Development of Condensed SAPRC-07 Chemical Mechanisms

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Outline

- Overview of the SAPRC-07 mechanism
- Objectives
- Condensation Approaches
- Effects of Condensations on Test Scenarios
- Recommendations

SAPRC Mechanism Use and Requirements

Used in airshed models to:

- Represent the chemistry of formation of secondary pollutants (e.g., O_3) from emitted VOCs and NO_x
- Predict relative ozone reactivity scales for VOCs ($\Delta O_3 / \Delta$ VOC) for regulatory applications (e.g, MIR scale used in California)

Requirements

- Represent current state of science of atmospheric chemistry
- Give predictions consistent with chamber and laboratory results
- Appropriately represent the hundreds of types of VOCs for reactivity scale calculations
- Represent complex ambient mixtures in airshed calculations in chemically appropriate but computationally efficient manner

Major Components of SAPRC Mechanisms

Base Mechanism

- Reactions of inorganics and common organic products

Mechanisms for individual VOCs (hundreds of VOCs represented)

- Mechanism generation system used where data and estimation methods exist, estimated or simplified mechanisms used otherwise.
- Uncertain parameters adjusted to fit chamber data if needed.

Condensed mechanisms for airshed models

- Mechanisms for limited number of “lumped model species” are derived from those of the mixture of individual VOCs they represent
- These depend on the composition of the mixture taken as representative of VOC emissions from all sources

Status of SAPRC Mechanisms

The version primarily currently in use is SAPRC-99

- Represents the state of the science as of 1999
- Used to calculate the MIR reactivity scale used in some regulations.
- Many airshed models use “Fixed Parameter” SAPRC-99 with condensed model species based on a “base ROG” mixture.

An updated version, SAPRC-07, is now complete

- Represents state of the science as of 2007. Undergoing peer review
- Used to calculate updated MIR and other VOC reactivity scales
- Fixed parameter versions developed, but not yet widely implemented
  - A “toxics” version with more species being developed for the EPA
  - More condensed versions have been developed for the CARB

SAPRC-07 Condensation Project

Problem

- SAPRC-07 may be larger than necessary for some applications
- Condensation frees computer resources for other priorities.

Objectives: Develop condensed SAPRC-07 where

- Validity based directly on that of the detailed mechanism
- Gives predictions as close as possible to detailed under wide range of model conditions
- The effects of condensations on predictions are understood
- Straightforward to update when detailed mechanism updated

Mechanism Condensation Project (continued)

Approach

- Current fixed-parameter SAPRC-07 used as the starting point
  - Based on detailed SAPRC-07 and a “Base ROG” mixture used to represent ambient reactive VOCs.
- Identify possible condensations approaches that may be used
- Develop set of test calculation scenarios representing range of atmospheric conditions, and special scenarios sensitive to specific parts of the mechanism that are changed
- Examine effect of each condensation sequentially on species of interest in the test calculations.
- Compile mechanisms with sets of condensations appropriate for various applications

Condensation Approaches Examined

Alternative peroxy radical representations:

A. Use representation in SAPRC-99 (and CB4/05) (SAPRC-07A)
B. Retain SAPRC-07 peroxy representation (no condensation)

Additional Condensations (made relative to SAPRC-07A):

1. Lump low reactivity products and other minor condensations
2. Lump Higher PANs with PAN2 (but PAN still explicit)
3. Use 1-product isoprene mechanism
4. Simplify aromatics mechanisms
5. Simplify chlorine mechanism
6. Reduce number of lumped alkane species for ambient mixtures
7. Lump PAN with PAN2
8. Lump acetaldehyde with higher aldehydes

Mechanism Comparison Model Scenarios: General Mechanism Tests

- Static Scenarios (5 cases)
  - 12 hour, constant light, all reactants at start, no dilution
  - VOC, NO_x and VOC/NO_x varied. VOC is ambient mixture
  - NO_2 injected hour 6 for some high VOC/NO_x cases
- Multi-Day Scenarios (5 cases)
  - EKMA-type airshed scenarios but with 5-day continuous emissions. Diluted with clean air during day
  - NO_x levels varied but VOC levels same. VOC is ambient mix
- Reactivity Scale Scenarios (39 x 5 cases + Average Cond's)
  - Scenarios used to calculate the MIR, MOIR, EBIR and base case reactivity scales
  - "Averaged Conditions" scenario with NO_x varied.

Mechanism Comparison Model Scenarios: Special Mechanism Tests

- Specific VOC Mechanism Tests - Static Scenarios (3 x 5 cases)
  - Similar to general static mechanism tests but but VOCs replaced by isoprene, toluene (ARO1), or m-xylene (ARO2).
  - VOC, NO_x, and VOC/NO_x varied. NO_2 injected hour 6 in some high VOC/NO_x cases
- Chlorine Mechanism Tests (5 cases)
  - Similar to general static mechanism tests but with Cl_2 or $CHCl_3$ added (fast or slow Cl atom formation)
  - VOC, NO_x, and VOC/NO_x varied
  - Cl_2 added at hour 6 in one added Cl_2 case.

Alternative Representations of Peroxy Radical Reactions

- Approximate methods are required to represent the peroxy + peroxy reactions important under low NOx conditions for the mechanisms to have reasonable size.
- SAPRC-99, like CB4 and CB05, uses a “chemical operator” method that assumes the same organic products are formed regardless of how the peroxy radical reacts. (Method “A”)
- SAPRC-07 uses a new representation of peroxy radical reactions that permits use of separate hydroperoxide and organic nitrate species, depending on the reactant. (Method “B”)
  - Better suited to SOA modeling
  - Requires more species and reactions, and its efficient implementation usually requires changes to model software.

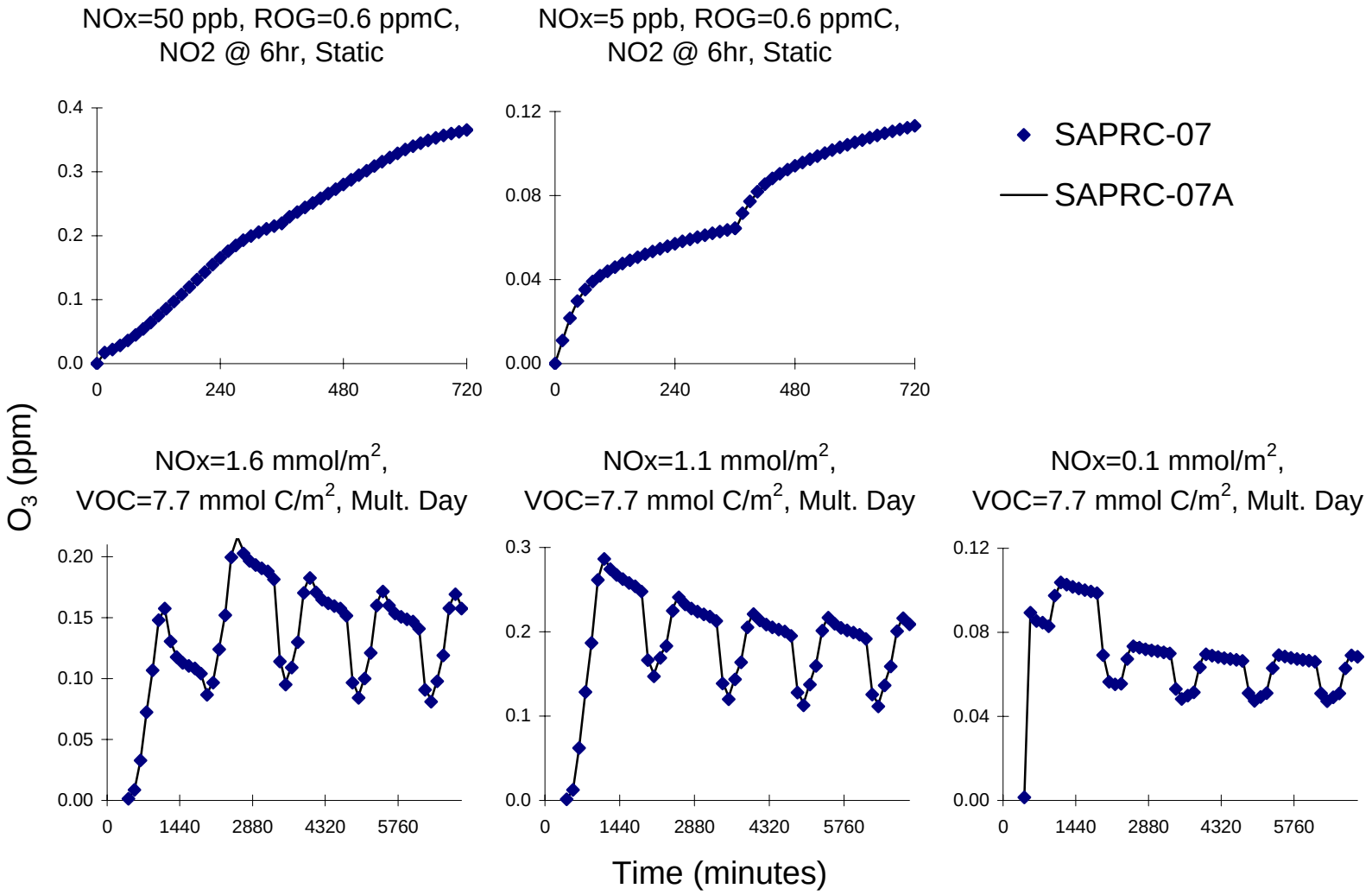
Comparison of Peroxy Representations

(Excluding nitrate formation)

