

Response to Peer Review Comments on the SAPRC Chemical Mechanism

William P. L. Carter
CE-CERT, University of California, Riverside, CA
March 25, 2009

Outline

- Discussion of the four peer review reports
 - Summary of the review comments and recommendations
 - Responses to comments
- Changes made to the SAPRC-07 mechanism resulting from this review and other considerations

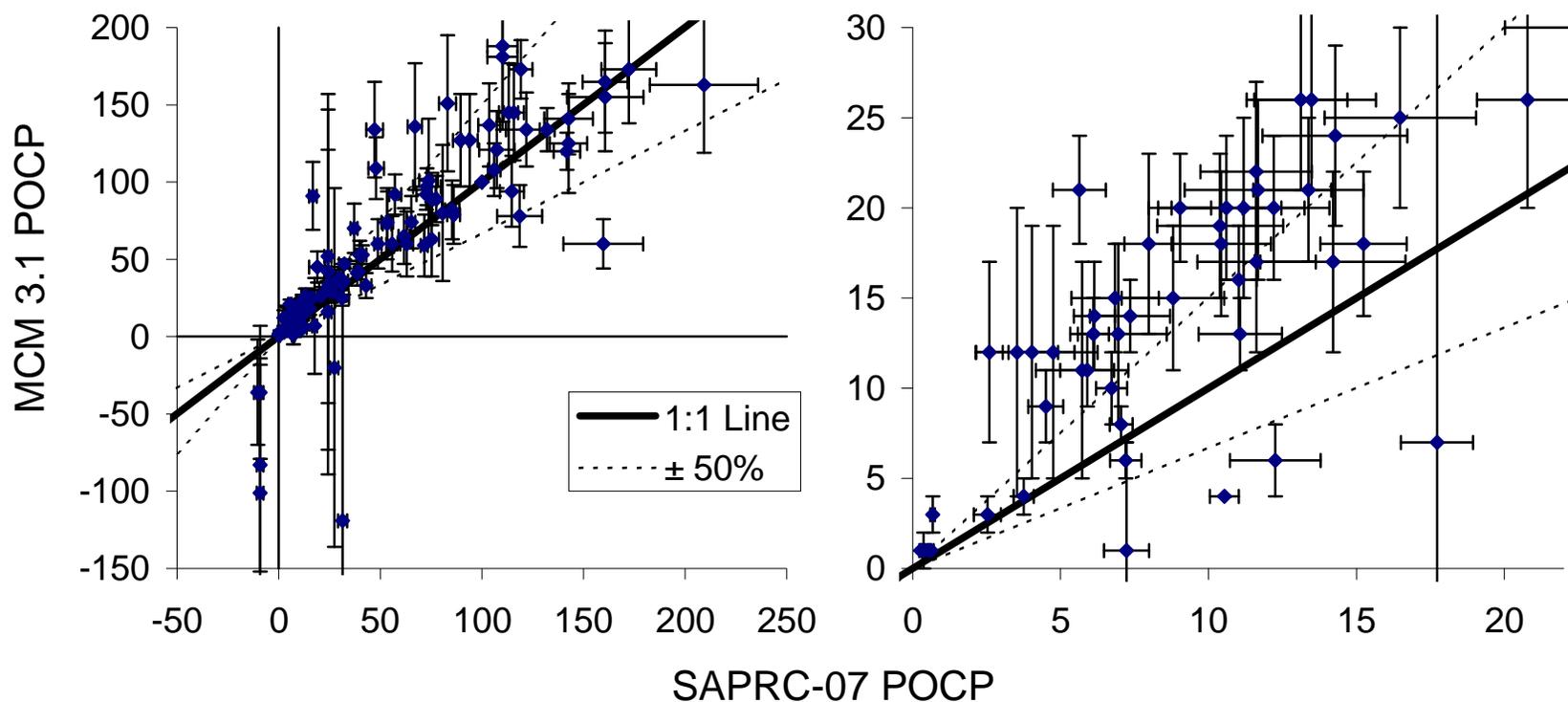
SAPRC-07 Peer Review Reports

- R. Derwent, M. Jenkin, and M. Pilling: “Reactivity Scales as Comparative Tools for Chemical Mechanisms: SAPRC vs. MCM”
- M. Azzi, S. White and D. Angove (2008): “Review of the SAPRC-07 Chemical Mechanism”
- R. Harley: “SAPRC-07 Chemical Mechanism Peer Review Comments”
- W. Stockwell (2009): “Peer Review of the SAPRC-07 Chemical Mechanism of Dr. William Carter”

Review by Derwent et al.

- Compared POCPs (reactivities relative to ethene) for 121 representative compounds calculated using MCM Version 3.1 and 5 selected MIR scenarios with SAPRC-07 MIRs
- It is actually more useful to compare SAPRC-07 POCPs for the same 5 scenarios, but the general conclusions are the same.
- In most cases reasonable correspondences between MCM and SAPRC-07 MIR POCPs were found. But there were differences:
 - Significant differences for some compounds found
 - Tendency for SAPRC-99 to give slightly higher POCPs
