Discussion of SAPRC-16 Mechanism and Modeling System

William P. L. Carter
University of California, Riverside, CA
Revised November 20, 2017

Overview

- Current status
- Available documentation and web sites
- Overview of components
  - Excel files, sheets, and macros used for SAPRC-16
  - Mechanism Generation system
  - SAPRC Modeling software
- Simple model preparation and simulation
- Spreadsheet files useful for SAPRC modeling
- Discussion and Recommendations

Current Status

- The SAPRC mechanism system has been developed in over 40 years of mechanism development work. No one yet has been trained to use it.
- Some groups use programs derived from older versions of some of the SAPRC Fortran programs. No one uses the rest of the SAPRC system
- Excel files with macros are extensively used to develop and evaluate the mechanism, but none have been made available to others yet.
  - Not documented except some limited internal documentation
  - Most files require modifications for use on other computers.
- Use of the SAPRC Fortran modeling programs is only partially documented. Draft documentation exists but is incomplete.
- The Mechanism Generation System has very limited documentation. Some capabilities are available online, but only a few have used it.
- SAPRC-16 is still being developed and documentation is incomplete.
  - A version was provided to CARB and reviewers but needs for some changes are becoming evident during the documentation process.
  - Reactivity scale calculations not yet supported because of the need to change the lumping approach in SAPRC-16.

SAPRC Web Sites

www.cert.ucr.edu/~carter/SAPRC

Documentation, and files for SAPRC-07 and SAPRC-11 mechanisms and reactivity scales for SAPRC-07

www.cert.ucr.edu/~carter/SAPRC/16

Available documentation and files for the current preliminary version of SAPRC-16. (For CARB staff and peer reviewers)

www.cert.ucr.edu/~carter/SAPRC/SAPRCfiles.htm

Fortran programs and files for box modeling and implementing versions of SAPRC through SAPRC-11. Includes available documentation.

mechgen.cert.ucr.edu

Web access to the new SAPRC-16 mechanism generation system

mechgen.cert.ucr.edu:7000

Web access to legacy SAPRC-07/11 mechanism generation system

www.cert.ucr.edu/~carter/emitdb

Emissions speciation assignments for SAPRC and other mechanisms

Files on CE-CERT Network

Toaster.engr.ucr.edu/locker/CERT/APL/Data/Carter/SAPRC

- Full distribution of files for SAPRC-07 and SAPRC-11 that is available at www.cert.ucr.edu/~carter/SAPRC
- Files to run a preliminary version of SAPRC-16

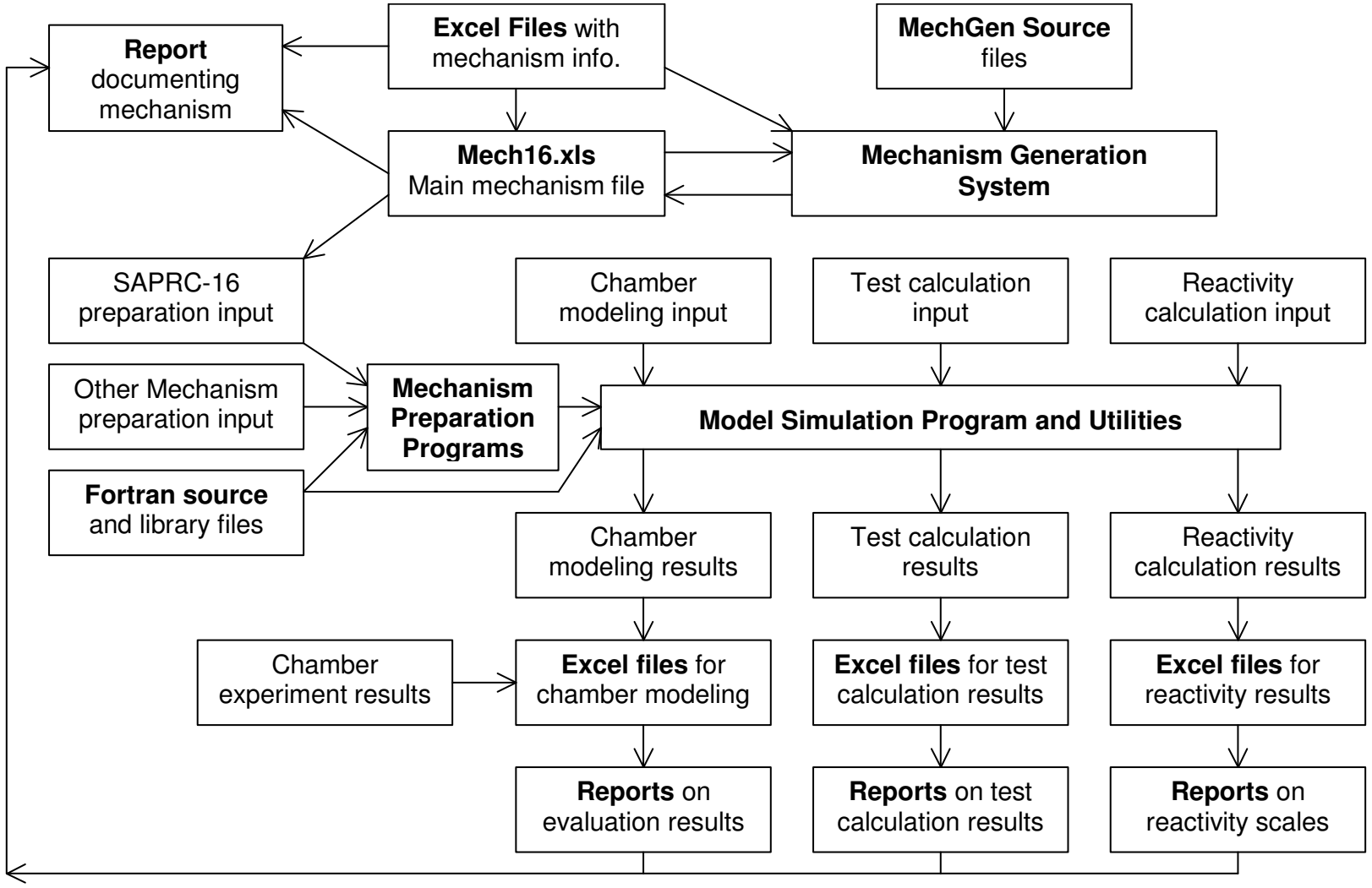
Toaster.engr.ucr.edu/locker/CERT/APL/Data/Carter/Training

- Current available documentation
- Spreadsheets discussed in this presentation
- Simple model preparation and simulation files discussed in this presentation and in documentation
- Folder with chamber model performance summary files
- This and other related presentations

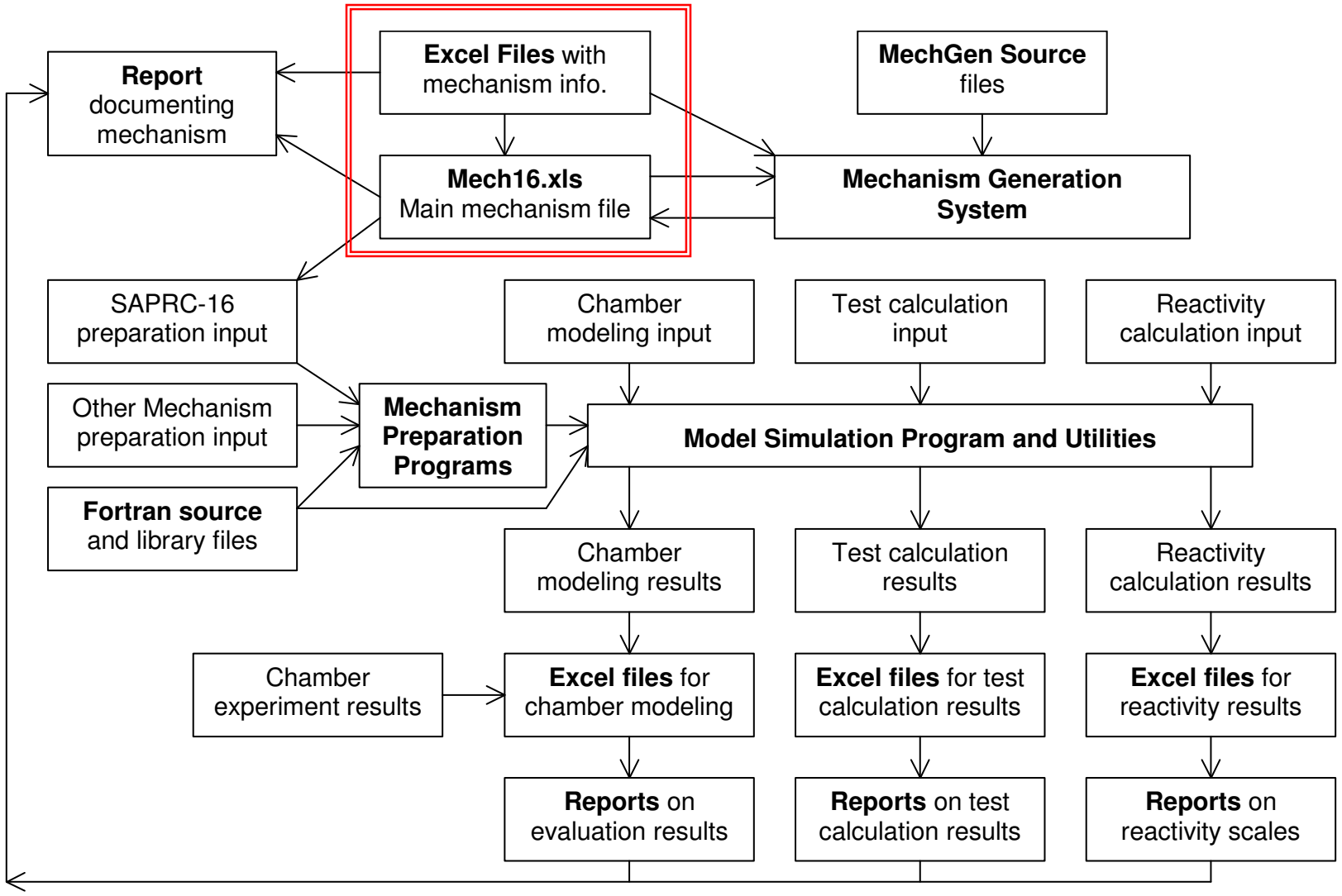
Available documentation

File(s)	Description
	SAPRC-16
This presentation	Overview and summary of SAPRC-16 system
S16doc.doc	Preliminary SAPRC-16 documentation in preparation (incomplete)
MechGen.doc	Draft documentation of SAPRC-16 mechanism generation system in preparation (incomplete)
MechGenChem .doc	Draft documentation of the treatment of chemistry in the SAPRC-16 MechGen system in preparation (incomplete)
	SAPRC Modeling Files and Programs
SAPRCfiles.pdf	Description of SAPRC modeling program and files for SAPRC versions up to SAPRC-11.
ModelPgm.pdf	Indcomplete documentation of distributed Fortran programs in SAPRC modeling
	Previous SAPRC Versions
SAPRC07.doc SAPRC07.xls	Documentation of SAPRC-07 mechanism, mechanism generation system, and reactivity scales (also journal article)
MIR10.pdf, scales07.xls	SAPRC-07 reactivity scales used in California regulations
CSAPRC07.doc	Documentation of condensed SAPRC-07 (also journal article)
SAPRC11.pdf	Documentation of SAPRC-11 mechanism (also journal article)