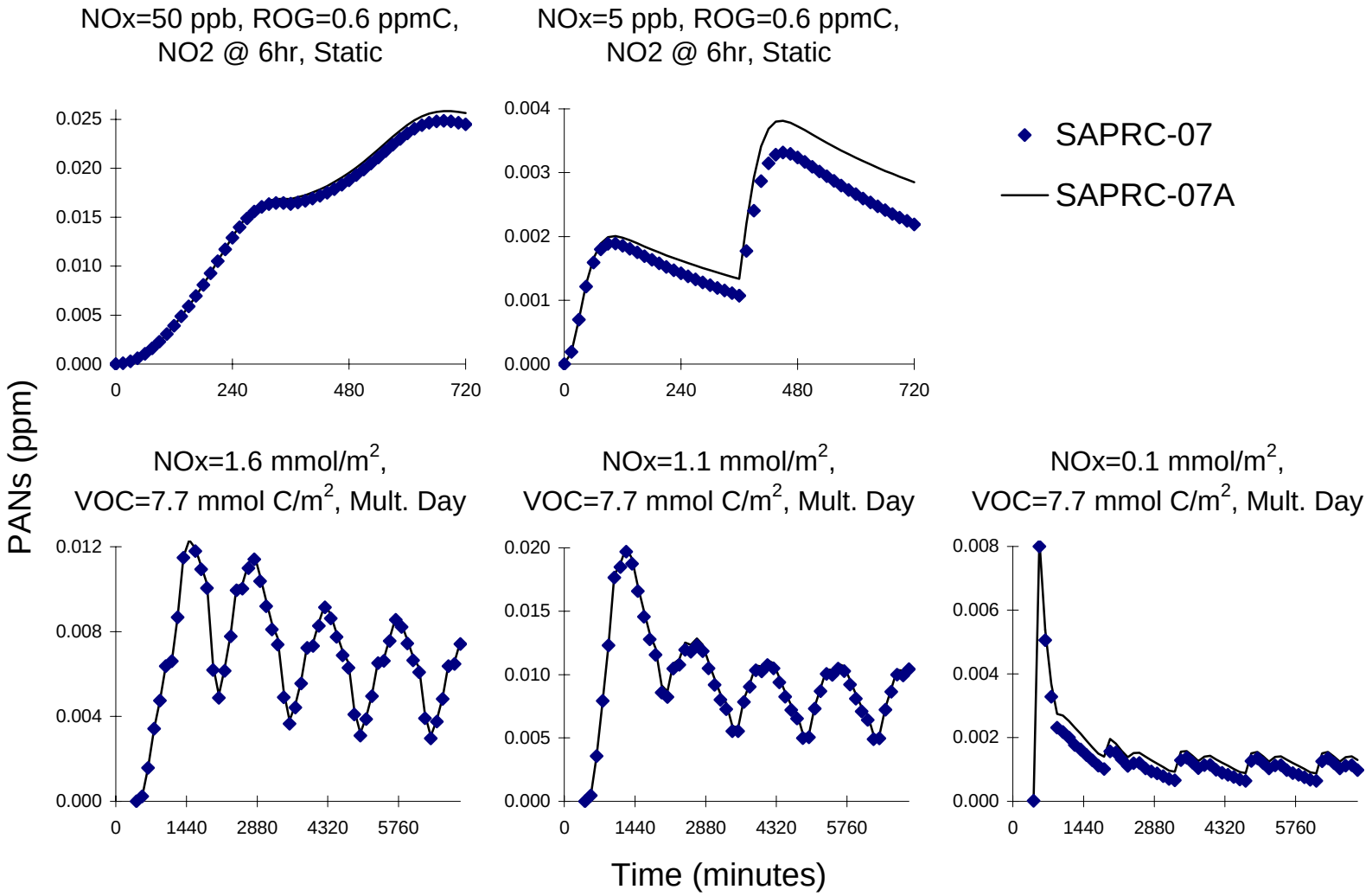
Reaction	Explicit Products	SAPRC-99 (A)	SAPRC-07 (B)
$RO_2 + NO$	Alkoxy radical products	Alkoxy radical products	Alkoxy radical products
$RO_2 + HO_2$	Hydroperoxide product	Alkoxy radical products + single lumped ROOH	Hydroperoxide product depends on RO_2
$RO_2 + RCO_3$	Disproportionation products	Alkoxy radical products	Ketone product depends on RO_2
$RO_2 + RO_2$	½ disproportionation products		Ketone product depends on RO_2
	½ Alkoxy radical products		Alkoxy radical products

Major Reaction when Ozone formation occurs

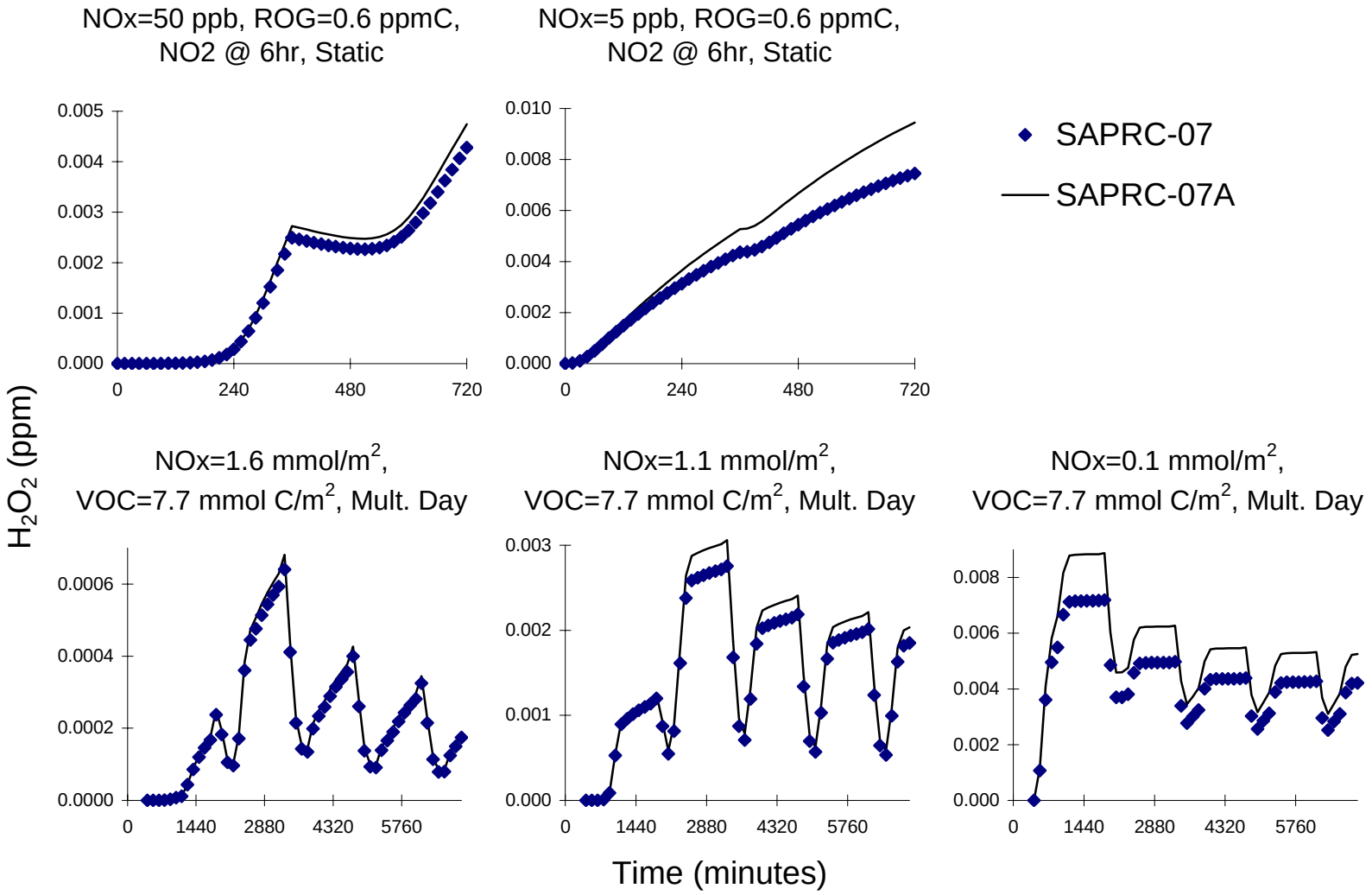
Effect of Peroxy Radical Condensation on <u>Ozone</u> in Selected Test Scenarios



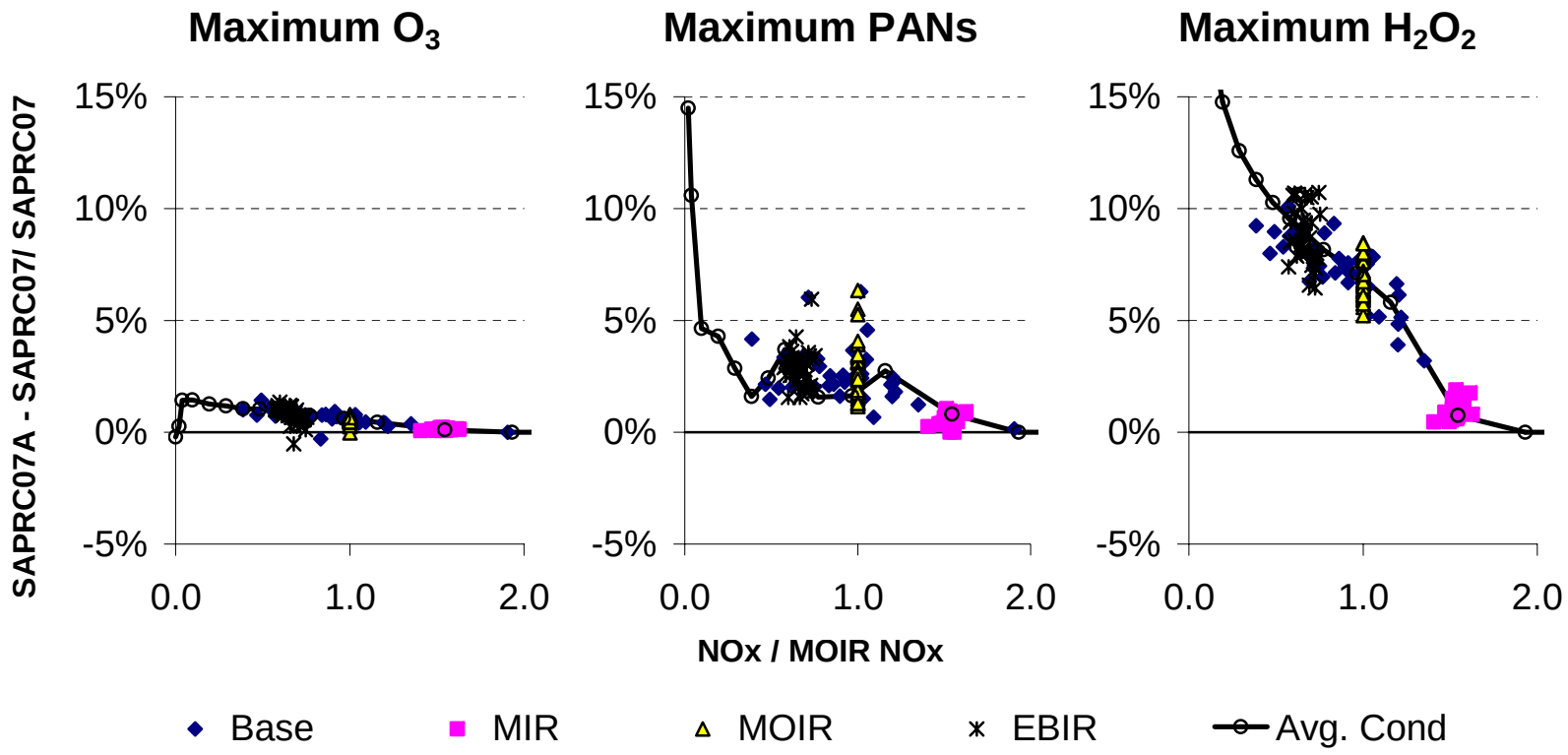
Effect of Peroxy Radical Condensation on PANs in Selected Test Scenarios



