SAPRC Gas-Phase Atmospheric Chemical Mechanisms

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Overview

- General discussion of mechanism development and evaluation
- Overview of SAPRC mechanisms
- SAPRC mechanism generation system
- Updates for SAPRC-18
- Future of SAPRC mechanisms

Gas-Phase Atmospheric Chemical Mechanisms

- Used to represent gas-phase reactions in air quality models to predict formation of secondary pollutants from emissions.
- Such models needed for the development of efficient control strategies to reduce O_3, and other secondary pollutants
  - Current gas-phase mechanisms were developed and tested primarily for predicting ozone and other oxidants.
  - Representing gas-phase processes leading to particle formation and air toxics is now also a priority.
- Reactions of hundreds of emitted compounds and many thousands of intermediates and products need to be represented.
  - Condensation necessary for practical applications.
  - Mechanisms differ in condensation levels and approach
- Mechanisms have many uncertainties, assumptions and estimates. Predictions need to be tested using observations.

Mechanism Development Objectives

- **Predictive capability**
  - First priority for mechanisms for regulatory models.
  - Requires evaluation of predictions against measurement data representing environments to be modeled.
- **Consistency with accepted laboratory data and theories**
  - Necessary for scientific credibility.
  - First priority for research mechanisms.
  - Reduces chance of compensating errors .
  - *Sometimes consistency with accepted data appears to be in conflict with predictive capability.*
- **Appropriate size for the modeling application**
  - Too much condensation limits utility and accuracy.
  - Too much detail wastes resources and may give illusion of accuracy that does not exist.

Alternative Mechanism Development Approaches for Scientific Acceptability

All Approaches

- Assemble and evaluate available relevant data and theories.

"Bottom Up" Approach

- Systematically add and evaluate mechanisms for representative compounds in order of dependence and complexity.
- Derive a surrogate species or lumped mechanisms based on those of the representative compounds.

"Top Down" Approach

- Develop protocols to estimate uncertain reactions and use them to derive a "master mechanism" for most relevant compounds.
- Evaluate portions of the master mechanism; revise if needed,
- Systematically derive reduced versions for modeling.

The alternative approaches will be discussed tomorrow

Evaluating Predictive Capability

- Conditions used to derive the evaluation data must be less uncertain than the mechanism being evaluated.
- Environmental chamber data are widely used because of much lower uncertainty in conditions than ambient data.
  - Experiments with varying complexity allow for a systematic evaluation approach.
  - However, the advocated “hierarchical” evaluation approach cannot really be fully implemented in practice:
    - Many simple chemical systems (e.g., alkane-NO_x) are so sensitive to chamber effects to be useless for evaluation.
    - Other simple systems (e.g., aldehyde-NO_x) have very different sensitivities to uncertainties than ambient air.
    - Incremental reactivity experiments better for such cases.
- Ambient measurements are valuable for evaluating completed mechanism, but not as much for mechanism development.

What Is Adjusted to Improve O_3 Predictions in Environmental Chamber Experiments?

- **Mechanism adjustment is not a "curve fitting" exercise.** Mechanisms not really "derived" from chamber data.
- Usually the adjustment is made to improve fits to *rates* of NO oxidation and O_3 formation. Usual adjustments:
  - $RONO_2$ yield from RO_2 + NO (VOCs with no radical sources)
  - Photoreactive product yields or k_{phot}'s (aromatics)
  - Radical yields in O_3, O^3P reactions (alkenes)
- Modeling several types of experiments is needed if more than one parameter is to be adjusted.
- If reasonable parameter adjustment does not fit data, it means the mechanism has missing or incorrect reactions.

There have been (and are) cases where predictive capability and accepted data and theories appear to be in conflict.

Examples where Predictive Capability and Accepted Data and Theories Conflict

Historical example (subsequently resolved)

- The need for a chamber radical source to model chamber experiments had no scientific credibility when first proposed. (Subsequently found to be due to HONO offgasing.)

