EVALUATION OF A GAS-PHASE ATMOSPHERIC MECHANISM FOR LOW NO_x CONDITIONS

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- Background and Objectives
- Environmental Chambers Employed
- Chamber Effects Characterization
- Evaluation Results
- Modeling assessment of relative rates of low NO_x reactions
- Discussion and Conclusions

BACKGROUND

- Ground-level ozone O_3 is formed in complex reactions of emitted VOCs with NO_x in sunlight
- The mechanisms representing these reactions in models are critical to accurate O_3 control strategy predictions.
- Environmental chamber data provide the best way to test these mechanisms independent of other uncertainties
- However, current mechanisms were evaluated using data with higher NO_x levels than most current ambient conditions.
- This is a concern because the nature of the oxidation processes change as NO_x is reduced.
- Opportunities exist for lower NO_x mechanism evaluation:
  - Existing Low NO_x data from CSIRO and TVA Chambers
  - Experiments from the new UCR EPA Chamber designed for low NO_x evaluations are becoming available

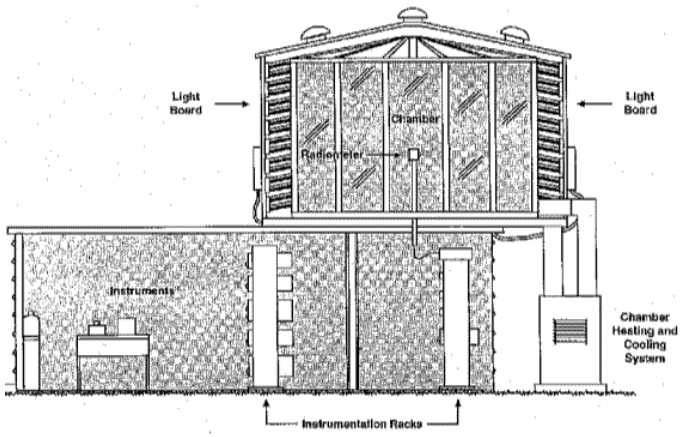
OBJECTIVES

- Evaluate the SAPRC-99 mechanism (the most up-to-date and detailed mechanism used by the CARB) for low NO_x conditions.
- Obtain and characterize existing TVA and CSIRO chamber data for mechanism evaluation
- Conduct experiments in the new UCR EPA chamber most needed for low NO_x evaluation
- Evaluate mechanism using available TVA, CSIRO, and UCR EPA chamber data
- Investigate modifications to SAPRC-99 to better represent low NO_x conditions
- Recommend research needed to improve mechanism performance

SUMMARY OF ENVIRONMENTAL CHAMBERS USED IN THE LOW NO_x EVALUATION

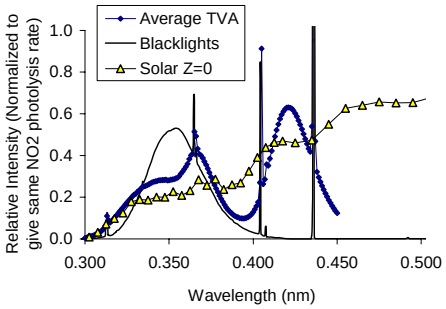
	TVA	CSIRO	UCR EPA
Volume (m^3)	28	2 x 20	2 x 85
Walls	FEP Teflon® Film		
Lighting	Fluorescents	Sunlight	Argon Arc
Number of Experiments	32 Char. 48 Mech Eval	19 Mixture experiments	36 Char 42 Mech Eval
Dates of Runs	1993-96	1995-1996	2003
Measured Species Used in Evaluation	O_3, NO, CO, HCHO, PAN, VOCs	O_3, NO, NO_y-NO	O_3, NO, NO_2, CO, HCHO, PAN, HNO_3, VOCs

DIAGRAM OF TVA INDOOR CHAMBER



DISCUSSION OF TVA INDOOR CHAMBER

- Experiments conducted by Simonaitis and Bailey of TVA in 1993 through 1995 for low NO_x mechanism evaluation
- Steps taken to reduce background by extensive purging between runs
- 3 types of fluorescent lamps used to approximate solar spectrum
- NO_2 actinometry results averaged 0.392 min^{-1}
- Temperature during runs varied from ~295 - 315 ^oK
- TVA Chamber no longer operational



- Data made available for modeling by Jeffries and Co-workers for an RRWG project