- Some but not all of the differences can be explained by known differences between the MCM 3.1 and SAPRC-07 mechanisms

Average POCPs* for Five MIR Scenarios: MCM 3.1 vs. SAPRC-99



* Incremental Reactivities relative to Ethene = 100

Representative Compounds with Significant Differences in MCM vs. SAPRC-07 POCPs

Compound	POCP		Possible Reason for POCP difference
	S-07	MCM	
Methyl Acetate	0.7	3	MCM forms more reactive products (formaldehyde)
Tetrachloroethylene	0.3	1	Phosgene photolyzes in MCM. Inert in SAPRC
Glyoxal	160	60	Glyoxal photolysis 4 x faster in SAPRC
Acetylene	11	4	
Methacrolein	67	136	Methacrolein photolysis 3 x faster in MCM
Isoprene	119	173	
d-Limonene	47	135	MCM terpene mechanisms too complex to readily assess
α -Pinene	48	109	

Responses to Review by Derwent et al.

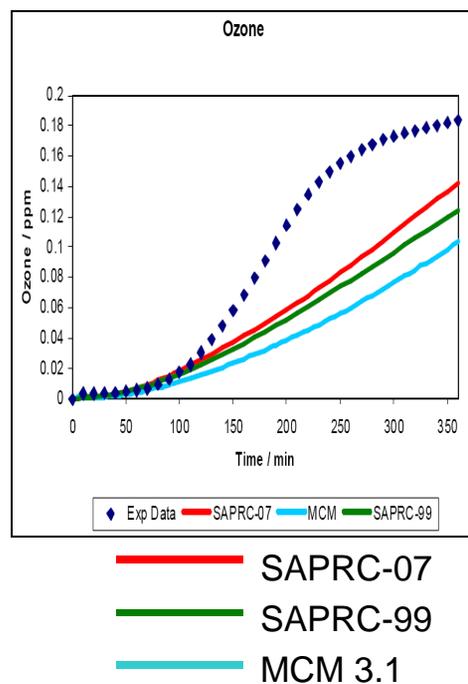
- The review of Derwent et al. is a useful comparison for individual VOCs that may reveal cases where VOC mechanisms need to be changed
- MCM tends to have higher POCPs than SAPRC-07 overall. This may be due to differences in base mechanisms
- The large differences for some VOCs appear to be primarily due to different estimates and approximations for uncertainties. In most cases both mechanisms are not unreasonable.
- The comparison did not reveal clear cases where I thought SAPRC-07 needed to be corrected at this time. **Therefore, no changes to SAPRC-07 were made as a result of this review**

Review by Azzi et al.

