Supplemental Material for "Evaluating Simplified Chemical Mechanisms within CESM Version 1.2 CAM-chem (CAM4): MOZART-4 vs. Reduced Hydrocarbon vs. Super-Fast Chemistry"

Benjamin Brown-Steiner[1,2,3], Noelle E. Selin[3,4,5], Ronald Prinn[2,3,5], Simone Tilmes[6], Louisa Emmons[6], Jean-François Lamarque[6], Philip Cameron-Smith[7]

[1]Now at Atmospheric and Environmental Research, 131 Hartwell Avenue, Lexington, MA 02421-3126
[2]Center for Global Change Science, Massachusetts Institute of Technology, 77 Massachusetts Ave, Cambridge, MA 02139
[3]Joint Program on the Science and Policy of Global Change, Massachusetts Institute of Technology, 77 Massachusetts Ave, Cambridge, MA 02139
[4]Institute for Data, Systems, and Society, Massachusetts Institute of Technology, 77 Massachusetts Ave, Cambridge, MA 02139
[5]Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, 77 Massachusetts Ave, Cambridge, MA 02139
[6]Atmospheric Chemistry Observations and Modeling Lab, National Center for Atmospheric Research, 3450 Mitchell Lane, Boulder, CO 80301
[7]Lawrence Livermore National Laboratory, 7000 East Ave, Livermore, CA 94550

Correspondence to: Benjamin Brown-Steiner (bbrownst@aer.com)

	CO	NO	NO2	SO2	C2H4	CH2O	CH3CHO	TOLUENE	NH3	ISOP	C10H16	OLE	PAR
CO	1												
NO		1											
NO2			1										
SO2				1									
BIGALK													5
BIGENE												1	2
C2H4					1								
C2H5OH													
C2H6													0.4
C3H6												1	1
C3H8													1.5
CH2O						1							
CH3CHO							1						
CH3COCH3													2
CH3OH													1
MEK													3
TOLUENE								1					
NH3									1				
ISOP										1			
C10H16											1		

Supplemental Table S1: Mapping of MOZART species (rows) to the lumped Reduced Hydrocarbon mechanism species (columns)

Photolysis Reactions

	Reactant		Products	Relation to Emmons et al. (2010)
(i)	$O_3 + hv$	→	$2{\cdot}OH$	simplified, includes reaction of $O(^1D)$ with H_2O
(ii)	$H_2O_2 + hv$	→	$2{\cdot}OH$	identical
(iii)	$NO_2 + hv$	→	$NO + O_3$	simplified, $O \rightarrow O_3$
(iv)	$CH_2O + hv$	→	$CO + 2{\cdot}HO_2$	identical
(v)	$CH_2O + hv$	→	CO	simplified, no H_2
(vi)	$CH_3OOH + hv$	→	$CH_2O + HO_2 + OH$	simplified, $H \rightarrow HO_2$