CSIRO OUTDOOR CHAMBERS

DISCUSSION OF CSIRO OUTDOOR CHAMBER

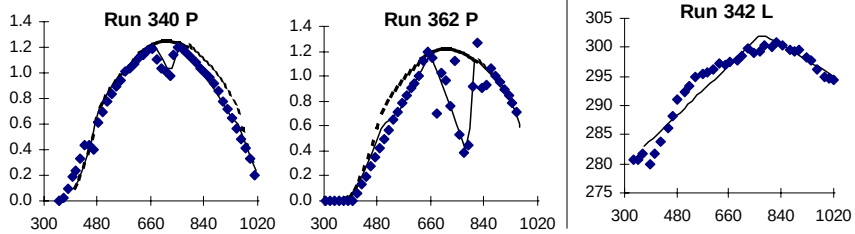
- Located outdoors in a suburb of Sydney, Australia
- Multiple complex surrogate – NO_x experiments conducted by Johnson and co-workers to test and derive parameters for Johnson's parameterized "extent of reaction" model
- Data used from 10 dual chamber surrogate experiments conducted in a collaborative project with Jeffries and co-workers
- Data made available for modeling as part of an RRWG project
- Photolysis rates for modeling derived as follows:
  - NO_2 photolysis rates as function of time estimated from TSR data using relationship of Demerjian and Schere
  - Ratios of other photolysis rates to NO_2 calculated using Peterson (1977) actinic fluxes as function of time of day
- Other characterization parameters estimated based on characterization results for other chambers

EXAMPLES OF CSIRO TEMPERATURE AND LIGHT CHARACTERIZATION ASSIGNMENTS

Experimental and Model Fit TSR

(Modeled TSR derived from calculated NO_2 photolysis rates and Demerjian and Schere Relationship)

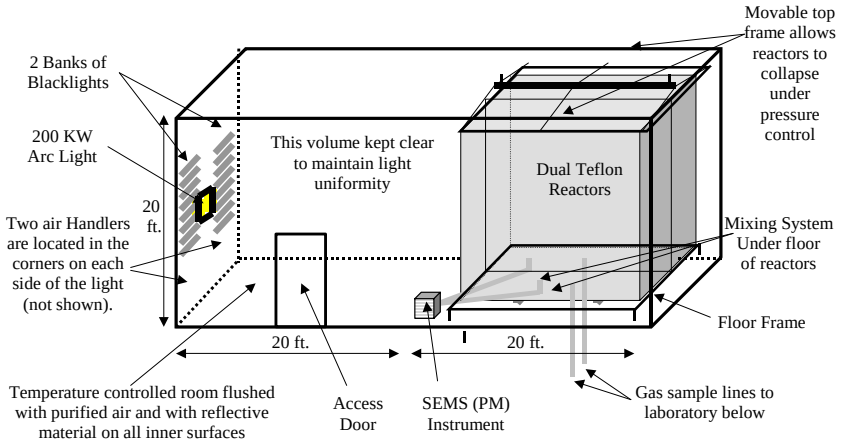
Temperature (Experimental and Model Input)



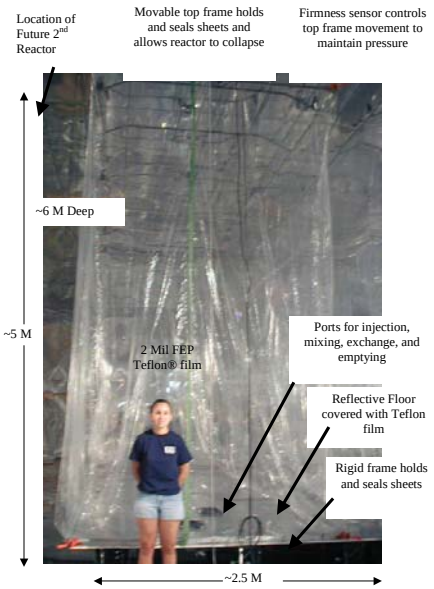
TSR or temperature vs. minutes after midnight

◆ **Experimental** —— **Model** - - - **No HV adj.**

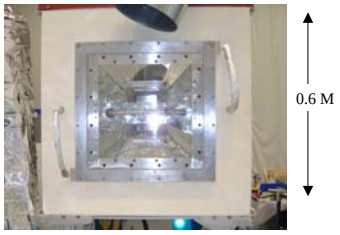
DIAGRAM OF UCR EPA CHAMBER

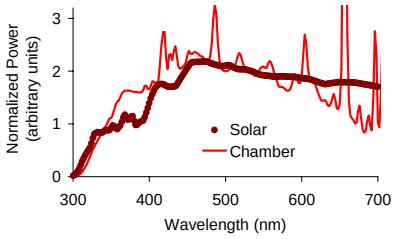


PICTURES OF UCR EPA CHAMBER



Light Source and Spectrum





DISCUSSION OF UCR EPA CHAMBER

- Constructed using a $2.9 Million EPA earmark to develop a "Next Generation" chamber for mechanism evaluation
  - Large volume to minimize background and permit PM studies and instrumentation with large sample requirements
  - Indoor chamber for maximum characterization and control
  - Light source simulating sunlight
  - Low background to permit well-characterized experiments at low pollution levels
  - Advanced analytical instrumentation
  - Temperature control to ±1°C in ~5° - ~50°C range
- Experiments with current configuration began in early 2003:
  - Initial characterization and evaluation runs funded by EPA
  - Very low NO_x surrogate experiments run for this project