SAPRC Mechanism Development System



Excel Files in SAPRC System



Excel Files with Mechanism Information

Main Mechanism File	
Mech16	• Base mechanism; • Information and assignments for VOC detailed model species; • MechGen lumping and several other MechGen assignments; • Other mechanism information; • Macros to input data from MechGen and output mechanism preparation files
Other Mechanism Data Files (partial list)	
Phf-16	Photolysis absorption cross section and quantum yields
DMSk	Data on rate constants for initial VOC reactions
Mechanism Generation Information and Assignments (partial list)	
MechGen	MechGen summary information and links
Groups	Information and properties of MechGen molecular groups
AbstEst	Assignment data for estimating rate constants for initial VOC reactions (OH, O_3, etc.)
HVasn	Assignments for photolysis reactions
(various)	Assignment data for estimating radical reactions (to be reorganized)
NewThermo	Thermochemical group assignments used for radical reaction estimates
MechAsn	Rate constant and mechanism assignments to be used instead of estimates (other than those in DMSk.xls)

Information in Mech16.xls (partial list)

Sheet	Contents (partial listing)
Log	Summary of mechanism changes since SAPRC-07
Info	• Links to other Excel files used for SAPRC-16 and MechGen • Description of sheets and data in this file • MechGen commands used to re-generate the complete mechanism
Parms	• Parameters and control tables used by various macros and calculations • List of macros used and controls to run them
LMS	List and information on all model species in base and lumped mechanism
Rxns Rxn Notes	• Reactions, rate constants and notes (in "Rxn Notes") for base mechanism. • Reactions imported from MechGen (produced from data in other sheets)
DMS	Information about detailed VOC model species (DMS) including: • Description, atom numbers, molecular weight, Mechgen and Smiles structure • Lumped model species assignments for explicitly represented compounds • Categorization codes and other Information. Codes in "Info Tables" sheet
Phens, Naps	Parameters used to derive mechanisms for compounds not supported by MechGen
LumpMole	"Lumped molecule" or simple mixture assignments for detailed model species whose mechanisms are derived from those of other compounds (for reactivity or ambient mixture modeling)

(continued)

Information in Mech16.xls (continued)

Sheet	Contents (partial listing)
MG Lumping	• Various parameters controlling the operations of MechGen • "Lumping Rules" for assigning lumped model species to compounds
Info Tables	Various tables given for information purposes or referenced in other sheets
DMS Tables	Various tables of detailed model species, including but not limited to: • Compounds in the base mechanism for mechanism generation • Compositions of ambient and biogenic mixtures used • MechGen input for VOCs needing special processing • Names of compounds represented explicitly for chamber modeling
MechGen Output	
MG Data	MechGen output giving lumped mechanisms and model species for compounds and mixtures whose mechanisms are derived using MechGen. This is used by macros to derive all MechGen-dependent data in the "LMS" and "Rxns" sheets.
(One sheet for each mixture. See next slide for mixture list)	• Tables listing compositions of various mixtures used to derive lumped mechanisms, sorted by the lumped model species representing the compounds in ambient simulations, then by mole fraction (descending) • Where applicable, these tables indicate which compounds are used to derive mechanisms of the lumped model species (see next slide) • The derivation and use of these mixtures are summarized on the next slide

Mixtures Used for Deriving Lumped Mechanisms

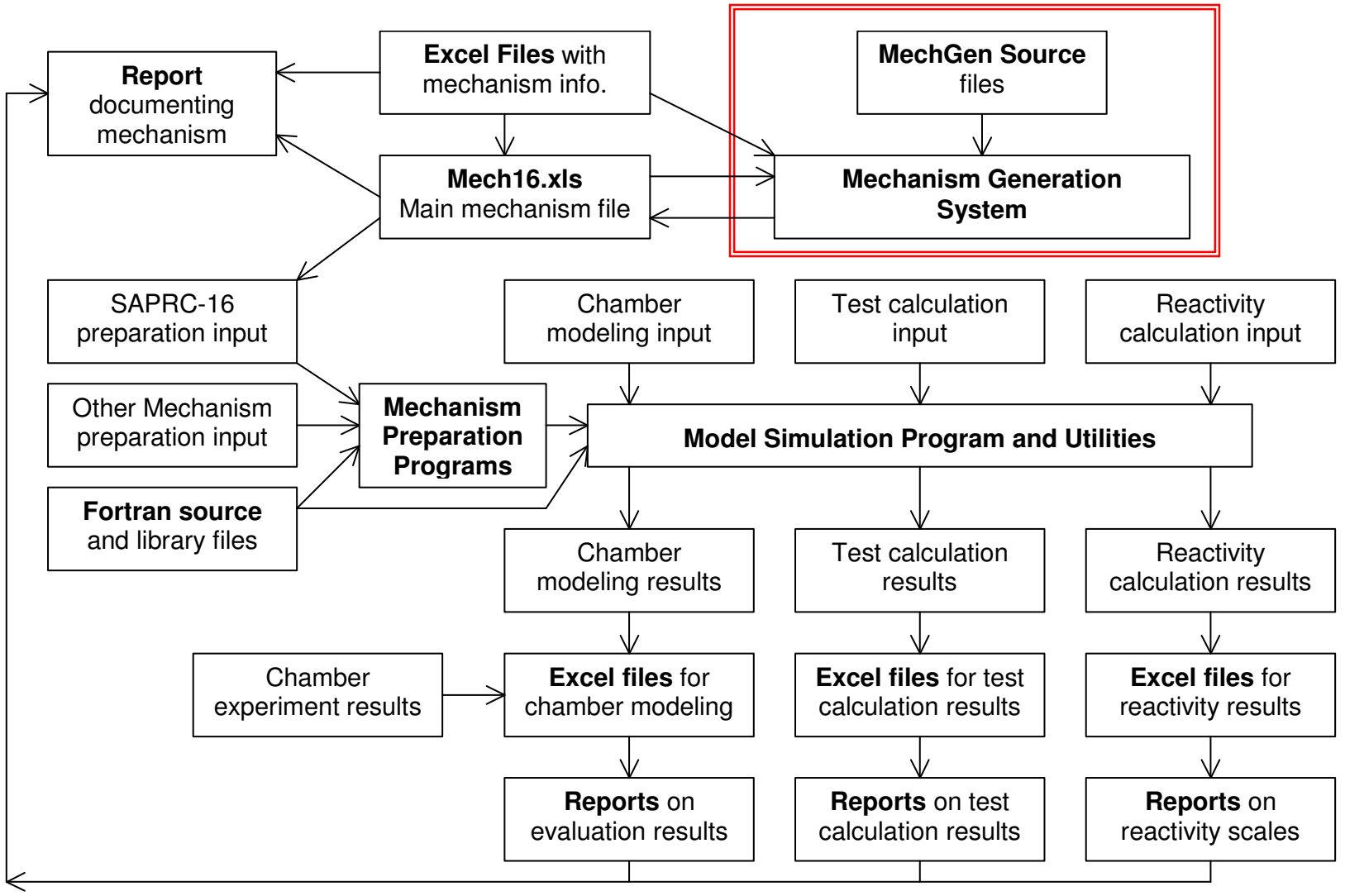
Mixture	Description	Lumped Species
EmitMix	Mixture representing ambient VOC emissions (Based on emissions data to so more types of compounds can be included than mixtures based on ambient measurements)	ALKx, OLEx *, AROx, OTH2+, AMINS, FURNS
Megan2	Mixture representing biogenic VOC emissions	TERP
EmitProds	Mixture of first-generation products formed with OH reacts with compounds in EmitMix	KET2, OTH1, RCHO, OLEP, AFGx, RxNO3 *
NEmitProds	Mixture of first-generation products formed with NO_3 reacts with compounds in EmitMix	RCNO3, RDNO3
HEmitProds	Mixture of first-generation products formed when HO_2 reacts with peroxy radicals formed when OH reacts with compounds in EmitMix	ROOH, RAOOH, CROOH
IsoProds	Mixture of first-generation products formed with OH reacts with isoprene	OLEA1, OLEA2, LVKS, HPALD
HIsoProds	Mixture of first-generation products formed when HO_2 reacts with peroxy radicals formed when OH reacts with isoprene	RUOOH

* Except as noted otherwise

Macros in Mech16.xls

Macro	Function
Write Rxns	Outputs .RXN files giving reactions and rate parameters from reactions in "Rxns" sheet. These are included in the mechanism preparation input. Output files are: • SAPRC16.RXN .. Base + lumped mechanism for ambient modeling • S16cham(2).RXN: Base + semi-lumped mechanism for chamber modeling.
Write Mec	As above, but output in CMAQ 'mech def' format and only for ambient modeling.
Write LCC	Write lumping assignment files giving model species for supported VOCs • SAPRC16.LCC: read by modeling programs for ambient modeling • S16cham.LCC: read by modeling programs for chamber modeling
Write DMS.PRM	Outputs the "DMS.PRM" file that has information about detailed model species that is used by some of the Fortran modeling and utility programs.
Fill Species	Prepare reactions in 'Rxns' sheet for output and and also check for carbon and nitrogen balances. Automatically run by some other macros that need this.
Load MG	Loads output file produced by MechGen and sent by FTP into the "MG Data" sheet.
Process MG	Processes data giving reactions of compounds and mixtures in the "MG Data" sheet and outputs their reactions in the "Rxns" sheet and their intermediate peroxy model species in the "LMS" sheet. The above two macros must be run every time new data obtained from MechGen.

SAPRC Mechanism Generation System



SAPRC-16 Mechanism Generation System

Capabilities

- Derives explicit mechanisms for:
  - Most non-aromatic VOCs with C, H, O, and/or N atoms
  - Monocyclic alkylbenzenes
  - Some chlorine-containing compounds.
- Measured rate constants and branching ratios used where available
- Displays documentation of the chemical estimates and assignments used if reactions run in 'single step react' mode.
- Generates subsequent reactions of radicals formed, and of radicals they form, if run in ''react completely' mode.
  - Reactions of stable products formed are not automatically generated. These can be generated separately if desired.

