

CURRENT STATUS OF THE ENVIRONMENTAL CHAMBER DATA BASE FOR EVALUATING OXIDANT MECHANISMS

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Extended Abstract

Because of the importance of environmental chamber data to the development and evaluation of chemical mechanisms used in airshed models for regulatory applications (Jeffries et al., 1993), the U.S. Environmental Protection Agency initiated a program to assemble and document a quality-assured chamber data base for this purpose. The objectives included selecting past chamber runs whose data are potentially useful for mechanism evaluation, evaluating and correcting data where applicable, giving recommended input data for modeling, and providing the data in documented and computer-readable format useful to the modeler. This program has involved researchers at the University of North Carolina and elsewhere, but the discussion here will focus on work carried out at our laboratories in developing and documenting the data base for the past SAPRC environmental chamber experiments.

Five indoor and one outdoor chamber have been used at SAPRC to generate data suitable for modeling, though presently only the indoor chamber data are on the data base. The chambers and data which are included are summarized below.

- The Evacuatable chamber (EC) is a 5800-liter metal cylinder with quartz end windows and Teflon-coated aluminum walls and a xenon arc light source. It was used between 1978-1983 to generate a variety of single compound experiments and a more limited number of mixture runs specifically for mechanism development and evaluation. The data base includes 216 EC runs.
- The Indoor Teflon Chamber (ITC) is a ~6400-liter reaction bag constructed of FEP teflon film with a blacklight light source. It was used between 1982-1986 (with a few runs in 1989) for a variety of single compound experiments for mechanism development, multi-day surrogate - NO_x experiments to assess effects of ROG/NO_x and methanol substitution, and a preliminary series of low NO_x incremental reactivity experiments. The data base includes 346 ITC runs.
- The Indoor Teflon Chamber #2 (ETC) is similar to the ITC except for a smaller reaction volume (~3000 liters). This was used between 1989 and 1993 primarily for a large number of incremental reactivity experiments using a simple "mini-surrogate" under relatively low ROG/NO_x conditions. A few experiments with single compounds were also conducted, including a number of experiments involving isoprene and selected terpenes. The data base includes 413 runs from this chamber.
- The Dividable Teflon Chamber (DTC) consists of two ~5000-liter FEP teflon film reaction bags with a blacklight light source designed for simultaneous irradiations of two different mixtures under the same conditions. This was used in 1993 primarily for incremental reactivity experiments with more complex ROG surrogates, though experiments with simpler ROG surrogates and some single compound runs, including experiments with isoprene and terpenes, were also conducted. The data base includes 66 dual chamber runs (132 separate mixtures irradiated) from this chamber.
- The SAPRC Xenon Teflon Chamber (XTC) consisted of a ~5000-liter FEP teflon film reaction bag with a xenon arc light source. A total of 31 experiments involving selected single compounds and mixtures were

carried out in 1993 for the purpose of assessing effects of chamber and light source on mechanism evaluation results, and are included on the data base.

The preparation of the data base involved the following activities. Spreadsheets were created listing and classifying all runs on data base, noting special conditions, problems, initial NO_x, VOCs, other relevant data. Calibration factors were re-assigned based on trend data. Non-negligible changes were made for some NO_x data. Uncertainties for calibration factors and zero corrections added to data sets and used to estimate uncertainties in initial reactant concentrations. All actinometry data were re-analyzed using updated calculations, and light intensities were reassigned for all runs. Recommended spectra were derived for modeling all runs, with significant corrections being made to the recommended spectra for EC and blacklight chamber runs. Each run was assigned a "characterization Set", where chamber effects parameter recommendations are given. Computer programs were developed to extract data from files for modeling, and to prepare summaries and plots of performance results. A report was prepared documenting experiments, methods, data base, and corrections made to it.

The distributed data base include the following types of files: (1) files containing data specific to each run, including measurements, comments, run-specific model input, etc; (2) various types of spreadsheet files containing summary data for all runs and actinometry experiments in a chamber; (3) chamber dependent model input parameters for each "characterization set"; (4) available relevant calibration data for each instrument where such data are available; (5) programs for data conversion and example model simulations; (6) mechanism implementation and other files necessary for example simulations of the experiments using the SAPRC-90 and the Carbon Bond 4 mechanisms; (7) "Batch" file for installing the files and programs on a PC-compatible computer and conducting example model simulations; and (8) the two-volume report and data base documentation as Portable Document Format (PDF) files which can be read and printed using software available on the Internet¹.