Effect of Peroxy Radical Condensation on H_2O_2 in Selected Test Scenarios



Effects of Peroxy Condensations in the Reactivity Scenarios

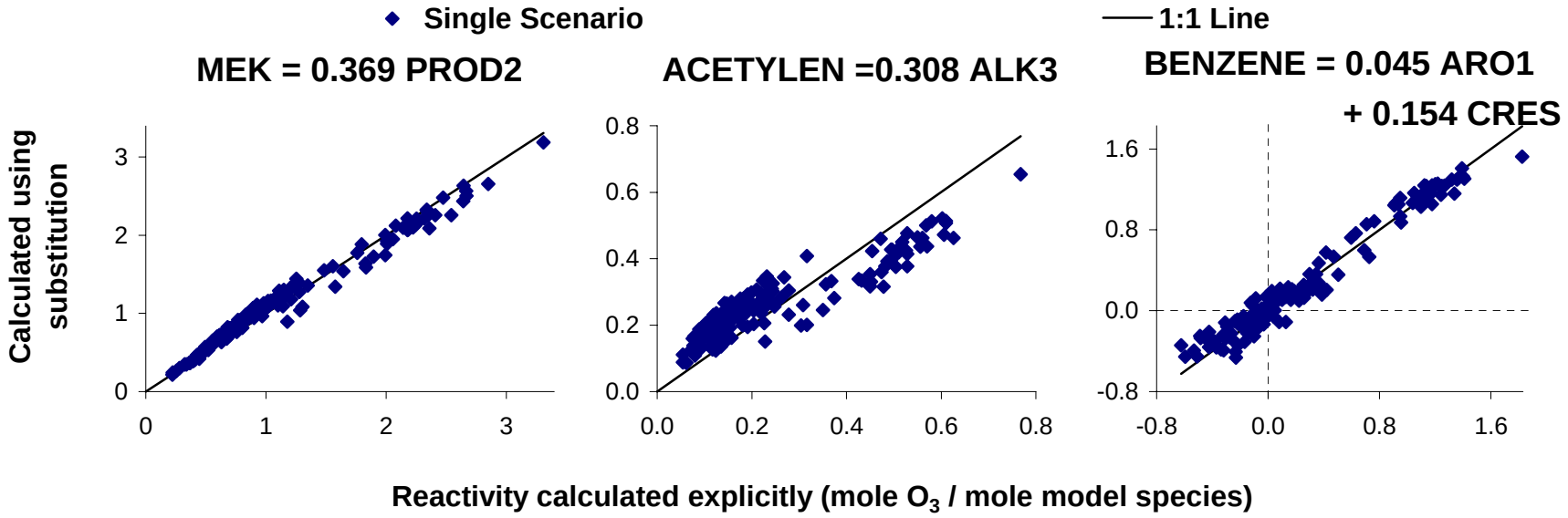


Level 1 Condensations

- Several radical species replaced by species they primarily form
  - MEO2 = RO2R + HCHO
  - TBUO = ACET + HCHO + RO2R
  - RO2CL = CL + R2O2
- Low reactivity species lumped using “reactivity weighting”
  - HCOOH = 0.048 ALK3
  - CCOOH = 0.243 ALK3 + 0.086 CCHO
  - RCOOH = 0.526 ALK3 + 0.190 CCHO
  - MEOH = 0.288 ALK3
  - MEK = 0.369 PROD2
  - ACET = 0.071 PROD2
  - METHANE = 0.003 ALK3
  - BENZENE = 0.045 ARO1 + 0.154 CRES
  - ACETYLEN = 0.308 ALK3

Reactivity Weighting

- The reactivity weighting factors were derived to match incremental reactivities in the 1-day EKMA scenarios used to calculate the MIR, MOIR, and EBIR VOC reactivity scales.
- Example plots showing performance of substitutions:

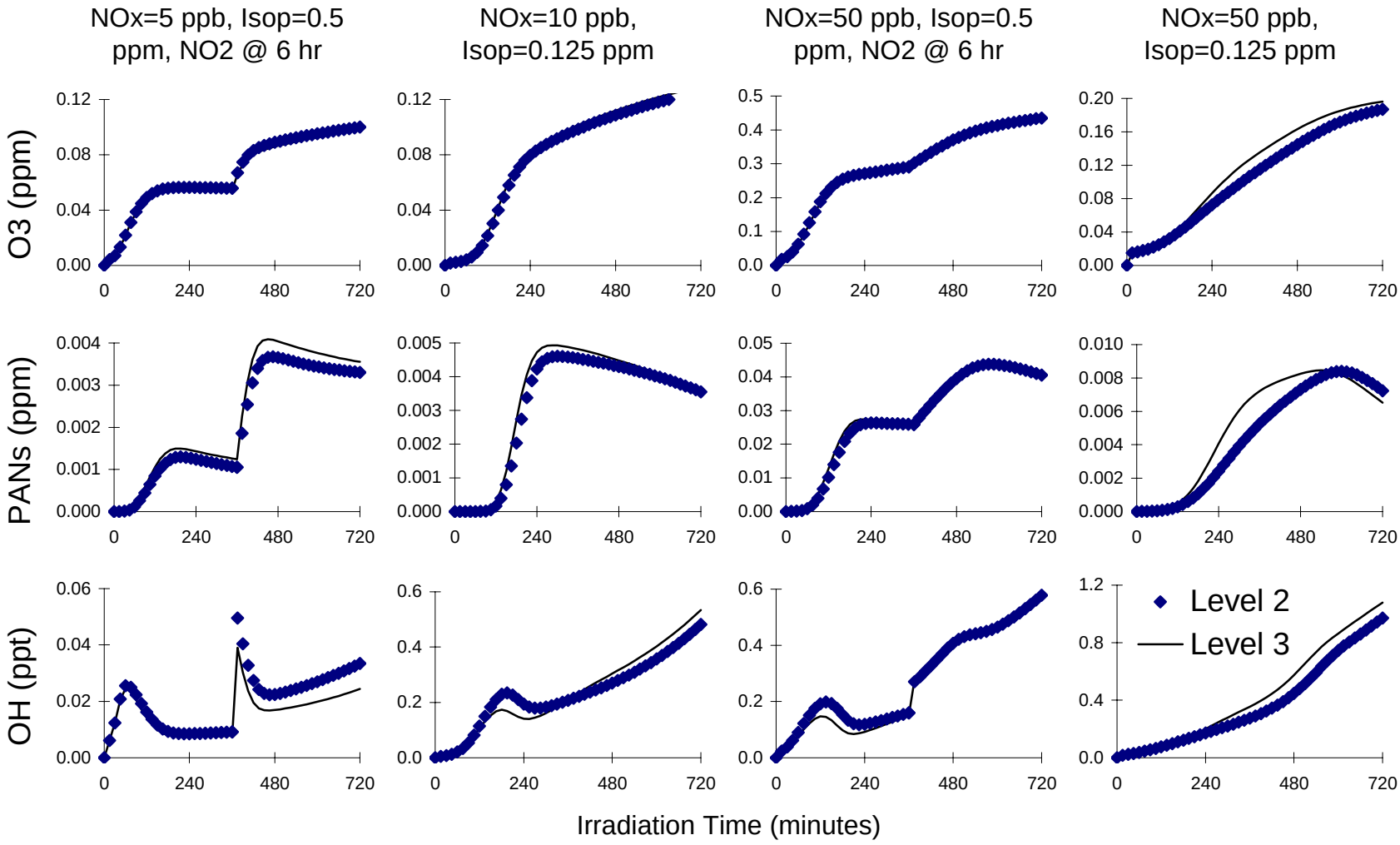


Additional Condensations

- Level 2: Higher PANs lumped
  - BZCO3 and MACO3 represented by RCO3
  - PBZN and MAPAN represented by PAN2
  - Relatively small effect on test calculations

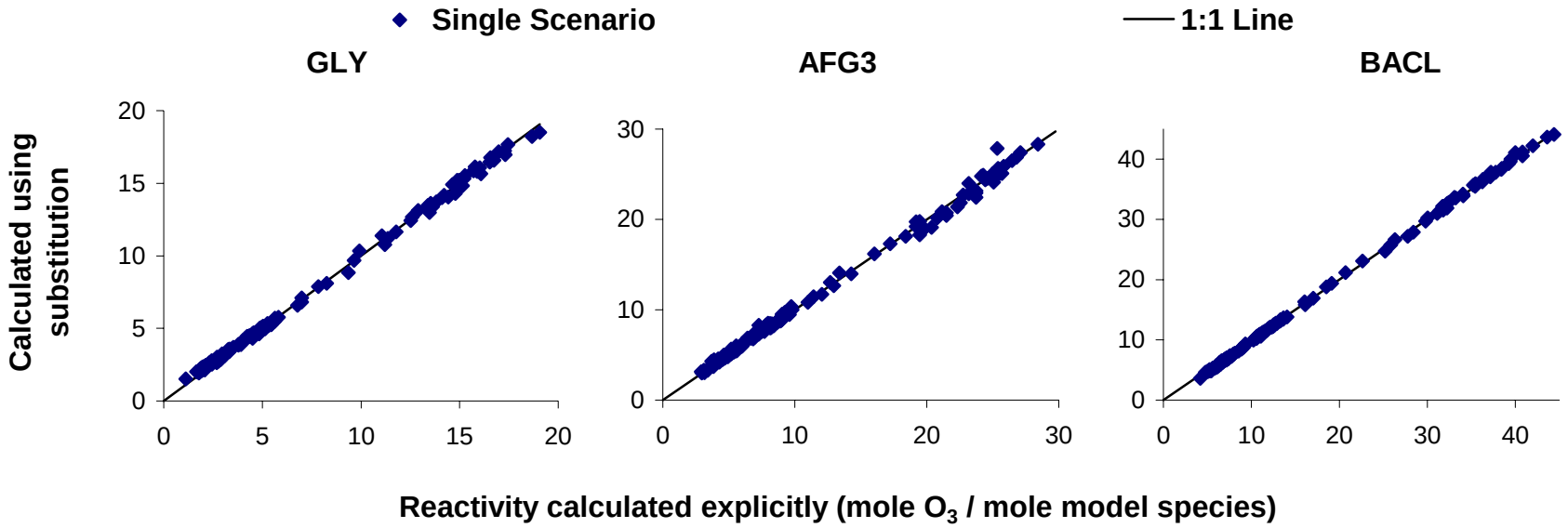
- Level 3: 1-Product Isoprene Mechanism
  - MVK and MACR represented by IPRD (Lumped C_5 product)
  - IPRD mechanism revised to incorporate MVK and MACR (weighted average parameters of IPRD, MVK, and MVK)