Limitations (partial)

- Does not understand steric effects.
- Not usable or reliable for all types of compounds or radicals.
- Valid mainly for a atmospheric temperature and pressure.

SAPRC-16 Mechanism Generation System:
Other Capabilities

Capabilities used for SAPRC-16 integration

- Provides means for processing many reactants at once.
- Derives mechanisms for mixtures from generated mechanisms of the components, given the mole fractions.
- Derives lumped mechanisms from the generated explicit mechanisms.
- Accepts input pasted from Mech15.xls and other files to update assignments and generate desired output.
- Uses FTP to output data that can be pasted into Mech16.xls or other files for implementation into SAPRC-16.

Other Capabilities

- Estimates vapor pressures of non-aromatic hydrocarbons using EVAPORATION method of Compernolle et al (2011).

SAPRC Mechanism Generation System:
Representation of Molecules

- Each molecule is split into groups, including:

Stable groups					Radical Groups				Criegee
-CH3	=CH2	#CH	-OH	-ONO2	-CH2.	-CH2OO.	-CH2O.	-NH.	-CHOO[excited]
-CH2-	=CH	#C-	-O-	-NO2	-CH[.]-	-CH[OO.]-	-CH[O.]-	-N[.]-	-COO[excited]-
>CH-	=C	-aC-	-CHO	-NH2	>C[.]-	>C[OO.]-	>C[O.]-		-CHOO[stab]
>C<	=C=	-aCH-	-C[O]-	-NH-	=CH.	-C[O]OO.	-C[O]O.		-COO[stab]-
				-N<	=C[.]-	Not listed: Zero valence groups and groups that are not fully supported			
					-C[O].				

Alkyne

Aromatic

- Each group is assigned properties giving:
  - Type of group it is converted to in various types of reactions;
  - Parameters for rate constant or branching ratio estimates;
  - Which groups are neighbors (can affect estimates).
- Each type of group has procedures (verbs) that controls its reactions and rate constant or branching ratio estimates.

SAPRC Mechanism Generation System:
Examples of Structure Specifications

Compound	Smiles	MechGen Structures
propane	CCC	CH3-CH-CH3
propene	C=CC	CH2=CH-CH3; CH3-CH=CH2
methyl acetylene	C#CC	CH#C-CH3; CH3-C#CH
2-methyl-2-ethyl butane	CCC(C)(C)CC	CH3-CH2-C(CH3)(CH3)-CH2-CH3
isoprene	C=CC(=C)C	CH2=CH-C(=CH2)-CH3; CH2=CH-C(-CH3)=CH2
2-butenes (mixed isomers)	CC=CC	CH3-CH=CH-CH3
cis-2-butene	C/C=C\C	CH3-^CH=CH-vCH3; CH3-vCH=CH-^CH3
trans-2-butene	C/C=C/C	CH3-^CH=CH-^CH3; CH3-vCH=CH-vCH3
cyclopropane	C1CC1	CH2*-CH2-CH2*; *CH2-CH2-*CH2
bicyclo [1.1.1] heptane	C1C2CC1C2	CH2*1-CH*2-CH2-CH*1-CH2*2
toluene	Cc1ccccc1	CH3-aC*-aCH-aCH-aCH-aCH-aCH*
naphthalene	c12ccccc1cccc2	aC*12-aCH-aCH-aCH-aCH-aC*1-aCH-aCH-aCH-aCH*2
2-propyl nitrate	CC(C)ON(=O)=O	CH3-CH(CH3)-ONO2; CH3-CH(ONO2)-CH3
ethylene glycol ethyl ether acetate	CCOCCOC(C)=O	CH3-CH2-O-CH2-CH2-O-CO-CH3
2-propyl radicals	C[CH]C	CH3-CH[.]-CH3
2-propyl peroxy radicals	CC(C)O[O]	CH3-CH[OO.]-CH3
methyl allyl radicals	C=C[CH]C	CH3-aCH[.]-aCH-aCH2; CH3-CH[.]-CH=CH2
OH+benzene adduct	OC1C=CC=C[CH]1	HO-CH*-aCH[.]-aCH-aCH[.]-aCH-aCH[.]*

SAPRC Mechanism Generation System:
Types of Supported Reactions

Type of reactant	**Types of reactions**
Stable organics	H-abstractions by OH, NO_3; Additions by OH, O_3, NO_3, O^3P; Photolyses
Carbon-centered radicals	O_2 additions; O_2 abstractions; Decompositions
Peroxy radicals	Isomerizations; Reactions with NO, NO_2, HO_2, NO_3, or RO_2
Alkoxy radicals	Decompositions; Isomerizations; O_2 abstractions
Criegee biradicals	Stabilizations; Decompositions; Reactions with H_2O (if stabilized)
Other Excited species	Decompositions; stabilizations
Nitrogen-centered radicals	O_2 abstractions; NO_2 additions

SAPRC-16 Mechanism Generation System:
Programming Platform and Access Methods

Platform and Programming Language

- Coded in MOO code as an extension of a now-obsolete text-based virtual reality system. Built on the LamdaMOO system.
- Uses a programming language similar to Python. Software objects are used to organize data, procedures, and relationships. Much better suited for a mechanism generation application than Fortran.
- Runs continuously with Telnet or Web access on Unix or Windows-type computers with internet access.

Telnet (Command Line) Access (at mechgen.cert.ucr.edu:8888)

- Required to program and use MechGen for mechanisms development.
- Anyone can log as a guest on but only one user has the ability to effectively use or update the system.

Web Access (at mechgen.cert.ucr.edu)

- Anyone can access the system using a menu interface to generate reactions and see documentation output and other information.

SAPRC-16 Mechanism Generation System:
Representative Types of Software Objects Used

Note that generic or parent objects contain procedures (verbs) and default properties for the various types of objects, while descendant objects contain properties for specific cases.

- Reactants. Contains information about specific molecules and and also contains mechanism generation results, if available.
- Groups. Structural groups in a molecule. Default properties control reactions at groups. Other properties identify neighbor groups, how bonded, and the reactant containing the group.
- Chamber. Contains main user interface. Properties specify the various assignment objects and options that control mechanism generation.
- Lumping Control. Controls how lumped mechanisms are derived from explicit mechanisms and how the reactions are generated.
- Mixture Databases. Defines mixtures either input by the user or derived from results of reactions of compounds or other mixtures.
- Reactant Containers. Used to simplify operations on multiple reactants and mixture objects. Needed for full mechanism development.

SAPRC-16 Mechanism Generation System:
Examples of Commands using Telnet Access

build MyVOC as CH3-CH2-CH3

Creates a reactant named “MyVOC” with the structure of propane

react MyVOC with OH

Does a single step reaction with OH. Output includes documentation, and reactant objects for products are also produced.

react CH3-CH2O.

Creates a reactant object with the structure of ethoxy and does a single step reaction of this radical. Documentation and product objects output.

fullreact MyVOC with OH

Does a complete reaction of the reactant with OH, with the results on properties of the MyVOC object.

@ftpout log on MyVOC --or-- @ftpout rxninfo on MyVOC

Sends a file with the generated and lumped mechanism and processing information (log) or the lumped mechanism in a format that is recognized by Mech16.xls (rxninfo) to an FTP site defined for the user.

Mechanism Generation System Web Interface

Login page at mechgen.cert.ucr.edu

- Provide a user name and password if this is the first time or a new computer. No other login information needed. (No 'cookies' used.)

Available options at the Main Menu (partial list)

- Create a new reactant (a 'help' link is provided).
  - Shows a 'reactant page' screen if the reactant is stable compound.
  - Generates reactions in single step mode if the reactant is a radical.
- Obtain information about or delete stable reactants created before.
  - Nothing shown if no previous reactants saved.
  - If complete reactions were previously generated (using the reactant page) there will be links to see or download the results.
- Obtain information about assignments used in place of estimates.
- Obtain information on estimation methods used. This is a work in progress and currently only covers initial thermal VOC reactions.
- Log out of system (only needed if you want to go back to login page).

Mechanism Generation System Web Interface
(continued)

Reactant Page

- Shows structure, formula, molecular weight, heat of formation*, vapor pressure estimates*, and how lumped in SAPRC-16 (*=if available)
- Shows menu of options for each type of initial reaction, including:

  'Single step react': Shows reactions, documentation, and products formed for selected type of reaction.
  - Can 'click' on products formed to see their reactions or page.

  'React completely': Generates the full set of reactions leading to stable products or explicitly represented radicals.
  - Links to the results will be shown when the reactant is listed in when you return to the 'main menu'.
  - If the process takes less than 5 seconds you will see the generated reactions listed, a summary of products formed and the lumped mechanism what was derived.
  - If the process takes longer, you will get a page where you can either abort the process or return to the main menu. If you don't see links to the results there, wait a while and refresh the page.

Mechanism Generation System Web Interface
(continued)

