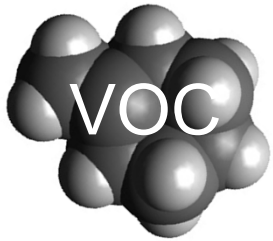
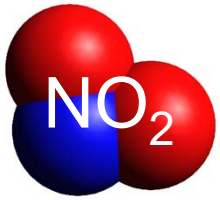
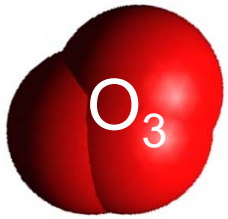
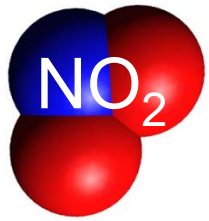




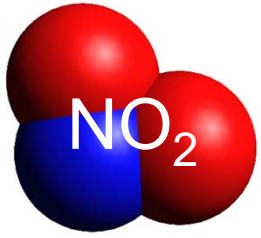


Review of the SAPRC-16 Chemical Mechanism and Comparison with the Regional Atmospheric Chemistry Mechanism, Version-2



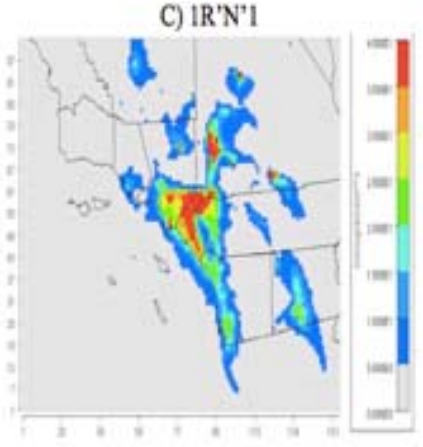
William R. Stockwell[a], Emily Saunders[b], Rosa Fitzgerald[a]

[a]University of Texas El Paso, [b]NASA Goddard Space Flight Center

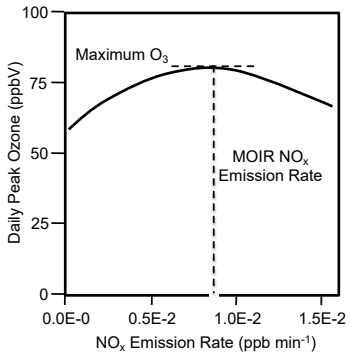


Applications of Air Quality Mechanisms such as SAPRC

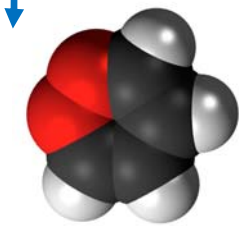
Mechanisms should be constructed with the application in mind.



- Used in 3D Air Quality Models such as CMAQ, CAM-X and WRF-Chem for ozone and particulate matter simulations.
- Detailed/explicit mechanisms designed to be used for VOC-ozone reactivity calculations.

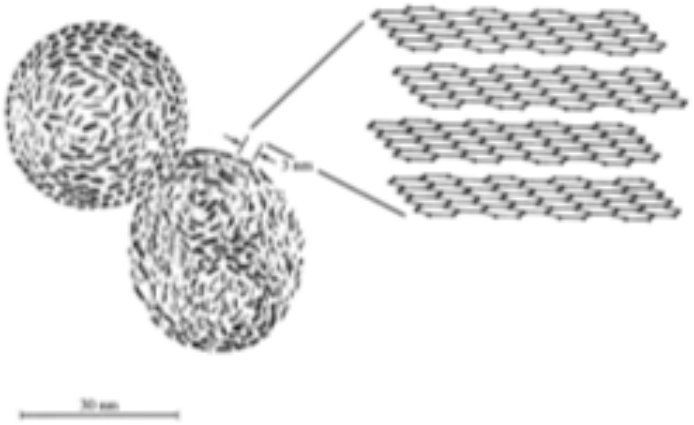


- Used to simulate air toxics (such the SAPRC-07T mechanism (Hutzell et al, 2012).
- The biggest is not necessarily the best given constraints such as the available experimental kinetic data base and available computational resources.



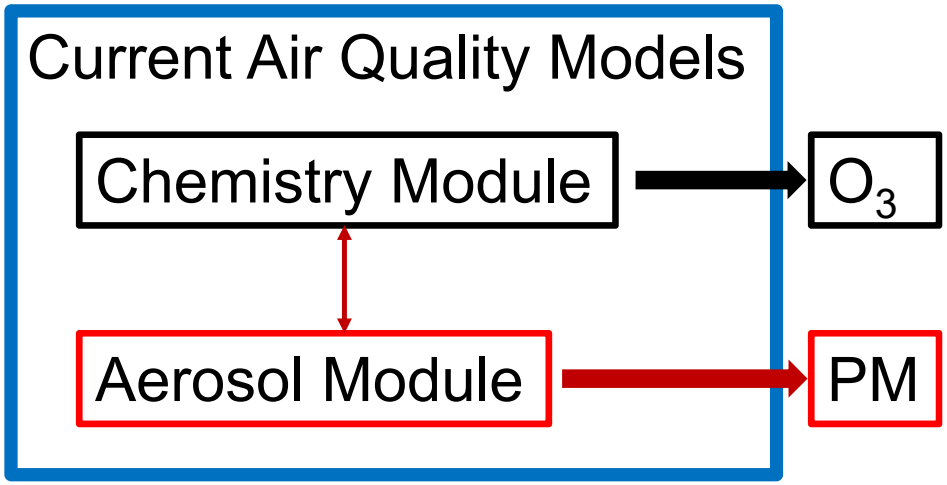
A Major Focus of New SAPRC Development is Secondary Organic Aerosol Modeling (SOA)