Gas-Phase Reactions

	Reactants		Products	Rate	Relation to Emmons et al. (2010)
(1)	$O_3 + OH$	→	$HO_2 + O_2$	$1.70E\text{-}12{\cdot}\exp(-940/T)$	identical
(2)	$HO_2 + O_3$	→	$2{\cdot}O_2 + OH$	$1.00E\text{-}14{\cdot}\exp(-490/T)$	identical
(3)	$HO_2 + OH$	→	$H_2O + O_2$	$4.80E\text{-}11{\cdot}\exp(250/T)$	identical
(4)	$HO_2 + HO_2$	→	$H_2O_2 + O_2$	$(2.3E\text{-}13{\cdot}\exp(600/T)+1.7E\text{-}33{\cdot}[M]{\cdot}\exp(1000/T)){\cdot}\ (1 + 1.4E\text{-}21{\cdot}[H2O]{\cdot}\exp(2200/T))$	identical
(5)	$H_2O_2 + OH$	→	$H_2O + HO_2$	$1.80E\text{-}12$	identical
(6)	$NO + O_3$	→	$NO_2 + O_2$	$3.00E\text{-}12{\cdot}\exp(-1500/T)$	identical
(7)	$HO_2 + NO$	→	$NO_2 + OH$	$3.50E\text{-}12{\cdot}\exp(250/T)$	different rates
(8)	$NO_2 + OH + M$	→	HNO_3	$ko=1.80E\text{-}30{\cdot}(300/T)^{3.00}$; $ki=2.80E\text{-}11$; $f=0.60$	identical
(9)	$CH_4 + OH$	→	$CH_3O_2 + H_2O$	$2.45E\text{-}12{\cdot}\exp(-1775/T)$	identical
(10)	$CO + OH$	→	HO_2	$ko\_m/(1+(ko\_m/k_\infty\_m)){\cdot}0.6{\cdot}\exp((1/(1+\log(ko\_m/k_\infty\_m))^2))$ $+(k0/(1+(k0/k_\infty\_m))){\cdot}0.6{\cdot}\exp((1/(1+(\log(k0/k_\infty\_m))^2)))$	simplified: no CO_2, $H \rightarrow HO_2$, see note A
(11)	$CH_2O + OH$	→	$CO + H_2O + HO_2$	$5.50E\text{-}12{\cdot}\exp(125/T)$	rates identical, simplified: $H \rightarrow HO_2$
(12)	$CH_3O_2 + HO_2$	→	$CH_3OOH + O_2$	$4.10E\text{-}13{\cdot}\exp(750/T)$	identical
(13a)	$CH_3OOH + OH$	→	$CH_3O_2 + H_2O$	$2.70E\text{-}12{\cdot}\exp(200/T)$	in combination, equivalent
(13b)	$CH_3OOH + OH$	→	$CH_3O + H_2O + OH$	$1.10E\text{-}12{\cdot}\exp(200/T)$	
(14)	$CH_3O_2 + NO$	→	$CH_2O + HO_2 + NO_2$	$2.80E\text{-}12{\cdot}\exp(300/T)$	idential
(15)	$CH_3O_2 + CH_3O_2$	→	$2{\cdot}CH_2O + 0.80{\cdot}HO_2$	$9.50E\text{-}14{\cdot}\exp(390/T)$	different rates, simplified: 1 reaction instead of 2
(16)	$H_2O + NO_2$	→	$0.50{\cdot}HNO_3$	$4.00E\text{-}24$	no equivalent in MOZART, see note B
(17a)	$DMS + OH$	→	SO_2	$1.100E\text{-}11{\cdot}\exp(-240/T)$	different, see note C
(17b)	$DMS + OH$	→	$0.75{\cdot}SO_2$	$2.00E\text{-}10{\cdot}\exp(5820{\cdot}[M])/((2.00E29/[O2]) + \exp(6280{\cdot}[M]))$	
(18)	$OH + SO_2 + M$	→	SO_4	$ko=3.30E\text{-}31{\cdot}(300/T)^{4.30}$; $ki=1.60E\text{-}12$; $f=0.60$	different, see note C
(19)	$H_2O_2 + SO_2$	→	SO_4	aqueous chemistry (see note D)	no equivalent, see note C
(20)	$O_3 + SO_2$	→	SO_4	aqueous chemistry (see note D)	no equivalent, see note C
(21a)	$ISOP + OH$	→	$2{\cdot}CH_3O_2$	$2.70E\text{-}11{\cdot}\exp(390/T)$	different, see note E
(21b)	$ISOP + OH$	→	$ISOP$	$2.70E\text{-}11{\cdot}\exp(390/T)$	
(21c)	$ISOP + OH$	→	$ISOP + 0.5{\cdot}OH$	$2.70E\text{-}11{\cdot}\exp(390/T)$	
(22)	$ISOP + O_3$	→	$.87{\cdot}CH_2O + 1.86{\cdot}CH_3O_2 + 0.06{\cdot}HO_2 + 0.05{\cdot}CO$	$5.59E\text{-}15{\cdot}\exp(-1814/T)$	different, see note E

NOTES:

A: For rate: $ko = 5.90E\text{-}33{\bullet}(300/T)1.4$; $k_\infty = 1.10E\text{-}12{\bullet}(T/300)1.3$; $ko\_m = ko{\bullet}[M]$; $k0 = 1.50E\text{-}13{\bullet}(T/300)0.6$; $k_\infty\_m = (2.10E9{\bullet}(T/300)6.1)/[M]$

B: HNO_3 chemistry included only as reaction 8 and 16, with reaction 16 involving heterogeneous chemistry paramaterization

C: DMS chemistry limited only to reaction with OH (reaction 17), SO_4 production simplified to reactions 18 with OH and 19 and 20 with aqueous chemistry (with a fixed pH in the cloud droplets)

D: Rate equations are included within the aerosol routines adapted from the MOZART-4 mechanism implimentation within CAM-chem

E: Isoprene chemistry paramaterized from UCI for ISOP + OH and from LLNL-IMAPCT for ISOP + O_3, see text for full details

Table S2: Full description of Super-Fast chemical mechanism as compared to the MOZART-4 mechanism of Emmons et al. (2010). Reaction rates are written out if they are of the Arrenhius form, or otherwise formulated. If the reaction rates are of the Troe form, they list the ko and ki parameters, as in Emmons et al. (2010). The simplifications made in the SF are noted by indicating what species is missing or modified when compared to Emmons et al. (2010). Chemical species are the same as in Emmons et al. (2010).