Effects of Isoprene Condensations on Selected Isoprene Test Calculations

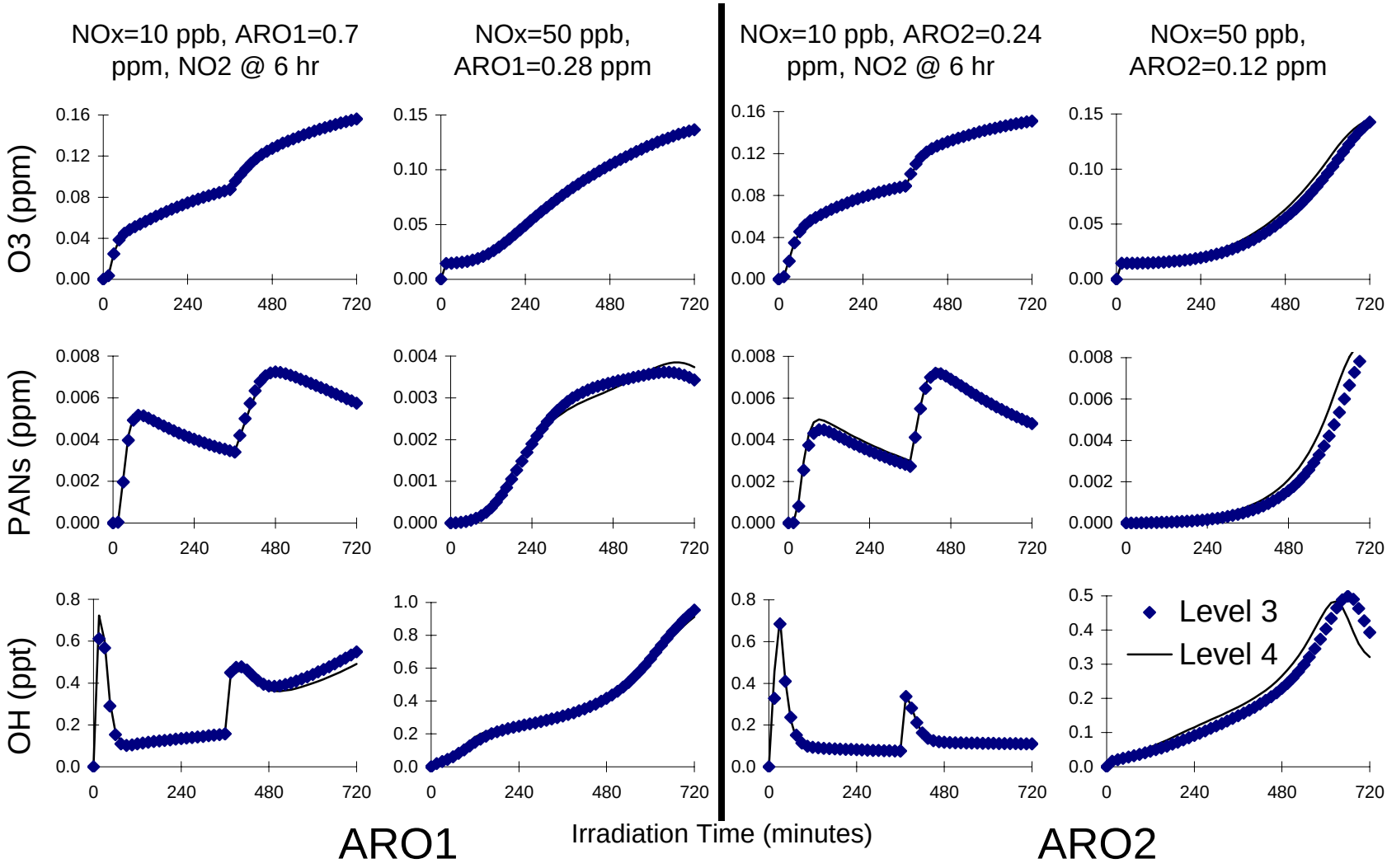


Additional Condensations (continued)

- Level 4: Aromatics mechanisms simplified
  - BALD (Benzaldehyde) removed
  - NPHE formed on NO3 + CRES replaced by 0.5 CRES
  - Several reactive products lumped using reactivity weighting
    - GLY (Glyoxal) = 0.582 MGLY + 0.016 AFG1
    - BACL (Biacetyl) = 1.455 MGLY
    - AFG3 (Non-photoreactive dicarbonyls) = 0.724 MGLY + 0.918 AFG2

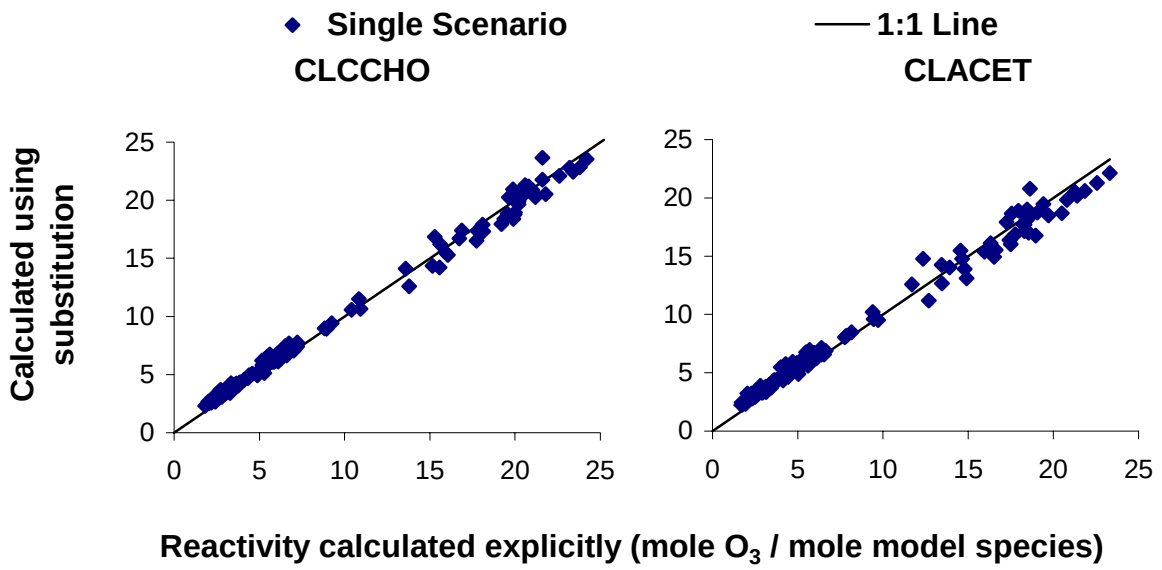


Effect of Aromatic Condensations on Selected Aromatic Test Calculations



Additional Condensations (continued)

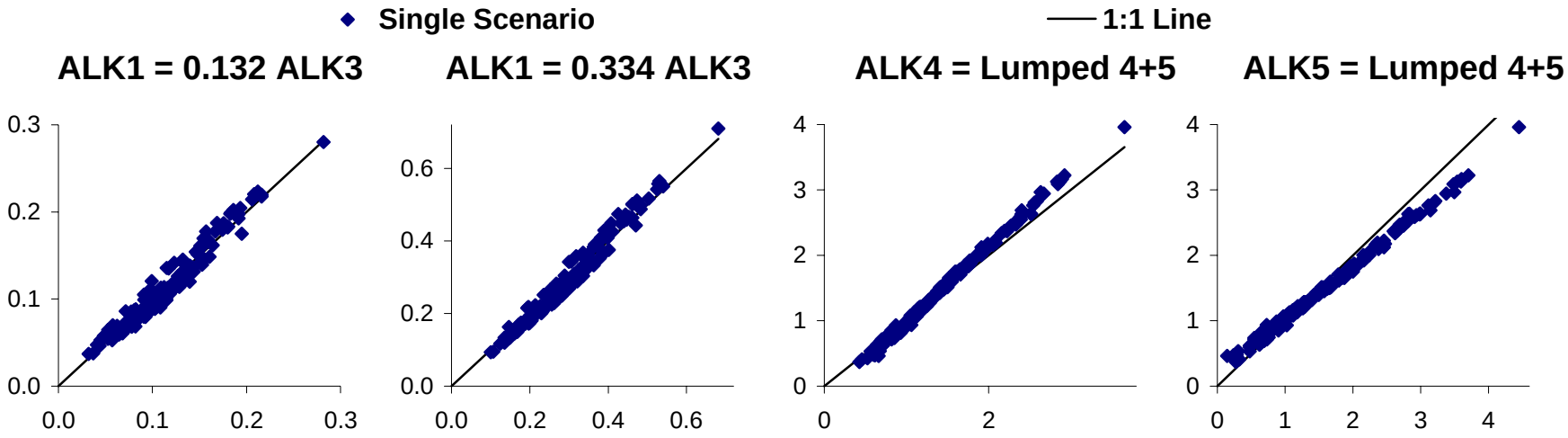
- Level 5: Chlorine Mechanism simplified
  - Formation and reactions of CLNO, CLNO2, CLONO, and HOCL removed. No significant effects on test calculations
  - Following substitutions made using reactivity weighting
    - CLCCHO (Chloroacetaldehyde) = 0.261 RCHO + 0.713 MGLY
    - CLACET (Chloroacetone) = 0.400 RCHO + 0.583 MGLY



Additional Condensations (continued)

- Level 6: Number of lumped alkane species reduced from 5 to 2
  - ALK1 represented by ALK3 using reactivity weighting ALK3 unchanged (used for for some product substitutions)
  - ALK4 and ALK5 lumped together and parameters changed to reflect mixtures of both