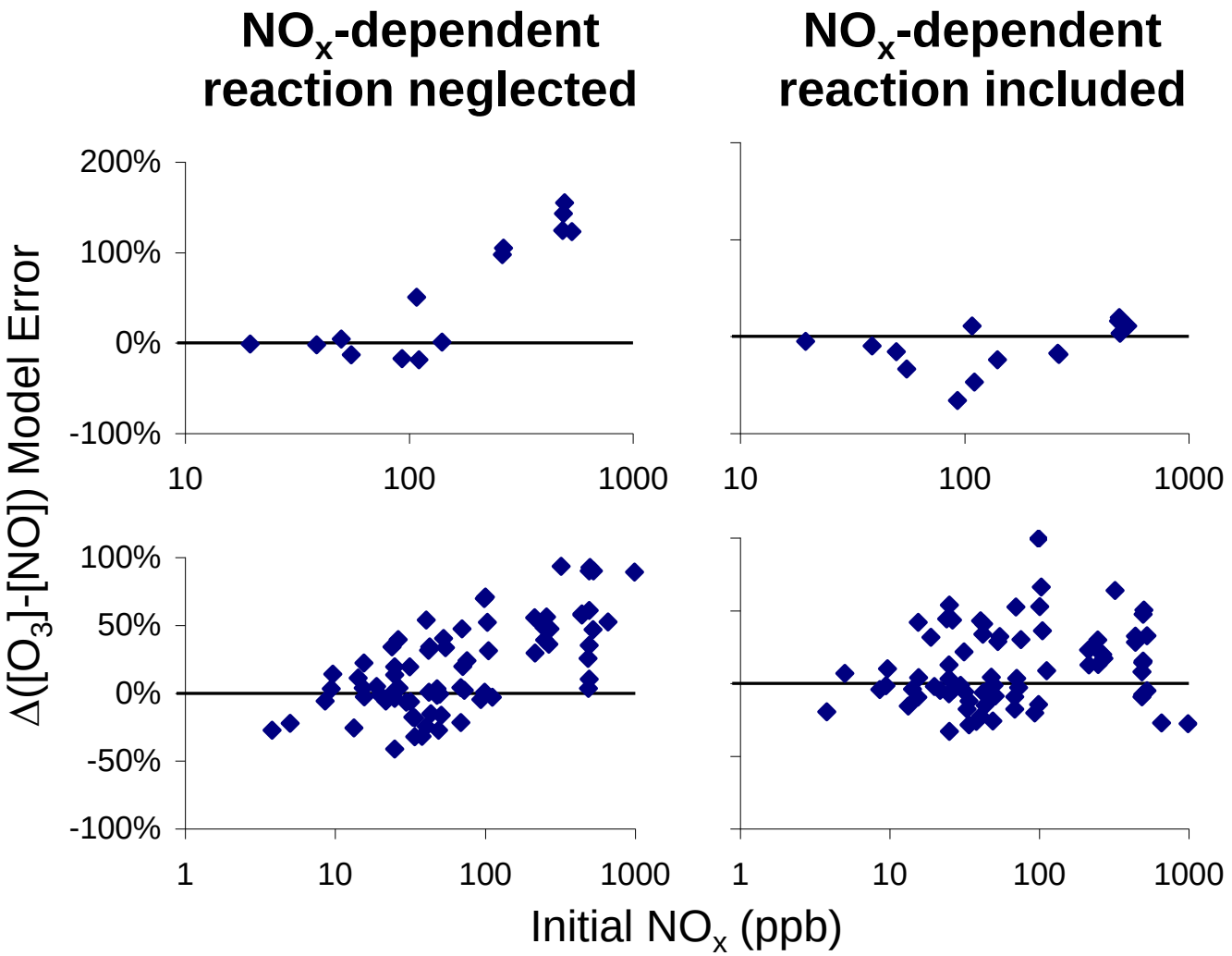
Current examples (still need to be resolved)

- Accepted aromatics mechanisms underpredict OH and under-predict NO_2 levels where OH-adduct + NO_2 reduces reactivity:

Compound(s)	Fits Chamber Data	Based on Accepted Data
Benzene	~ 10 ppb NO_2	~ 1000 ppb NO_2
Toluene	~ 200 ppb NO_2	~ 3000 ppb NO_2
Most others	(Reaction not needed)	Higher NO_2

- Accepted radical yields in O_3 + 1-alkene reactions overpredict rates of reaction in 1-alkene - NO_x chamber experiments.

Plots of Δ([O_3]-[NO]) Model Errors vs. NO_x for Benzene and Toluene Chamber Experiments



SAPRC-11 results shown, but SAPRC-18 similar.