		[ppbv] Mean	[ppbv] Median	[ppbv] Standard Deviation	[%] Variability	[ppbv] 90th Percentile	[ppbv] 99th Percentile	[ppbv] 99th - 90th Percentile	[%] 99th - 90th Percentile
W US	**CASTNET**	49.9	49.6	4.82	9.66	56.4	61.3	4.87	109
	MO	54.9	54.9	3.37	6.14	59.4	62.4	2.99	105
	RH	55.9	55.8	3.58	6.41	60.6	64.0	3.47	106
	SF	50.5	50.5	3.22	6.38	54.7	57.8	3.15	106
MW US	**CASTNET**	57.3	57.0	7.57	13.2	67.1	76.9	9.77	115
	MO	71.0	70.7	11.03	15.5	85.5	96.0	10.6	112
	RH	72.6	72.1	11.26	15.5	87.4	98.8	11.4	113
	SF	70.6	69.8	13.44	19.0	88.7	104	15.1	117
MW US single grid cell	**CASTNET**	62.4	60.6	14.5	23.2	81.7	104	22.7	128
	MO	84.6	83.8	16.2	19.2	106	126	19.4	118
	RH	86.2	85.3	15.8	18.4	107	126	19.5	118
	SF	85.4	82.5	22.4	26.2	116	149	32.8	128
SE US	**CASTNET**	51.5	51.3	8.18	15.9	62.3	71.9	9.64	115
	MO	60.2	59.5	9.22	15.3	72.5	83.7	11.2	115
	RH	61.3	60.5	10.1	16.6	74.9	87.9	12.9	117
	SF	58.6	57.8	11.4	19.4	73.9	87.1	13.2	118
SE US single grid cell	**CASTNET**	53.8	53.1	12.8	23.8	68.7	93.5	24.8	136
	MO	83.4	84.7	19.1	22.9	107	124	17.3	116
	RH	85.2	86.1	20.4	24.0	111	131	20.1	118
	SF	83.6	82.1	27.0	32.3	120	153	33.1	128

Table S3: Summary Statistics for the Daily Maximum 8-Hour (DM8H) O_3 over the globe other regions, accompanying Table 2. The last two columns indicate the difference between the 99th percentile and the 90th percentile, expressed both in absolute values (ppb) and as a percent.

5

Supplemental Description of the Super-Fast Chemical Mechanism

The SF mechanism has been included in several model inter-comparison projects, including the ACCMIP (e.g. Lamarque et al., 2013), a comparison of stratospheric dynamics and ozone production (Hsu et al., 2013), a comparison of isoprene mechanisms and ozone changes (Squire et al., 2015), and a multi-model assessment of surface ozone and observations (Schnell et al., 2015). The SF mechanism was also used to examine the role of DMS within ENSO (Xu et al., 2016). Here we briefly review the findings of these four model inter-comparison projects.

The SF only simulates sulfate (SO_4) and not the other aerosols, so the SF mechanism was not included in many of the ACCMIP aerosol comparisons (Lamarque et al., 2013). While the inclusion of non-sulfate aerosols within the CESM can be easily accomplished, there are two aerosol modules (either bulk or modal) to which aerosols could be added, which was beyond the scope of this project, so aerosol model capabilities are not examined in the present study.

We now summarize the ACCMIP results as they pertain to the SF mechanism. Within the ACCMIP, the SF mechanism has lower rates of ozone production and loss compared to the ACCENT models (biases of -24% and -22% respectively), as well as low ozone deposition (bias of -38%) (Young et al., 2013). In this comparison, natural emissions were not prescribed and different treatments of meteorology were used, which may account for some of the noted differences. This results in a high bias for the ozone lifetime (+3 days, or +14%), as well as a low ozone burden bias (-34 Tg, or -10%) (Young et al., 2013). In addition, the models that showed similarly low ozone production and loss rates have lower emissions of VOCs. The SF mechanism falls within the ACCMIP range for human health results due to ozone exposure (Silva et al., 2013). The SF mechanism simulated the 1850-2000 changes in the tropospheric ozone column within the range of the ACCMIP models, and projected changes to the ozone radiative forcing for future RCP scenarios also fell within the ACCMIP range (Stevenson et al., 2013). However, the calculated historical change in ozone RF fell outside of the ACCMIP range (+20% bias). The SF mechanism also has a high bias for global-mean OH (+16% compared to the ACCMIP mean) and a low bias for the calculation of the methane lifetime due to OH oxidation (-14%) (Voulgarakis et al., 2013).