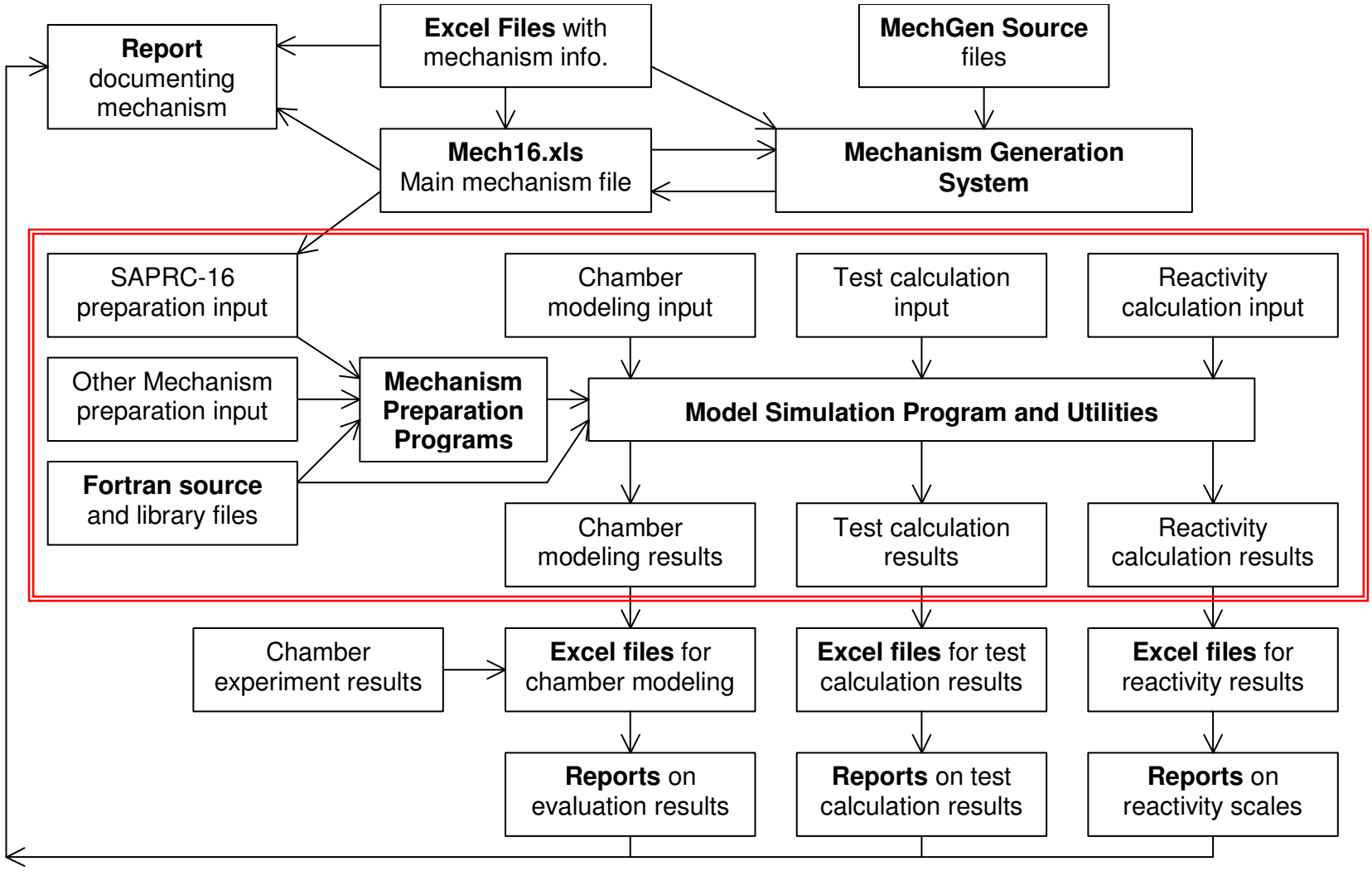
Links for information on previously created reactants (in 'Main Menu')

- Delete: Only available link if 'react completely' not previously run.
- Show reactions and products: Shows page listing generated reactions and products (similar to page shown if 'react completely' takes less than 5 seconds).
- Send reactions: Sends user a text file containing the reactions in tab separated format.
- Send products: Sends user a text file listing the final products formed in the various types of reactions, with final overall yields (if NO=0.5 ppb) and lumped model species representing them (tab separated)
- Send lumped mechanism (in tab separated or SAPRC .RXN format): Sends the user a text file with the lumped mechanism.

How to manually generate reaction sequences

- Create reactant and a 'single step react' for a selected reactant.
- Click on a radical product formed to generate its reactions, do this again react a selected product, etc.
- Stable products formed in these steps will appear in the 'main menu'.

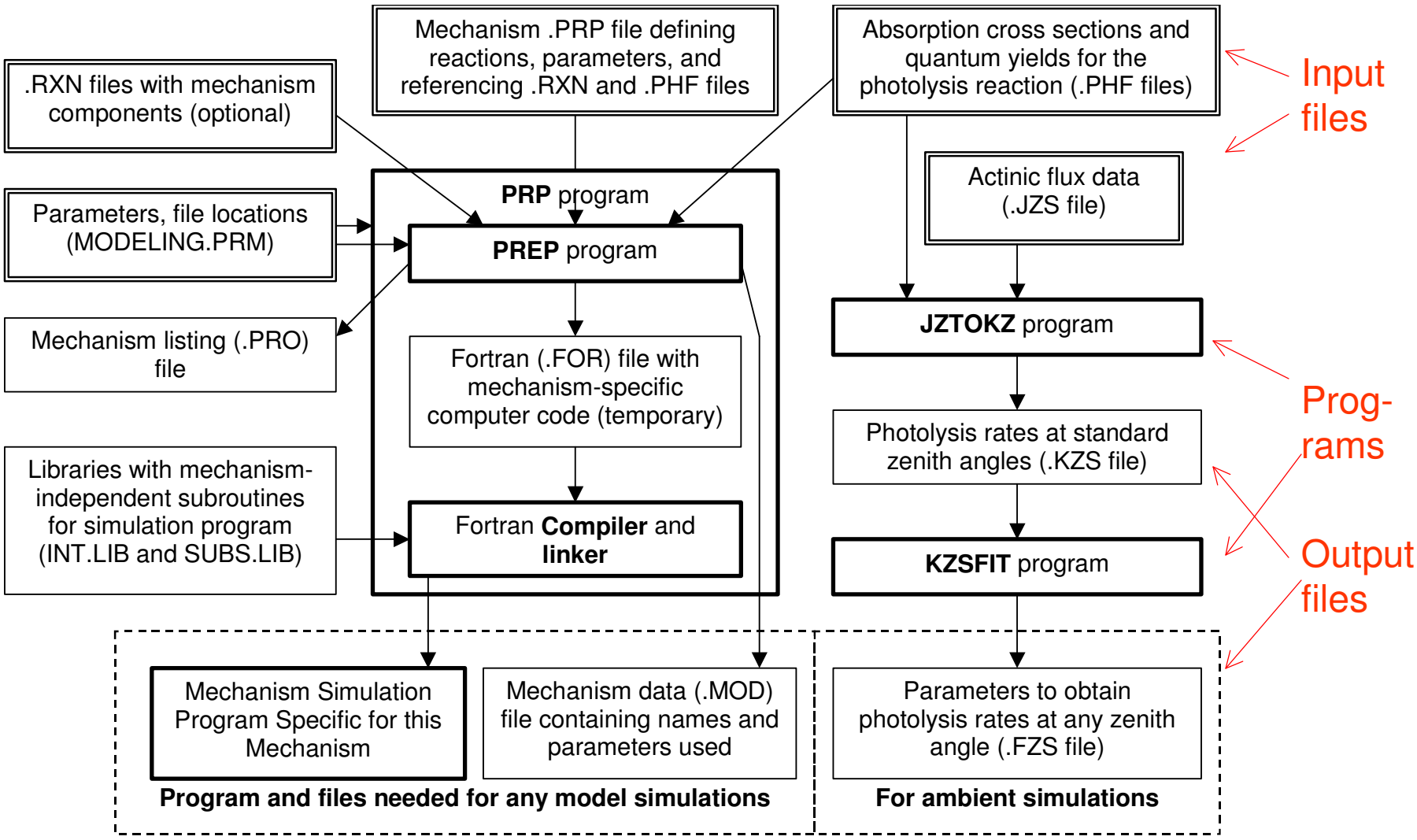
Modeling Programs in the SAPRC System



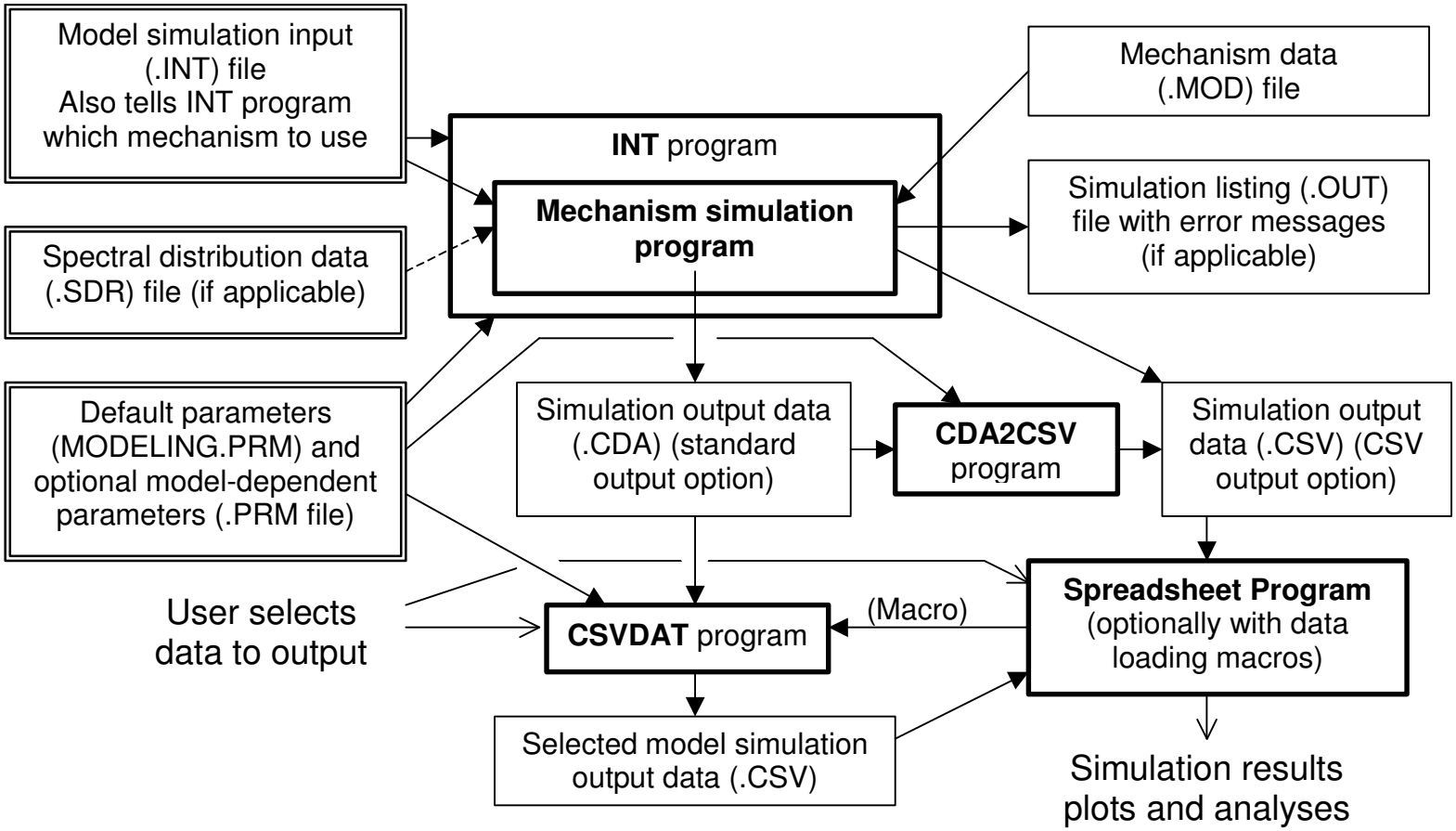
SAPRC Modeling Programs

- Used to conduct model simulations of chamber experiments and ambient box model scenarios and analyze results.
- Programs, input files examples, and (incomplete) documentation available at SAPRC web site. These include:
  - All programs used for mechanism preparation and basic, chamber, test calculation, and reactivity simulations.
  - Mechanism files for SAPRC-99, -07, and –11 (SAPRC-16 files not included in online distribution, but available to CARB).
  - Excel files and templates useful for analysis of results.
- Major programs include:
  - Mechanism preparation programs.
  - “Lumping” programs to prepare mechanism-dependent simulation input from mechanism-independent simulation input files.
  - Box model simulation programs.
  - Utility programs for gathering results for spreadsheet input.
  - Programs for processing reactivity calculation results (not yet supported for SAPRC-16).

