Photochemical Mechanism Reduction for the SAPRC Mechanism

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Introduction

Mechanism Reduction

- Mechanism reductions of a system:
  - Intrinsic low dimensional manifolds (ILDM), sensitivity analysis, species lumping, repro-modeling, etc
  - Elimination of redundant species and reactions
  - Providing reasonable representations

- Reduction methods based on sensitivity analysis:
  - Reduced mechanisms represent the behavior of key species with significant computer time saving
  - Applied to troposphere systems several times

Introduction

Objective of the Study

- To apply mechanism reduction methods to SAPRC:
  - Evaluate predictions of reduced mechanisms over a wide range of conditions
  - Compare computational resources of mechanisms

Methods

Chemical Mechanism

- SAPRC-99 chemical mechanism:

  - Employed to study the applicability of the reduction methods to a realistic atmospheric mechanism
  - Representing the detailed gas phase atmospheric reactions used in Models-3/CMAQ→72 species, 216 reactions and 25 photolytic reactions

Methods

Numerical Model

- Model description: simple box model
  - 1500 test cases representing the range of air quality, temperature and relative humidity in the San Joaquin Valley of California (July 30-31, 2000)
    a) 500 represent daytime conditions
    b) 500 represent nighttime conditions
    c) 500 represent sunset/sundown transitions
  - Concentrations of species simulated for 10 minute period
  - LSODES with low tolerances used to obtain a highly accurate solution for the full mechanism→Gold standard
  - **O_3 concentration** prediction accuracy used as a primary consideration when reducing the full mechanism

Identification of Redundant Species

- Identification of redundant species:

- ***Important*** species→O_3 concentration
- ***Necessary*** species→the species have direct or indirect effects on O_3 concentrations
- ***Redundant*** species →the effects on predictions of the important and necessary species concentrations are negligible

- The sum of squares of normalized Jacobian elements $\boldsymbol{B_i}$:

$$B_i = \sum_{n=1}^{N} \left(\frac{\partial \ln f_n}{\partial \ln c_i} \right)^2$$

f_n : the net rate of reaction of the N-membered group of ***important*** and ***necessary*** species

- Species identified as redundant for all 1500 cases are eliminated from the mechanism

Identification of Redundant Reactions

- Additional identification of redundant reactions:

- Redundant reactions are identified using rate-sensitivity analysis that calculates the log-normalized rate sensitivity matrix:

$$F_{ij} = \frac{\partial \ln f_i}{\partial \ln k_j} = \frac{\nu_{ji} R_j}{f_i}$$

k_j : the rate parameter

ν_{ji} : the stoichiometric number of species i in reaction j

R_j : the rate of reaction j

f_i : the net rate of reaction of species i

- The matrix is interpreted using principle component analysis (PCA) based on an eigen-decomposition of the cross-product matrix F^TF
- Thresholds are defined for eigenvalues and eigenvector magnitudes to determine which reactions are redundant

Methods

QSSA

- QSSA (quasi-steady-state approximation):

- Species can be placed in steady state if their reaction rates are much faster than the rates of related species
- The concentrations of the species with fast timescales can be computed algebraically in terms of other species concentrations
- QSSA species selected by calculating instantaneous errors
- If the single and group errors are small at all chosen time points, these species are identified as QSSA species and the differential equations are replaced by algebraic equations
- Nonlinear QSSA species are not removed due to computational considerations

Results

Mechanism Reduction

- Mechanism reduction:
  - Redundant species were identified using concentration sensitivity analysis→19 species were removed from the mechanism
  - Redundant reactions were identified using rate sensitivity analysis→104 reactions were removed from the mechanism
  - As a result of the QSSA reduction two reduced mechanisms were developed

    O^1D^2 and O^3P (reduced model I)

    O^1D^2, O^3P and OH (reduced model II)

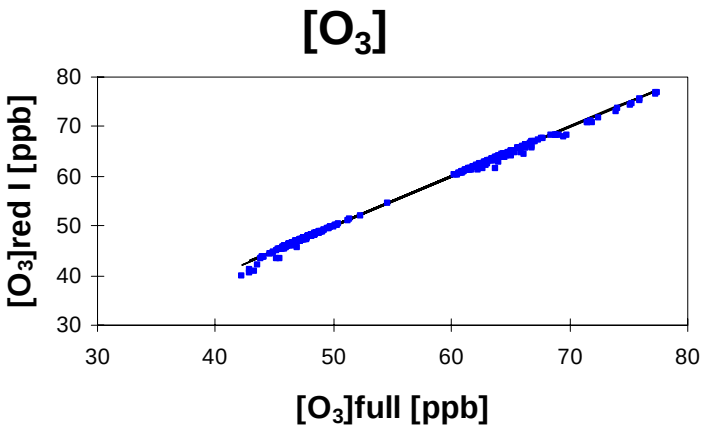
Number of reactions and species of full and reduced mechanisms