The SF mechanism was tested against MOZART by Hsu et al. (2013) who concluded that the selection of a chemical mechanism was only a secondary influence on the stratospheric chemistry since they used a linearized scheme. However, the SF mechanism did produce a less stratified tropopause and a warmer troposphere due largely to the impact of ozone forcings on the simulated dynamics and thermodynamics. Unfortunately, the Hsu et al. (2013) analysis had a bug with their SF simulations, which resulted in the aerosols not being communicated to the cloud nucleation routines, but this didn't affect their conclusions on the sensitivity of the stratosphere to uncertainty in the O_2 photolysis cross-section.

Squire et al. (2015) compared the SF isoprene scheme with three other schemes of much greater complexity. They concluded that the "1-species, 2-reaction" isoprene scheme from the SF mechanism, as simple as it is, is preferable to neglecting biogenic chemistry entirely, although the SF mechanism shows the highest biases in regions where isoprene chemistry is important for simulating accurate ozone concentrations. They also explored some of the other biases within the SF mechanism scheme, which include: (1) under high-isoprene conditions, the SF mechanism overestimates O_3; (2) under

low-isoprene and low-NO_x conditions, the SF mechanism overestimates O_3; (3) due to the simplicity of SF mechanism, HO_x is sequestered into the organic hydroperoxides, and methyl hydroperoxide (CH_3OOH) has low reactivity, which results in high levels of the peroxy radicals, an enhanced rate of CH_3O_2 + NO, and therefore a high bias (up to +80%) for ozone; and (4) the NO_x lifetime is too short, except in high-NO_x emission regions. They conclude that the addition of a PAN formation scheme would significantly improve the O_3 distribution. Finally, they find that many of the errors described above largely cancel each other out, which results in the globally averaged O_3 bias for SF mechanism to be small (-2.6% compared to the Master Chemical Mechanism).

The SF mechanism has a known anomalous annual cycle (see Schnell et al., 2015), in which peak ozone occurs in March/April rather than May. In the main article we show that this anomaly exists at global scales, but not within all regions. In addition, the size and extent of ozone pollution episodes is anomalously high, and these large events occur mainly in the springtime (Schnell et al., 2015). Interestingly, the SF mechanism outperforms many of the more sophisticated mechanisms in simulating the observed summertime diurnal cycle for ozone (Schnell et al., 2015).

References for Supplemental Material:

Emmons, L. K., Walters, S., Hess, P. G., Lamarque, J.-F., Pfister, G. G., Fillmore, D., Granier, C., Guenther, A., Kinnison, D., Laepple, T., Orlando, J., Tie, X., Tyndall, G., Wiedinmyer, C., Baughcum, S. L., and Kloster, S.: Description and evaluation of the Model for Ozone and Related chemical Tracers, version 4 (MOZART-4), Geosci. Model Dev., 3, 43-67, https://doi.org/10.5194/gmd-3-43-2010, 2010.

Hsu, J., Prather, M. J., Bergmann, D., and Cameron-Smith, P.: Sensitivity of stratospheric dynamics to uncertainty in O_3 production, J. Geophys. Res. Atmos., 118, 8984-8999, https://doi.org/10.1002/jgrd.50689, 2013.

Lamarque, J.-F., Shindell, D. T., Josse, B., Young, P. J., Cionni, I., Eyring, V., Bergmann, D., Cameron-Smith, P., Collins, W. J., Doherty, R., Dalsoren, S., Faluvegi, G., Folberth, G., Ghan, S. J., Horowitz, L. W., Lee, Y. H., MacKenzie, I. A., Nagashima, T., Naik, V., Plummer, D., Righi, M., Rumbold, S. T., Schulz, M., Skeie, R. B., Stevenson, D. S., Strode, S., Sudo, K., Szopa, S., Voulgarakis, A., and Zeng, G.: The atmospheric chemistry and climate model intercomparison Project (ACCMIP): Overview and description of models, simulations and climate diagnostics, Geosci. Mod. Dev., 6, 179–206, https://doi.org/10.5194/gmd-6-179-2013, 2013.

