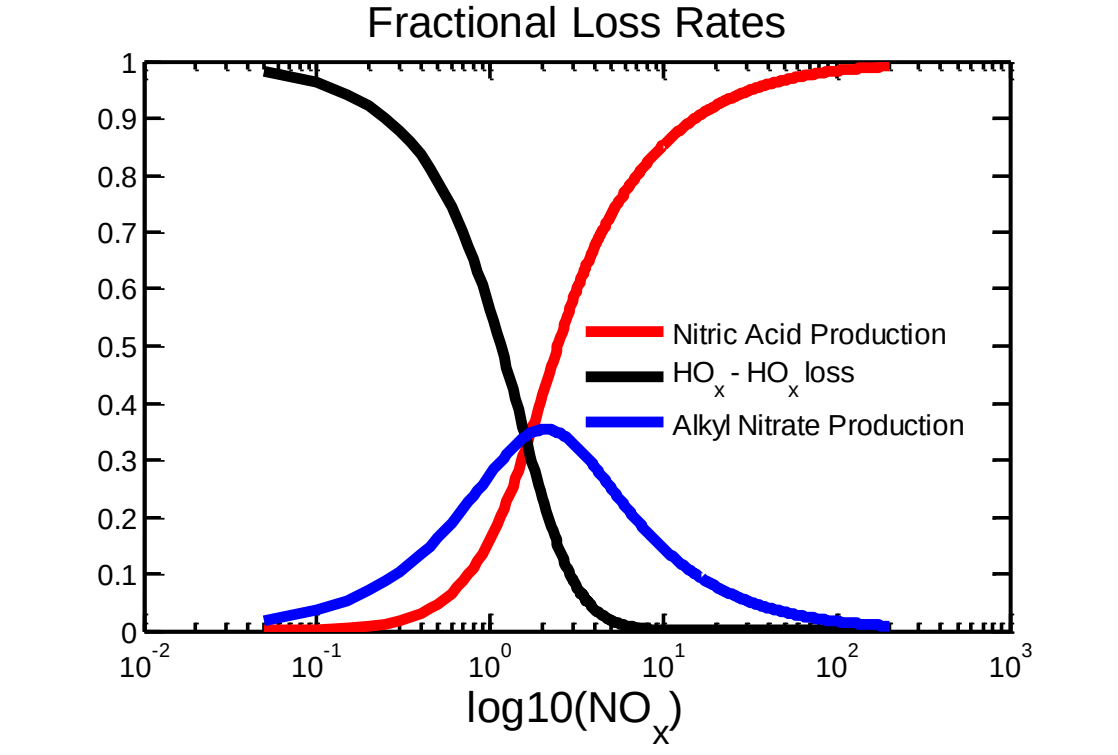
Perring and Cohen, in prep., 2011

Organic Nitrate formation effectively couples NO_x and HO_x to reduce ozone production