- Evaluated ability of SAPRC-07, SAPRC-99 and MCM-3.1 to simulate results of new CSIRO chamber experiments
- **M-Xylene – NO_x**: SAPRC-07 performed satisfactorily and better than other mechanisms
- **Isoprene – NO_x**: SAPRC-07 performance was within variability observed in simulating isoprene experiments in other chambers
- **Toluene – NO_x**: All mechanisms performed poorly simulating the three CSIRO toluene runs
- **Evaporated unleaded gasoline – NO_x**: SAPRC-99 simulated the data within uncertainties. Some problems with SAPRC-07:
 - Headspace fuel runs: SAPRC-07 results consistent
 - Whole fuel runs: Results inconsistent. Model input problems for SAPRC-07 more likely than mechanism problems

Mechanism Performance Simulating Toluene – NO_x Runs in Various Chambers

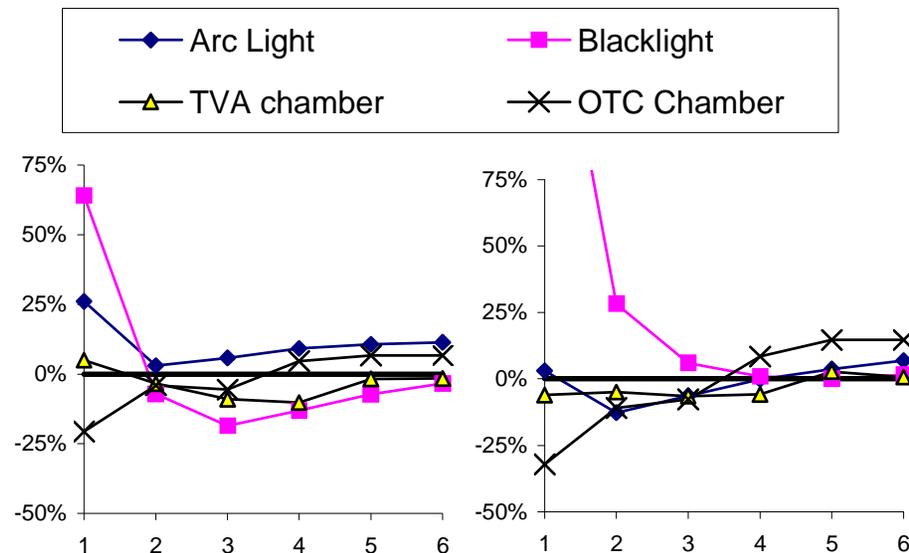
CSIRO Run 431:
O₃ vs. time



UCR and TVA Chamber Data:
Average model error vs. hour of run

SAPRC-99

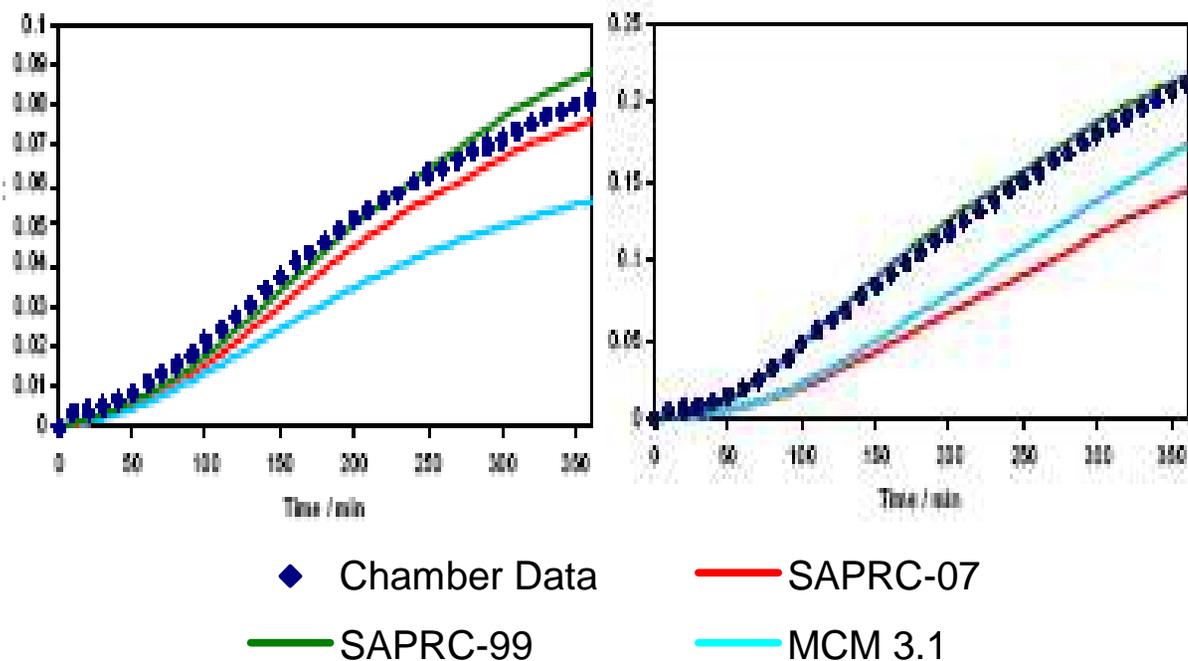
SAPRC-07



Mechanism Performance Simulating O₃ in Two CSIRO Gasoline Experiments

Headspace Vapor

Whole Fuel



Note inconsistent differences of SAPRC-07 relative to the MCM

Responses to Review by Azzi et al.

- The review of Azzi et al. provides useful independent mechanism evaluation against new environmental chamber data
- The results for m-xylene, isoprene and headspace gasoline were within the variability and uncertainty of the previous chamber evaluations and indicate no new mechanism problems
- The results for toluene suggest mechanism problems, but are insufficient in themselves to justify for changing the mechanism.
- The possibility of input problems when modeling the whole gasoline experiments need to be investigated
- **Therefore, no changes to SAPRC-07 were made as a result of this review**

Review by Harley

- Implemented condensed SAPRC-07 (CS07A) into a 3-D model of the CSCAB and compared simulations with SAPRC-99
 - Condensed SAPRC-07 required less computer time than SAPRC-99 because of its smaller size