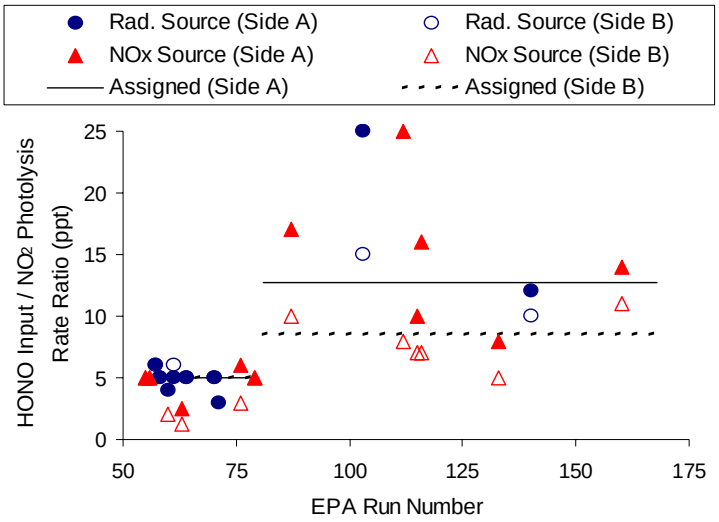
DERIVATION OF MAJOR CHAMBER CHARACTERIZATION PARAMETERS

Parameter	TVA	CSIRO	UCR EPA
Continuous Radical source (HONO offgasing)	Negligible compared to high HCHO offgasing	T-Dependent rate assumed to be same as SAPRC OTC or 3 x higher	Model char. runs sensitive to HONO offgasing
NO_x Offgasing	Model CH_3CHO - Air runs	Assume same as radical source	Approx. same as radical source
HCHO background and offgasing	Model HCHO in CO - NO_x or NO_x - air runs	Assumed to be unimportant compared to R.S.	Model HCHO in char. runs w/o HCHO source
Initial HONO	Model CO - NO_x, NO_x - Air, and CH_4 - NO_x runs	No data – varied in evaluation simulations	Model char. runs sensitive to initial HONO
O3 Decay	Measured	Estimated	Measured
Dilution	Derived from tracer data	Estimated to be minor	Believed to be low in most runs

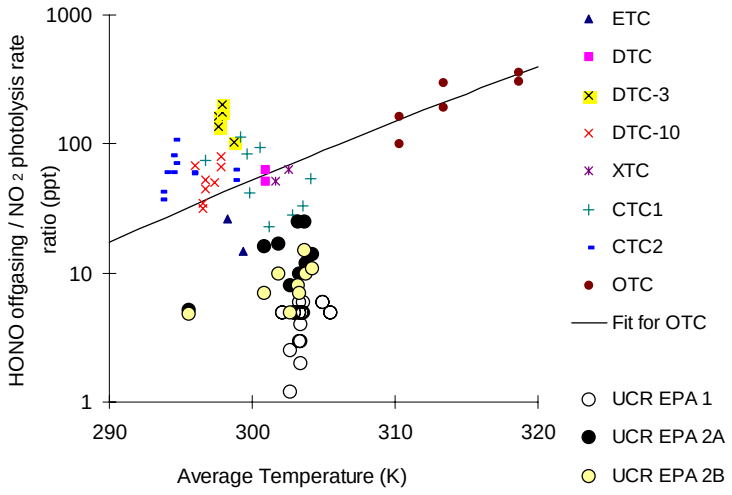
VALUES OF MAJOR CHAMBER CHARACTERIZATION PARAMETERS

Parameter	TVA	CSIRO (varied)	UCR EPA
HONO or NO_x offgasing / NO_2 photolysis rate ratio	7.2 ppt (as NO_x offgasing only)	Standard: Temp.-dependent fit for OTC (10-100 ppt) High RS: 3 x Std.	Runs 55-80: 5 ppt Runs 81-168: •Side A: 8.5 ppt •Side B: 12.5 ppt
HCHO offgasing / NO_2 photolysis rate ratio	HCHO: 45 ppt HCHO precursor: 135 ppt	Assumed to be low compared to other sources	10 ppt
Initial HONO	0.5 ppb	Standard: ~0 High RS: 2 ppb	0.05 ppb
O3 Decay	7% /hour	1.3% /hour	1.1% /hour
Light Intensity	$k_1 = 0.392\ min^{-1}$	Standard: Deriv'd from TSR data High: 1.15 x Std.	$k_1 = 0.284\ min^{-1}$

UCR-EPA HONO INPUT PARAMETER VS. RUN NO.