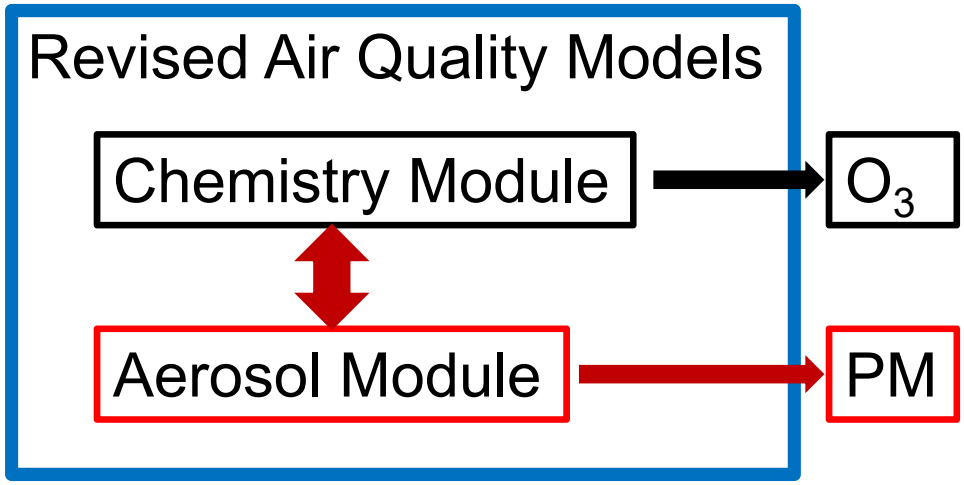
- SAPRC development is moving in the right direction for simulating SOA.
- Need to treat higher molecular weight VOC.
- Secondary organic aerosol (SOA) simulation requires larger, more explicit gas-phase mechanisms than required for ozone.
- SAPRC includes more species and reactions focused on the prediction of the formation of the condensable species that are SOA precursors than previous versions.



Improved SOA Modeling Will Require Revision of Models

Some serious revision of air quality models will be required to take advantage of mechanisms like SAPRC-16 and future versions. Current air quality models do not make full use the gas-phase mechanism to calculate SOA. They use mostly separate and parameterized SOA modules.

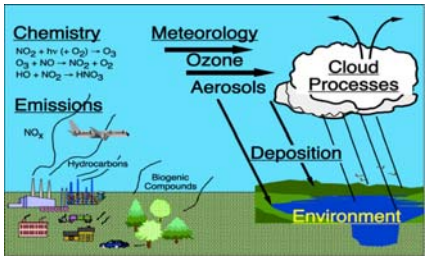




SAPRC-16

There are two versions of SAPRC-16 mechanism

- One for atmospheric simulations
- One used for evaluations against chamber data.

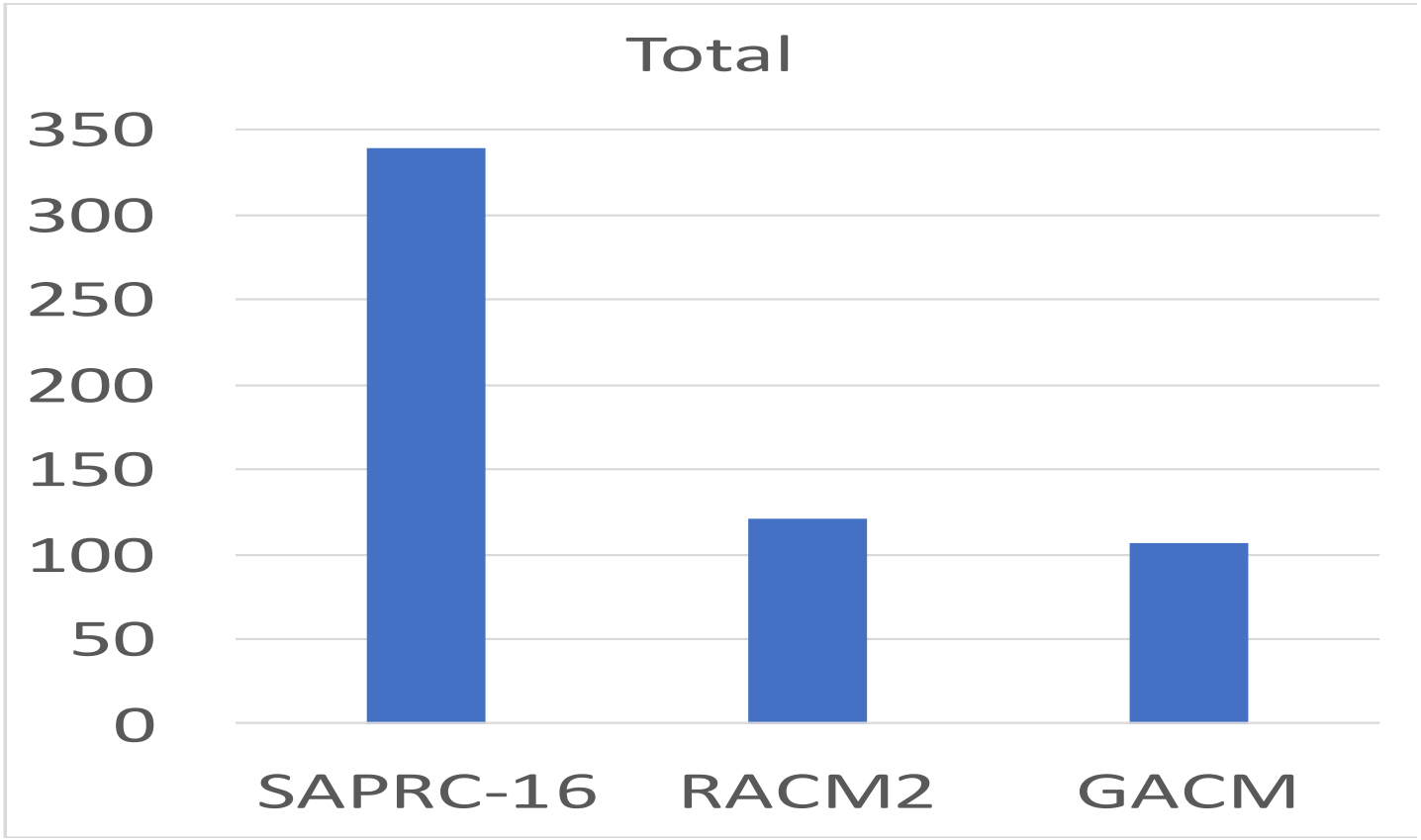


Here we discuss the SAPRC-16 mechanism for atmospheric simulations and make some comparisons with RACM2 and GACM.

Why compare with simpler mechanisms?

Total Species Treated by SAPRC-16 vs RACM2 & GACM

- SAPRC-16 treats more model chemical species.