NO_x Limited

Termination Reactions

$HO_2 + HO_2$
$RO_2 + HO_2$
$RO_2 + RO_2$



VOC Limited

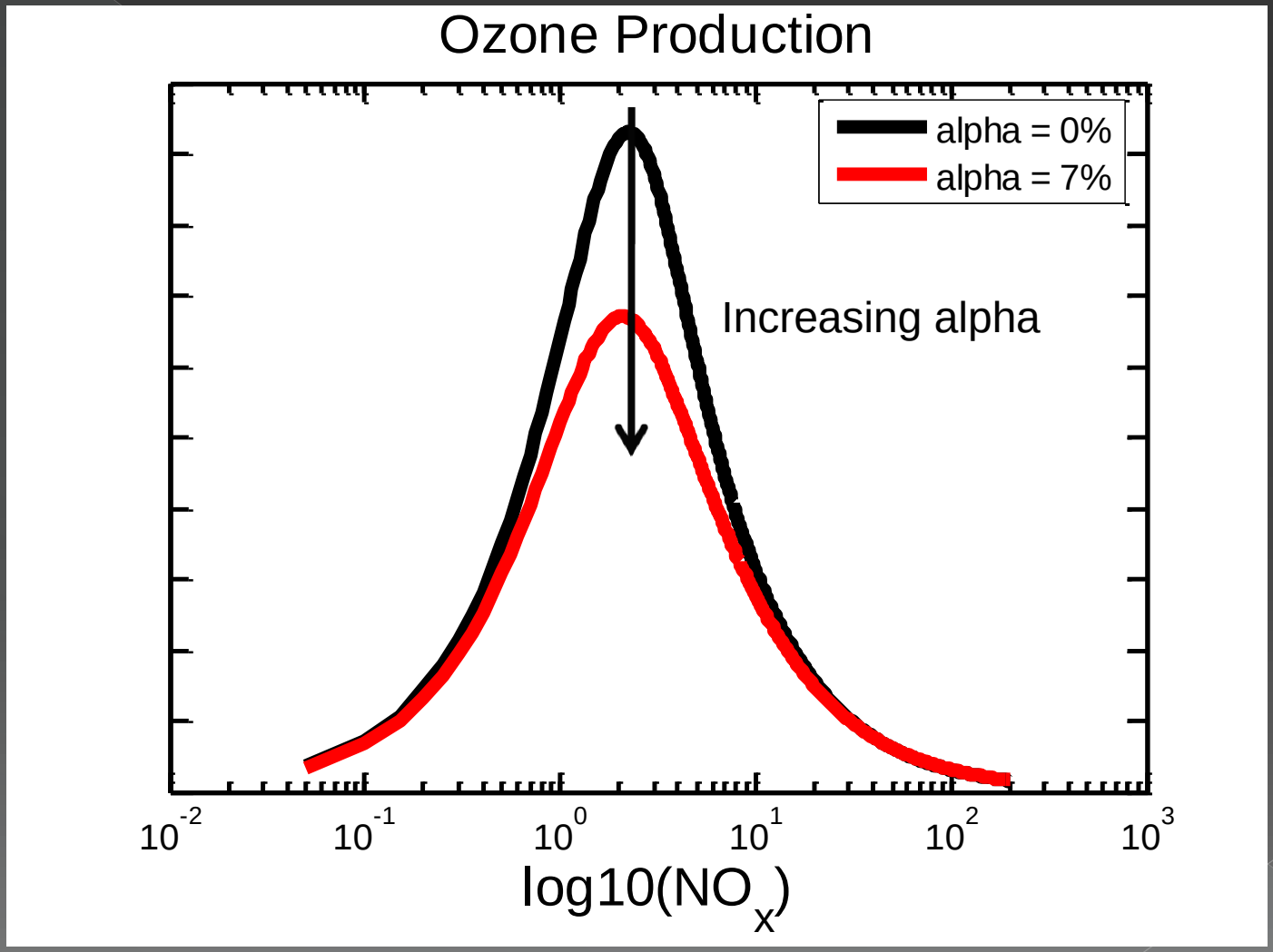
Termination Reactions

$NO_2 + OH$

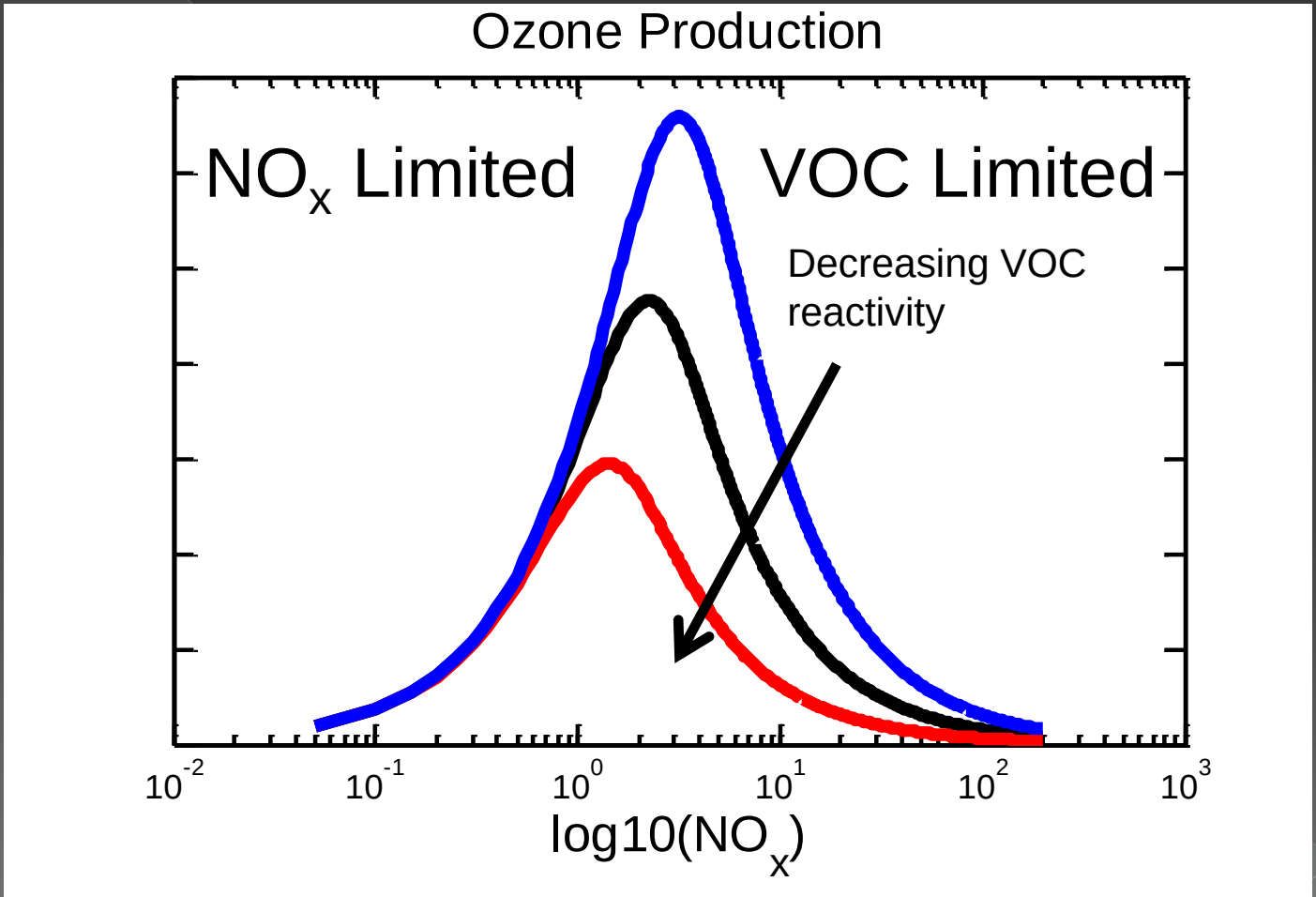
Organic Nitrate Production

$\alpha(NO + RO_2)$

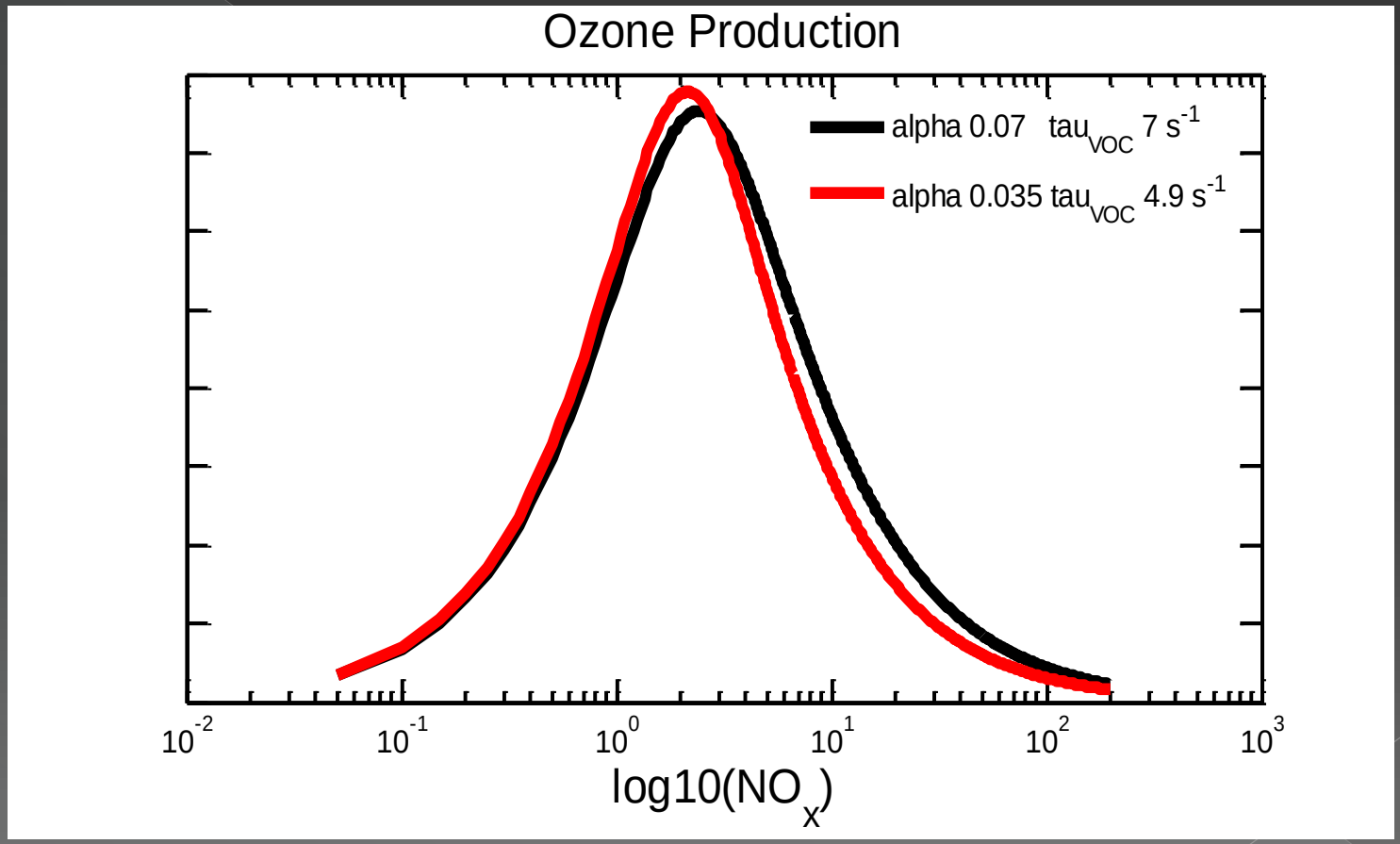
Organic Nitrate formation decreases peak ozone production



Decreasing VOC reactivity decreases ozone production



- ↓ VOC reactivity and
- ↓ organic nitrate formation
- ↑ peak ozone production
- ↑ ozone production at low NO_x