The full data base and documentation is available by anonymous FTP at the Internet address cert.ucr.edu, subdirectory pub/carter/chdata. The source files for the modeling programs used in the example and other SAPRC modeling software and mechanism files are also available from the same FTP site in the subdirectory pub/carter/model. Hard copies of the documentation and the data base on diskettes are available from the EPA on request.

Reference

Carter, W. P. L., D. Luo, I. L. Malkina, and D. Fitz (1995): "The University of California, Riverside Environmental Chamber Data Base for Evaluating Oxidant Mechanism. Indoor Chamber Experiments through 1993," Report submitted to the U. S. Environmental Protection Agency, EPA/AREAL, Research Triangle Park, NC., March 20.

¹The main body of the documentation is in the file DATABAS2.PDF, while the appendices are in DATBAS2A.PDF. Software for reading or printing PDF files are available for anonymous FTP from ftp.adobe.com, subdirectory pub/Adobe/Applications/Acrobat.

**CURRENT STATUS OF THE ENVIRONMENTAL
CHAMBER
DATA BASE FOR EVALUATING OXIDANT
MECHANISMS**

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OBJECTIVES

ASSEMBLE AN EVALUATED AND DOCUMENTED CHAMBER DATA BASE FOR EVALUATING OXIDANT MECHANISMS.

EVALUATE DATA AND CORRECT WHERE APPLICABLE.

DOCUMENT METHODS, DATA QUALITY, PROBLEMS, UNCERTAINTY, SPECIAL CONDITIONS FOR EXPERIMENTS.

GIVE RECOMMENDED INPUT DATA FOR MODELING.

PROVIDE DATA IN COMPUTER-READABLE FORMAT USEFUL TO MODELER.

SELECT AND PRIORITIZE RUNS FOR MODELING

DEVELOP RECOMMENDED PROTOCOL FOR EVALUATING OXIDANT MECHANISMS

SAPRC ENVIRONMENTAL CHAMBERS

ID	VOL.¹ (L)	WALLS	LIGHTS	RH¹
EC	5800	TEFLON-COATED AL. & QUARTZ WINDOWS	XENON ARC	50%
ITC	6400	FEP TEFLON BAG	BLACKLIGHTS	50%
ETC	3000	FEP TEFLON BAG	BLACKLIGHTS	<5%
DTC	2 X 5000	FEP TEFLON BAGS	BLACKLIGHTS	<5%
XTC	5000	FEP TEFLON BAG	XENON ARC	<5%
OTC²	2 X 25,000	FEP TEFLON BAGS	SUNLIGHT	<5%

¹ Approximate

² OTC runs not on current SAPRC Documented data base

MAJOR TYPES OF EXPERIMENTS IN THE VARIOUS SAPRC CHAMBERS

EC (216 runs)

- RUN DATES: 9/75 - 11/83
- SINGLE COMPOUND RUNS FOR MECHANISM EVALUATION (EPA FUNDED)
- SOME ISOPRENE, ISOPRENE PRODUCT RUNS
- LIMITED NUMBER OF MIXTURE EXPERIMENTS
- **USED FOR DEVELOPMENT OF SAPRC-90, CB4, RADM2**

ITC (346 runs)

- RUN DATES: 1/82 - 8/86; 10/89
- SINGLE COMPOUND AROMATIC, ALKANE RUNS FOR MECHANISM DEVELOPMENT (USAF FUNDED)
- SOME ISOPRENE, ISOPRENE PRODUCT RUNS
- MULTI-DAY MIXTURE EXPERIMENTS (ROG/NO_x, MEOH SUB EFFECTS.)
- PRELIMINARY, LOW NO_x REACTIVITY EXPERIMENTS
- **USED FOR DEVELOPMENT OF SAPRC-90, RADM2**

OLD OTC (not on distribution)

- RUN DATES: 6-10/83; 5-11/85
- MULTI-DAY MIXTURE EXPERIMENTS (ROG/NO_x, MEOH SUB EFFECTS)
- **USED FOR EVALUATION OF SAPRC-90, RADM2**
- (NOT ON PRESENT DOCUMENTED DATA BASE)