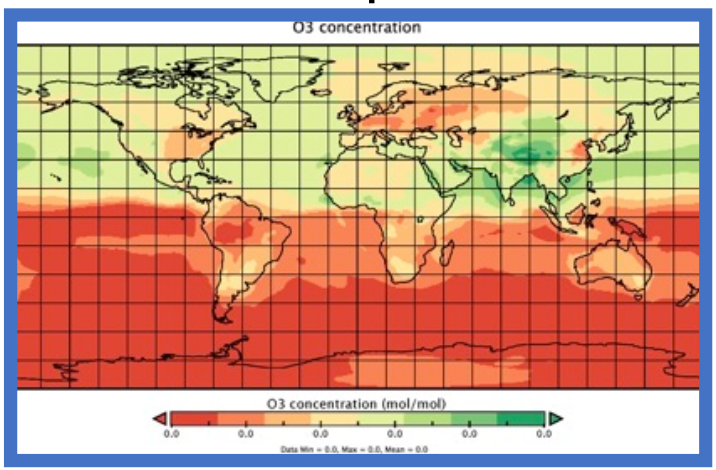
Regional Atmospheric Chemistry Mechanism, Version 2 RACM2

- Both SAPRC-16 and RACM2 use aggregation by molecule approaches. Comparison examines SAPRC-16 core.
- The RACM2 mechanism is designed to simulate remote to polluted conditions from the Earth's surface through the upper troposphere.
- The RACM2 been tested against selected environmental chamber data and compared with previous RACM/RADM scenario simulations.
- RACM2 is implemented in CMAQ and WRF-Chem.

Global Atmospheric Chemistry Mechanism (GACM)

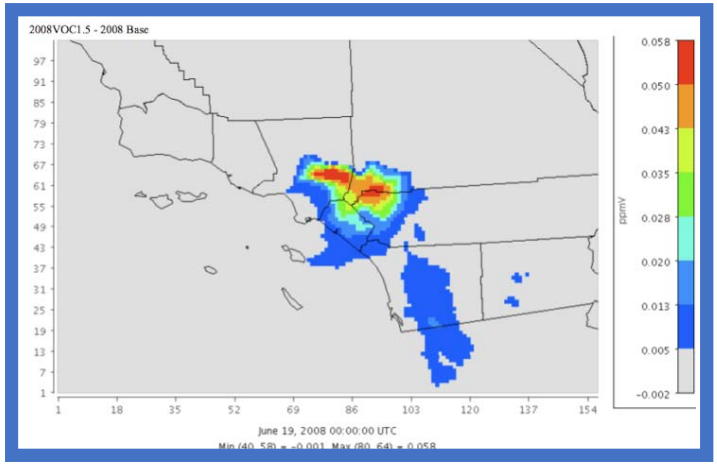
GACM is the global version of RACM2 used to run global atmospheric chemistry simulations and produce chemical boundary conditions for regional and urban models with consistent VOC chemistry.

Global Atmospheric Model



Boundary Conditions

Regional & Urban Models



Saunders, E. W.S. Goliff … and W.R. Stockwell, paper in preparation

Global Atmospheric Chemistry Mechanism (GACM)

Includes more Inorganic Chemistry than RACM2 or SAPRC-16

Such as Chlorine, Bromine and Iodine:

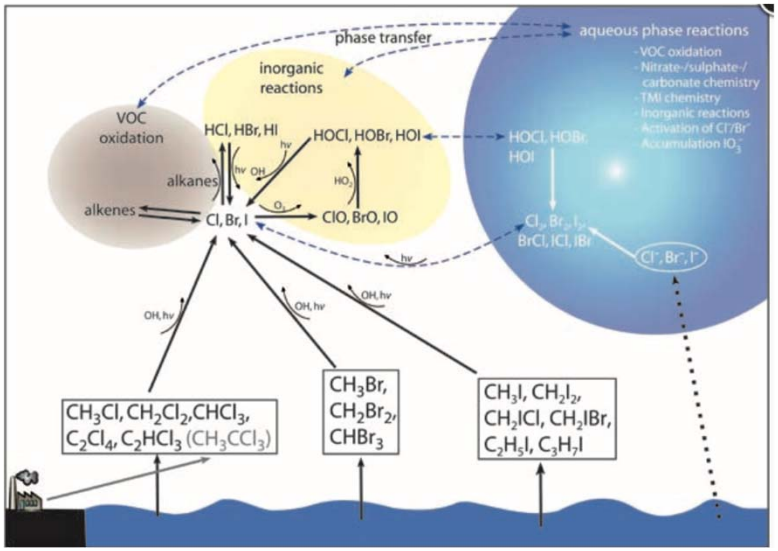
$X\bullet + O_3 \rightarrow O_2 + XO\bullet$

$XO\bullet + O(^3P) \rightarrow O_2 + X\bullet$

More Sulfur Chemistry

$H_2S \rightarrow$ Products

$CH_3SCH_3 \rightarrow$ Products



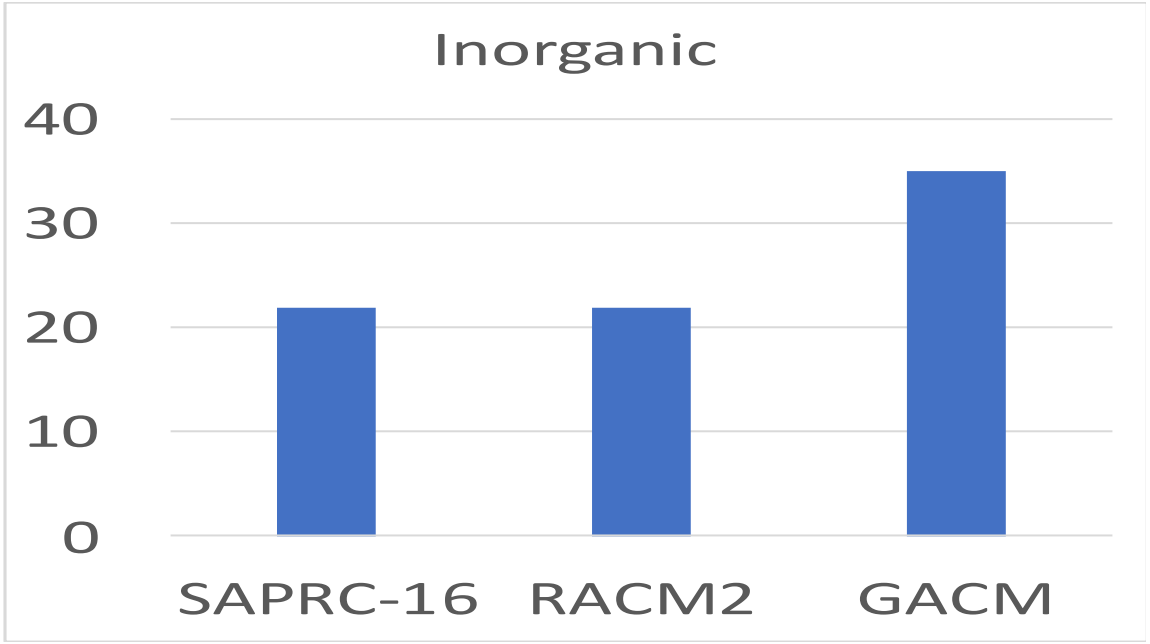
Hartmut Herrmann and Colleagues, TROPOS, Leibniz Institute for Tropospheric Res.

