

Review of SAPRC-07 Chemical Mechanism

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Presentation to RSAC

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Review Elements

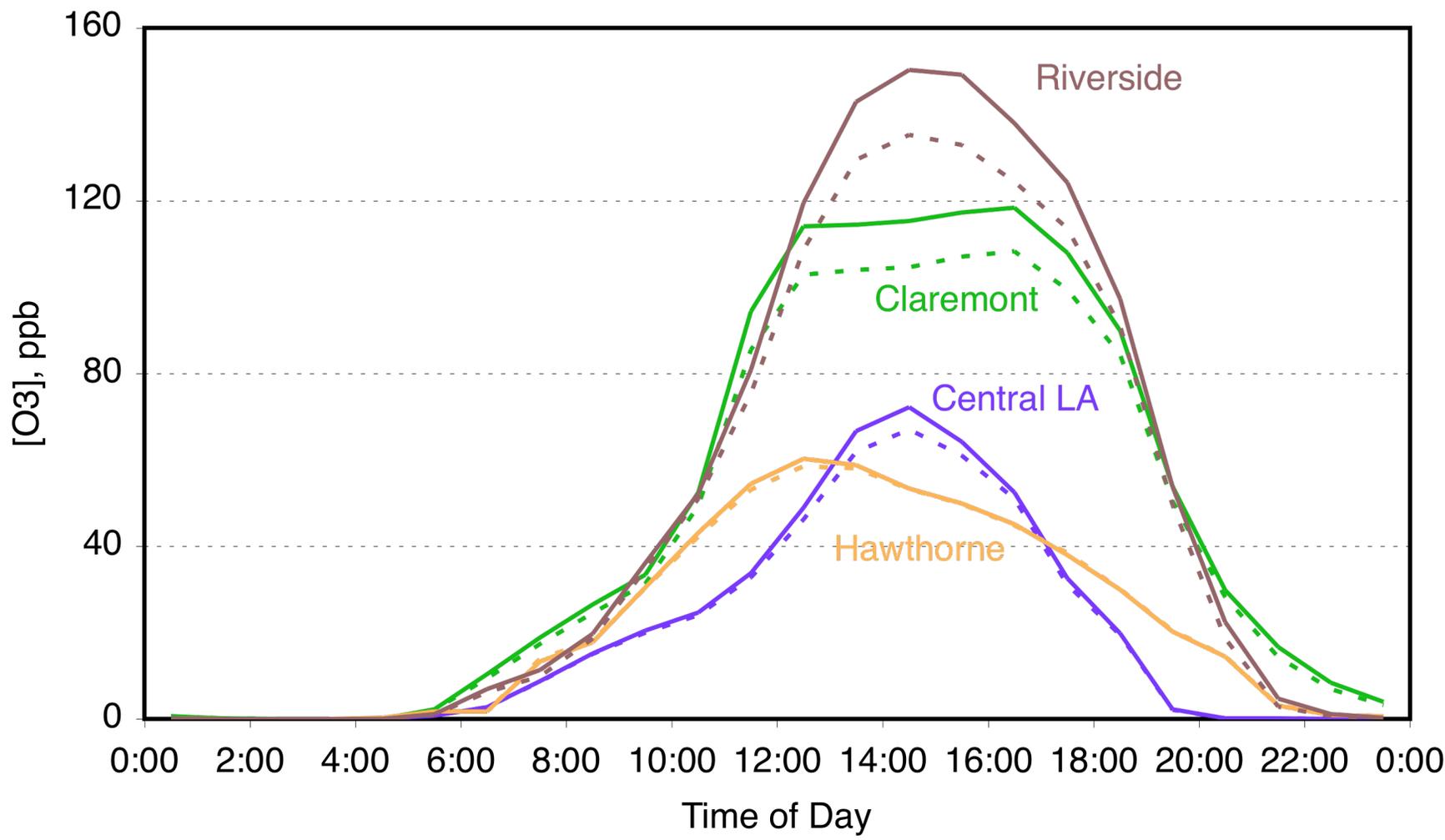
- Implementation of SAPRC-07 (CS07A) in 3-D air quality model
- Rate of nitric acid formation from OH+NO₂ reaction
- Lumped VOC species definitions