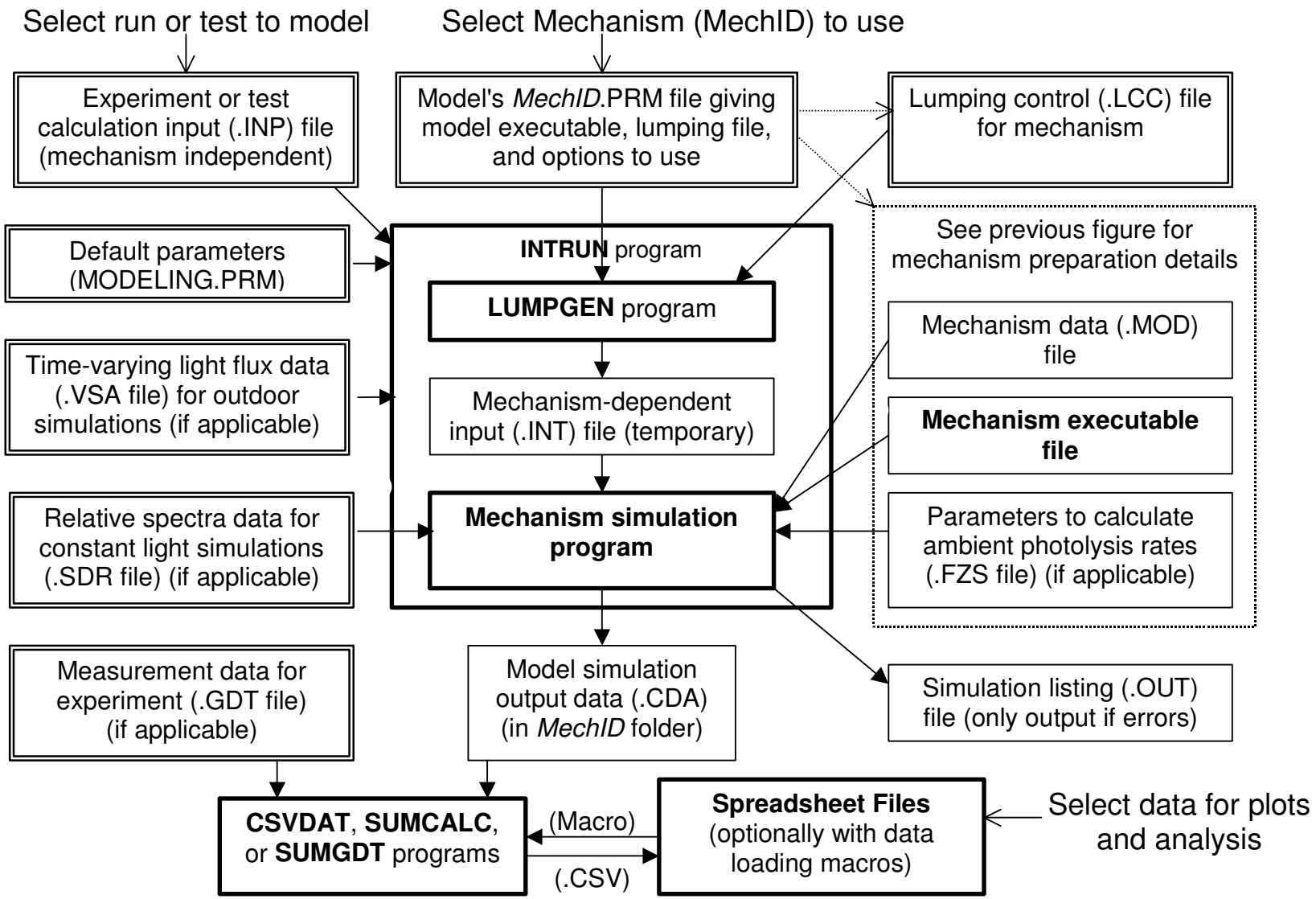
Mechanism Preparation Overview



Basic Model Simulation Overview



Chamber and Test Calculation Overview



Distributed SAPRC Files and File Locations

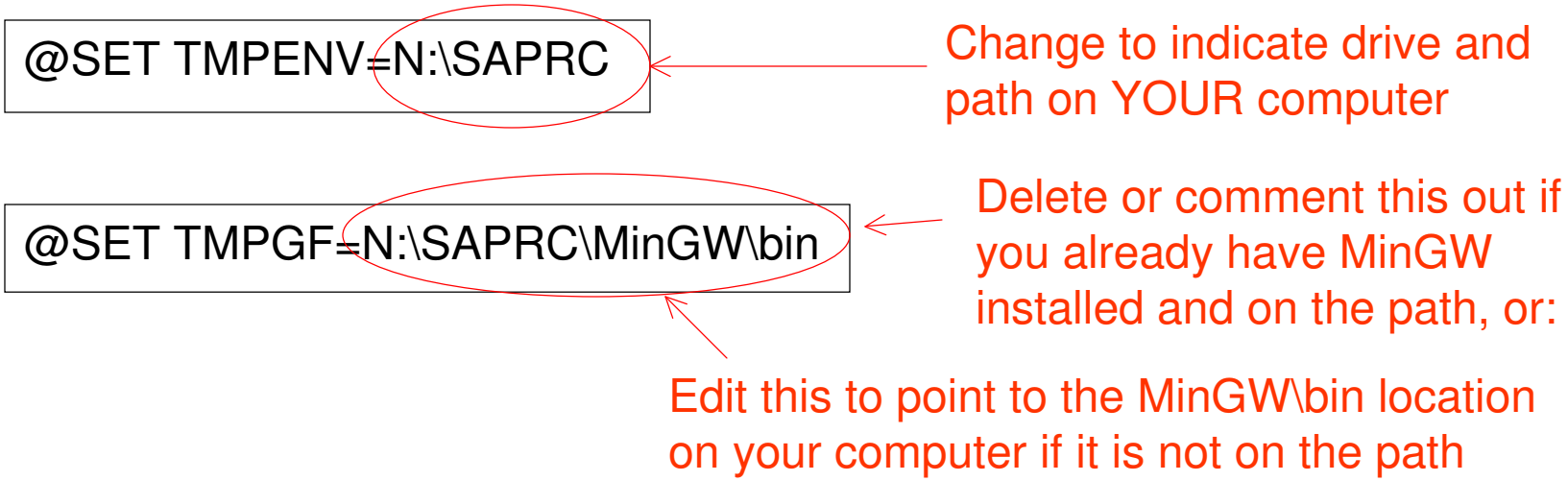
Directory Structure			Contents
Level 1	**Level 2**	**Level 3**	
PGMS	(root)		Executable files for distributed programs
	SOURCE	One for most programs	Source and library files for distributed programs, in organized into subfolders (requires Gfortran to compile)
	TEMPLATES		Templates for spreadsheets useful for analysis of results
MECH	One for Each mechanism		Files for SAPRC-99, SAPRC-07, and SAPRC-11. SAPRC-16 files also go here but are not distributed
TESTCALC	(root)		Test calculations run from this folder
	INPFILES		Input files for standard test calculations
	CDTFILES	One for each .PRM file used	Calculation data files, organized in subfolders for each .PRM file used.
CHAMCALC	(root)		Chamber calculations run from this folder
	INPFILES		Input files for all experiments
	CHDfiles		Experimental data files for experiments
	CHAR	LIGHT	Spectral distribution files
		One for most mechanisms	Characterization input files for sets of runs. Can depend on mechanism.
REACT	Not discussed today		Files for reactivity simulations

Installing and Testing the SAPRC Software System

- Available at SAPRC web site and provided with this training. Look at SAPRCfiles.doc or ModelPgm.doc for installation instructions
- Install the freeware Gfortran compiler (preferably MinGW version), available from GNU websites (or MinGW files can be provided)
- Copy files to a PC-type computer with at least 1 GB free
  - Create an empty folder, e.g., D:\SAPRC, on a PC-type computer with at least 1 GB free
  - Copy distributed PGMS, MECH, TESTCALC, CHAMCALC, (optionally) REACT, and (if available) S16DIST.ZIP to that folder
  - Unzip each of these .ZIP files, then you can delete them.
  - Alternatively, copy all the files from a provided USB drive.
  - Make sure directory structure as shown on previous slide.
- Edit NEWENV.BAT in root folder (next slide)
- Open DOS window, navigate to folder, then run NEWENV.BAT
- Run test compilations, preparations, and simulations (next slides)

Configuring DOS Window to Run Programs

- A DOS window is used to run SAPRC Fortran programs manually.
- The Batch file NEWENV.BAT, to be run right after the DOS window is opened, is provided to assure environment is as needed. Edit this as follows to properly set the environment for your system:



- Alternately, configure your default DOS path environment to include following on path, so you won't have to run NEWENV every time:
  - SAPRC\PGMS folder
  - MinGW\bin folder (should be there if MinGW installed properly)

Testing Installation and Configuration

- Open DOS window and navigate to installation folder (e.g. D:\SAPRC)
- Run NEWENV.BAT if unless default path already set
- Run TESTGF.BAT to test Fortran instillation
  - Should show date and time if successful
- Test mechanism preparation (e.g., SAPRC-11)
  - CD \SAPRC\MECH\SAPRC11
  - PRP TESTS11 (Should see 'Model prepared' if no errors)
- Test chamber simulation
  - CD \SAPRC\CHAMCALC
  - INTRUN EC340 SAPRC11 (Should see .CDA file created)
  - CDA2CSV EC340 SAPRC11 (TMP.CSV will have calc data)
- Test calculations
  - CD \SAPRC\TESTCALC\
  - Run EXAMPLE.BAT (Look for error messages)
  - Results should be in various .CSV files. See EXAMPLE.BAT

Simple Model Preparation

SIMPLE.PRP file

```
Simple example preparation file
.ACT
= A + P1 + P2 + P3
.STS
R1
.CON
HV  1.0
.RXN
R1) PF=SIMPNO2  ;A + HV = P1 + R1
R2)        1.0          ;P1 = P2 + P2a
R3)        1.0E+4       ;R1 + A = P3
.END
```

Units are ppm and minutes

SIMPNO2.PHF file

```
Simple approximation of NO2 + HV
0.250 0.00e+00 1.0
0.300 1.30e-19 1.0
0.350 4.50e-19 1.0
0.400 6.00e-19 1.0
0.415 6.00e-19 0.0
```

MODELING.PRM file

```
SOURCE=D:\SAPRC\PGMS\
```

Open DOS box, go to D:\SAPRC and run NEWENV.BAT if needed.