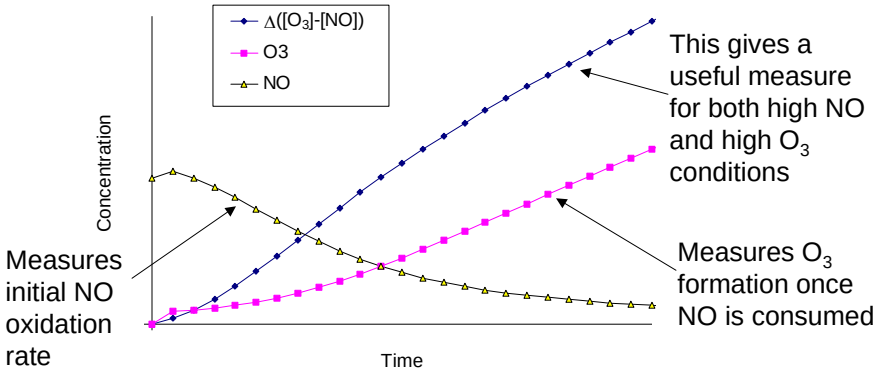
COMPARISONS OF RADICAL SOURCE PARAMETERS FOR UCR EPA AND PREVIOUS CHAMBERS



MEASURE OF MODEL PERFORMANCE FOR OZONE

Model performance for simulating both ozone formation and NO oxidation is measured by ability to predict $\Delta([O_3]-[NO])$:

$$\Delta([O_3]-[NO]) = ([O_3]-[NO])_{FINAL} - ([O_3]-[NO])_{INITIAL}$$



UCR EPA RUNS AND FITS TO $\Delta([O_3]-[NO])$

Run Type	Runs	NO_x Range (ppb)	Average Model Fits	
			Bias	Error
Characterization	32	0 - 200	-2%	31%
Formaldehyde - NO_X	2	8 - 25	-23%	23%
Formaldehyde - CO - NO_x	2	15-20	-10%	10%
Ethene - NO_x	2	10 - 25	-15%	15%
Propene - NO_x	2	5 - 25	16%	16%
Toluene or m-Xylene - NO_x	4	5 - 25	10%	10%
Aromatic - NO_x + CO	6	5 - 30	-17%	18%
Ambient Surrogate - NO_x	24	2 - 110	-11%	15%

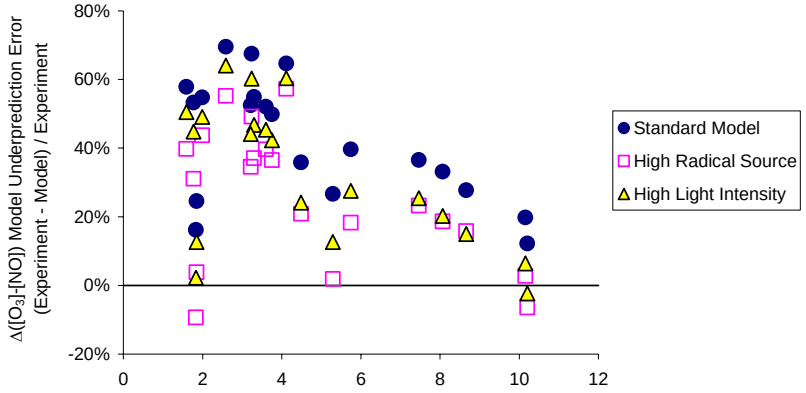
SUMMARY OF TVA RUNS AND FITS TO Δ([O_3]-[NO]

Run Type	Runs	NO_x Range (ppb)	Average Model Fits	
			Bias	Error
Characterization	32	0 - 54	1%	15%
Formaldehyde - NO_x	4	39 - 42	-4%	10%
Isopentane - NO_x	1	18	-28%	28%
Ethene, Propene, or trans-2-Butene - NO_x	7	22 - 54	10%	10%
Toluene or m-Xylene - NO_x	5	50 - 266	1%	8%
Simple Mixture - NO_x	23	50 - 100	6%	7%
Ambient Surrogate - NO_x	12	25 - 169	-8%	9%

CSIRO RUNS AND FITS TO Δ([O_3]-[NO]

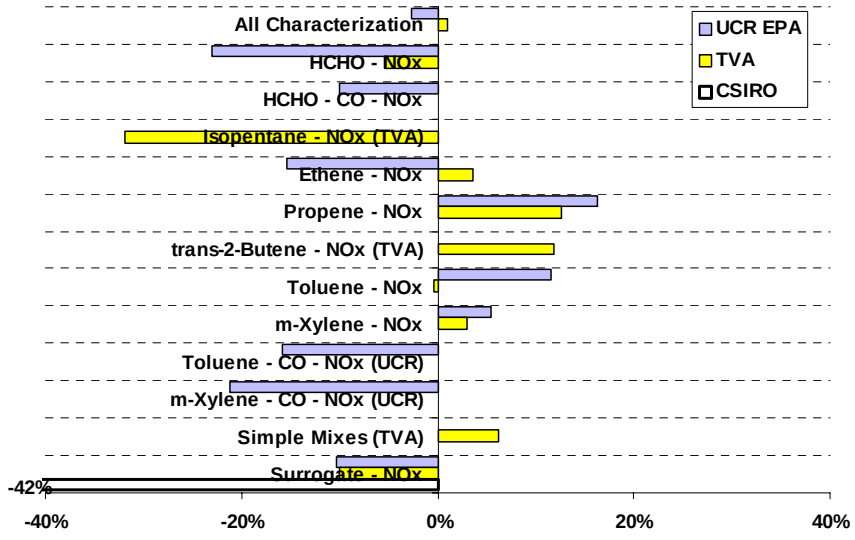
Run Type	Runs	NOx Range (ppb)	Average Model Fits	
			Bias	Error
Ambient Surrogate – NO_x				
Standard Char. Model	20	17 - 100	-42%	42%
High Radical Source			-26%	27%
High Light Intensity			-33%	33%