**MAJOR TYPES OF EXPERIMENTS
IN THE VARIOUS SAPRC CHAMBERS
(CONTINUED)**

ETC (413 runs)

- RUN DATES: 10/89 - 2/93
- LARGE NUMBER OF REACTIVITY EXPERIMENTS WITH SIMPLE SURROGATE, HIGH NO_x.
- NEW ISOPRENE AND TERPENE EXPERIMENTS
- **USED TO UPDATE SAPRC MECHANISM FOR TERPENES AND OTHER INDIVIDUAL VOCs**

DTC (66 dual chamber runs)

- RUN DATES: 5-8/93
- REACTIVITY EXPERIMENTS (COMPLEX SURROGATE, HIGH AND LOW NO_x) FOR SELECTED VOCs
- ISOPRENE AND TERPENE REACTIVITY EXPERIMENTS
- **USED TO EVALUATE SAPRC MECHANISMS**

XTC (31 runs)

- RUN DATES: 8-11/93
- RUNS WITH SELECTED COMPOUNDS AND MIXTURES TO ASSESS CHAMBER AND LIGHT SOURCE EFFECTS
- **AROMATIC, MIXTURE RUNS INDICATE MECHANISM PROBLEMS.**

NEW OTC (not on distribution)

- RUN DATES: 6-10/93
- RUNS WITH SELECTED COMPOUNDS AND MIXTURES TO ASSESS CHAMBER AND LIGHT SOURCE EFFECTS.
- **AROMATIC, MIXTURE RUNS SUGGEST MECHANISM PROBLEMS.**

PREPARATION OF SAPRC CHAMBER DATA BASE

SPREADSHEETS CREATED LISTING AND CLASSIFYING ALL RUNS ON DATA BASE, NOTING SPECIAL CONDITIONS, PROBLEMS, INITIAL NO_x, VOCs, OTHER RELEVANT DATA.

CALIBRATION FACTORS RE-ASSIGNED BASED ON TREND DATA. NON-NEGLIGIBLE CHANGES FOR SOME NO_x DATA.

NO_x ZERO CORRECTIONS FOR EARLIER EC, ITC RUNS

UNCERTAINTIES FOR CALIBRATION FACTORS AND ZERO CORRECTIONS ADDED TO DATA SETS. USED TO ESTIMATE UNCERTAINTIES IN INITIAL REACTANT CONCENTRATIONS.

RE-ANALYZED ALL ACTINOMETRY DATA USING UPDATED CALCULATIONS, RE-ASSIGNED K₁'S FOR ALL RUNS.

DERIVED NEW SPECTRA FOR MODELING. CORRECTED EC SPECTRA, IMPROVED BLACKLIGHT SPECTRUM.