Farmer et al., ACP 2011

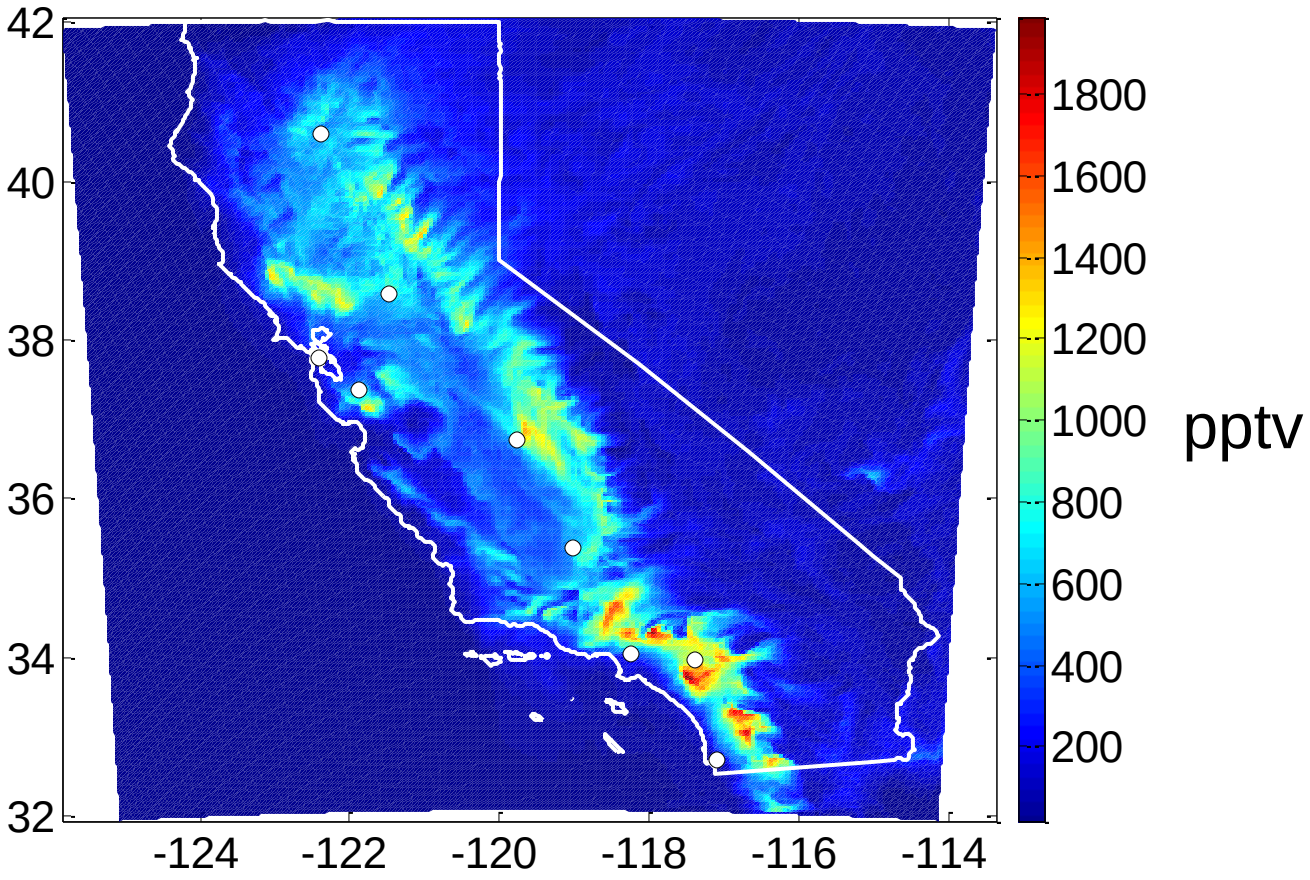
Research Questions

- If we implement a more realistic treatment of organic nitrates in a regional chemistry mechanism:
  - What does resulting organic nitrate speciation look like?
  - How are NO_y composition, NO_x lifetime and ozone production affected?
  - What are the air quality and policy implications?
    - Do we see increasing ozone with decreasing VOC reactivity in a regional model?
    - What role do biogenic emissions play?

New organic nitrate chemistry

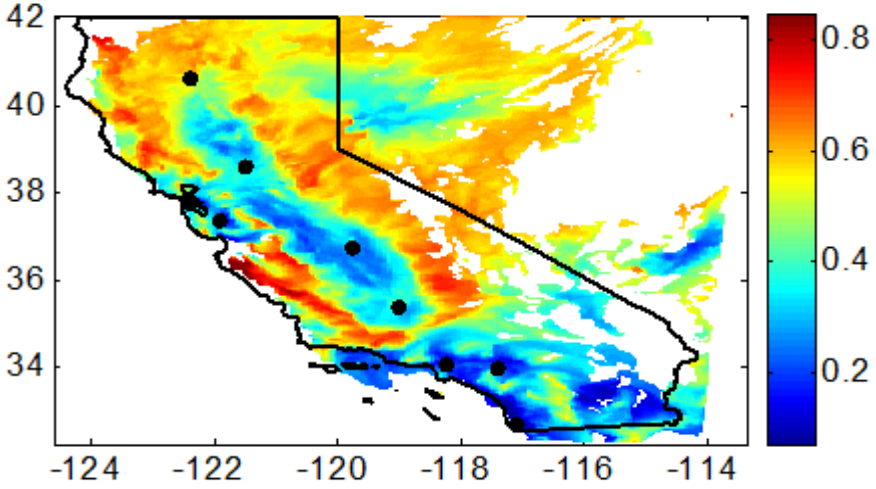
- Approach of Middleton et al., 1990 and branching ratios from MCM v3.1 and Arey et al., 2001
- Aromatic-derived nitrates (AONIT)
- Mulifunctional unsaturated nitrates (DONIT)
- Multifunctional saturated nitrates (MONIT)
- Monofunctional nitrates (ONIT)
- Terpene-derived nitrates (TONIT)
- Isoprene-derived nitrates from Paulot et al., 2009

Large concentrations of organic nitrates near urban centers and areas of high biogenic emissions