 - SAPRC-07 gave less O₃ and more HNO₃ than SAPRC-99
This may be due to 19% higher k(OH + NO₂) in SAPRC-07
- Recommended that a version of SAPRC-07 with lower k(OH + NO₂) be developed for sensitivity studies
- Recommended that the base ROG mixture used to derive the fixed parameter mechanism be updated and simplified
- Recommended that the dividing line between the lumped alkenes OLE1 and OLE2 be changed so 1-butene and isobutene are lumped together because of GC separation problems

Responses to Harley's Review

- Condensed SAPRC-97 vs. SAPRC-99 comparison:
 - CS07A should give the same O_3 as SAPRC-07 so the test calculations give a good indication SAPRC-07 vs. SAPRC-99
 - The change in $k(OH + NO_2)$ is probably the most important reason for the differences, but this needs to be examined.
- The recommendations to develop a version of SAPRC-07 with a lower $k(OH + NO_2)$ for sensitivity studies has merit, **but**
 - Cannot justify changing this important rate constant until new data are published or given in updated evaluations
 - Developing a mechanism with a different $k(OH + NO_2)$ will be a major effort that requires funding
 - Would it be better to wait until the NASA and/or IUPAC evaluations are updated?

Responses to Harley's Review (continued)

- The recommendation to update the base ROG has merit, but requires work that is beyond the scope of the present project
 - A project for the University of Texas to update the base ROG is being initiated. The fixed parameter mechanism can be updated once this work is completed and undergone review
 - It is not necessary at this time to simplify the base ROG. This can be considered after it is updated.
- It is more appropriate to continue to represent isobutene by OLE2 because its rate constants are closer to those of OLE2.
 - Changing the lumping does not eliminate the effects of the GC uncertainties on the OLE_n mechanistic parameters
- **Therefore, no changes to SAPRC-07 as a result of this review could be made at this time**