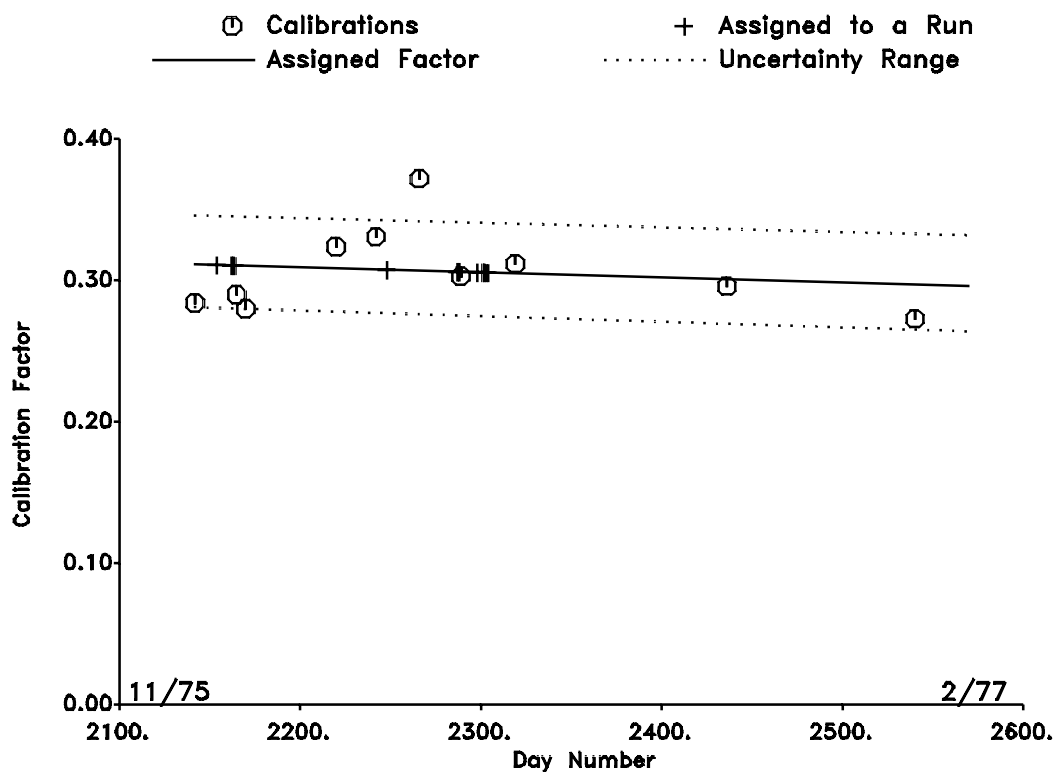
EACH RUN ASSIGNED A "CHAR. SET", WHERE CHAMBER EFFECTS PARAMETER RECOMMENDATIONS ARE GIVEN.

PROGRAMS DEVELOPED TO EXTRACT DATA FROM FILES FOR MODELING, PREPARE SUMMARIES AND PLOTS OF PERFORMANCE RESULTS.

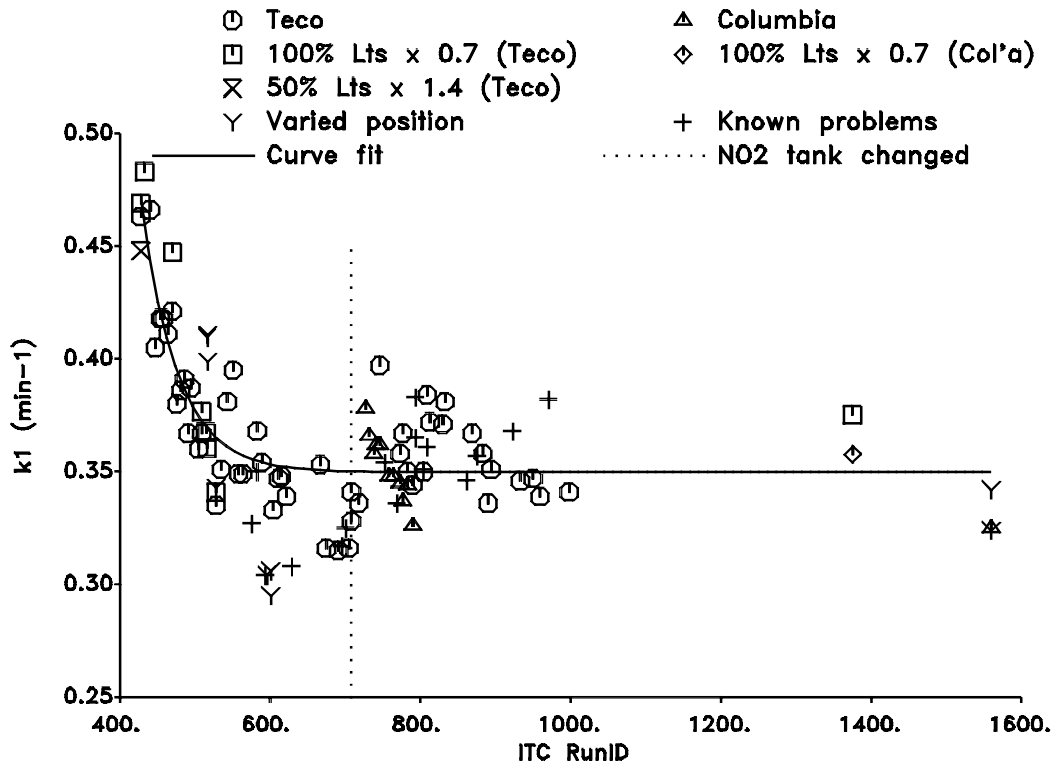
REPORT PREPARED DOCUMENTING EXPERIMENTS, METHODS, DATA BASE, AND CORRECTIONS MADE TO IT.