3-D Modeling w/SAPRC-07

- Implemented condensed version (CS07A) of SAPRC-07 in CIT airshed model
 - CS07A (47 species, 139 rxns, w/o chlorine chem)
 - SAPRC-99 (74 species, 210 rxns)
- Compared to SAPRC-99 predictions for southern California (3-day simulation)
- CS07A 30% faster than SAPRC-99 (with dry deposition & secondary aerosols turned off). Output file size & memory reqts reduced also.

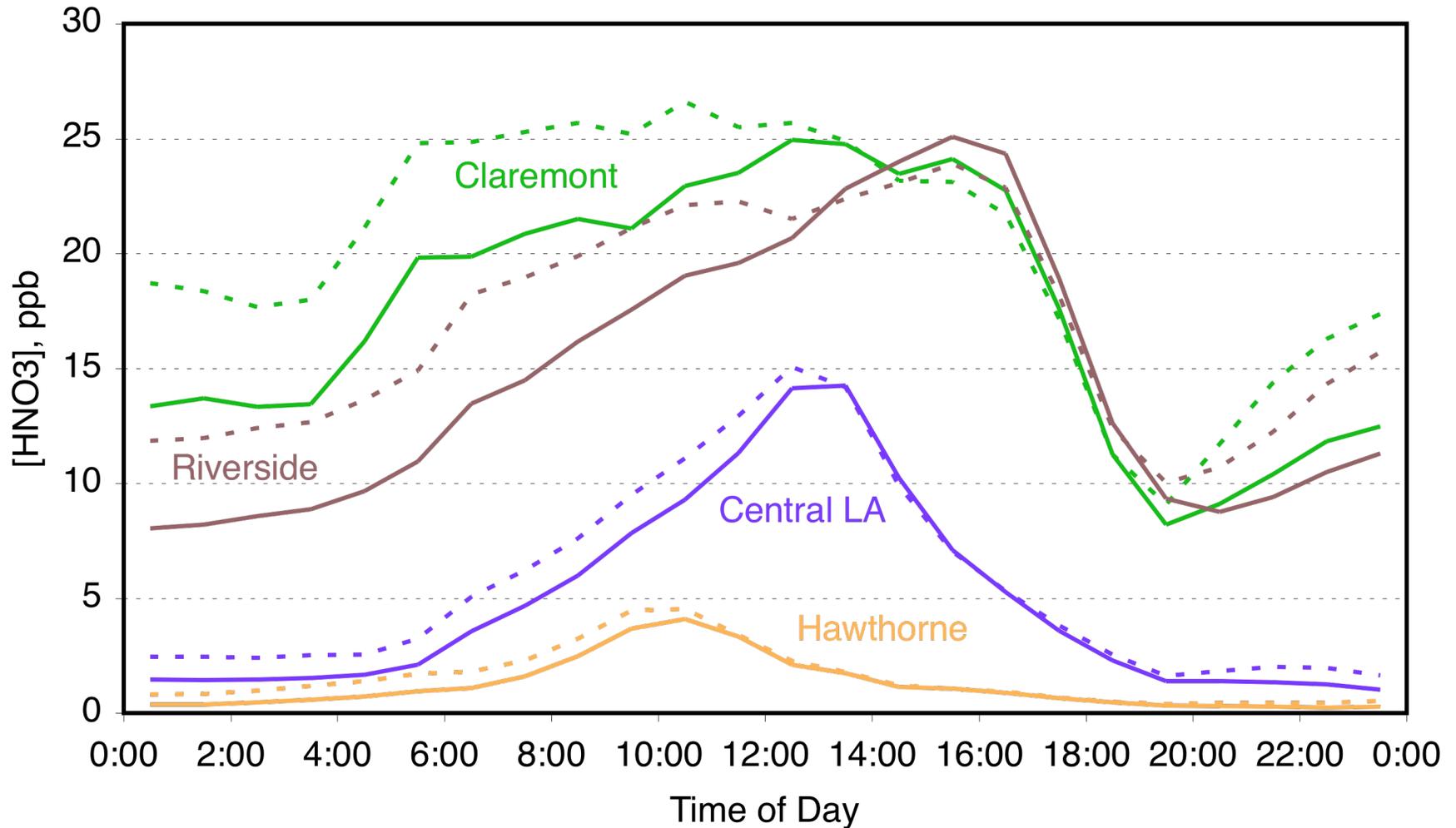
Predicted O₃ in Southern California

Airshed Model Predictions for Ozone
(SAPRC99 = solid lines; SAPRC07 = dashed lines)

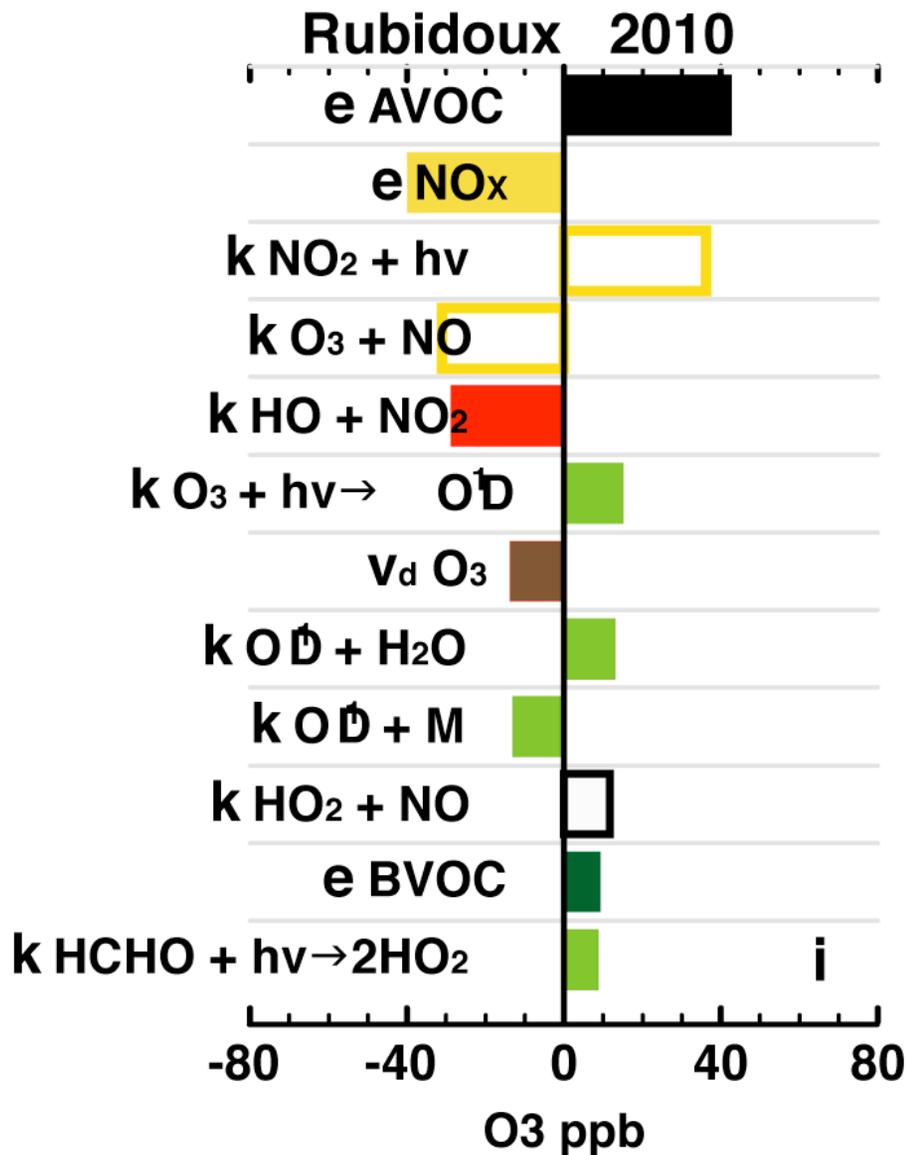


Predicted HNO₃ in So Cal

Airshed Model Predictions for Nitric Acid
(SAPRC99 = solid lines; SAPRC07 = dashed lines)