EFFECTS OF ALTERNATIVE CHARACTERIZATION ASSUMPTIONS ON CSIRO SIMULATIONS

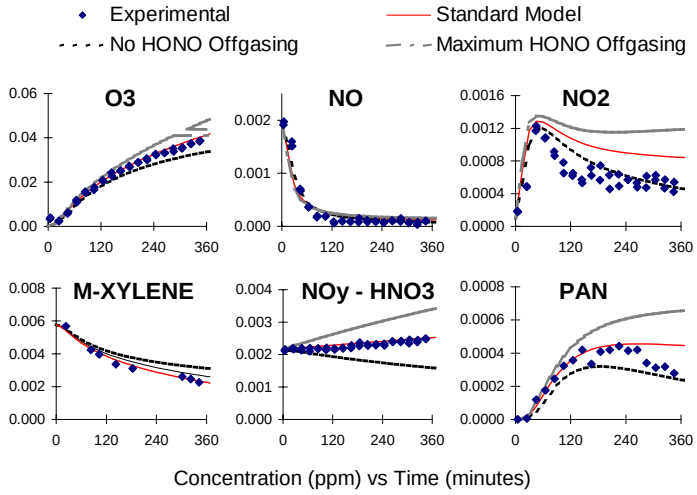


Δ([O_3]-[NO]) Underprediction error vs. Surrogate / NO_x ratio

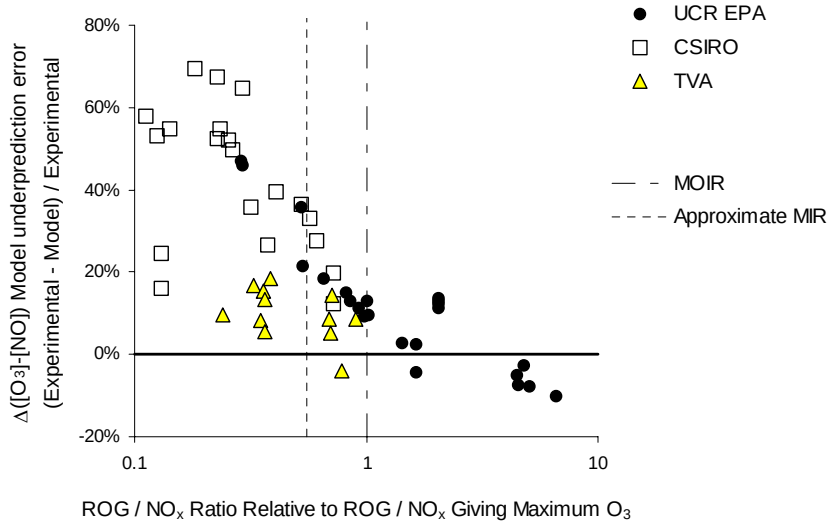
MODEL BIASES FOR PREDICTION OF Δ([O3]-[NO])



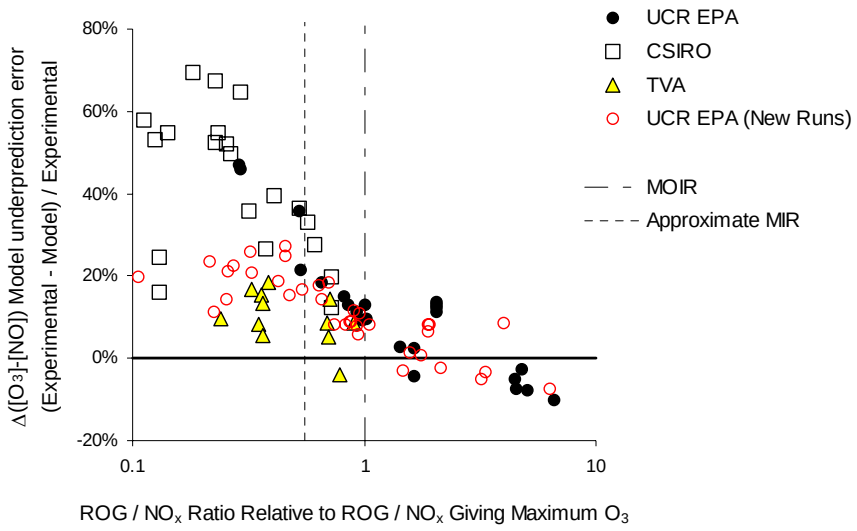
LOWEST NOx UCR EPA SURROGATE EXPERIMENT
(ROG SURROGATE = 300 PPBC, NOx = 2 PPB)