Effects of substitutions on ozone reactivity of alkane species:



Reactivity calculated using substitution vs. calculated explicitly (mole O_3 / mole model species)

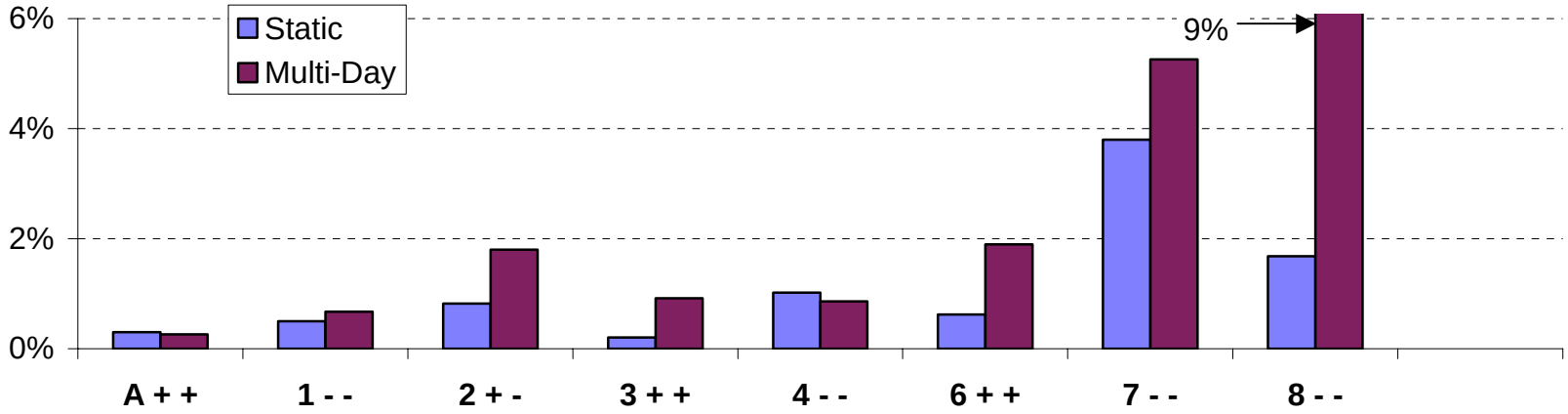
Additional Condensations Considered

- Level 7: PAN lumped with PAN2 (only one PAN species left)
  - MECO3 lumped with RCO3
  - Rate constants of PAN2 used because it caused least O_3 change in test calculations
- Level 8: RCHO lumped with CCHO
  - Rate constants of CCHO (acetaldehyde) used

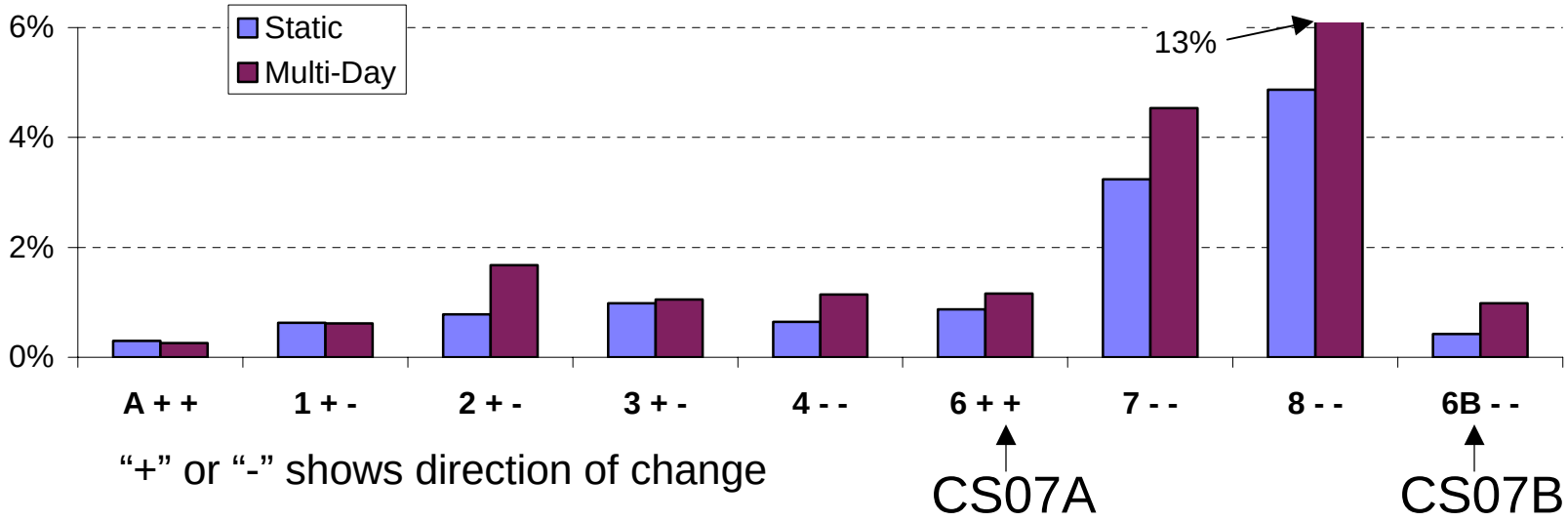
These condensations were not adopted because they caused larger changes in ozone than the others that were considered.