Less need for highly detailed VOC chemistry – not many cities in the middle of the Pacific Ocean.

Compound Class	SAPRC	RACM2	GACM
Constant	5	6	6
Active Inorganic Species	11	12	22
Active Radical Species and Operators	4	2	5
Steady State Inorganic Radical Species	2	2	2
Explicitly Represented Organics	42	9	9
Lumped Organic Compounds – Mechanism for representative compounds or estimated parameterized mechanisms used	16	43	30
Lumped Organic Compounds – SAPRC – Mechanism for representative mixture nitrites or chloropicrin used, derived using MechGen	39	N/A	N/A
PAN and PAN Analogues PAN	8	3	2
Non-Reacting Species (Active for testing other unsaturated PAN analogues. -- can be removed if not needed)	8	1	1
Non-reacting counter species (Set to "dummy" as distributed to avoid numerical problems. Set to "Active" for testing.)	2	N/A	N/A
Peroxy Radical Species in Base Mechanism	7	37	27
Acyl peroxy radical species	8	3	2
Other organic radical or reactive intermediate species	5	2	0
Radical operator species	12	1	1
Peroxy radical intermediates in generated mechanisms (slow or no unimolecular reactions)	138	N/A	N/A
Peroxy radical intermediates in generated mechanisms (relatively fast unimolecular and NO reactions only)	32	N/A	N/A
Total	**339**	**121**	107

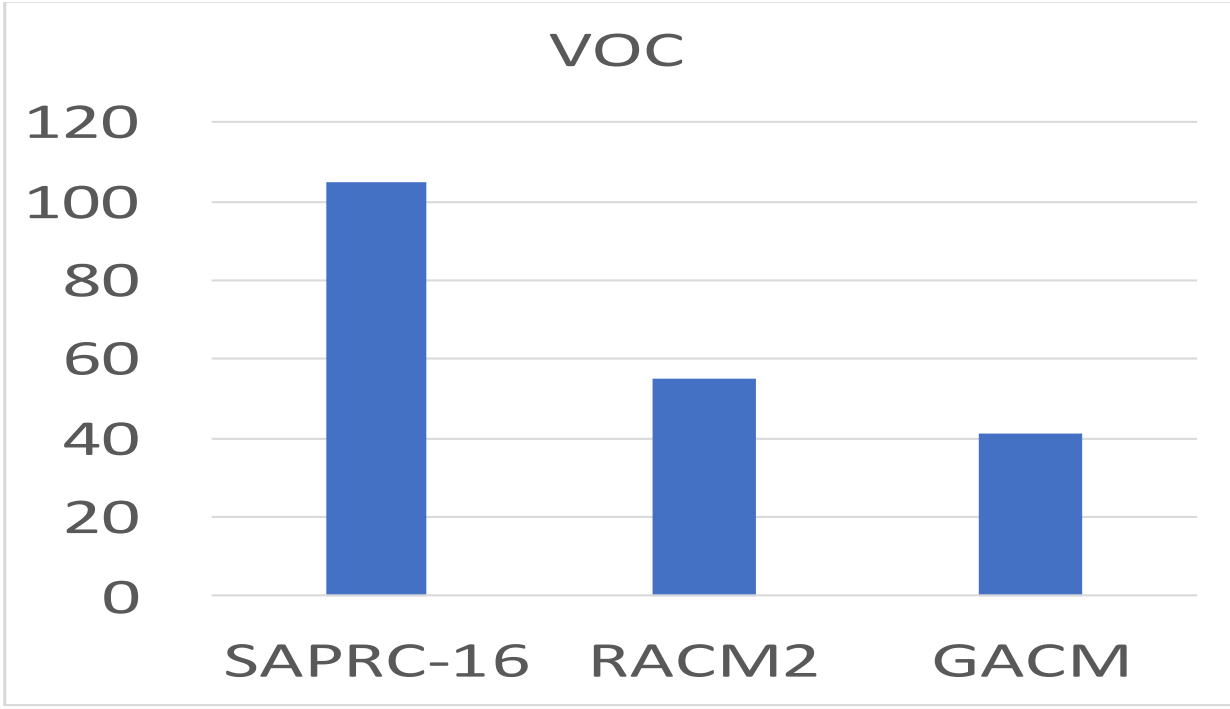
Species Treated by SAPRC-16 vs RACM2 & GACM

- SAPRC-16 and RACM2 have very similar, explicit chemistry for inorganic compounds.
- GACM has more inorganic species due to its need to treat halogen chemistry and reduced sulfur compounds over the oceans.



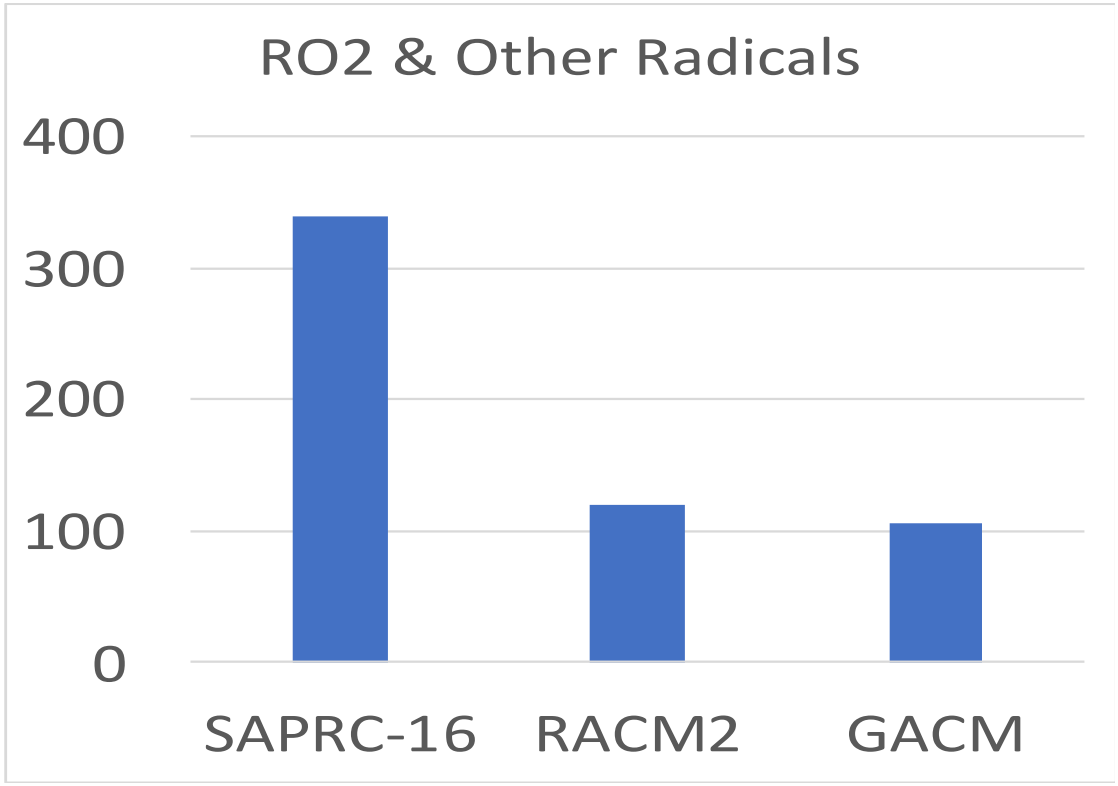
Species Treated by SAPRC-16 vs RACM2 & GACM