SAPRC Mechanisms

- The SAPRC* mechanisms provide examples of chemically consistent mechanisms with varying levels of chemical detail.
- SAPRC mechanism development began in the early 1980's and is continuing today.
- SAPRC-07 is now widely used. Later versions are SAPRC-11 (updated aromatics) and SAPRC-18 (complete update).
- Currently used for research and regulatory modeling in California and the U.S.
  - More detailed versions used for ozone reactivity scales
  - More condensed versions used for regional modeling.
- The earliest SAPRC mechanisms were developed primarily using a "bottom up" approach, but the more recent versions increasingly employ the "top down" method.

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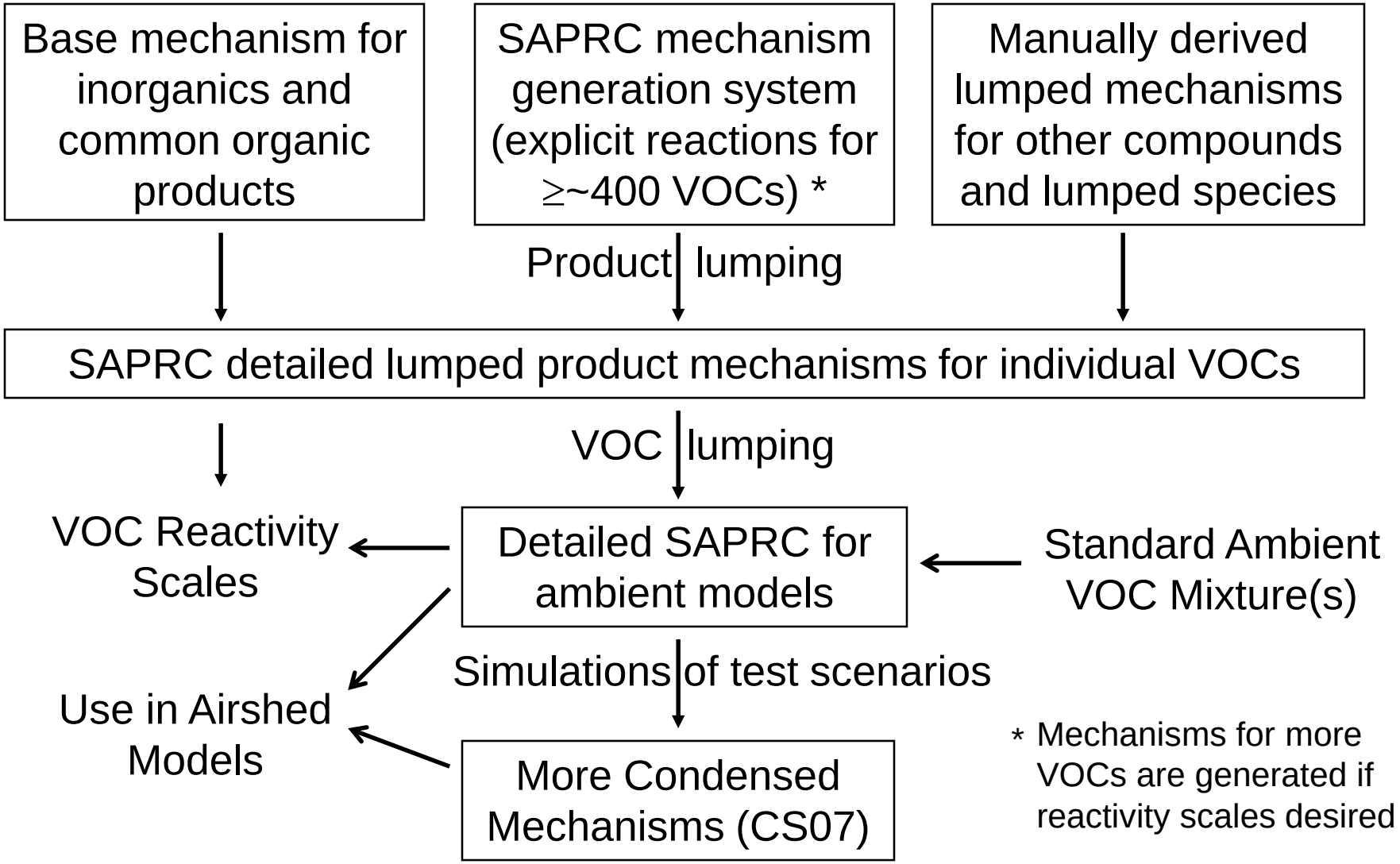
* SAPRC originally stood for (California) Statewide Air Pollution Research Center, which no longer exists.