Ozone Changes Caused by Condensations

Average of absolute change, relative to previous condensation level

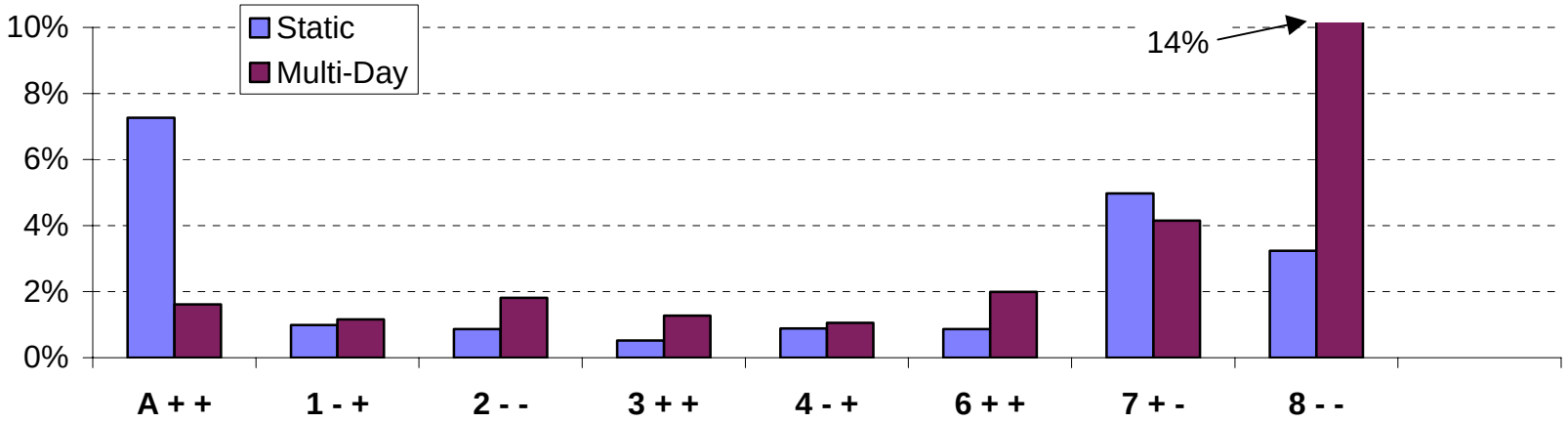


Average of absolute change, relative to uncondensed SAPRC-07

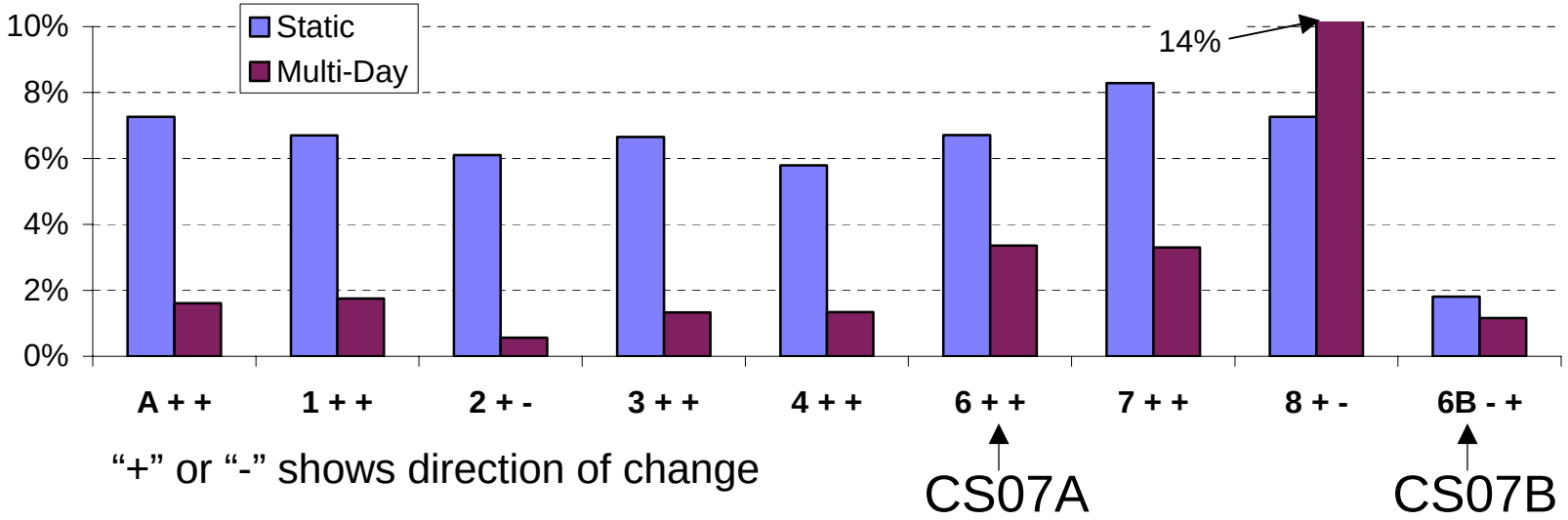


PANs Changes Caused by Condensations

Average of absolute change, relative to previous condensation level



Average of absolute change, relative to uncondensed SAPRC-07



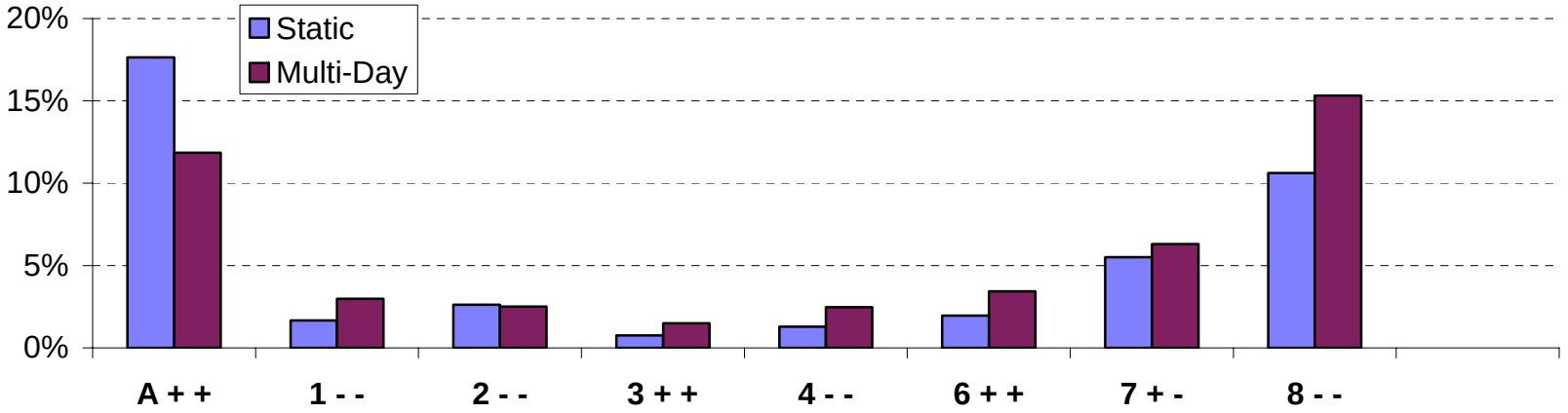
"+" or "-" shows direction of change

CS07A