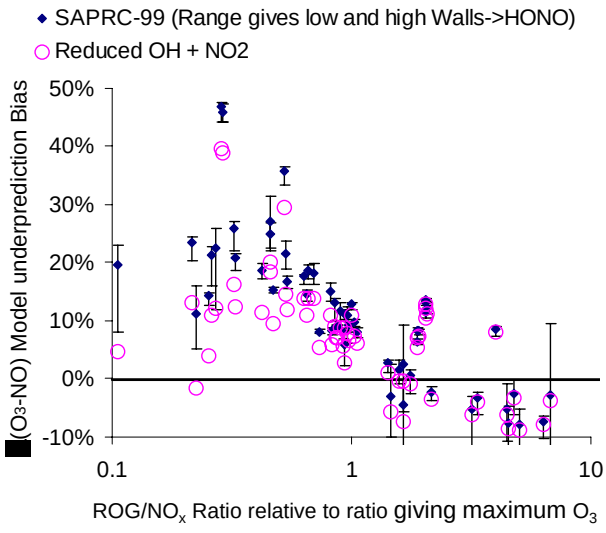
MODEL UNDERPREDICTION BIASES FOR SURROGATE – NOx RUNS VS. ROG/NO_x RATIO



MODEL UNDERPREDICTION BIASES FOR SURROGATE – NOx RUNS VS. ROG/NO_x RATIO

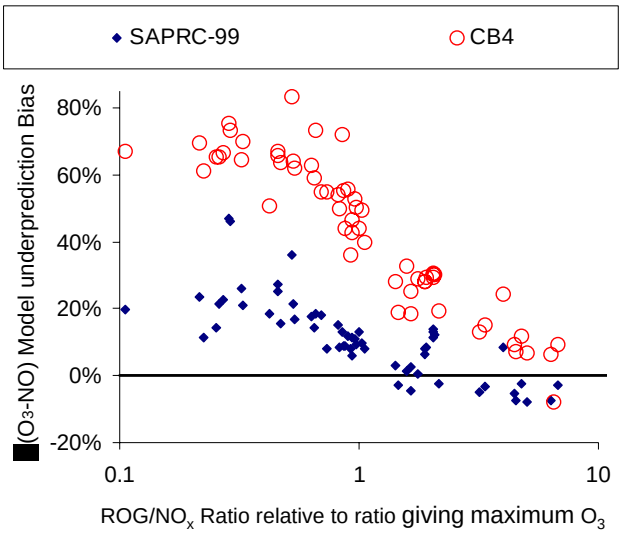


MODEL UNDERPREDICTION SENSITIVITIES FOR UCR EPA RUNS



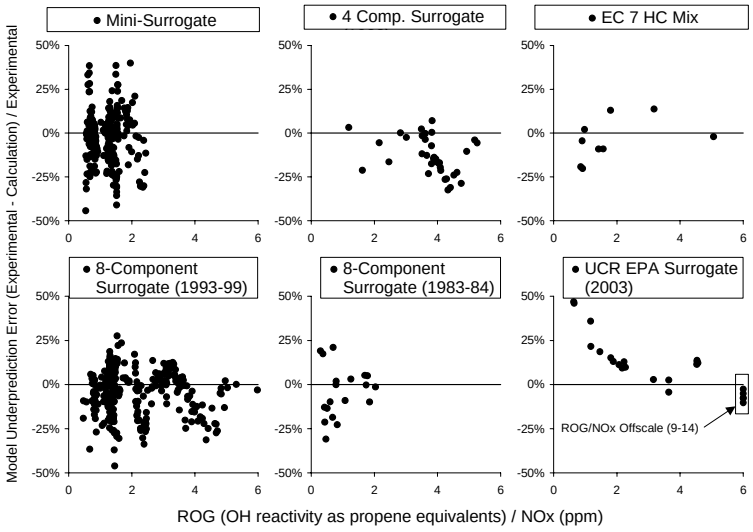
This includes more recent runs carried out for EPA OBM project

COMPARISON OF CB4 AND SAPRC-99 MODEL ERRORS FOR UCR EPA SURROGATE RUNS



This includes more recent runs carried out for EPA OBM project

COMPARISON OF CURRENT SURROGATE FITS WITH DATA USED IN PREVIOUS EVALUATION

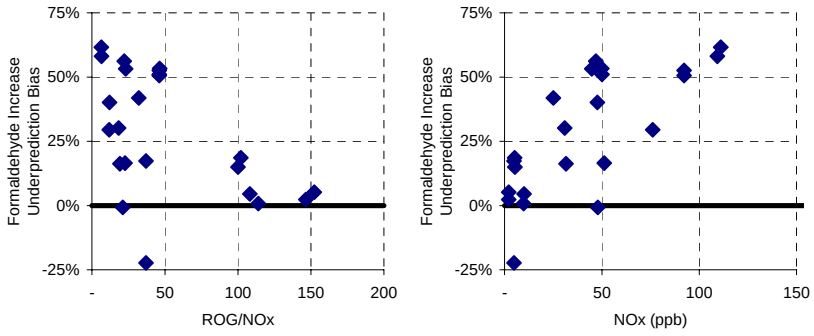


MODEL PERFORMANCE IN SIMULATING OTHER MEASUREMENTS IN SURROGATE RUNS

Compounds	TVA	UCR EPA
NO_2	No data (NO_Y-NO only)	Tends to underpredict consumption following maximum
PAN	Very significantly underpredicted	Reasonably well simulated in runs where O3 well simulated
Formaldehyde	Tendency to underpredict (depends on offgasing model)	Tendency to underpredict depends on NO_x levels
Reactant VOCs	Generally consistent with data	Tendency to underpredict final consumption rates
HNO_3	No data	Generally consistent with available data ([NO_x]>50 ppb)