- SAPRC-16 has the largest number of explicitly represented organic compounds. The total number of stable organic compounds treated by SAPRC-16 is 111 and RACM2 treats 55. GACM has simplified aromatic chemistry and other organic chemistry was simplified to keep GACM near the size of RACM2.

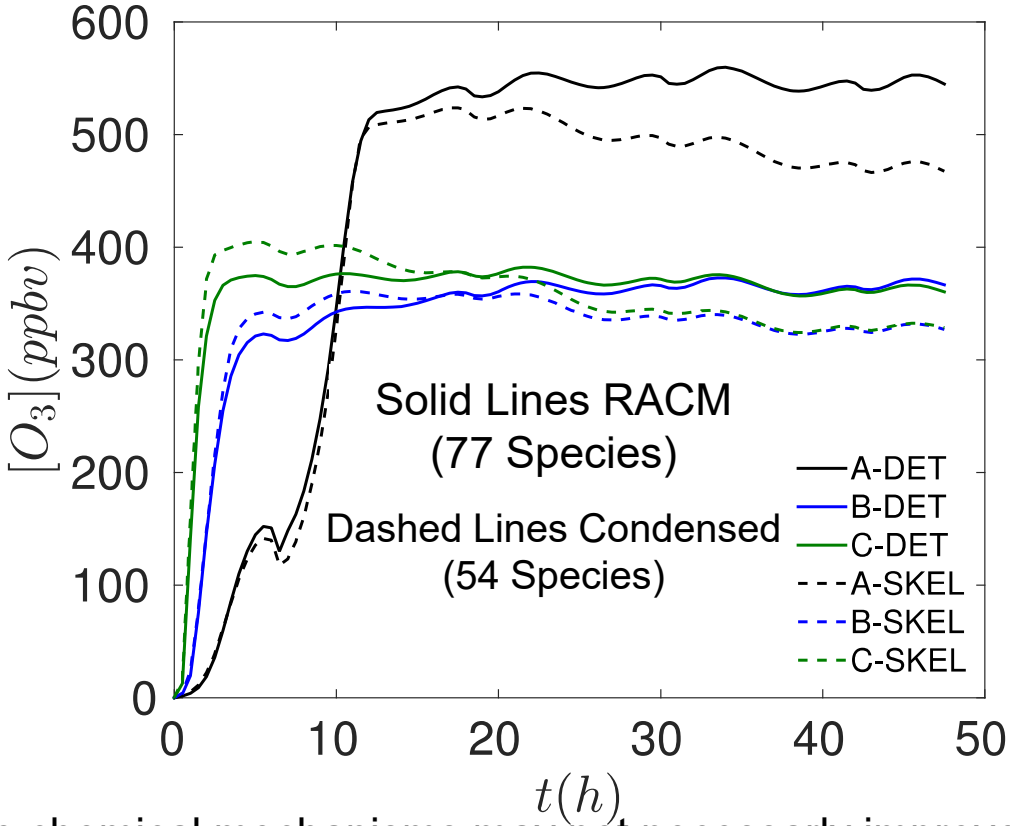


Species Treated by SAPRC-16 vs RACM2 & GACM

- SAPRC-16 has a detailed set of proxy radicals, radical operators and other radicals compared with RACM2 and GACM. Good for SOA Modeling.



Do highly detailed mechanisms have that great of an impact on ozone concentrations simulated by 3D models?



Highly detailed gas-phase chemical mechanisms may not necessarly improve ozone simulations by meteorological three-dimensional air quality models. (Nikolaou et al., Accelerating simulations using REDCHEM_v0.0 for atmospheric chemistry mechanism reduction, Geosci. Model Dev., 11, 3391–3407, 2018 https://doi.org/10.5194/gmd-11-3391-2018)

Photolysis Frequencies

Calculated photolysis frequencies do not compare well between SAPRC and RACM2 & GACM. Probably a presentation issue.

For example formaldehyde and acetaldehyde appear to be very different.

$HCHO + h\nu \rightarrow H_2 + CO$

SAPRC16	$3.49 \times 10^{-3}\ s^{-1}$
RACM2/GACM	$4.02 \times 10^{-5}\ s^{-1}$

$CH_3CHO + h\nu \rightarrow HO_2 + CH_3O_2 + CO$

SAPRC16	$4.65 \times 10^{-4}\ s^{-1}$
RACM2/GACM	$3.45 \times 10^{-6}\ s^{-1}$

Photolysis Frequencies Large Changes

Changes to photolysis frequencies within SAPRC versions suggest that better measurements of dicarbonyls: glyoxal and methyl glyoxal and others: monounsaturated 1,4 aldehyde-ketones, monounsaturated 1,4-diketones … are desirable.