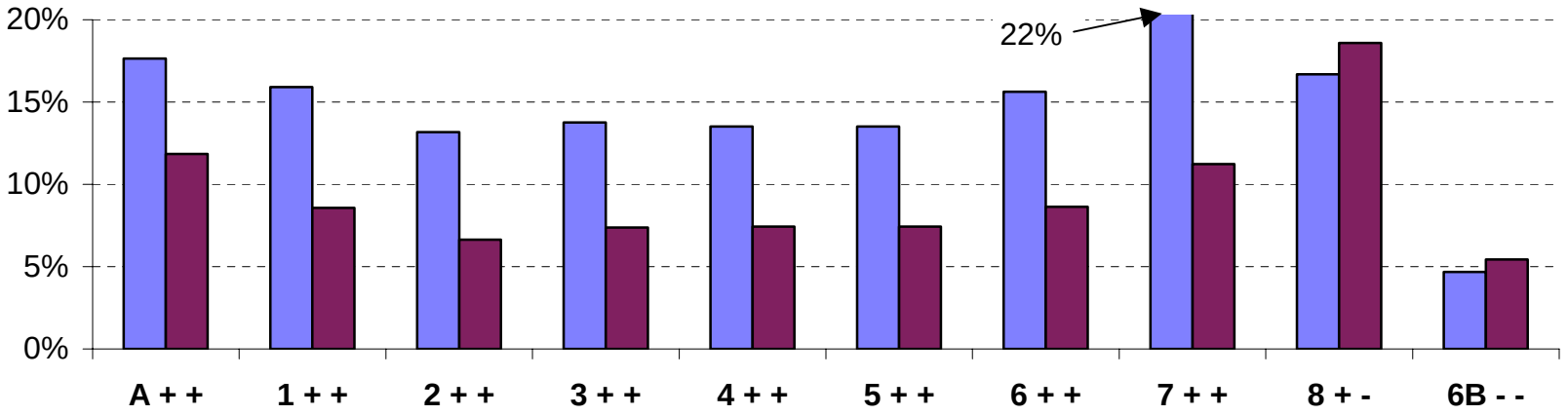
CS07B

H_2O_2 Changes Caused by Condensations

Average of absolute change, relative to previous condensation level



Average of absolute change, relative to uncondensed SAPRC-07

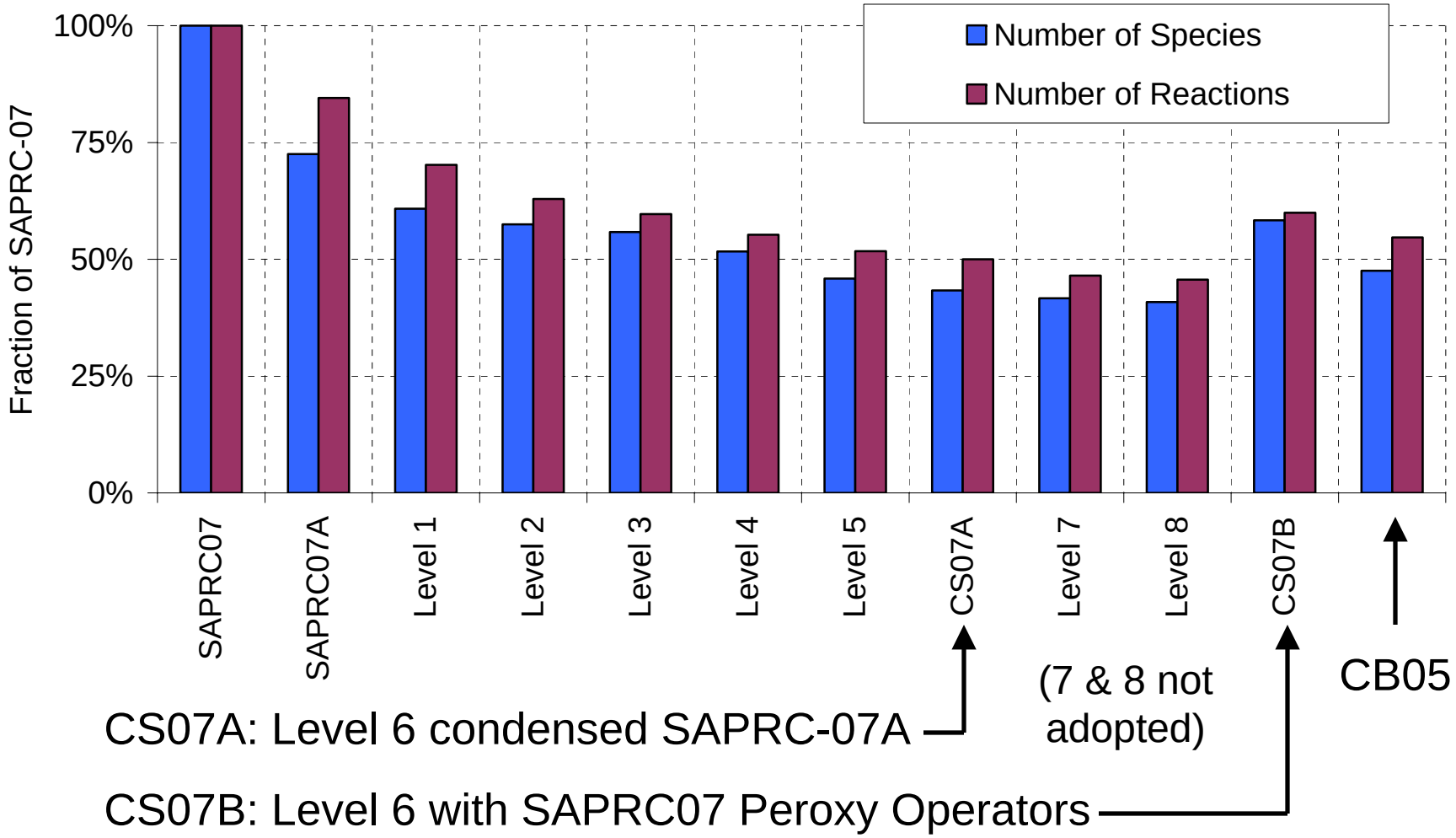


"+" or "-" shows direction of change

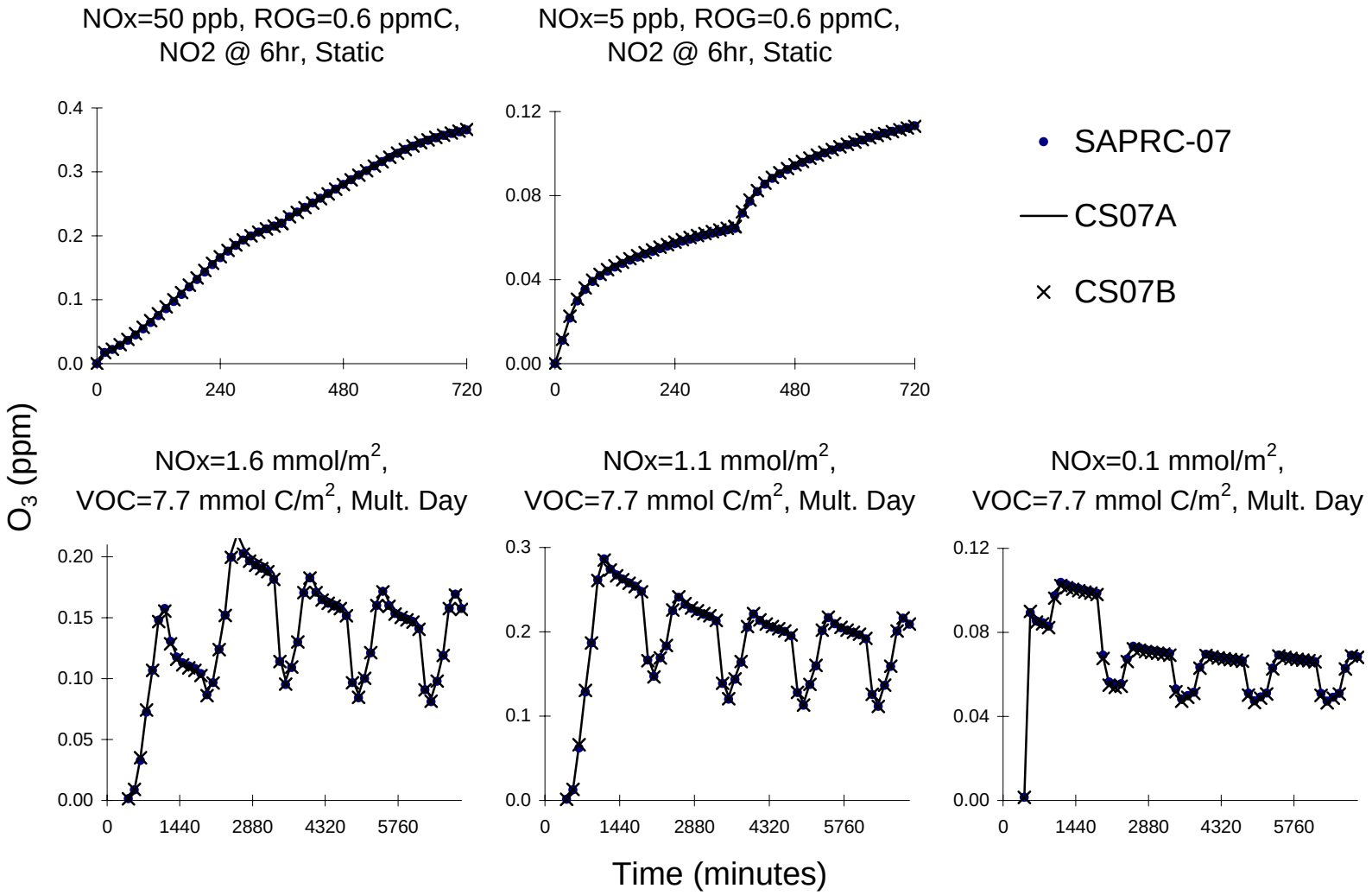
CS07A

CS07B

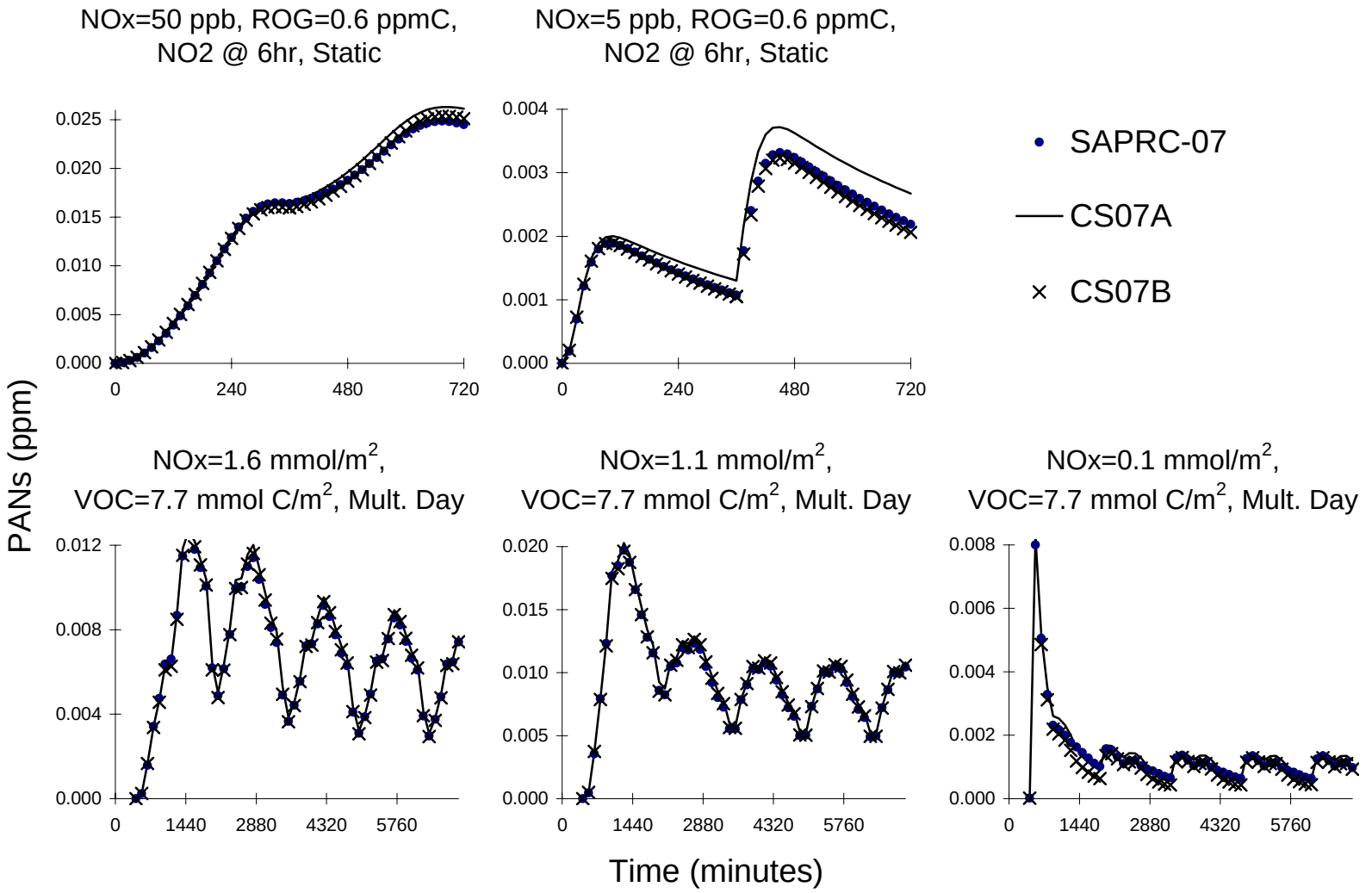
Comparison of Mechanism Sizes



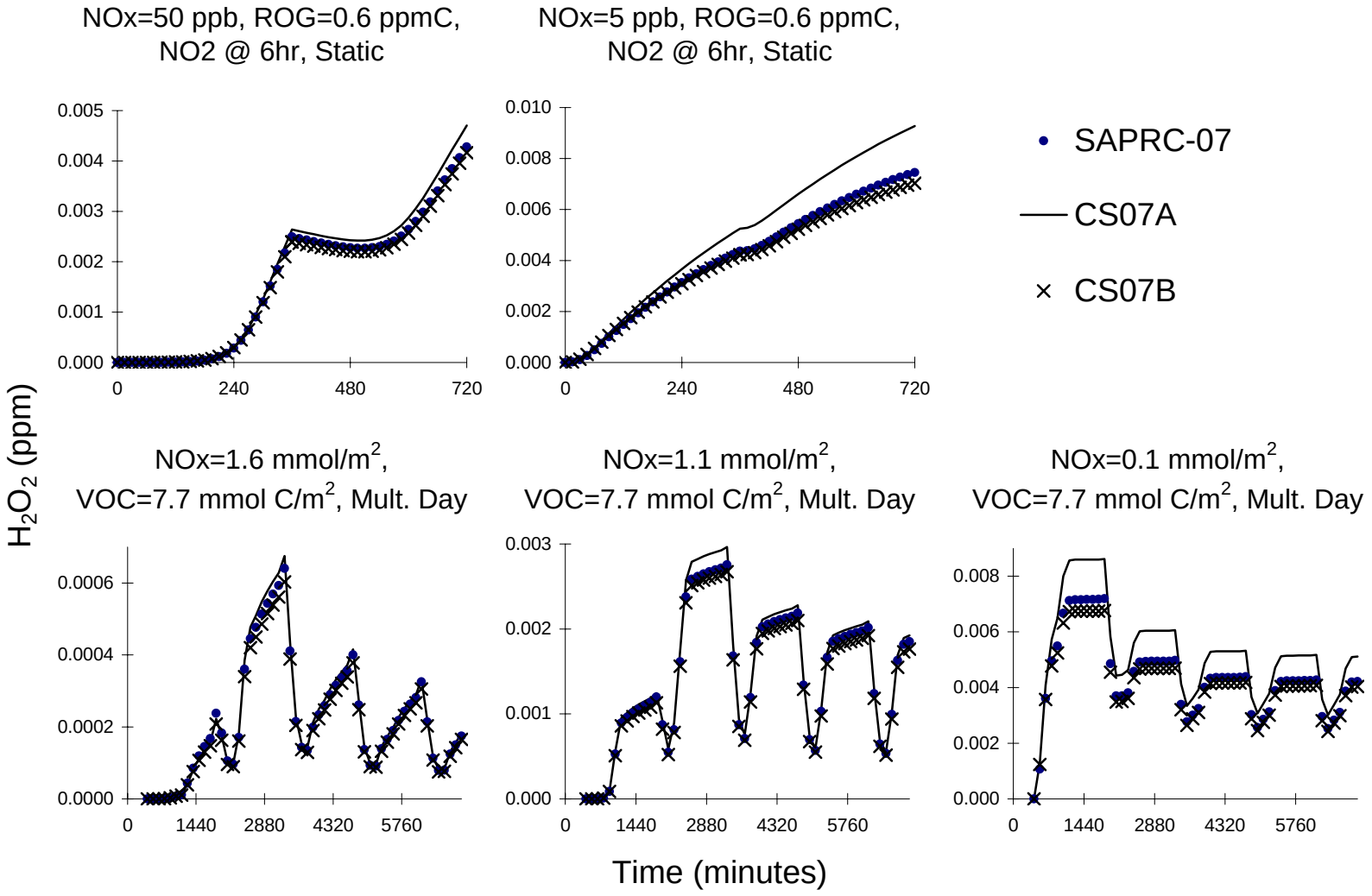
Effect of Mechanism Condensation on $\underline{O_3}$ in Selected Test Scenarios