Relationships Between Components of the Current SAPRC Mechanisms



SAPRC Mechanism Generation System

General Capabilities

- Generates near-explicit mechanisms for most VOCs of interest.
- Uses measured rate constants and branching where available, various estimation methods otherwise.
- Optionally applies “lumping rules” to mechanisms for output.

Mechanism Coverage

- Full capability for hydrocarbons, compounds with -O-, -OH, -CO-, -CHO, and $-ONO_2$ groups, and simple amines.
- Partial capability or less reliable for polycyclic compounds, multiple double bonds, and halogenated compounds.
- Generates reactions of stable compounds with: OH, O_3, NO_3, $h\nu$, and Cl, and subsequent reactions of intermediates formed.
- Not usable for oxygenated or polycyclic aromatics.

SAPRC Mechanism Generation System
(continued)

Other Capabilities

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

Simplifications

- Reaction pathways <1% for single steps are ignored.
- Reactions of stable products formed are not automatically generated. These can be generated separately when needed.

Limitations (partial)

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

SAPRC Mechanism Generation System
(continued)

Capabilities used for SAPRC integration

- Provides means for easily processing many reactants at once.
- Derives mechanisms for mixtures from generated mechanisms of the components, given the mole fractions.
- Applies the reductions used in detailed SAPRC-18.

Availability and Documentation

- Available online at http://mechgen.cert.ucr.
- Documentation at http://www.cert.ucr.edu/~carter/SAPRC
- Documentation of estimation methods not yet complete, but descriptions can be obtained using the online version.

Differences Between the SAPRC System and Gecko-A

Gecko-A Mechanism Generation System

- Described by Aumont et al (2005) (http://geckoa.lisa.u-pec.fr)
- Generates complete mechanisms for selected organics, including reactions of all generations of non-negligible products.
- Allows for simulations using very large generated mechanisms.
- Used extensively in published work on chemical complexity.
- Project is now underway to integrate Gecko-A with MCM.

SAPRC Mechanism Generation System

- Not yet described in the peer-reviewed literature.
- Only generates 1st generation products, one organic at a time.
- Currently no simulation capability with generated mechanisms.
- Has been increasingly used as a tool for developing or updating SAPRC since SAPRC-07

Discussion of Research Needs for Mechanism Estimation Systems

- Estimation of reactions of hundreds of VOCs and thousands of products and radicals are needed for a comprehensive system.
- Many types of reactions need to be considered, including some that have not yet been imagined.
- Quantum calculations are providing useful input data for estimations, but are needed for a wider range of species.
- Quantum calculations can also fill gaps in thermochemical group to aid estimation methods using heats of reactions.
- Comprehensive data compilations, including useful quantum calculation results, needed for estimation development.
- A knowledge of mechanism estimation needs can provide input for priority experimental and quantum calculation studies.

The author is participating in a SAR evaluation panel to evaluate structure-reactivity and other estimation methods.

SAPRC Update Project

Objectives

- Update SAPRC-11 to current literature and recommendations, and include new types of reactions based on recent research.
- Continue using the “top down” development approach, using mechanism generation with updated estimates where possible.
- Improve linkages to SOA models and representation of NO_x sources and sinks.
- Useable in 3D and box models as a **reference mechanism** (minimal reduction needed for usability in 3D models).

Following is beyond the scope of the initial update project:

- Developing more condensed mechanisms (separate project)
- Including halogen chemistry
- Updating MIR and other reactivity scales

Summary of Major Changes for SAPRC-18

- Base mechanism updated to current literature as of 2018.
- Made major updates to methods for estimating VOC reactions:
  - New types of reactions added (e.g., peroxy H-shifts, others)
  - Increased utilization of mechanism generation to derive explicit mechanisms for single compounds or mixtures.
- Increased numbers of explicit VOCs and lumped VOC groups
- Increased number organic product model species to improve:
  - Representing NO_x sinks and reservoirs.
  - Representing more photoreactive bifunctional compounds
  - Integration with mechanistic-based SOA models.
- More detailed representation of peroxy reactions used to allow for auto-oxidations and improve model for low NO_x conditions.
  - Requires an increase number of reactions and many more peroxy radical species in the mechanism than SAPRC-11.