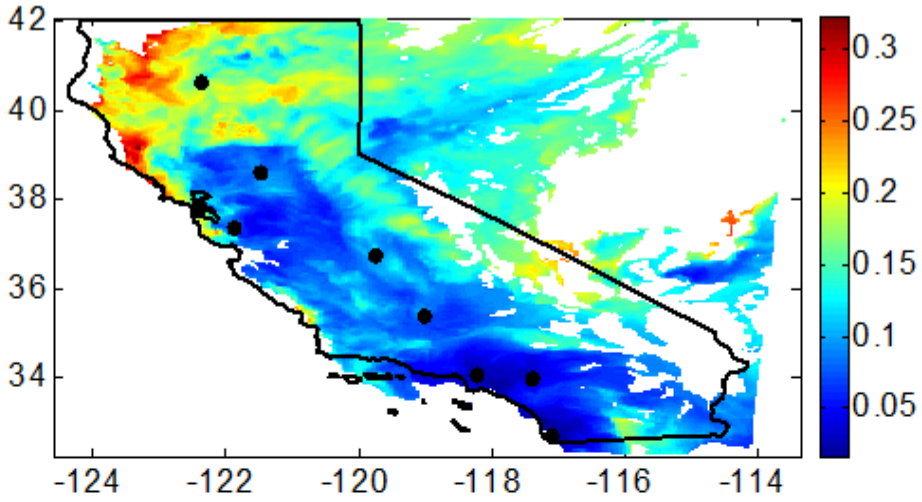


Fractional composition of organic nitrate

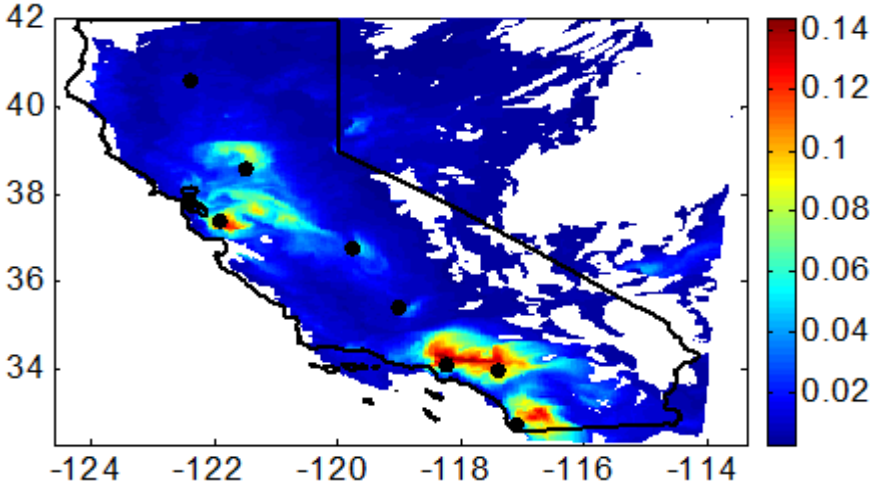
Isoprene-derived



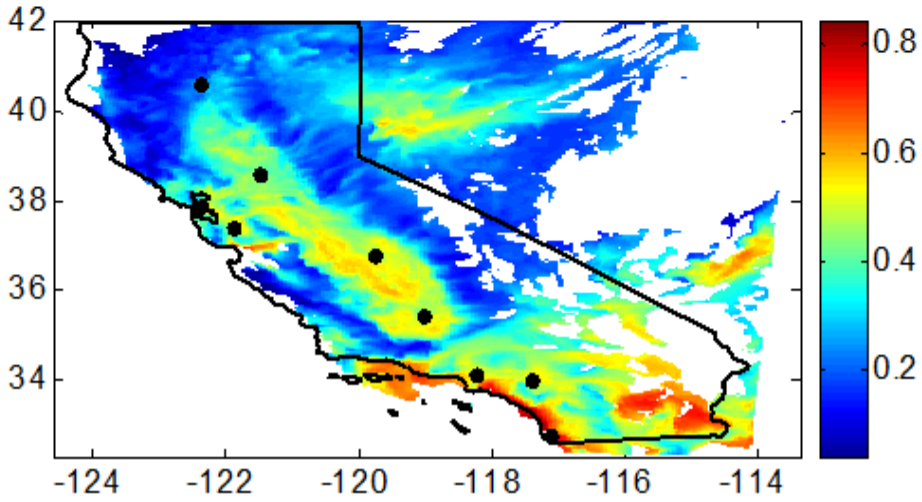
Terpene-derived



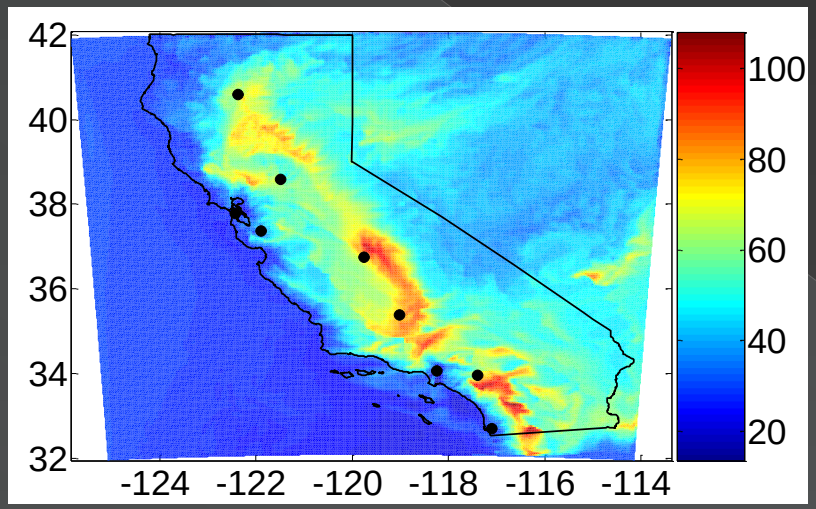
Aromatic-derived



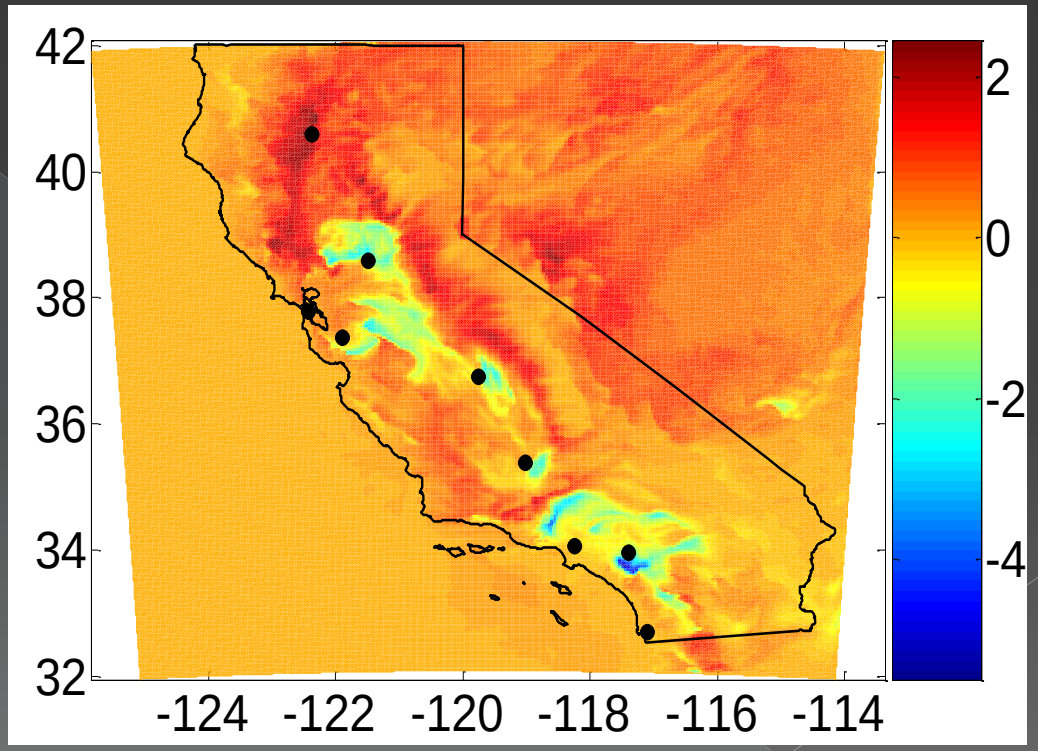
Monofunctional



New organic nitrate chemistry results in **increased background ozone** and **decreased ozone near urban areas**