Review by Stockwell

- Detailed comparison made of reactions and rate constants in the SAPRC-07, CB05, and RACM2 mechanisms
- Overall, Stockwell concludes that SAPRC-07 represents the state of the science and is complementary about
 - The approach used to represent peroxy reactions, and
 - The inclusion of chlorine chemistry
- Stockwell notes many differences among the mechanisms, but most are results of different approaches or approximations or use of different evaluations
- However, Stockwell found an inconsistency due to an error in SAPRC-07 and had several criticisms or recommendations that need to be addressed

Comments in Stockwell's Review that Need Responses

- The $\text{HO}_2 + \text{O}_3$ reaction has a different temperature dependence than the other mechanisms.
 - Response: SAPRC-07 had an error in the activation energy. Correcting it increases the rate constant by 20%
- The $\text{HO}_2 +$ formaldehyde reaction is unimportant and can be removed to improve computational efficiency
 - Response: This recommendation has merit and has been adopted. The reaction is rapidly reversed except when NO is so high that HO_2 is suppressed.
- The reactions of O^3P with alkenes in SAPRC-07 are only important in chamber simulations
 - Response: These reactions may be important in plumes and should be retained for models with plume-in-grid processes

Comments in Stockwell's Review that Need Responses (continued)

- The lumping of O₂ with N₂ as “M” may give errors in the temperature dependence of the O¹D quenching process
 - Response: The activation energy for O¹D + M is adjusted so this approximation is insignificant for atmospheric conditions
- HCl should not be treated as unreactive in aerosol models
 - Response: It is not unreactive in the full SAPRC-07 but is in the condensed versions. This condensation does not affect O₃ but should not be used if HCl is important in the model.
- SAPRC-07 should have a more detailed representation of alcohols, like RACM2
 - Response: The current level of detail is appropriate for most applications. Extended mechanisms with more alcohols can be developed using detailed SAPRC-07 if needed

Comments in Stockwell's Review that Need Responses (concluded)

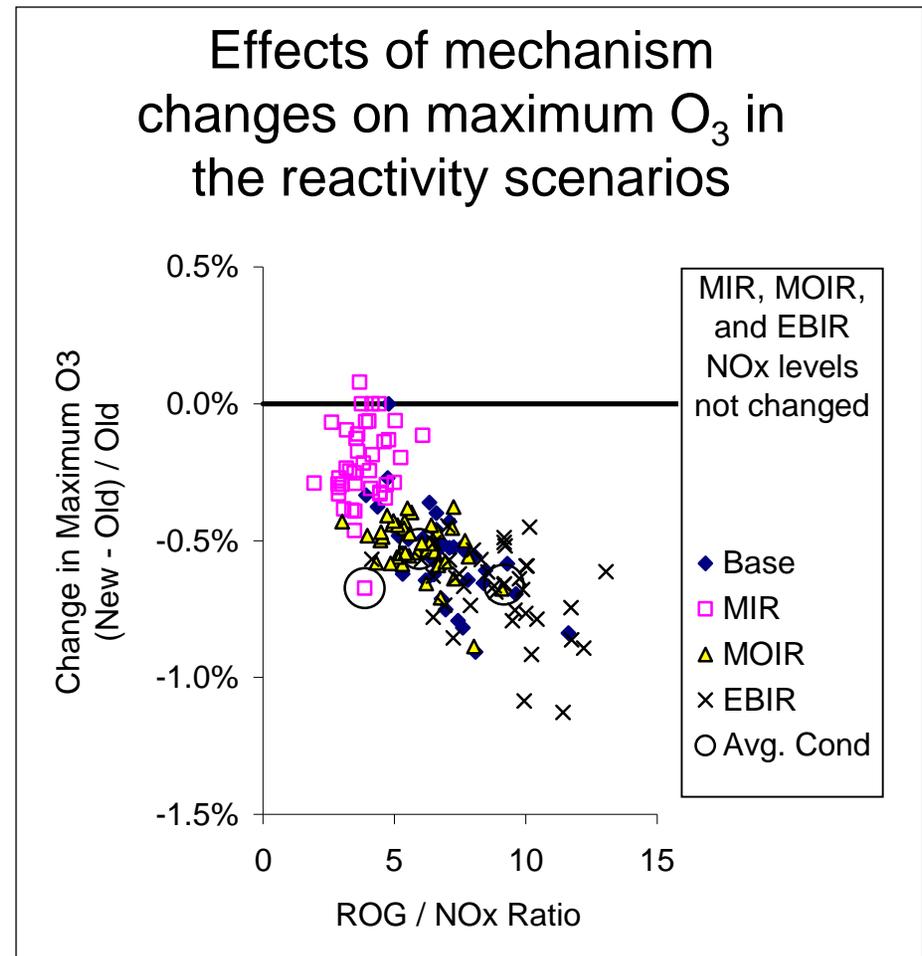
- The SAPRC-07 rate expression for $\text{CH}_3\text{O}_2\cdot + \text{NO}$ is different from that used in CB05 and RACM2
 - Response: SAPRC-07 uses the IUPAC recommendation while the others use NASA. They are the same at 300°K.
- Many rate constant and reaction differences between the three mechanisms are noted.
 - Response: Most of these differences are due to different approximations or assumptions made in the mechanisms, and do not necessarily indicate errors in SAPRC-07.
- **Corrections had to be made to the SAPRC-07 mechanism as a result of this review. However, these are not the only corrections found to be needed.**