$AFG2A + h\nu \rightarrow Products$

SAPRC11 3.87×10^{-1} s^{-1}

SAPRC16 3.87×10^{-2} s^{-1}

Difference: -90%

Others:

$HCHO + h\nu \rightarrow H_2 + CO$

$CH_3CHO + h\nu \rightarrow HO_2 + MO_2 + CO$

$RCHO + h\nu \rightarrow Products$

$RNO_3 + h\nu \rightarrow Products$

$ROOH + h\nu \rightarrow Products$

Dicarbonyls + $h\nu \rightarrow$ Products

$HCOCOH + h\nu \rightarrow HCHO + CO$

SAPRC-16 Thermal Reactions with Large Changes

Inorganics Involving HO_x & Its Production

$O^1D + M \rightarrow O^3P + M$

$2\ HO_2 \rightarrow H_2O_2 + O_2$

$2\ HO_2 + H_2O \rightarrow H_2O_2 + H_2O + O_2$

$HO_2 + NO + H_2O \rightarrow HNO_3 + H_2O$

$HO_2 + NO \rightarrow HNO_3$

$HO + HONO \rightarrow H_2O + NO_2$

$HO_2 + NO_2 \rightarrow HNO_4$

$HNO_4 \rightarrow HO_2 + NO_2$

Lumped $RO_2 + HO_2 \rightarrow$ Products

Inorganics Involving NO_3/N_2O_5

$NO_3 + HO_2 \rightarrow HO + NO_2 + O_2$

$NO_3 + HO \rightarrow NO_2 + HO_2$

$N_2O_5 + H_2O \rightarrow 2\ HNO_3$

$N_2O_5 + H_2O + H_2O \rightarrow HNO_3 + H_2O$

Organics Involving NO_3

$CH_3CHO + NO_3 \rightarrow ACO_3 + HNO_3$

$HCOCOH + NO_3 \rightarrow$ Products

$CH_3COCHO + NO_3 \rightarrow$ Products

SAPRC-16 Thermal Reactions with Large Changes

Dicarbonyls and Organic Acids

$HCOCOH + HO \rightarrow HO_2 + H_2O + 2\ CO$

$CH_3COCHO + HO \rightarrow Products$

$HCOOH + HO \rightarrow HO_2 + CO_2$

Aromatic Product Reactions with HO and NO_3

$CH_3C_6H_4OH + HO \rightarrow Products$

$C_6H_5OH + NO_3 \rightarrow Products$

$C_6H_5CHO + NO_3 \rightarrow Products$

Preliminary Tests of SAPRC 16
Automatic Mechanism Generation System
http://mechgen.cert.ucr.edu

Preliminary Tests of SAPRC 16
Automatic Mechanism Generation System

SAPRC 16-MECHANISM GENERATION SYSTEM

Web Reactor for william.r.stockwell@gmail.com [#3496]

Change: Temperature= 300 °K Presssure= 1.00 atm.

Lumping = SAPRC-16 Lumping

Create reactant: **Structure (help) or SMILES string:** CH3-CH2-CH3

Create from the list of SAPRC VOC Model Species

Other actions

- Reload
- Show SAPRC-16 Mechanism Assignments
- Show Estimation Methods (This is work in progress -- not all methods are shown.)

- Change password
- Delete user william.r.stockwell@gmail.com and log out (a new one will be created if needed)
- Log out

Preliminary Tests of SAPRC 16
Automatic Mechanism Generation System

PROPANE

CH_3-CH_2-CH_3

Smiles string: CCC
Molecular weight of C_3H_8 is 44.10

Assigned heat of formation is -25.02 kcal/mole.
NASA, 2011
Estimated heat of formation is -25.08 kcal/mole.
Estimated vapor pressure at 300.00 deg K is 6.36e+0 atm.
VOC Type = Normal alkane

Model species used with Preliminary SAPRC-16 lumping: PROP
(Propane)

Reactions

Reaction	Processing Method	
OH	Single step react	React completely
NO3	Single step react	React completely
React completely with OH		

Get reaction assignments

Groups

CH_3-CH_2-CH_3

#	Group	Bonded To	Heat of Formation	
1	-CH_3	3	-10.04	C_(C)
2	-CH_3	3	-10.04	C_(C)
3	-CH_2-	1,2	-5.00	C_(C)(C)

Full set of reactions with OH

Rxn	k	Factor	Overall	Reaction
1)	3.06e-13	27.2%	27.2%	CH3-CH2-CH3 + OH -> CH3-CH2-CH2. + H2O
2)	8.21e-13	72.8%	72.8%	CH3-CH2-CH3 + OH -> CH3-CH[.]-CH3 + H2O
3)		100.0%	27.2%	CH3-CH2-CH2. + O2 -> CH3-CH2-CH2OO.
4)		100.0%	72.8%	CH3-CH[.]-CH3 + O2 -> CH3-CH[OO.]-CH3
5)	8.68e-12	95.9%	26.0%	CH3-CH2-CH2OO. + NO -> CH3-CH2-CH2O. + NO2
6)	3.72e-13	4.1%	1.1%	CH3-CH2-CH2OO. + NO -> CH3-CH2-CH2-ONO2
7)	2.30e-12	100.0%		CH3-CH2-CH2OO. + NO3 -> CH3-CH2-CH2O. + NO2
8)	4.66e-12	100.0%		CH3-CH2-CH2OO. + HO2 -> CH3-CH2-CH2-O-OH
9)	3.80e-14	50.0%		CH3-CH2-CH2OO. + RO2. -> RO2. + CH3-CH2-CH2O.
10)	1.90e-14	25.0%		CH3-CH2-CH2OO. + RO2. -> RO2. + CH3-CH2-CHO
11)	1.90e-14	25.0%		CH3-CH2-CH2OO. + RO2. -> RO2. + CH3-CH2-CH2-OH
12)	7.78e-12	50.0%		CH3-CH2-CH2OO. + RCO3. -> RCO3. + CH3-CH2-CHO
13)	7.78e-12	50.0%		CH3-CH2-CH2OO. + RCO3. -> RCO3. + CH3-CH2-CH2O.
14)	8.68e-12	95.9%	69.9%	CH3-CH[OO.]-CH3 + NO -> CH3-CH[O.]-CH3 + NO2
15)	3.72e-13	4.1%	3.0%	CH3-CH[OO.]-CH3 + NO -> CH3-CH(CH3)-ONO2
16)	2.30e-12	100.0%		CH3-CH[OO.]-CH3 + NO3 -> CH3-CH[O.]-CH3 + NO2
17)	4.66e-12	100.0%		CH3-CH[OO.]-CH3 + HO2 -> CH3-CH(CH3)-O-OH
18)	3.80e-14	50.0%		CH3-CH[OO.]-CH3 + RO2. -> RO2. + CH3-CH[O.]-CH3
19)	1.90e-14	25.0%		CH3-CH[OO.]-CH3 + RO2. -> RO2. + CH3-CO-CH3
20)	1.90e-14	25.0%		CH3-CH[OO.]-CH3 + RO2. -> RO2. + CH3-CH(CH3)-OH
21)	7.78e-12	50.0%		CH3-CH[OO.]-CH3 + RCO3. -> RCO3. + CH3-CO-CH3
22)	7.78e-12	50.0%		CH3-CH[OO.]-CH3 + RCO3. -> RCO3. + CH3-CH[O.]-CH3
23)	5.67e+4	99.4%	25.9%	CH3-CH2-CH2O. + O2 -> CH3-CH2-CHO + HO2.
24)	3.56e+4	98.8%	69.0%	CH3-CH[O.]-CH3 + O2 -> CH3-CO-CH3 + HO2.
25)	4.33e+2	1.2%	0.8%	CH3-CH[O.]-CH3 -> CH3-CHO + CH3.
26)		100.0%	0.8%	CH3. + O2 -> CH3OO.