Changes in Organic Product Model Species
(SAPRC-11 → SAPRC-16)

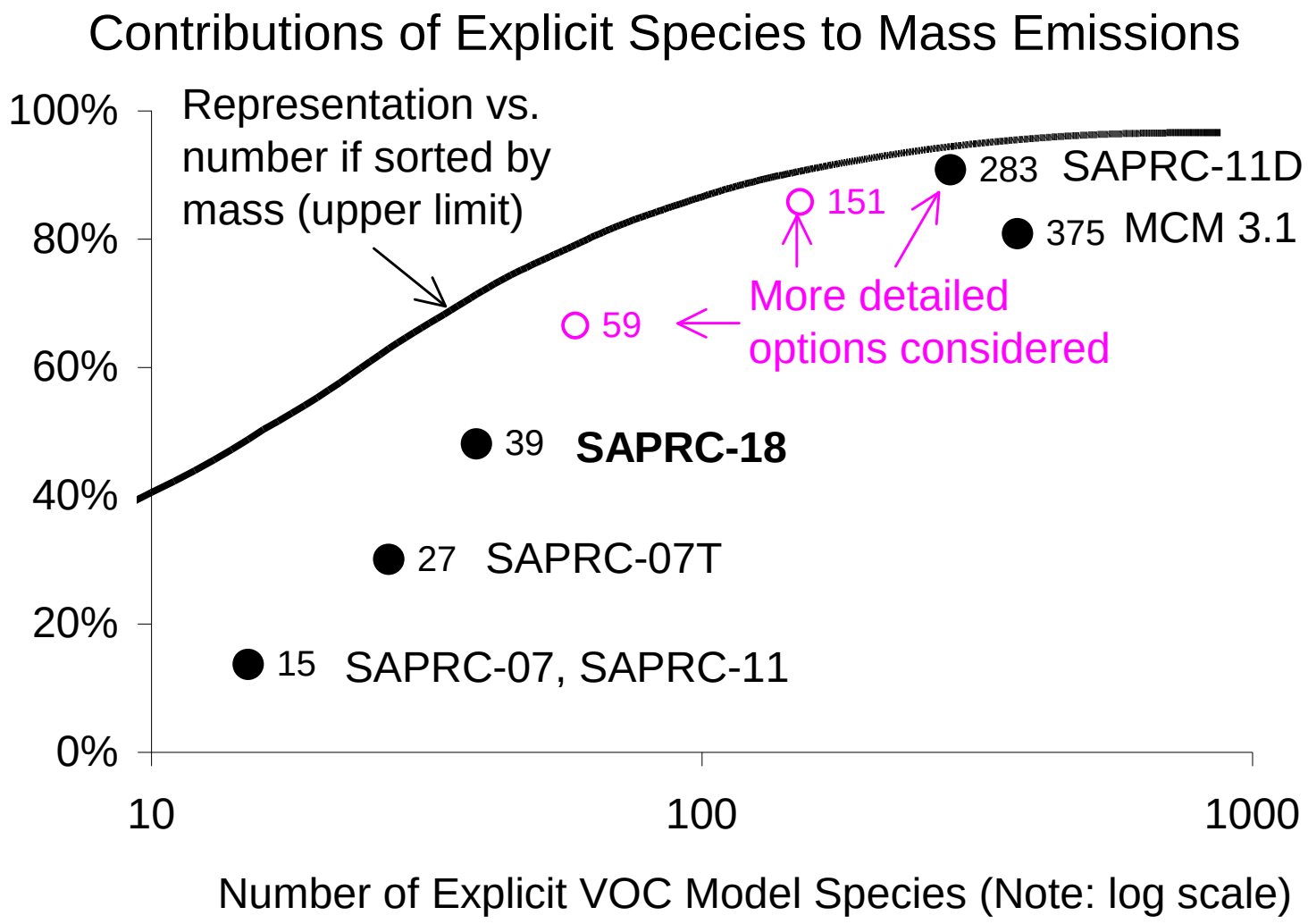
Type of Species	# Species	Compounds represented by new species
Organic nitrates	1 → 7	Slower vs fast reacting; Unsaturated; Hydroxy; Carbonyl; Aromatic; Peroxy-containing (from aromatics); Non-volatile
Hydroperoxides	4 → 7	Unsaturated; Carbonyl containing; Unsaturated carbonyl containing
PANs	4 → 8	PPN, HO-PAN, and acrolein's PAN explicit; Lumped PAN with 2nd nitrate group
Aromatic ring open products	5 → 6	2-Butene-1,4-dial explicit; Meanings of some other model species changed
Other Lumped aldehydes	10 → 12	Propionaldehyde explicit; α-Unsaturated aldehydes; Other unsaturated aldehydes
Other lumped oxygenates	5 → 7	MVK explicit; α-Unsaturated ketones; Other unsaturated ketones
Other new	0 → 3	IEPOX compounds; nitramines; non-volatiles
Total	**29 → 50**	