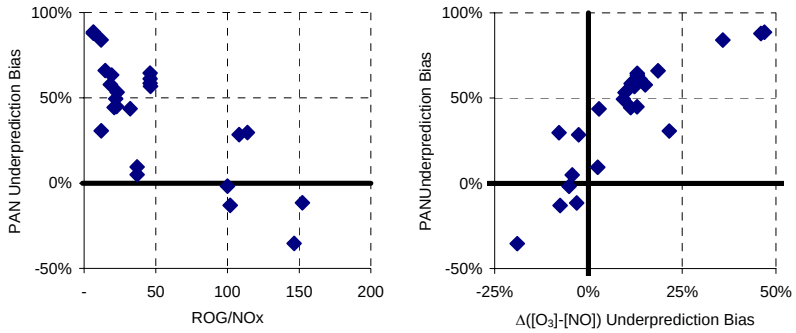
Note: Data for above compounds not available for CSIRO Runs

MODEL PERFORMANCE SIMULATING FORMALDEHYDE IN UCR EPA SURROGATE RUNS



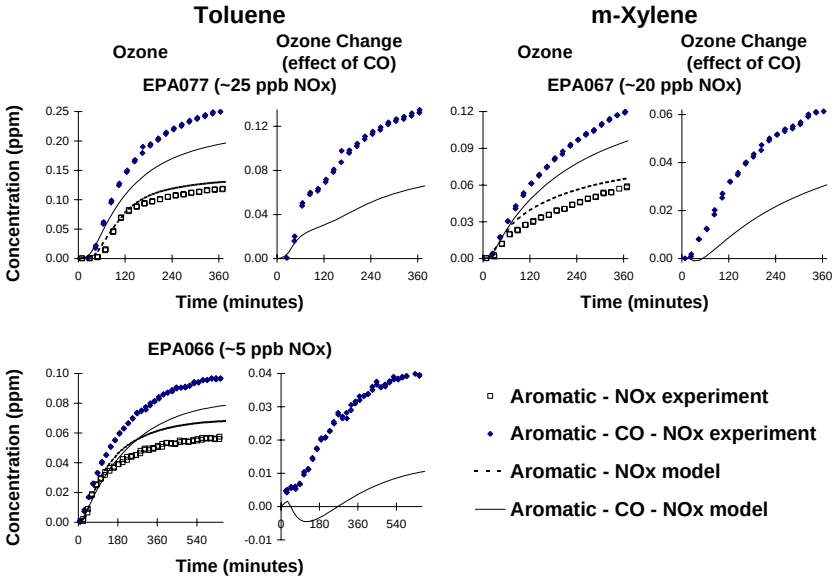
Formaldehyde Underprediction bias vs. ROG/NO_x or NO_x
(experimental - calculated) / experimental Δ[HCHO]

MODEL PERFORMANCE SIMULATING PAN IN UCR EPA SURROGATE RUNS

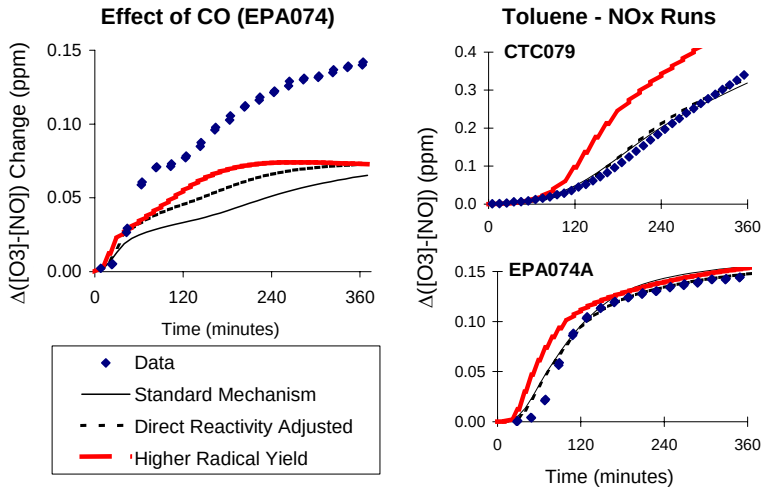


PAN Underprediction bias vs. ROG/NO_x or NO_x
(experimental - calculated) / experimental final PAN