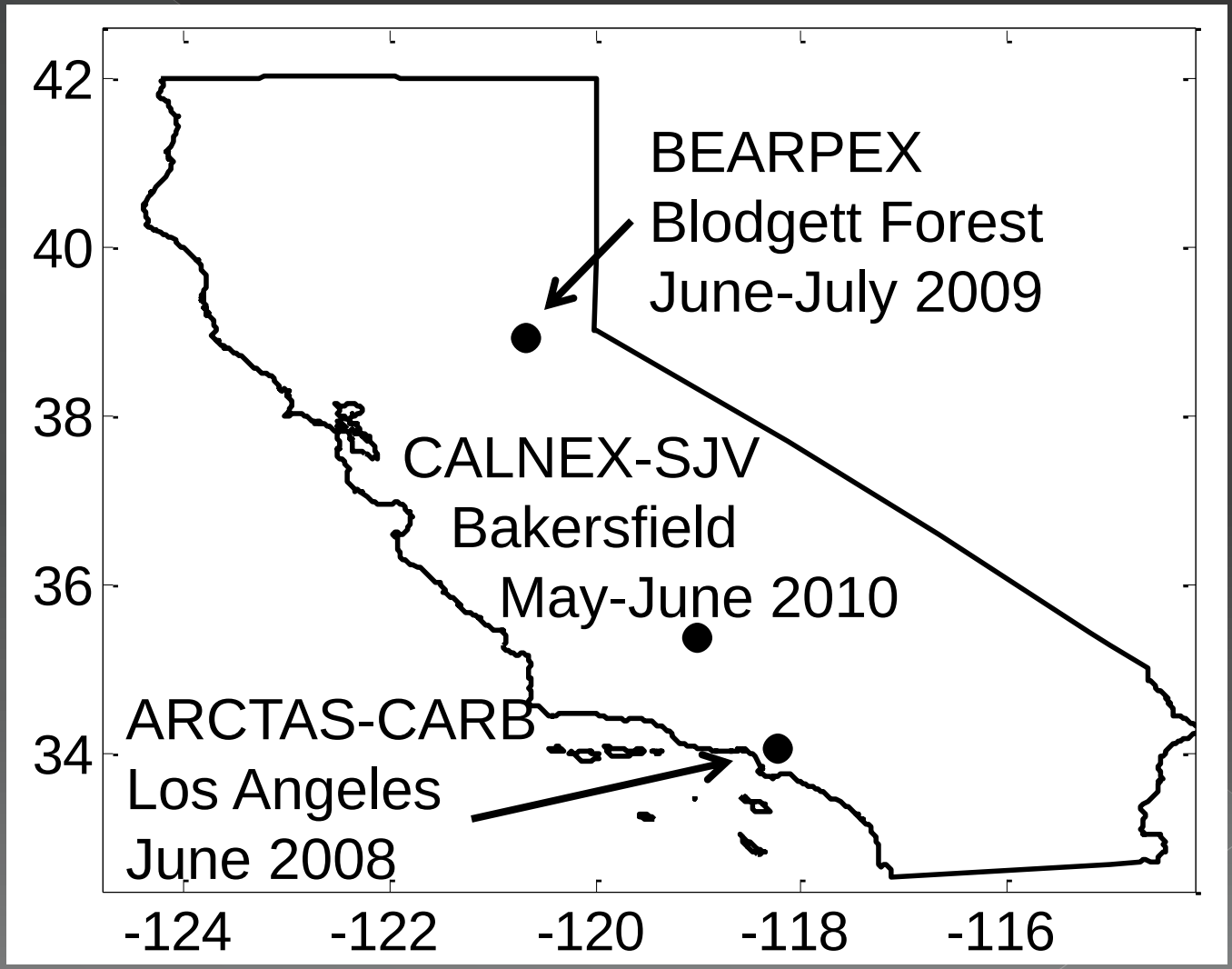


Standard chemistry surface ozone (ppbv)



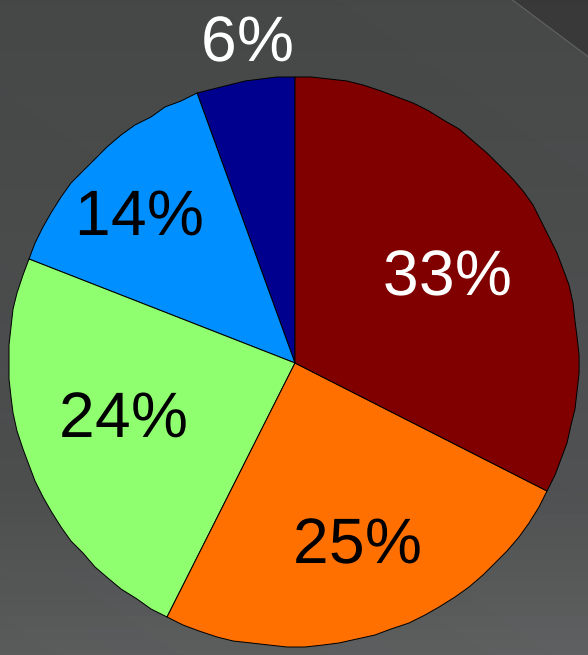
Surface ozone difference (ppbv)
New organic nitrates - standard

How do these results compare to measurements?