CD SIMPLE

Run PRP SIMPLE

Because of a program bug, you must have at least one product that does not react and is not declared active. Most models generally have this.

Simple Model Simulation

SIMPLE.INT file

```
Simple example simulation file
MODEL=SIMPLE
SAVE CSV
.
.SD-SIMPSUN
.DPRN 0.1
.TEND 5.0
A 1.0
.INT
```

Units are ppm and minutes

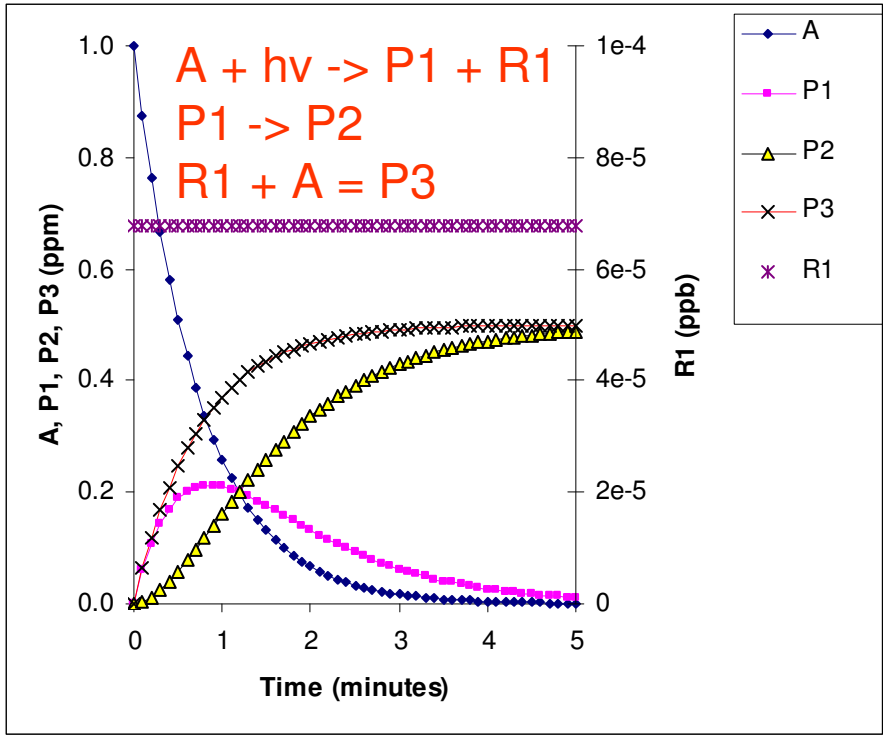
SIMPSUN.SDR file

```
Simple approximation of Solar Flux
0.300 0.0E+00
0.450 3.5E+19
1.000 3.5E+19
```

Run INT SIMPLE

Load SIMPLE.CSV into Excel

Create plots or analyze as desired



Spreadsheet Files Useful for SAPRC Modeling

Run simulations on test scenarios

- CalcTest.xls ...Compare, analyze simulations of scenario or test input
  - Flexible control over what is plotted and compared
  - Optionally shows rates or integrated rates
  - Optionally analyzes results
- Test1Day.xls ... Compares simulations with one day test scenarios
- TestMday.xls ... Compare simulations with multi-day test scenarios

Run chamber simulations and see calculation vs. experimental data

- RunCalc.xls or RunCalc.xlt ... Calculations for a single single experiment (optionally showing data from a 2nd run on the same plot)
- RunsFit.xls or RunsFit.xlt ... Calculations for multiple experiments
  - Number of experiments and plots can be increased using macros
- Spreadsheets exist to show results multiple chamber evaluation simulations but need to be configured to work on other computers

Considerations when Using SAPRC Excel Files

Font Color Conventions

Black Font	Text or data that usually are not changed
Red Font	Input that the user can or should change
Blue Font	Calculation input. Do not modify unless you want to use a non-default value, in which case you should change the font to red to avoid future confusion.
Purple Font	Data produced by macros.

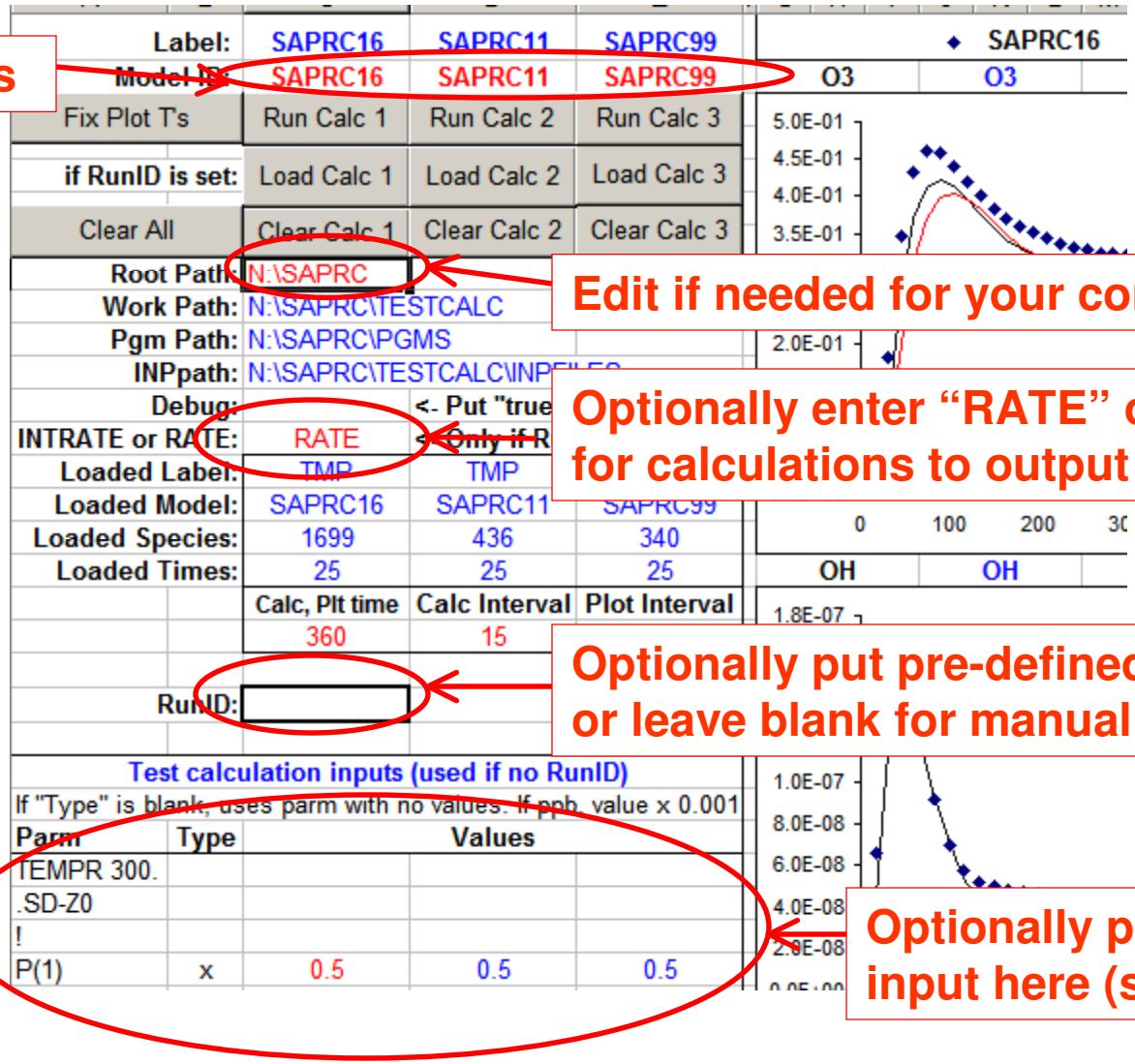
Developed and tested using Excel-2000

- Macros *should* work but not tested using newer versions of Office and proper functioning cannot be guaranteed
- May get “file error ... some formats have been list” because newer Excel versions don’t like “0.00e+00” in scientific notation. These formats lost but file otherwise ok. Change these formats to “0.00E+00”.

Sheets in CalcTest.xls

Sheet	Description
Work	Where parameters input and selected plots shown (see next slide)
Plots	Shows more plots. Channels to plot can be changed
Plots2	Shows more plots, with options to compare data in different ways
Analysis	Shows formation and loss rates of selected species or groups of species. (Useful only if "RATE" or "INTRATE" options used on the "Work" sheet)
CompCalc	Compare differences between two calculations (useful mainly if they are supposed to be nearly the same but aren't)
Rxns1 .. 3	Reaction listings from for the three calculations. Macros can be run to show rates if "RATE" or "INTRATE" used.
Calc1 ... 3	Concentration-time data for the three calculations

Portions of CalcTest.xls



Model IDs

Edit if needed for your computer

Optionally enter "RATE" or "INTRATE" for calculations to output reaction rates

Optionally put pre-defined input ID here, or leave blank for manual input

Optionally put manual input here (see next slide)

Portions of CalcTest.xls (continued)

Label:	SAPRC16	SAPRC11	SAPRC99
Model ID:	SAPRC16	SAPRC11	SAPRC99
Fix Plot T's	Run Calc 1	Run Calc 2	Run Calc 3
if RunID is set:	Load Calc 1	Load Calc 2	Load Calc 3
Clear All	Clear Calc 1	Clear Calc 2	Clear Calc 3

Model IDs (these could be the same if comparing calculations with different inputs)

Test calculation inputs (used if no RunID)

If "Type" is blank, uses parm with no values. If ppb, value x 0.001

Parm	Type	Values		
TEMPR 300.				
.SD-Z0				
!				
P(1)	x	0.5	0.5	0.5
H2O	ppm	2.00e+4	2.00e+4	2.00e+4
NO	ppb	50	50	50
NO2	ppb	50	50	50
!				
.LUMP				
T-HEXENE	ppm	1	1	1
!				
!				
!				
.				
.INT				

.INT simulation input that does not depend on model used

.INT simulation input of standard VOC names to be lumped or converted to mechanism-dependent model species go between ".LUMP" and "." lines.