OH+NO₂



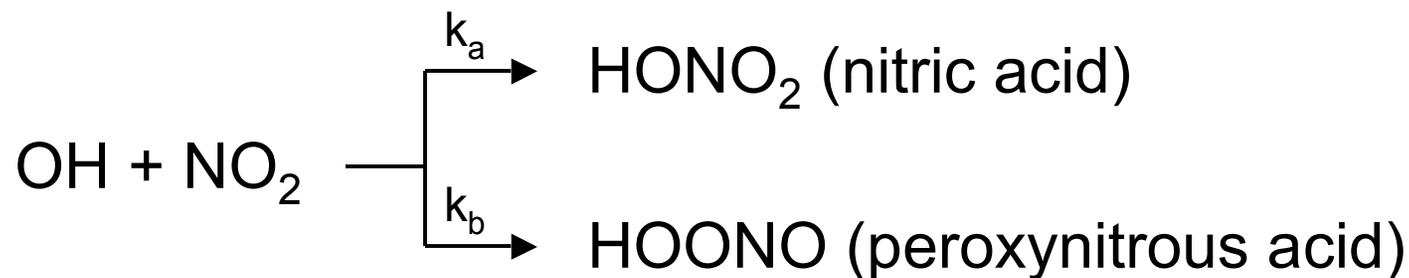
Martien & Harley (ES&T 2006) calculated and ranked sensitivity of O₃ to 900 airshed model inputs including rate coeffs, emissions, BC, IC, & deposition velocities.

k(OH+NO₂) is highly ranked (5th out of 900 parameters!)

Changes to k(OH+NO₂) require other revisions to mechanism to fit chamber data

OH+NO₂

- Reaction of OH+NO₂ has 2 pathways:



- Range of recommended values for k_a :
 - IUPAC (2004) $11.8 \times 10^{-12} \text{ cm}^3/(\text{molec-s})$
 - JPL (2006) 10.6
 - JPL (2000) 8.8
 - Okumura et al (2005) 8.7

VOC Lumping Strategy

- Most users of SAPRC mechanism use “fixed parameter” version rather than calculating oxidation product yields etc.
 - Review of lumped species definitions appropriate since others will typically use them “as is”
- SAPRC follows good practice of separating biogenic VOC (isoprene & lumped terpenes) from anthropogenic VOC

Lumped VOC Species

- Category 1 (definitions seem reasonable):
 - ALK1 (100% ethane)
 - ALK2 (100% propane)
 - ALK3 (68% n-C₄, 30% iso-C₄)
 - ALK4 (62% C₅, 29% C₆)

 - ARO1 (75% toluene, 10% ethylbenzene)
- Hard to define a universal lumped terpene:
 - TERP (38% α -pinene, 27% β -pinene, 17% β -carene, 10% sabinene, 9% *d*-limonene)

Lumped VOC Species

- Category 2 (updates may be appropriate):
 - ALK5 (C₇⁺ alkanes)
 - does not include trimethylpentanes
 - ARO2 (di/trialkyl benzenes)
 - m/p-xylene co-elution (ARO2 = 13% meta/13% para)
 - trimethylbenzene isomers (124 vs 123, 135 isomers)
 - OLE1 (terminal) and OLE2 (internal alkenes)
 - 1-butene (OLE1) and isobutene (OLE2)
- Base mixture may have more ALK & oxy-VOC, less OLE & ARO compared to 1980s