Schnell, J. L., Prather, M. J., Josse, B., Naik, V., Horowitz, L. W., Cameron-Smith, P., Bergmann, D., Zeng, G., Plummer, D. A., Sudo, K., Nagashima, T., Shindell, D. T., Faluvegi, G., and Strode, S. A.: Use of North American and European air quality networks to evaluate global chemistry-climate modeling of surface ozone, Atmos. Chem. Phys., 15, 10581–10596, https://doi.org/10.5194/acp-15-10581-2015, 2015.

Silva, R. A., West, J. J., Zhang, Y., Anenberg, S. C., Lamarque, J.-F., Shindell, D. T., Collins, W. J., Dalsoren, S., Faluvegi, G., Folberth, G., Horowitz, L. W., Nagashima, T., Naik, V., Rumbold, S., Skeie, R., Sudo, K., Takemura, T., Bergmann, D., Cameron-Smith, P., Cionni, I., Doherty, R. M., Eyring, V., Josse, B., MacKenzie, I. A., Plummer, D., Righi, M., Stevenson, D. S., Strode, S., Szopa, S., and Zeng, G.: Global premature mortality due to anthropogenic

outdoor air pollution and the contribution of past climate change, Environ. Res. Lett., 8, 034005, https://doi.org/10.1088/1748-9326/8/3/034005, 2013.

Squire, O. J., Archibald, A. T., Griffiths, P. T., Jenkin, M. E., Smith, D., and Pyle, J. A.: Influence of isoprene chemical mechanism on modelled changes in tropospheric ozone due to climate and land use over the 21st century, Atmos. Chem. Phys., 15, 5123–5143, https://doi.org/10.5194/acp-15-5123-2015, 2015.

Stevenson, D. S., Young, P. J., Naik, V., Lamarque, J.-F., Shindell, D. T., Voulgarakis, A., Skeie, R. B., Dalsøren, S. B., Myhre, G., Berntsen, T. K., Folberth, G. A., Rumbold, S. T., Collins, W. J., MacKenzie, I. A., Doherty, R. M., Zeng, G., van Noije, T. P. C., Strunk, A., Bergmann, D., Cameron-Smith, P., Plummer, D. A., Strode, S. A., Horowitz, L., Lee, Y. H., Szopa, S., Sudo, K., Nagashima, T., Josse, B., Cionni, I., Righi, M., Eyring, V., Conley, A., Bowman, K. W., and Wild, O.: Tropospheric ozone changes, radiative forcing and attribution to emissions in the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP), Atmos. Chem. Phys., 13, 3063–3085, https://doi.org/10.5194/acp-13-3063-2013, 2013.

Voulgarakis, A., Naik, V., Lamarque, J.-F., Shindell, D. T., Young, P. J., Prather, M. J., Wild, O., Field, R. D., Bergmann, D., Cameron-Smith, P., Cionni, I., Collins, W. J., Dalsøren, S. B., Doherty, R. M., Eyring, V., Faluvegi, G., Folberth, G. A., Horowitz, L. W., Josse, B., MacKenzie, I. A., Nagashima, T., Plummer, D. A., Righi, M., Rumbold, S. T., Stevenson, D. S., Strode, S. A., Sudo, K., Szopa, S., and Zeng, G.: Analysis of present day and future OH and methane lifetime in the ACCMIP simulations, Atmos. Chem. Phys., 13, 2563–2587

Xu, L., Cameron-Smith, P., Russell, L. M., Ghan, S. J., Liu, Y., Elliott, S., Yang, y., Lou, S., Lamjiri, M. A., and Manizza, M.: DMS role in ENSO cycle in the tropics, J. Geophys. Res. Atmos., 121, 537–558, https://doi.org/10.1002/2016JD025333, 2016.

Young, P. J., Archibald, A. T., Bowman, K. W., Lamarque, J.-F., Naik, V., Stevenson, D. S., Tilmes, S., Voulgarakis, A., Wild, O., Bergmann, D., Cameron-Smith, P., Cionni, I., Collins, W. J., Dalsøren, S. B., Doherty, R. M., Eyring, V., Faluvegi, G., Horowitz, L. W., Josse, B., Lee, Y. H., MacKenzie, I. A., Nagashima, T., Plummer, D. A., Righi, M., Rumbold, S. T., Skeie, R. B., Shindell, D. T., Strode, S. A., Sudo, K., Szopa, S., and Zeng, G.: Pre-industrial to end 21st century projections of tropospheric ozone from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP), Atmos. Chem. Phys., 13, 2063–2090, https://doi.org/10.5194/acp-13-2063-2013, 2013.