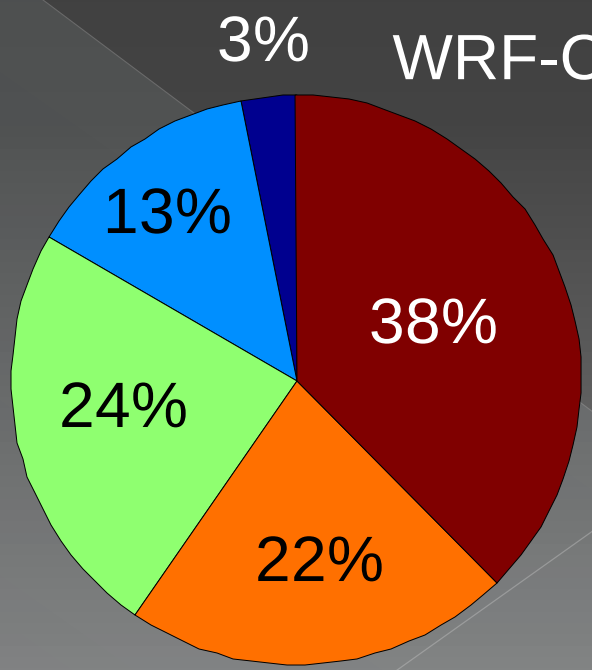


Organic nitrates account for ~25% of NO_y at Blodgett forest

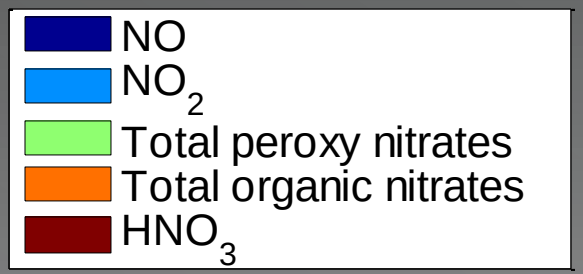
Average composition from 10-16 PST



Measurements

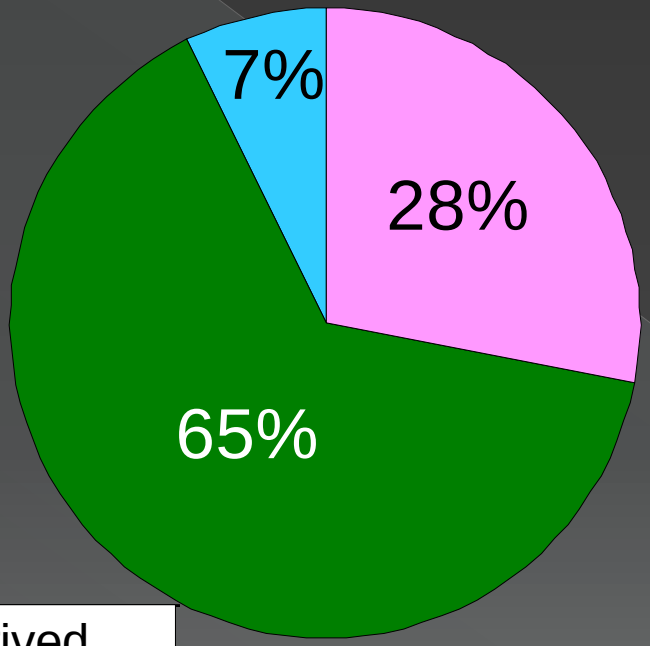


WRF-CHEM



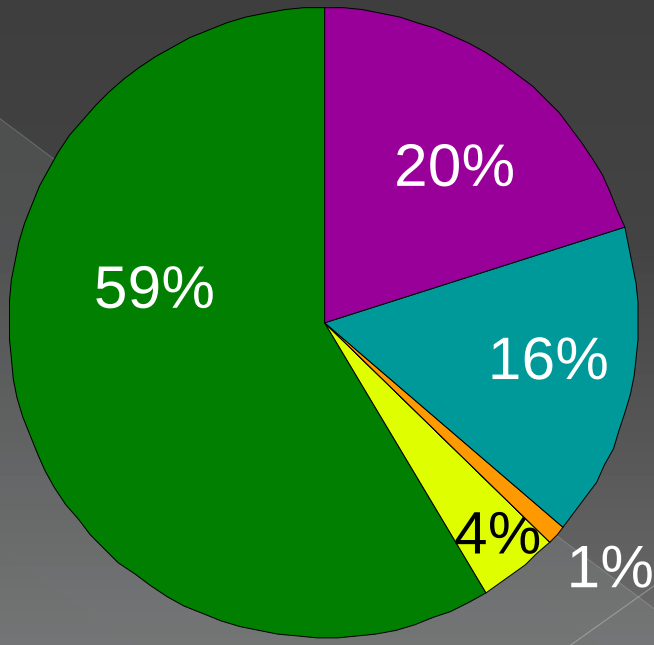
Isoprene-derived nitrates account for majority of organic nitrates at Blodgett

Measurements



MBO-derived
Isoprene-derived
Other

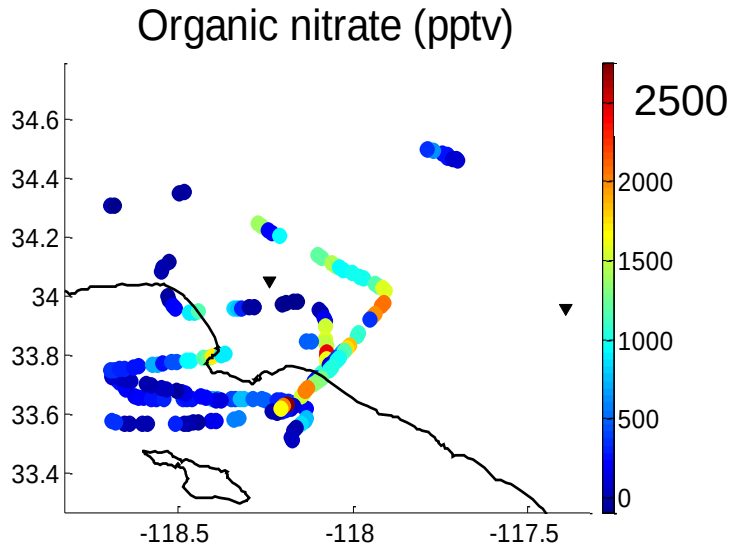
Isoprene and MBO nitrate data provided by Melinda Beaver

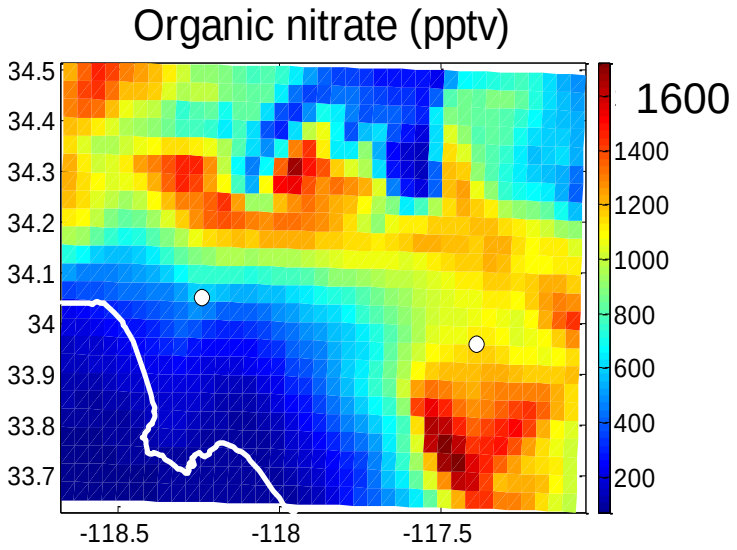


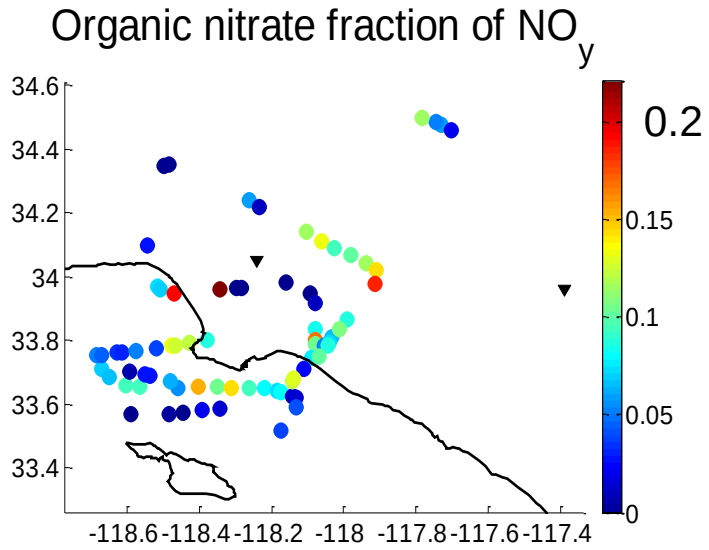
Isoprene-derived
Saturated-multifunctional
Unsaturated-multifunctional
Aromatic-derived
Terpene-derived
Monofunctional