Changes in Emitted VOC Model Species
(SAPRC-18 vs SAPRC-11)

Type of Species	# Species	Added or changed species
Explicit hydrocarbons	5 → 21	Ethane; Propane; n-Butane; Propene; 1,3-Butadiene; α-pinene; β-pinene; d-Limonene; Toluene; Ethylbenzene; All 6 xylene and trimethylbenzene isomers
Other explicit	0 → 2	Ethanol; Peroxy acetic acid
Lumped Alkanes	5 → 3	ALK1 and ALK2 no longer needed
Lumped Alkenes	3 → 8	Iso alkenes; 3- and 4-substituted; Cyclic; Conjugated dialkenes; Sesquiterpenes
Lumped Aromatics	2 → 5	Low reactivity (benzene-like) aromatics; Naphthalenes and tetralins; Styrenes
New model species	0 → 6	Acetylenes; Amines; Imines; Inhibitors; Other photoreactives
Others	0* → 4	Non-hydrocarbons previously lumped with alkanes

Total **15 → 49**

Contributions of Explicitly Represented Compounds to Anthropogenic Emissions



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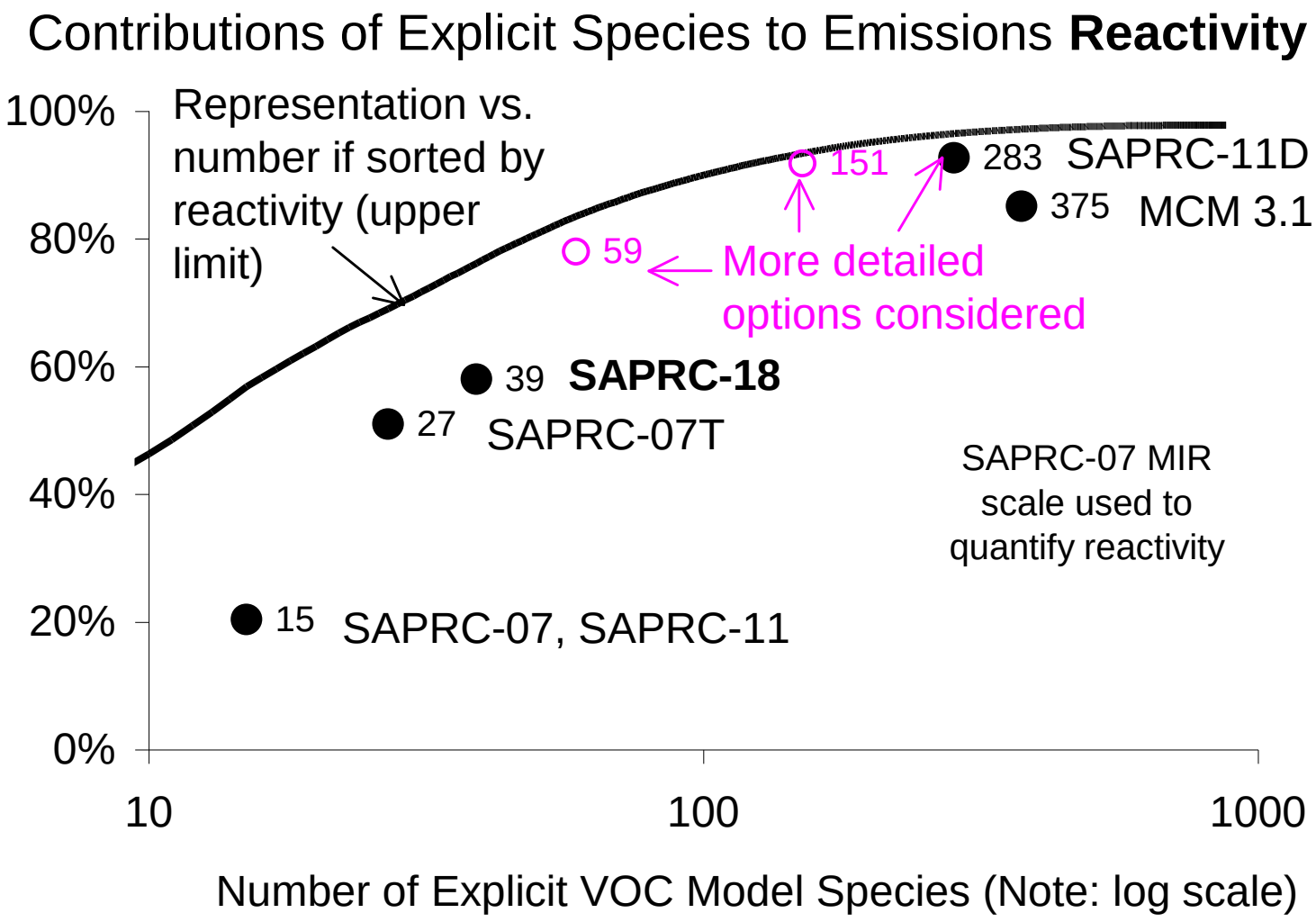
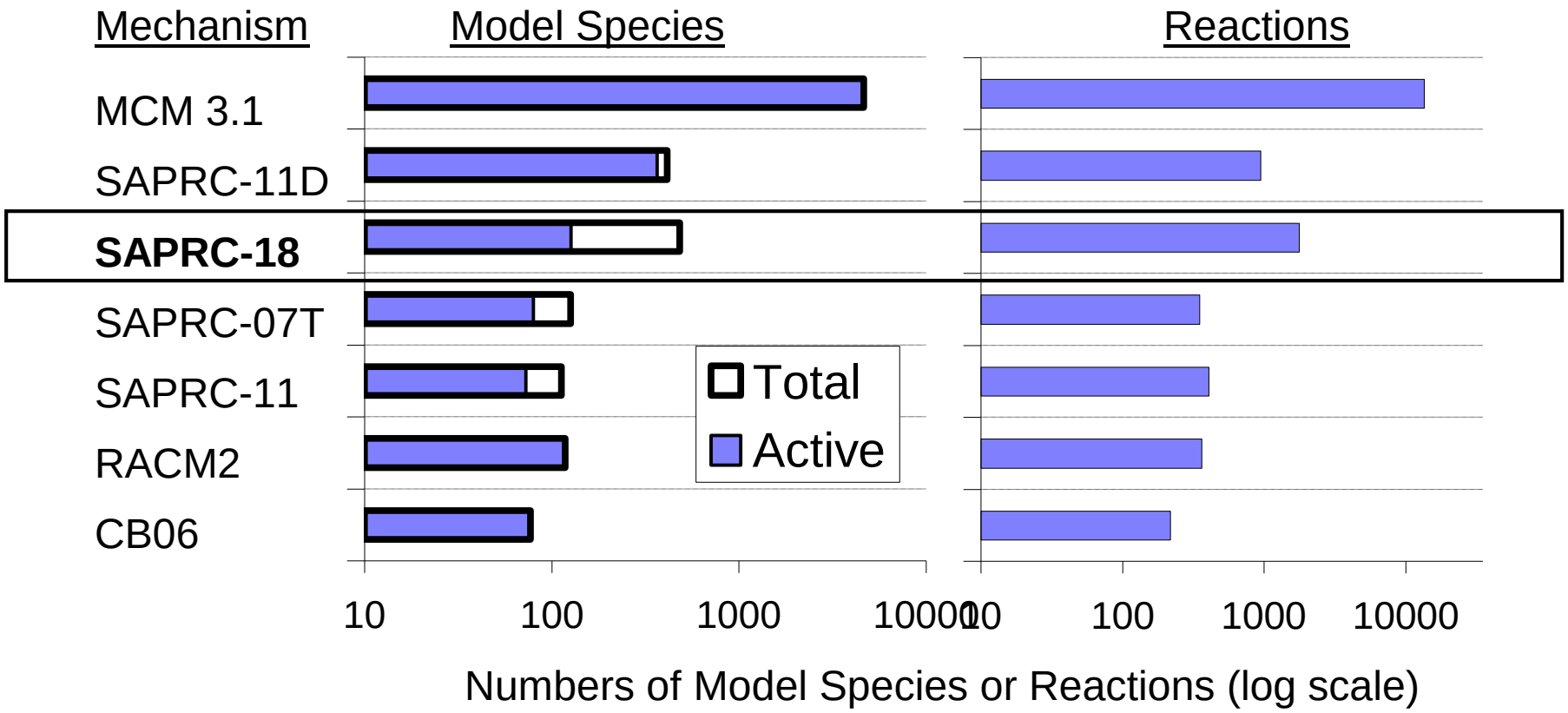