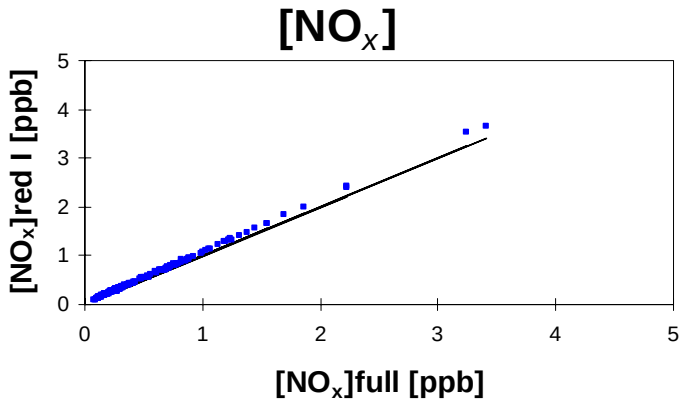
Mechanism	Full Model	Reduced Model I	Reduced Model II
Species	72	20	19
Reactions	216	55	55
QSSA species		2	3

Results

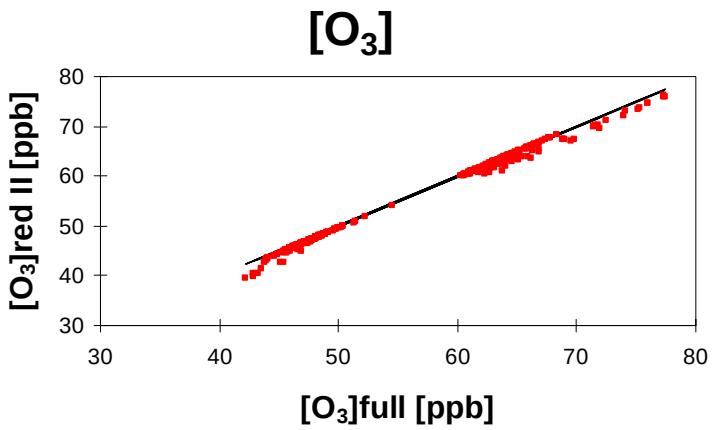
Comparison with SAPRC-full (Day)

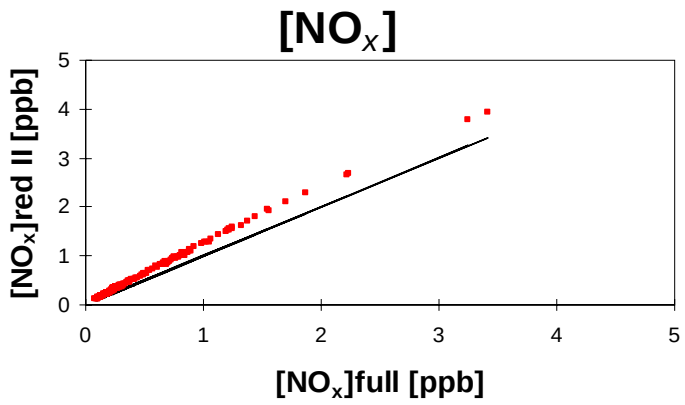
Reduced Mechanism I





Reduced Mechanism II





Results

Percentage Relative Errors

Percentage relative errors in concentration after reduction

Species	Reduced Mechanism I			Reduced Mechanism II		
	Nighttime (%)	Transition (%)	Daytime (%)	Nighttime (%)	Transition (%)	Daytime (%)
O_3	0.020	**0.015**	0.76	0.011	0.016	**1.43**
NO_x	7.23	1.59	8.93	6.95	2.18	17.71
HCHO	0.72	0.62	7.26	0.70	0.60	7.27

Computational Resources

CPU time for three different scenarios (500 runs)

	CPU time (s)			
Mechanism	Nighttime	Transition	Daytime	Average
Full model	35.31	32.70	29.52	**32.51**
Red model I	2.92	2.66	3.69	**3.09**
Red model II	2.44	1.80	3.07	**2.43**

Conclusions

- 19 species and 51 reactions were removed as a result of concentration sensitivity analysis→ 53 species and 162 reactions
- 104 reactions and 31 species were eliminated as a result of reaction rate sensitivity analysis and PCA →22 species and 55 reactions
- O^1D^2, O^3P and OH were selected as QSSA species in the reduced scheme I and II
- Reduced mechanisms reproduced O_3 concentration well with the percentage relative errors less than 1.5% and NO_x concentration relatively poorly
- The CPU time reductions for the reduced mechanism I and II were approximately a factor of 11 and 14, respectively
- Such speed improvements facilitate seasonal simulations predicting O_3 concentrations or numerous sensitivity analyses