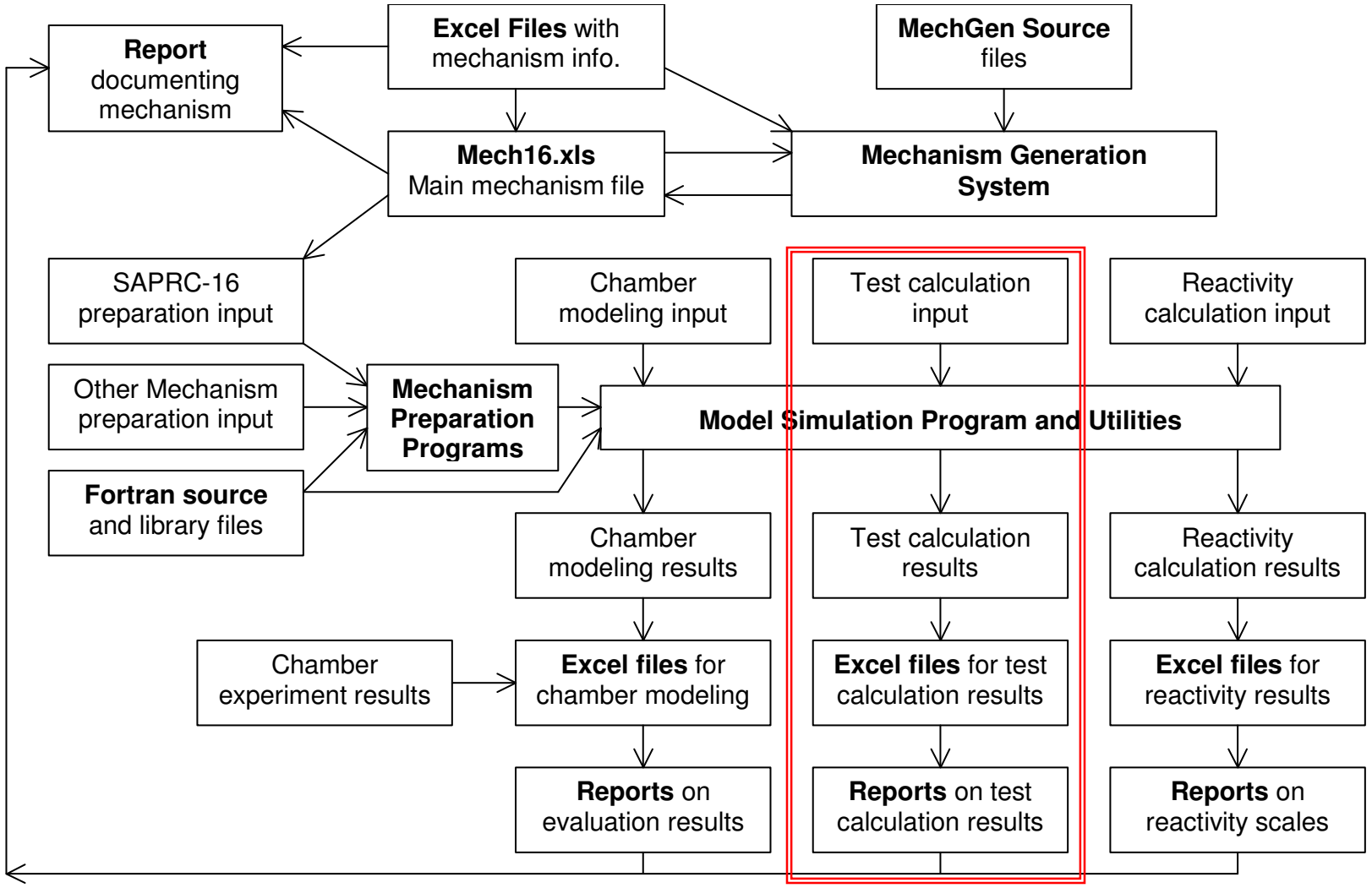
Input lines or species names

Concentrations or parameter values for each calculation

(Inputs can varied to compare effects)

Units or "x" if other columns used

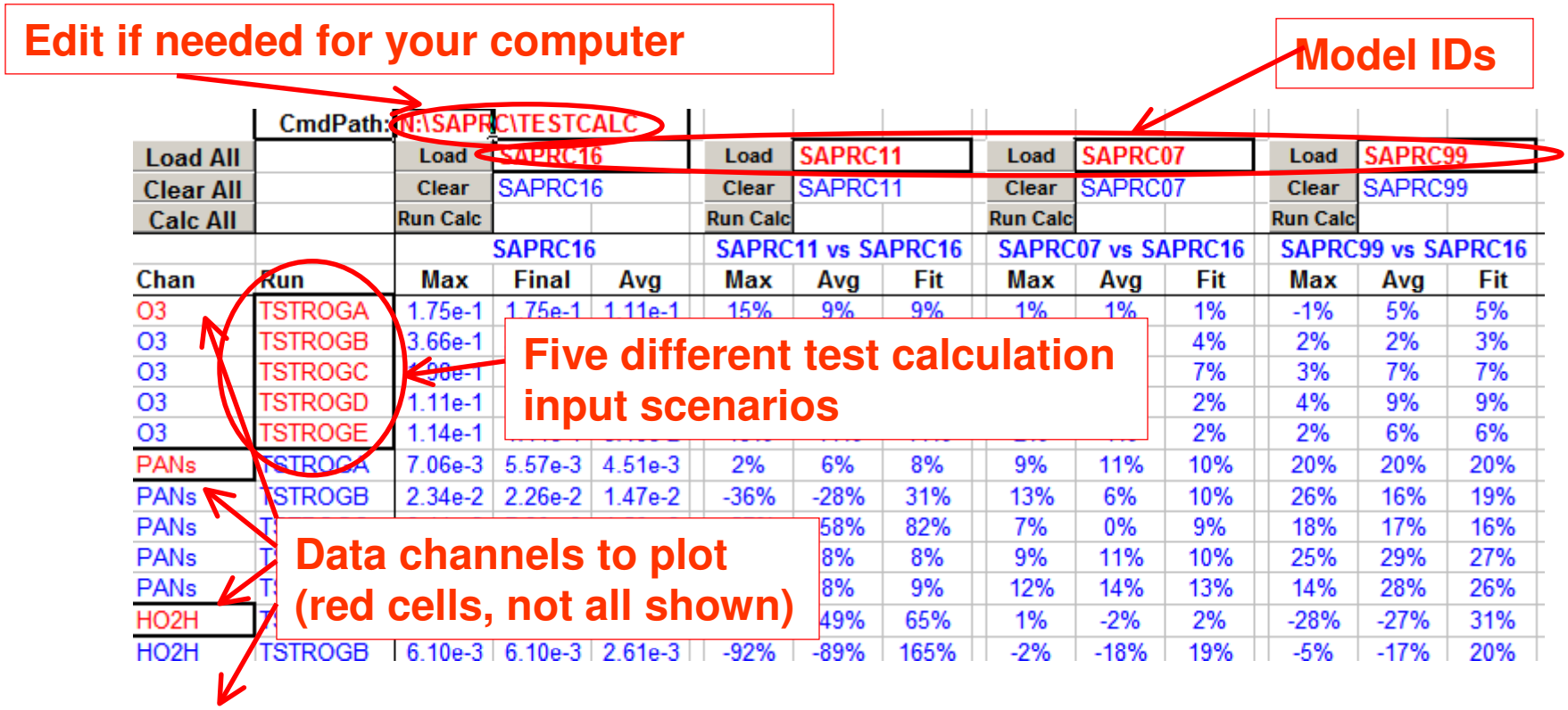
Files for SAPRC Test Calculations



Test Calculation Inputs Included in Distribution

Name	Type	Input
MD5TSTHN MD5TSTMR MD5TSTMO MD5TSTLN MD5TSTLN	5-Day simulations with continuous emissions during daylight hours. All inputs same except for NO_x	High NO_x MIR NO_x MOIR NO_x EBIR NO_x Very low NO_x
TSTROGA TSTROGB TSTROGC TSTROGD TSTROGE	Static 1-day calculation, with NO_x and ambient VOC Mixture varied. More NOx injected in middle of "A", "B", and "D" simulations. (NO_x in ppb, Ambient ROG in ppmC)	NO_x=10, ROG=0.6 NO_x=50, ROG=0.6 NO_x=50, ROG=0.3 NO_X=5, ROG=0.6 NO_x =50, ROG=0.6
(others)	Other test calculations used to develop and test condensed mechanisms (e.g., CSAPRC07)	