Comparison of Sizes of Mechanisms



- "Active" model species are those that cannot be eliminated using the steady state approximation. Only given for SAPRC mechanisms
- SAPRC-11D is SAPRC-11 but with the maximum reasonable number of emitted compounds represented explicitly

Future of SAPRC Mechanisms

- SAPRC mechanisms has been primarily developed by W.P.L. Carter, who is **now mostly retired**, but still committed to:
  - Completion of the documentation and peer review of SAPRC-18 and its mechanism generation system.
  - Collaborating with Kelley Barsanti at UCR and colleagues at NCAR on a new EPA project for the development of next generation detailed and reduced mechanisms.
  - Coordinating and encouraging activities of the Structure and Reactivity (SAR) evaluation panel.
- CARB and others would like the continuation of SAPRC mechanism development, but no replacement found thus far.
- Please contact me and/or the CARB if you are interested in SAPRC-like mechanism development work.
- Please contact me if you want to learn more about using any of the SAPRC mechanism development tools for your own work.

Acknowledgements

Primary Funding Sources

- NFS-RANN, U.S. EPA, USAF: Supported initial development work that led to SAPRC mechanisms.
- CARB: Primary support for SAPRC mechanism development
- Various industry groups: Mechanism development and chamber evaluation experiments for compounds of interest.

Collaborators in Mechanism Development (incomplete list)

- J. N. Pitts, Jr., Alan Lloyd, Fred Lurmann, Roger Atkinson, Dongmin Luo, Gookyoung Heo, others.

Programmatic Support and Helpful Discussions

- Marcia Dodge, Deborah Luecken, Bart Croes, Eileen McCauley, Dongmin Luo, Ajith Kaduwela, others.

Other collaborators and helpful discussions – too many to list.

SAPRC Web Sites

www.cert.ucr.edu/~carter

Main web site and links to reports, publications and other pages.

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

Documentation and files for recent SAPRC mechanisms and reactivity scales for SAPRC-07

www.cert.ucr.edu/~carter/SAPRC/18

Available documentation and files for SAPRC-18.

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

Fortran programs, files and documentation for box modeling and implementing versions of SAPRC through SAPRC-18.

mechgen.cert.ucr.edu

Web access to the SAPRC mechanism generation system

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

Emissions speciation assignments for various mechanisms

Thank You

History of the SAPRC Mechanisms

1979-1980	First papers by Carter et al. on mechanisms.
1985	Paper on mechanism generation for alkanes published.
1987	Reports to EPA, USAF and CARB on multi-VOC mechanisms that served as basis for subsequent detailed SAPRC.
1990	SAPRC-90 detailed mechanism developed and published.
1991	Condensed SAPRC-90 for airshed models developed.
1994	Paper on MIR and other reactivity scales using SAPRC-90.
1999-2000	Reports on SAPRC-99 mechanisms. Current SAPRC mechanism generation system first developed.
2008-2010	Reports and papers on SAPRC-07 detailed and condensed mechanisms. Mechanism generation system enhanced.
2011-2012	SAPRC-11 for aromatics and aromatic SOA developed.
2013-2020	Complete update to SAPRC-18. Still being evaluated.
2021+	Future of SAPRC and successor mechanisms is uncertain.