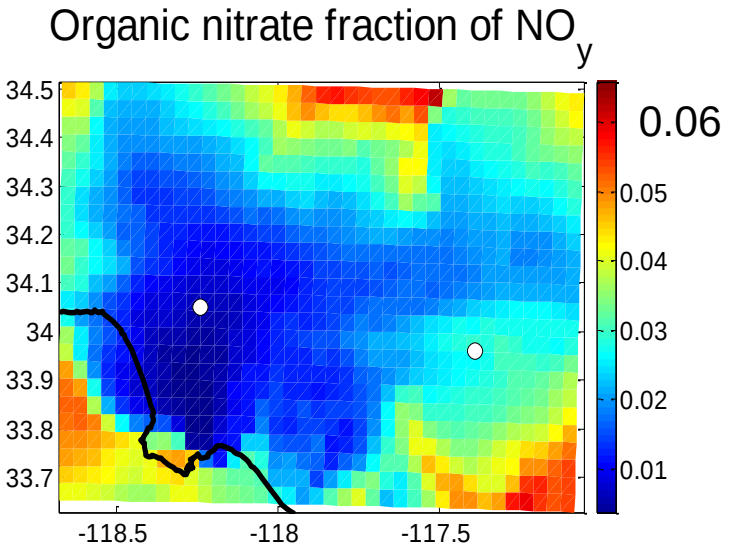
WRF-CHEM

ARCTAS-CARB, June 2008
Los Angeles





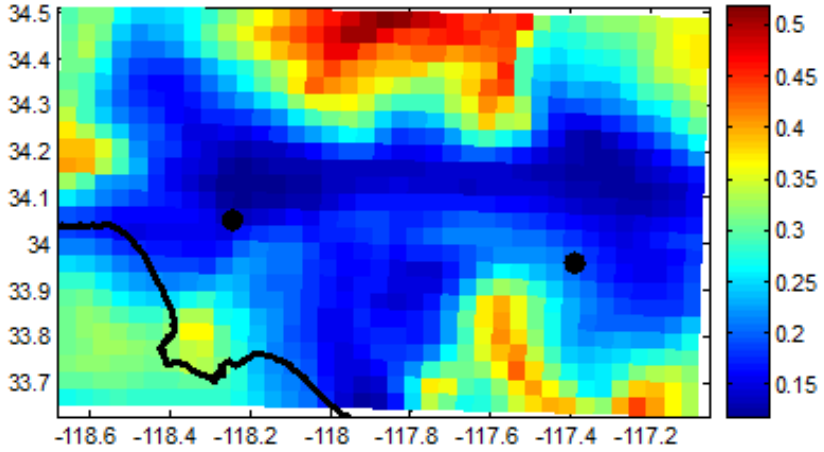




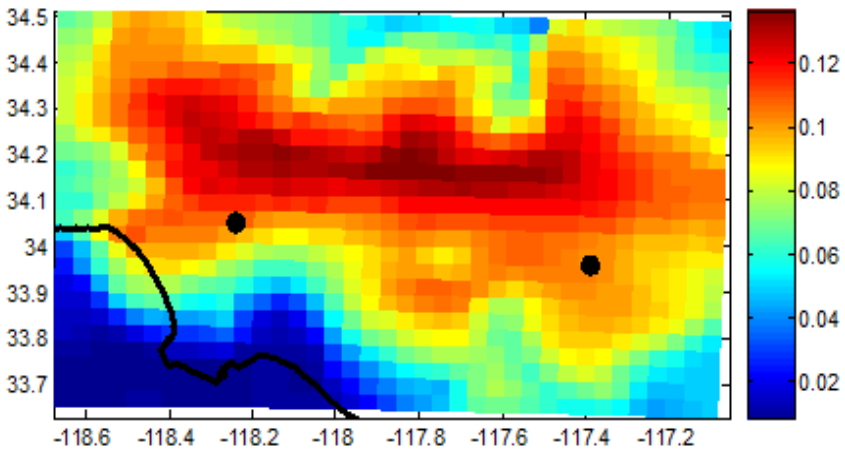
- Large variability in spatial distribution of organic nitrate consistent between measurements and model