Portions of Test1Day.xls

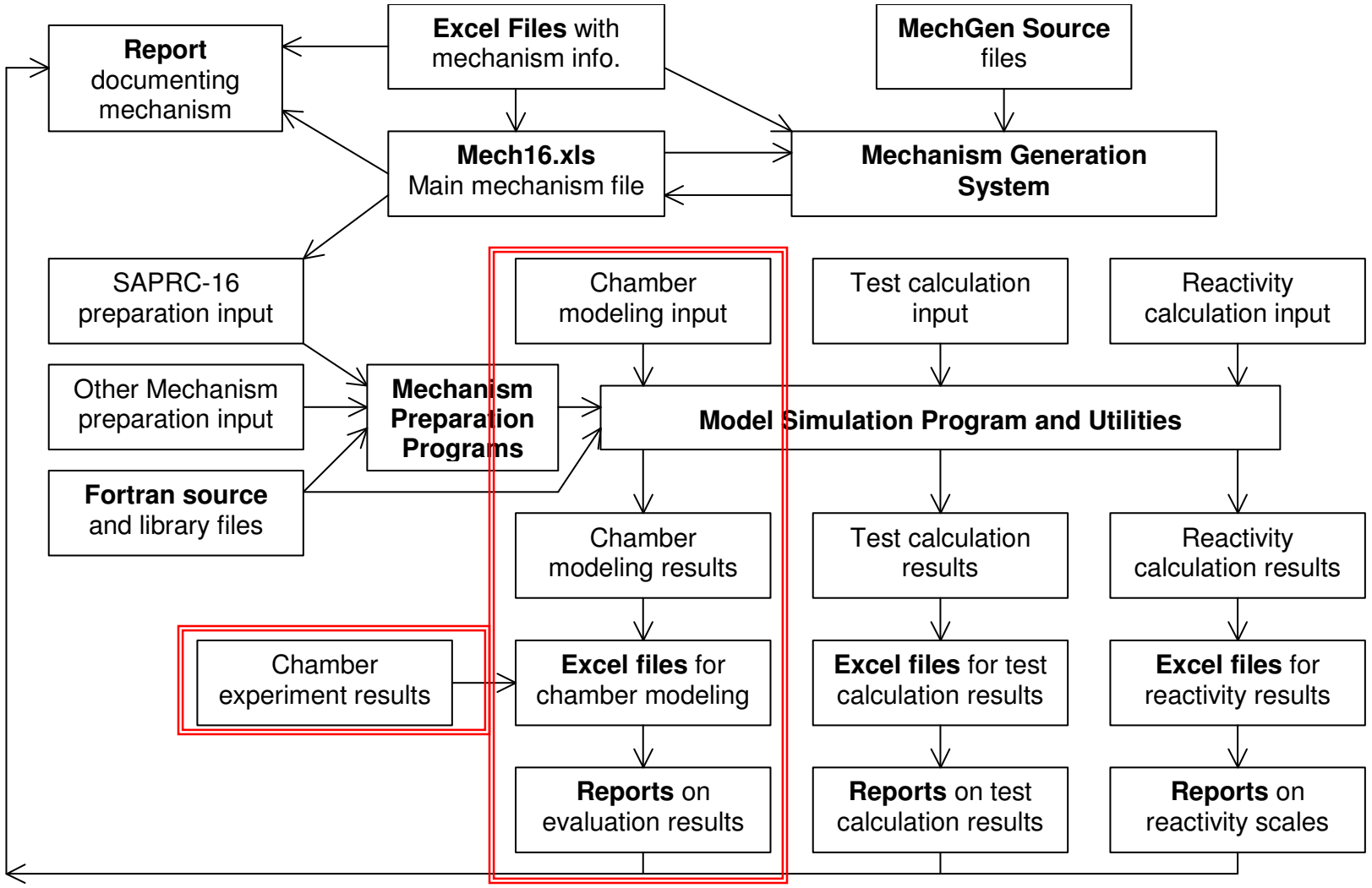


	CmdPath:	N:\SAPRC\TESTCALC											
Load All		Load	SAPRC16		Load	SAPRC11		Load	SAPRC07		Load	SAPRC99	
Clear All		Clear	SAPRC16		Clear	SAPRC11		Clear	SAPRC07		Clear	SAPRC99	
Calc All		Run Calc			Run Calc			Run Calc			Run Calc		
		SAPRC16			SAPRC11 vs SAPRC16			SAPRC07 vs SAPRC16			SAPRC99 vs SAPRC16		
Chan	Run	Max	Final	Avg	Max	Avg	Fit	Max	Avg	Fit	Max	Avg	Fit
O3	TSTROGA	1.75e-1	1.75e-1	1.11e-1	15%	9%	9%	1%	1%	1%	-1%	5%	5%
O3	TSTROGB	3.66e-1								4%	2%	2%	3%
O3	TSTROGC	[illegible]								7%	3%	7%	7%
O3	TSTROGD	1.11e-1								2%	4%	9%	9%
O3	TSTROGE	1.14e-1								2%	2%	6%	6%
PANs	TSTROGA	7.06e-3	5.57e-3	4.51e-3	2%	6%	8%	9%	11%	10%	20%	20%	20%
PANs	TSTROGB	2.34e-2	2.26e-2	1.47e-2	-36%	-28%	31%	13%	6%	10%	26%	16%	19%
PANs	T[illegible]					58%	82%	7%	0%	9%	18%	17%	16%
PANs	T[illegible]					8%	8%	9%	11%	10%	25%	29%	27%
PANs	T[illegible]					8%	9%	12%	14%	13%	14%	28%	26%
HO2H	T[illegible]					49%	65%	1%	-2%	2%	-28%	-27%	31%
HO2H	TSTROGB	6.10e-3	6.10e-3	2.61e-3	-92%	-89%	165%	-2%	-18%	19%	-5%	-17%	20%

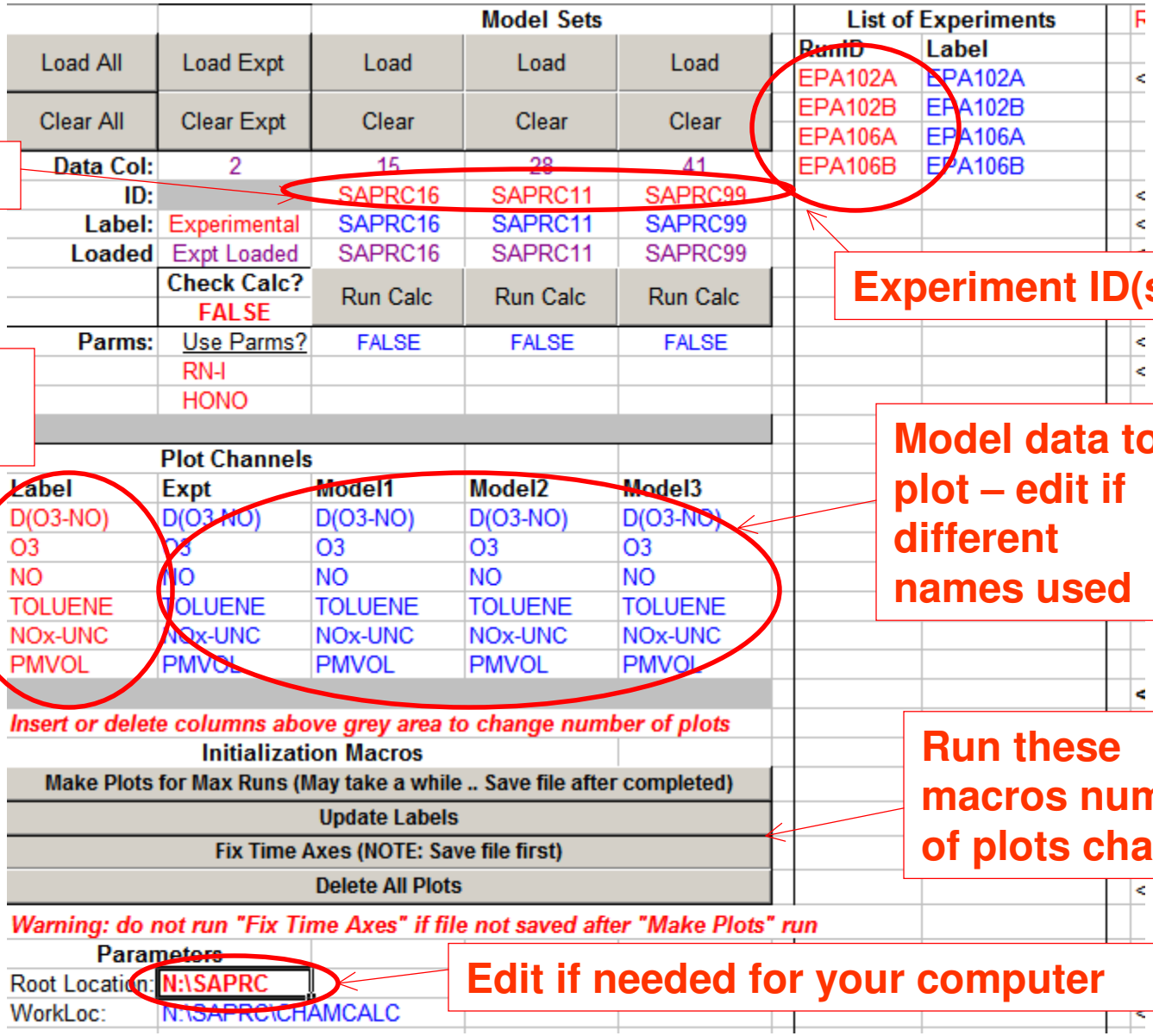
Plots are shown on a separate “Plots” sheet

TestMday.XLS is similar

Files for Evaluations Against Chamber Data



Portions of RunsFit.xls



		Model Sets		
Load All	Load Expt	Load	Load	Load
Clear All	Clear Expt	Clear	Clear	Clear
Data Col:	2	15	28	41
ID:		SAPRC16	SAPRC11	SAPRC99
Label:	Experimental	SAPRC16	SAPRC11	SAPRC99
Loaded	Expt Loaded	SAPRC16	SAPRC11	SAPRC99
	Check Calc? FALSE	Run Calc	Run Calc	Run Calc
Parms:	Use Parms?	FALSE	FALSE	FALSE
	RN-I			
	HONO			

List of Experiments	
RunID	Label
EPA102A	EPA102A
EPA102B	EPA102B
EPA106A	EPA106A
EPA106B	EPA106B

Plot Channels				
Label	Expt	Model1	Model2	Model3
D(O3-NO)	D(O3-NO)	D(O3-NO)	D(O3-NO)	D(O3-NO)
O3	O3	O3	O3	O3
NO	NO	NO	NO	NO
TOLUENE	TOLUENE	TOLUENE	TOLUENE	TOLUENE
NOx-UNC	NOx-UNC	NOx-UNC	NOx-UNC	NOx-UNC
PMVOL	PMVOL	PMVOL	PMVOL	PMVOL

Insert or delete columns above grey area to change number of plots

Initialization Macros

Make Plots for Max Runs (May take a while .. Save file after completed)

Update Labels

Fix Time Axes (NOTE: Save file first)

Delete All Plots

Warning: do not run "Fix Time Axes" if file not saved after "Make Plots" run

Parameters	
Root Location:	N:\SAPRC
WorkLoc:	N:\SAPRC\CHAMCALC

Model IDs

Experiment ID(s)

Experimental Data to plot

Model data to plot – edit if different names used

Run these macros numbers of plots change

Edit if needed for your computer

Excel Files for Full Chamber Evaluations

Note: These have not yet been configured yet for use on other computers.

File name	Contents
ModelFIt.xls	• Loads data to evaluate fits to rates of change of $\Delta([O_3]-[NO])$ and maximum O_3. • Up to three mechanisms can be compared • These data are used in the linked spreadsheets below. • Computes fit errors errors for all runs and average errors and biases for groups of runs.
FitSumPlts.xls	Shows bar plots of average errors and biases for the various groups of runs
SelFitPlts.xls	Shows experimental and calculated Δ([O3]-[NO]) for all single VOC - NO_x runs with a VOC selected by user
DistPlots.xls	Shows distributions of model errors for the groups of runs
RctRuns.xls	Shows ability of the models to simulate incremental reactivities relative to $\Delta([O_3]-[NO])$ for all reactivity runs.

Discussion and Recommendations

- CARB staff need to decide how it wants to use the SAPRC system and what it wants to learn.
- This system may be useful for researchers interested in taking over SAPRC development, though they will likely want to do it differently.
  - Presently no academic researchers are being trained, though there is interest by some graduate students at UCR.
- Currently, mechanism development funding is insufficient to support researchers doing this full time. This was not true in the past.
  - Attempts to use funds from projects to update SAPRC to identify and train new mechanism developers have been unsuccessful.
  - CARB needs to consider how to incentivize and support young researchers to continue this work. If not done within a few years, knowledge and capabilities used to develop SAPRC will be lost.
- Funds are needed make the Mechanism Generation System sustainable into the future, even if the documentation is completed.
  - Probably needs to be reprogrammed for a modern platform.
  - This capability will be lost of no one else learns how to maintain it.