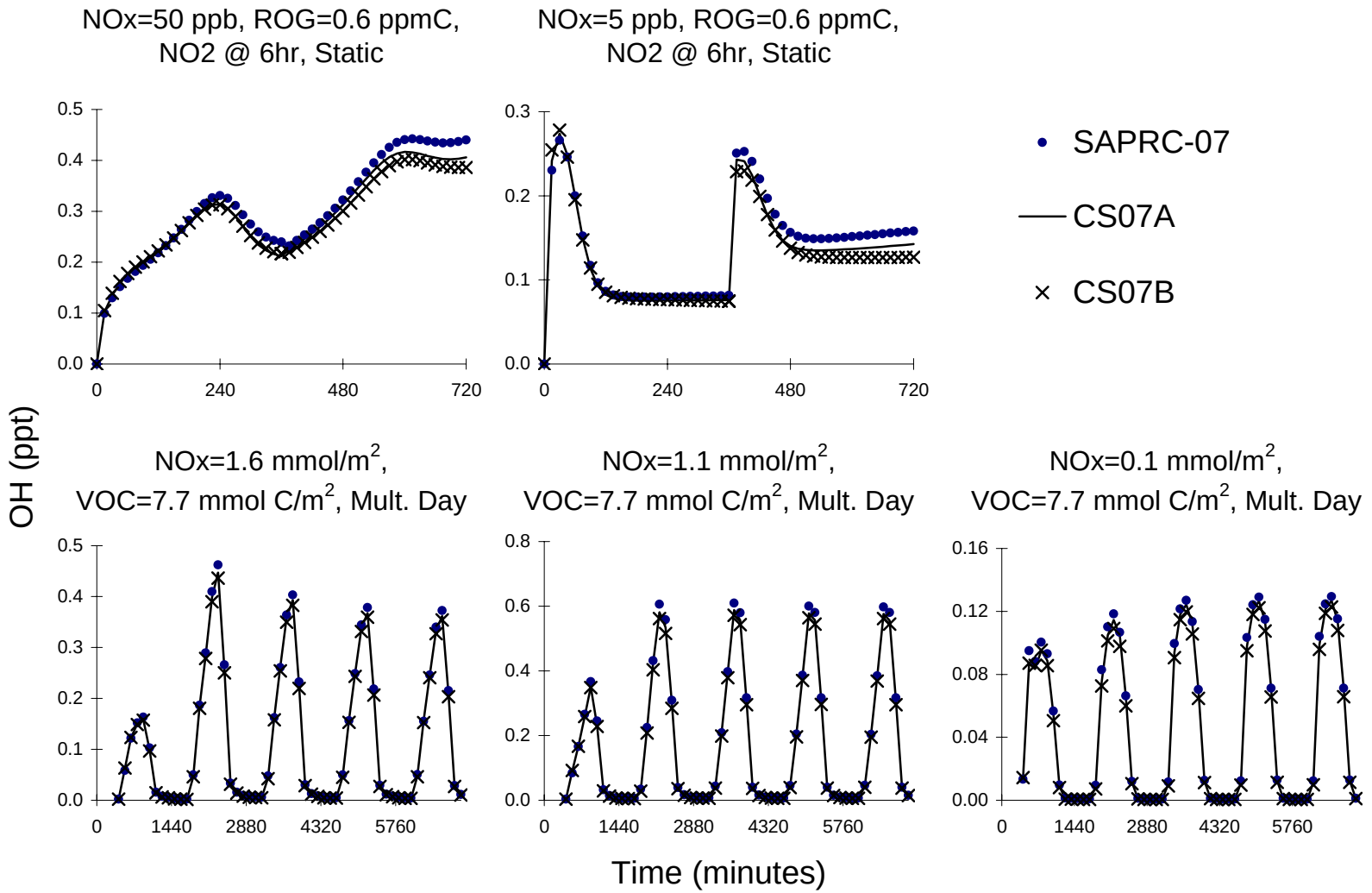
Effect of Mechanism Condensation on PANs in Selected Test Scenarios



Effect of Mechanism Condensation on H_2O_2 in Selected Test Scenarios

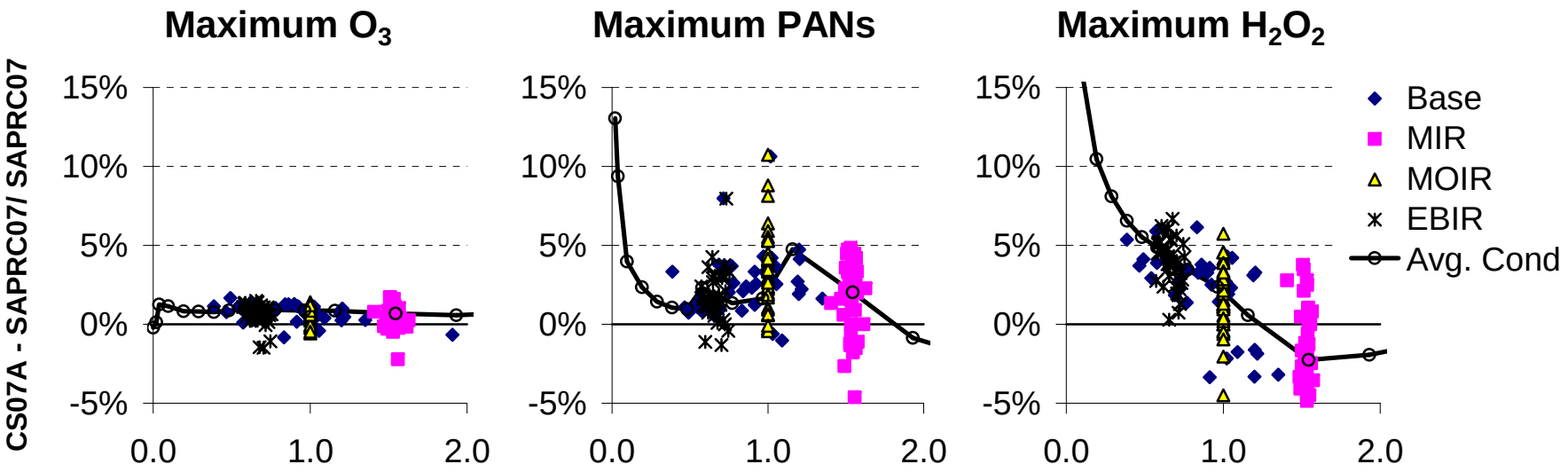


Effect of Mechanism Condensation on OH in Selected Test Scenarios

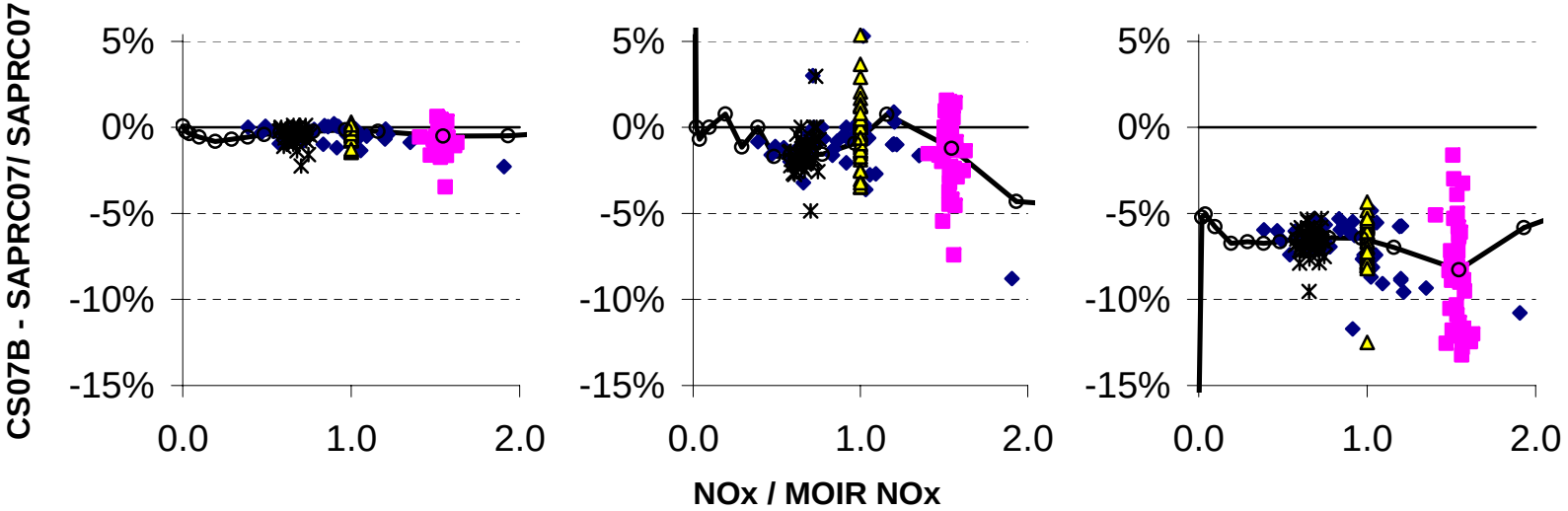


Results for Reactivity Scenarios

Condensed CS07A vs SAPRC-07



Condensed CS07B vs SAPRC-07



Summary of Results

- Condensed versions of SAPRC-07 have been developed
  - About half the number of species and reactions as uncondensed SAPRC-07. Comparable in size to CB05.
  - Essentially same O_3 predictions for wide range of conditions.
  - Changes small for PANs, OH radicals, most other species.
  - Effects on H_2O_2 usually less than 10%, but depends on which peroxy radical lumping method is used.
- Chemical validity is directly traceable to detailed SAPRC-07
  - Based on detailed mechanisms for hundreds of VOCs
  - Comprehensively evaluated against chamber data.
  - Can be readily modified if the base ROG mixture used to derive the lumped species parameters is changed
  - Can be readily updated if the underlying detailed mechanism is updated, by re-applying the condensation procedures.

Summary of Results (continued)

Two versions have been developed and are recommended for use

- CS07A: Incorporates SAPRC-99 peroxy representation
  - Recommended for applications where ozone is the priority.
  - Most condensed, easiest to implement in existing models.
  - Can be used in any application where CB4 or CB05 are considered appropriate. (Slightly smaller than CB05.)
- CS07B: Retains SAPRC-07 peroxy representation
  - Recommended when predictions of H_2O_2, hydroperoxides, or SOA are also important. (Hydroperoxides may be important SOA precursors under low NO_x conditions.)
  - Same ozone predictions as CS07A (and SAPRC-07).
  - 35% more species than CS07A, but most added species are in steady state. Requires software changes for most models.

Acknowledgements

- Development of condensed SAPRC-07 was supported by California Air Resources Board Contract No. 05-750, Dr. Ajith Kaduwela, CARB Project officer.
- The initial development of SAPRC-07 was supported by California Air Resources Board Contract No. 03-318., Dr. Dongmin Luo, CARB project officer.
- Development of a more detailed version of fixed parameter SAPRC-07 for toxics modeling is being supported by the EPA, Dr. Deborah Luecken, Project officer. This work underway.

Additional Information Available

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

- Information about the SAPRC-07 mechanism, including documentation, reactivity scales, and implementation files
- The report on the condensed SAPRC-07 is being finalized and will be posted here soon

http://www.engr.ucr.edu/~carter/SAPRC/files.htm

- Files for implementing various version of SAPRC-07, including CS07A, and CS07B in CMAQ.
- Files for running test simulations using the SAPRC modeling software.