Preliminary Tests of SAPRC 16
Automatic Mechanism Generation System

Products from reaction with OH (with NO = 0.50 ppb)

Yield	Lump	Product
100.0%	RO2C	RO2C
26.0%	ETCHO	CH3-CH2-CHO
95.1%	HO2	HO2.
95.9%	NO2	NO2
1.1%	R1NO3	CH3-CH2-CH2-ONO2
69.0%	ACET	CH3-CO-CH3
0.8%	MECHO	CH3-CHO
0.8%	MEO2	CH3OO.
3.0%	R1NO3	CH3-CH(CH3)-ONO2

Lumped reactions

No.	k	Reaction
1)	1.13e-12	PROP + OH = PROP_P1
2)	K(RO2+NO)	PROP_P1 + NO = #.959 NO2 + #.951 HO2 + #.69 ACET + #.26 ETCHO + #.041 R1NO3 + #.008 MECHO + #.008 MEO2 + #-0.079 XC
3)	K(RO2+NO3)	PROP_P1 + NO3 = NO2 + #.991 HO2 + #.72 ACET + #.272 ETCHO + #.009 MECHO + #.009 MEO2 + #-0.003 XC
4)	K(RO2+HO2)	PROP_P1 + HO2 = ROOH + #-1 XC
5)	K(RO2+RO2)	PROP_P1 + SumRO2 = #.542 ACET + #.496 HO2 + #.25 OTH3 + #.204 ETCHO + #.004 MECHO + #.004 MEO2 + #-0.25 XC
6)	K(RO2+RCO3)	PROP_P1 + SumRCO3 = #.724 ACET + #.496 HO2 + #.272 ETCHO + #.004 MECHO + #.004 MEO2

Preliminary Tests of SAPRC 16
Automatic Mechanism Generation System

SAPRC 16-MECHANISM GENERATION SYSTEM

Web Reactor for william.r.stockwell@gmail.com [#3496]

Change: Temperature= 300 °K Presssure= 1.00 atm.

Lumping = SAPRC-16 Lumping

Create reactant: **Structure (help) or SMILES string:**

Create from the list of SAPRC VOC Model Species

Get information on reactants in contents: (delete all reactants)

- PROPANE: CH3-CH2-CH3 [#7160] (reacted with OH) (delete)
  Full mechanism has 27 reactions and 26 species. Show (reactions and products). Send (reactions) or (products)
  Lumped mechanism has 6 reactions (show) (send in .RXN format) (Send in SAPRC spreadsheet format)
  Send version without peroxy lumping (in tab-separated format) or (in SAPRC .RXN format)
- ETHANE: CH3-CH3 [#4835] (reacted with OH) (delete)
  Full mechanism has 2 reactions and 5 species. Show (reactions and products). Send (reactions) or (products)
  Lumped mechanism has 1 reactions (show) (send in .RXN format) (Send in SAPRC spreadsheet format)
  Send version without peroxy lumping (in tab-separated format) or (in SAPRC .RXN format)
- ETHENE: CH2=CH2 [#6150] (reacted with NO3) (delete)
  Full mechanism has 3 reactions and 5 species. Show (reactions and products). Send (reactions) or (products)
  Lumped mechanism has 1 reactions (show) (send in .RXN format) (Send in SAPRC spreadsheet format)
  Send version without peroxy lumping (in tab-separated format) or (in SAPRC .RXN format)

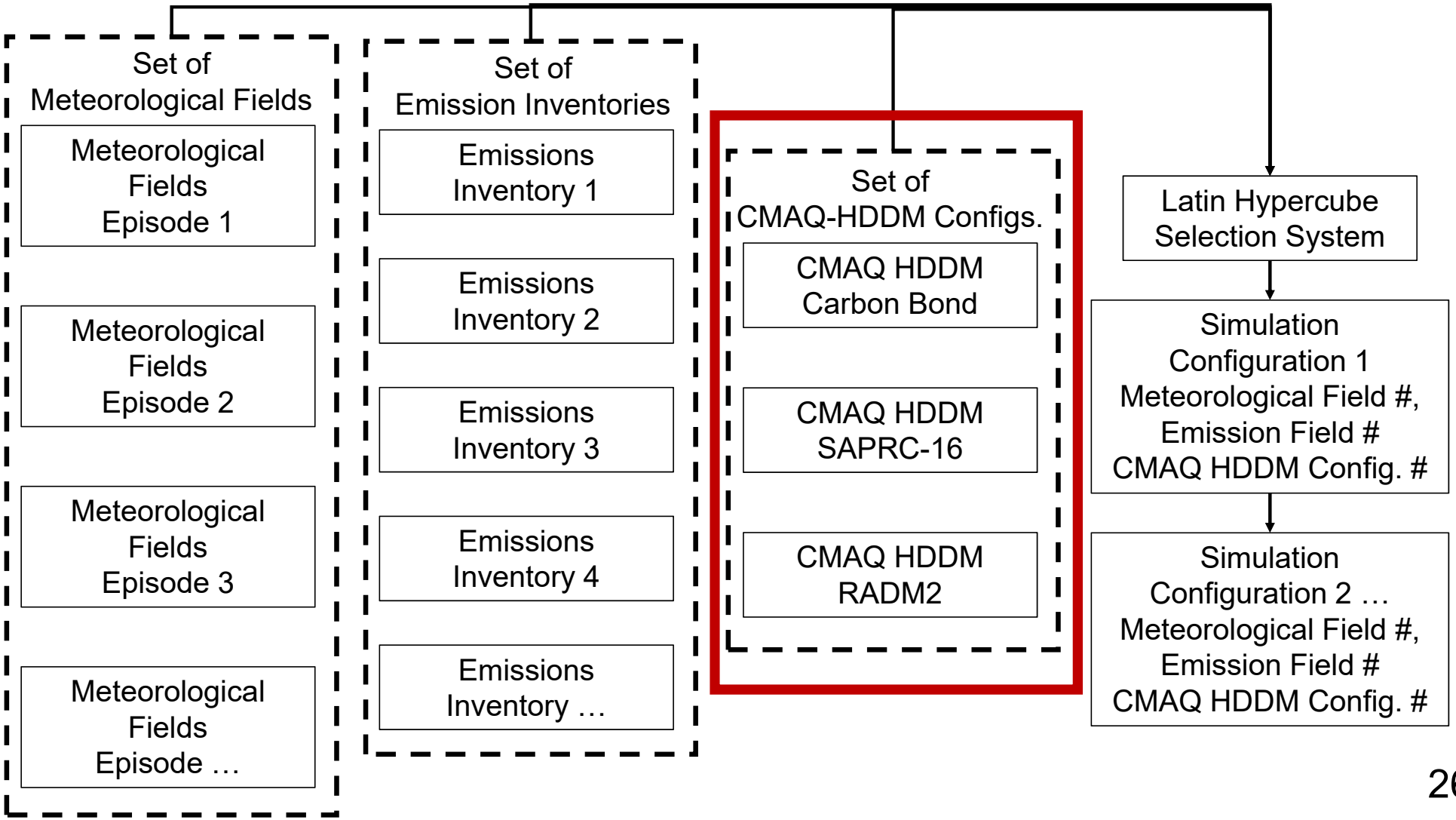
Should Policy be Made with Just One Mechanism?