Spatial distributions provide insight into SOA formation

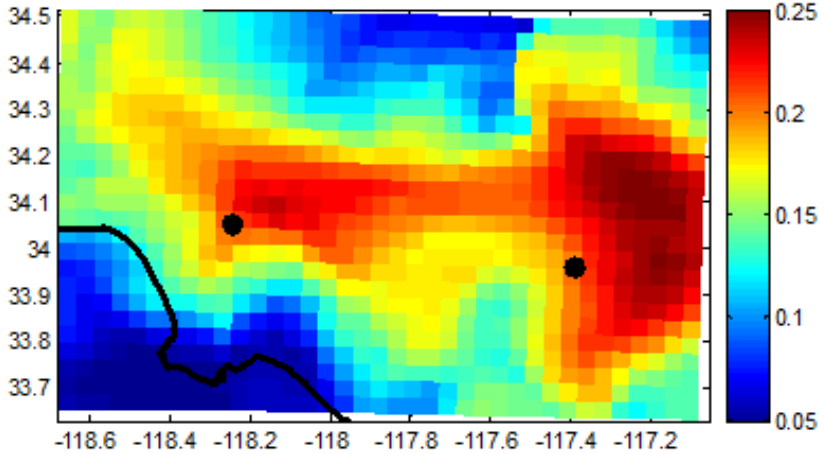
Isoprene-derived



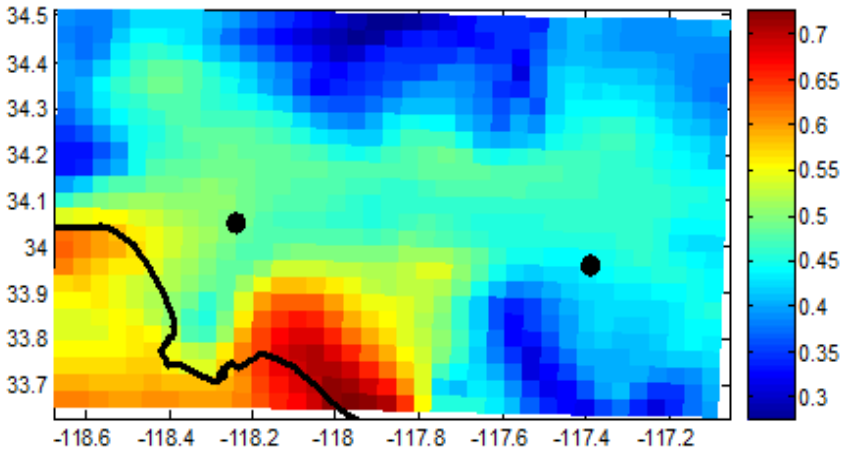
Aromatic-derived



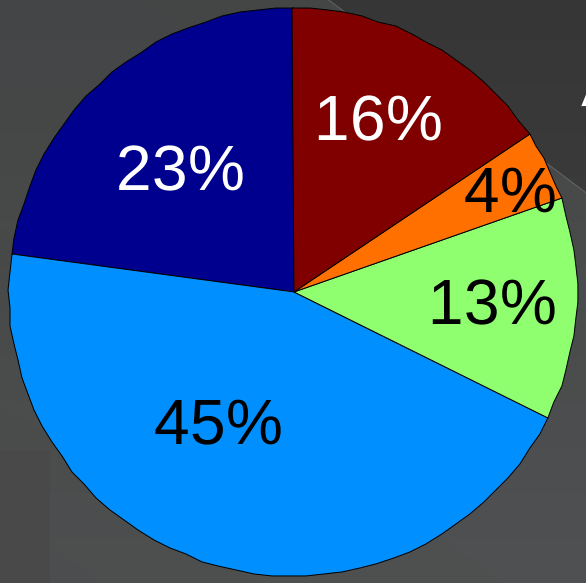
Multifunctional-saturated



Monofunctional

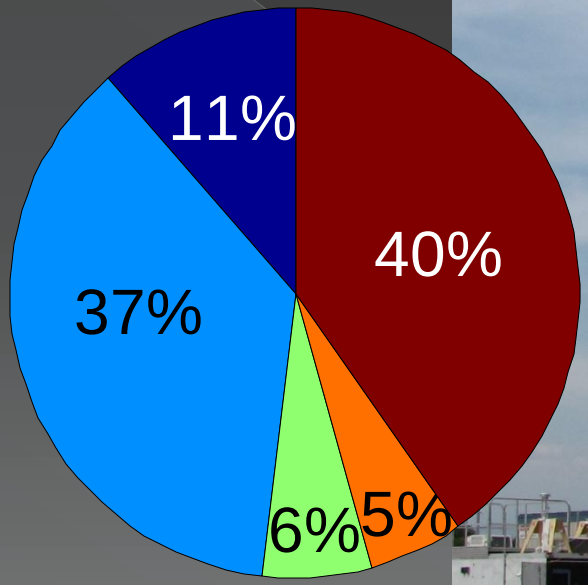


Organic nitrates are a small fraction of NO_y in Bakersfield



Average over 10-14 PST

Measurements

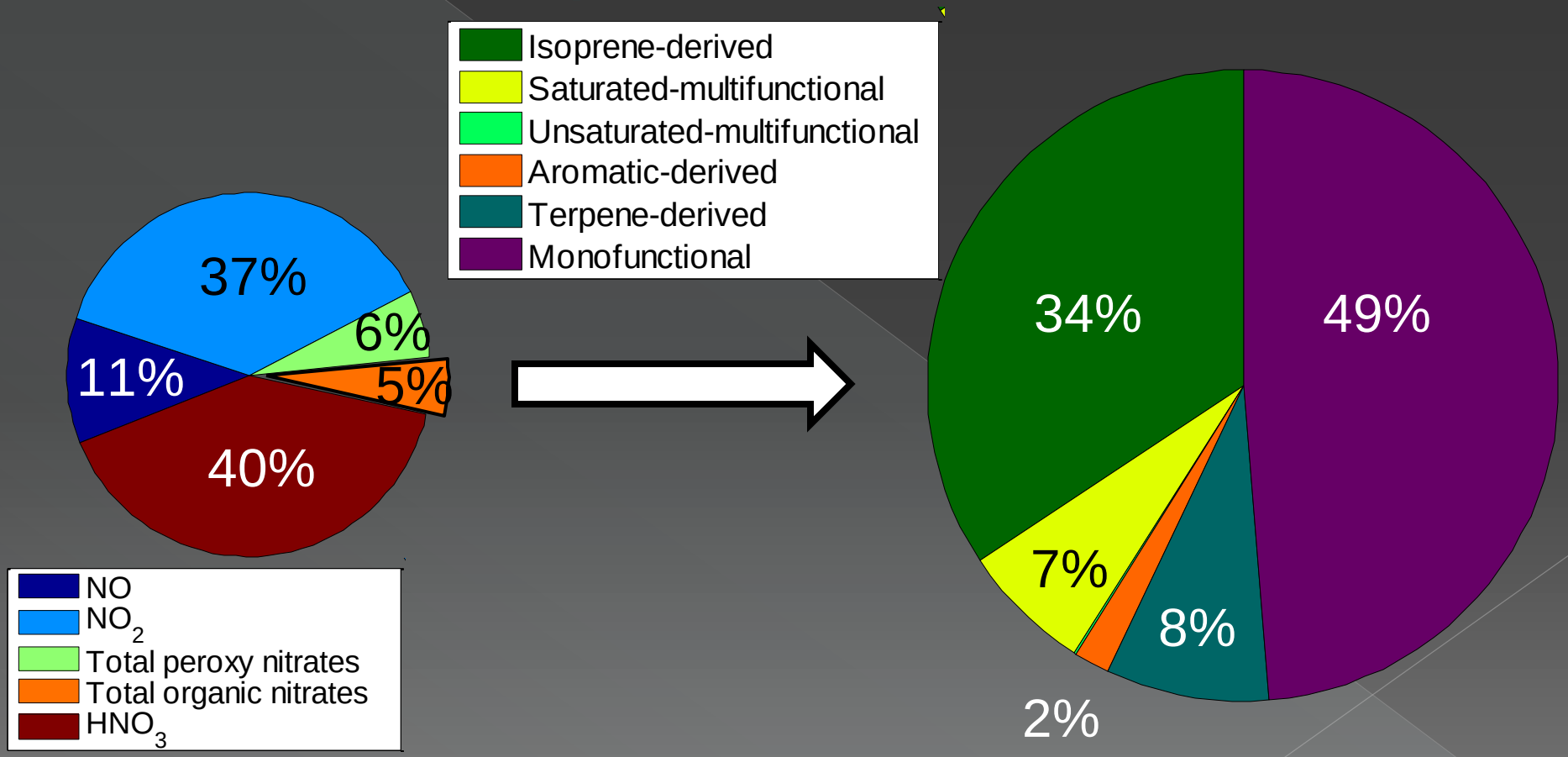


WRF-CHEM

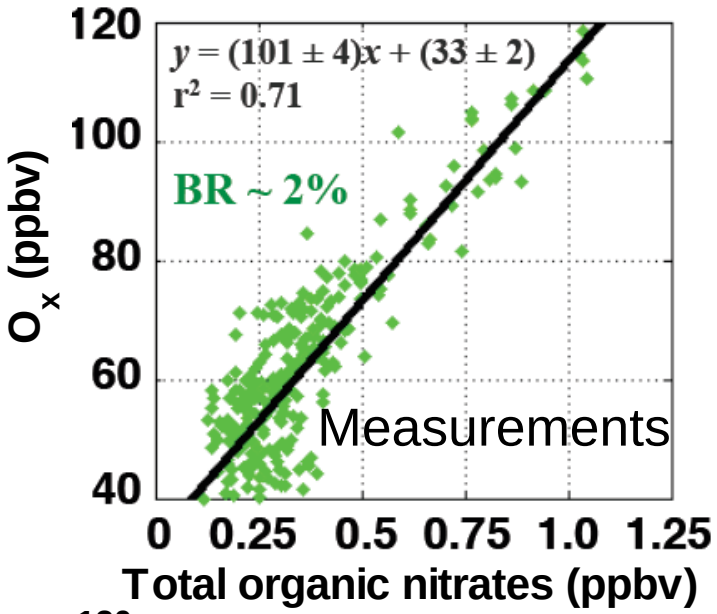
NO
NO_2
Total peroxy nitrates
Total organic nitrates
HNO_3

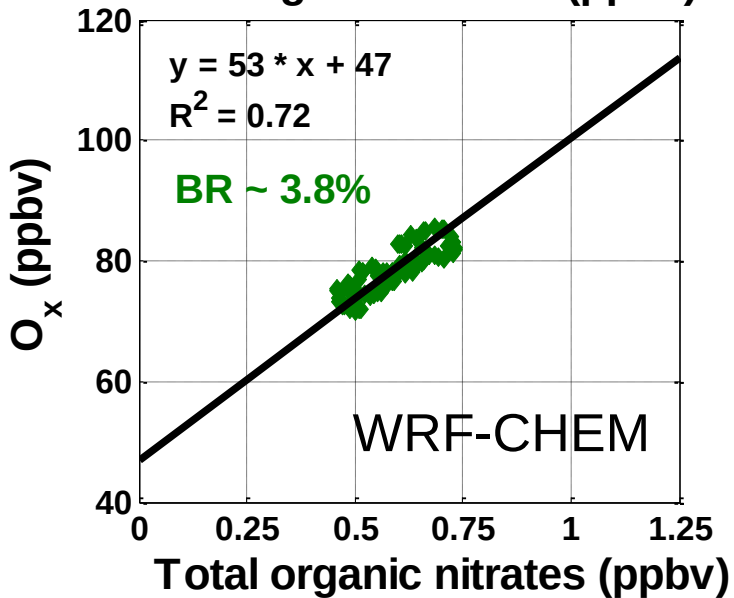
Photo credit: J. Karlik

Alkyl nitrates and long-lived isoprene-derived nitrates dominate organic nitrate composition



CALNEX measurements imply low effective organic nitrate formation





Measurements → 2% effective α
- Lowest branching ratio in an urban area
- Implications for ozone production (poster by Sally Pusede)

Model → 3.8% effective α
- Difference from measurements may help us constrain sources and lifetimes of organic nitrates

Summary

- Organic Nitrate formation effectively couples NO_x and HO_x and consequently affects ozone production.
- Improved representation of organic nitrates results in increased background ozone and decreased ozone near urban areas.
- Modeled organic nitrates and measurements of total organic nitrates in Blodgett forest, Los Angeles, and Bakersfield show strong similarities.
- Comparisons between model and measurement tests the lifetimes and sources of organic nitrates.
- Spatial and temporal distribution of organic nitrates will affect ozone production and SOA formation.
- Future work
  - NO_x recyling
  - Lifetimes
  - Aromatic-nitrate formation

Acknowledgments

- NASA
- CARB
- ARCTAS science team and flight crew
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- CalNex SJV science team, UC Kern county extension staff
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- Wendy Goliff