EFFECT OF CO ON AROMATIC - NO_x RUNS



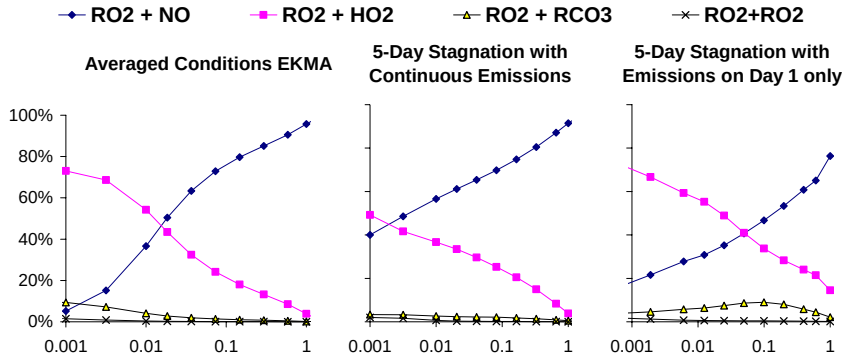
EFFECTS OF ADJUSTMENTS TO PARAMETERIZED TOLUENE MECHANISM



ASSESSMENT OF NEED TO MODIFY MECHANISM FOR LOW NO_x CONDITIONS

- Lower NO_x levels result in increased importance of peroxy + peroxy reactions, which form different organic products that the peroxy + NO reactions that dominate when NO_x is higher.
- SAPRC-99 uses an approximate “chemical operator” method for RO_2 reactions that neglects this change in products with NO_x
- Representing RO_2+RO_2 reactions more explicitly requires adding many reactions to the mechanism.
- Process analysis calculations were carried out to assess the relative importance of the different types of competing RO_2 reactions at low NO_x
- The results can then be used to assess priorities for mechanism modifications for more accurate low NO_x predictions

MODEL SIMULATIONS OF PEROXY REACTION INTEGRATED REACTION RATE RATIOS



Ratios of integrated reaction rates vs.
NO_x inputs relative to NO_x giving maximum O_3

IMPLICATIONS CONCERNING HOW TO MODIFY MECHANISMS FOR LOW NO_x CONDITIONS

- Results of test calculations of integrated peroxy radical reaction rates with three types of low NO_x scenarios indicate that:
  - Major low-NO_x sink for peroxy radicals is reaction with HO_2
  - Maximum importance of Alkyl Peroxy + Acyl Peroxy reaction is ~10%
  - Alkyl peroxy + Alkyl peroxy reactions negligible
- Adding reactions or species to improve representations of organic peroxy + peroxy reactions probably not worthwhile
- Higher priority is improving representation of:

$$RO_2 + HO_2 \rightarrow ROOH + O_2$$
$$ROOH + OH \text{ or } h\nu \rightarrow \text{Products}$$

- This requires adding more hydroperoxide species to the mechanism, whose reactions are uncertain.

DISCUSSION AND CONCLUSIONS: Good News

- Range of conductions where mechanisms have been evaluated has been significantly expanded
  - TVA data of comparable or better quality than previous runs in other chambers, despite formaldehyde contamination
  - CSIRO data proved to be useful in this evaluation, but more characterization information would increase its utility
  - Lower background in UCR EPA chamber permitted useful mechanism evaluation with NO_x as low as ~2 ppb and improves precision of evaluation
  - Simulations of lower NO_x characterization and most simple VOC – NO_x experiments generally satisfactory
- No apparent mechanism problem simulating very low NO_x conditions where maximum O_3 formation potentials achieved.
- Inaccuracies caused by approximate treatment of RO_2+RO_2 reactions in current mechanism are probably not important

DISCUSSION AND CONCLUSIONS: Bad News

- SAPRC-99 mechanism has consistent bias in underpredicting NO oxidation and O_3 formation rates at low ROG/NOx ratios
- Underprediction bias for CB4 even worse
- Significant problems with current aromatics mechanisms:
  - Ozone increase caused by adding CO “radical amplifier” to aromatic – NO_x systems underpredicted by factor of ~2
  - Adjustments to the mechanisms as currently parameterized cannot correct this problem
  - Aromatics mechanism problems *may* be the cause of the low ROG/NO_x underprediction bias, but this is not certain.
- Improving accuracy of low NO_x organic product predictions for requires explicit treatment of uncertain organic hydroxides

RESEARCH NEEDS

- The current parameterized aromatics mechanisms need to be reformulated and made consistent with available data
- The underprediction problem at low ROG/NO_x needs to be investigated and resolved
- Data are needed on effects of temperature on ozone and other secondary products. (UCR EPA chamber suitable for this)
- Well-characterized, low NO_x chamber data are needed to develop and test models for secondary PM formation. (UCR EPA chamber also suitable for this)
- SAPRC-99 needs to be updated to be consistent with latest recommendations and made more compatible with SOA models
- A new condensed mechanism, traceable to an updated and evaluated detailed version, needs to be developed to finally replace the out-of-date CB4 mechanism