- There are over 31* gas-phase chemical mechanisms used in 3-D air quality models. One mechanism for modeling is a bad idea
- Why not as a matter of best-policy – Run an Ensemble?
  - Detailed SAPRC
  - MCM
  - GECKOA
    SARS Constrained
  - Data Assimilated Mechanism (SCDAM)

Suite of Condensed:
$SAPRC_1$, $SAPRC_2$ …
MCM_1, MCM_2…
$GECKO_1$, $GECKO_2$ …

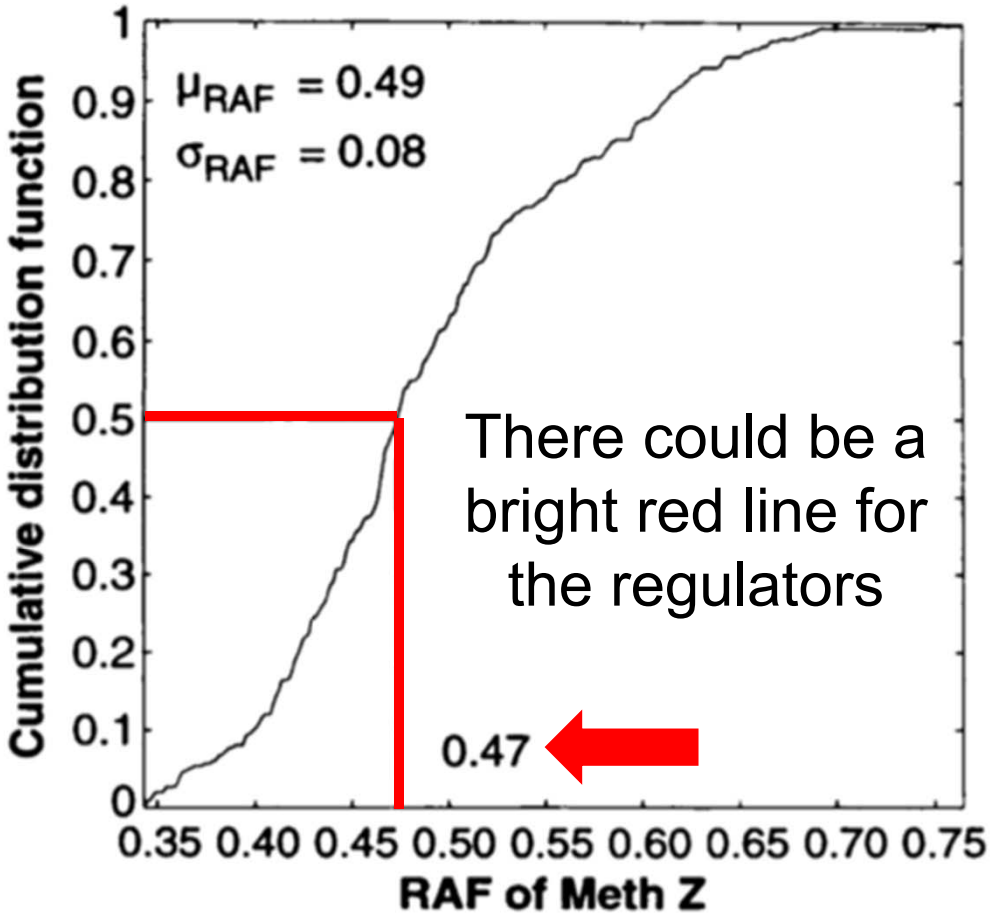
*Number extended from Baklanov, et al. (2014), Online Coupled Regional Meteorology Chemistry Models in Europe: Current Status and Prospects, Atmos. Chem. Phys., 14, 317–398.)

Ensemble HDDM Simulations



Potential Form of Results from an Ensemble Forecast

Russell, A., J.B. Milford, M.S. Bergin, S. McBride, L. McNair, Y. Yang, W.R. Stockwell and B. Croes, Urban Ozone Control and Atmospheric Reactivity of Organic Gases, Science, 269, 491-495, 1995.



Relative Adjustment Factor (RAF)

Fig. 4. Cumulative distribution function of the uncertainty in the RAF of prototype flexible-fueled M85 vehicles.

Conclusions / Observations

- Review is a work in progress and these results are preliminary.
- No major problems have been found.
- SAPRC-16 should be fine for reactivity calculations.
- Is the “condensed” SAPRC-16 overkill for 3-D air quality model *ozone* simulations? Previous condensed versions of appear more than sufficient.
- Increased detail for particulate matter simulations seems necessary and SAPRC-16 is a step in the right direction.
- Should there be only one mechanism be used for policy? Wouldn’t ensemble forecasts give a more robust picture?

Publication Plan

A major fraction of this review will be published as: The State-of-Science in the Atmospheric Chemical Mechanisms for Air Quality Modeling: Past, Present and Future, to be submitted to the Journal of the Air and Waste Management Association, March 2019.

Moral of this story: 'Tell the truth and . . .run!
Old Croatian proverb'

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