Changes Made to SAPRC-07 After Receipt of Reviews

- Errors were found in SAPRC-07 that needed to be corrected
 - 20% Error in the $\text{HO}_2 + \text{O}_3$ rate constant (noted by Stockwell)
 - The group additivity parameters used to derive OH + organic hydroperoxide reactions had errors. This affected the OH + ROOH, R6OOH, and RAOOH reactions
- Other updates and improvements were made to the base mechanism
 - The rate constant for OH + CH_3OOH was changed to that recommended by NASA (2006), which is more consistent with the recently revised IUPAC (2007) recommendation
 - The $\text{HO}_2 +$ formaldehyde reactions were deleted, removing one steady state species (recommended by Stockwell)
- Composition assignments were revised for some mixtures for consistency with the current emissions speciation database

Effects of Mechanism Modifications

- Effects of changes on one day O_3 is $\sim 1\%$ or less in the reactivity scenarios
- Effects of changes increase with decreasing NO_x because the $HO_2 + O_3$ reaction is more important at low NO_x
- Effects on MIRs less than 4% for all VOCs
- Effects on lower NO_x base case reactivities up to 30% for a few VOCs



Implementation of Recent Changes to SAPRC-07: Work Completed

- The mechanism was re-evaluated against the full chamber data base. There were no significant changes to the fits and therefore no need to change any of the adjustable parameters
- The MIR and other reactivity scales were recalculated. The current values submitted to the CARB reflect these updates
- The SAPRC-07 mechanism documentation report and all its appendices were updated to reflect the changes.
 - The updated report and tabulations are posted on the SAPRC web site at <http://www.cert.ucr.edu/~carter/SAPRC>
 - These supercedes the versions of the report and reactivity scales dated July, 2008 and earlier

Implementation of Recent Changes to SAPRC-07: Work Remaining

- The condensed SAPRC-07 mechanisms and the “toxics” version of SAPRC-07 have not yet been updated to be consistent with these changes.
 - These mechanisms, and their associated documentation, should be updated and available by the end of May, 2009
- Updated files implementing the various versions of the SAPRC-07 mechanisms have not yet been made available.
 - These will be made available at the SAPRC web site after the condensed and “toxics” version of SAPRC-07 are updated
- Persons needing updated mechanism implementation files sooner than end of May, 2009, should contact me at carter@cert.ucr.edu

Acknowledgements

- I wish to thank Ajith Kaduwela of the CARB for organizing this peer review and peer reviewers for their efforts and helpful comments