EXAMPLE OF RE-ASSIGNED CALIBRATION FACTORS: PROPENE "LOOP" ANALYSIS FROM 11/75 THROUGH 2/77

PROPENE Loop Calibration (DMS-1)

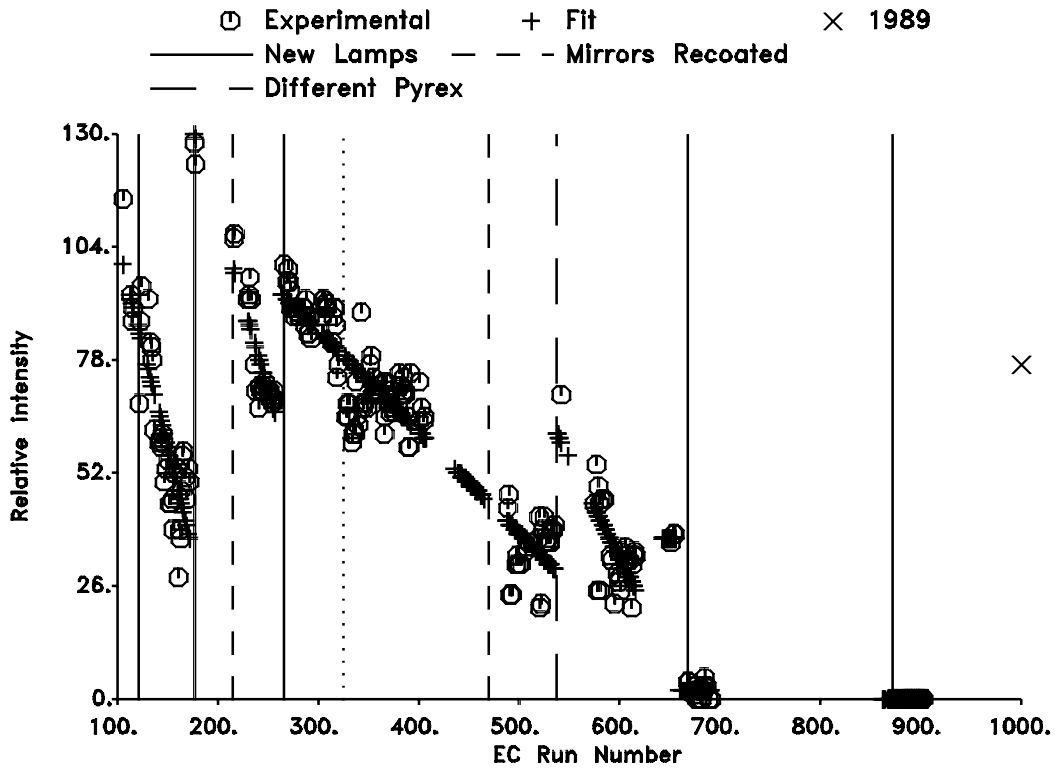


EXPERIMENTAL AND ASSIGNED NO₂ PHOTOLYSIS RATES FOR THE ITC

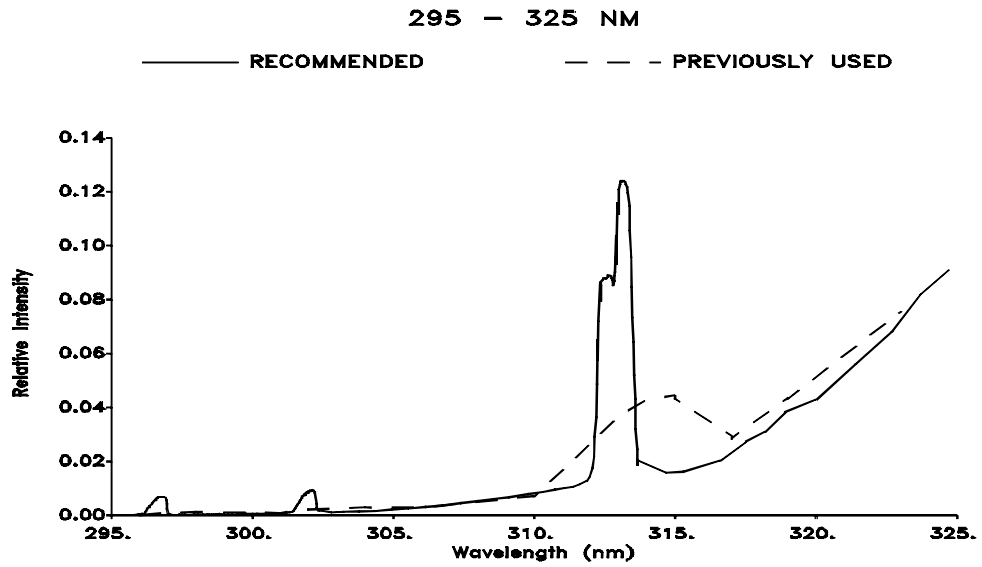
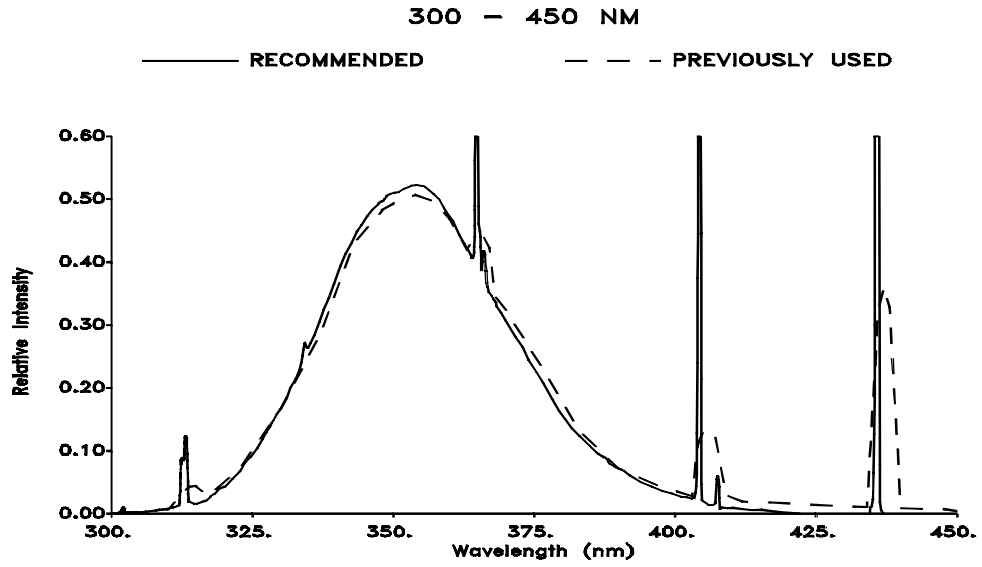


$$\text{Assigned } k_1 = 0.351 \times (1 + e^{-0.0023 (\text{RunID}-385.1)})$$

CHANGE IN RELATIVE 310 NM INTENSITY OF EC SOLAR SIMULATOR WITH TIME (NORMALIZED TO GIVE 1000 AT 380 NM)



PREVIOUS AND RECOMMENDED BLACKLIGHT SPECTRA IN SELECTED WAVELENGTH REGIONS



**EFFECT OF MODIFIED BLACKLIGHT SPECTRUM
ON REPRESENTATIVE PHOTOLYSIS RATES**
(FOR $K_1 = 0.3 \text{ MIN}^{-1}$)

REACTION	PHOTOLYSIS RATE (MIN^{-1})		
	OLD	NEW	CHANGE
HCHO \rightarrow radicals	5.90×10^{-4}	5.22×10^{-4}	-12%
NO ₂ \rightarrow NO + O	3.00×10^{-1}	3.00×10^{-1}	[a]
Methyl Glyoxal \rightarrow	7.34×10^{-4}	7.50×10^{-4}	2%
H ₂ O ₂ \rightarrow 2 OH	2.25×10^{-4}	2.29×10^{-4}	2%
HNO ₃ \rightarrow OH + NO ₂	6.86×10^{-6}	7.37×10^{-6}	7%
O ₃ \rightarrow O ¹ D	3.05×10^{-4}	3.99×10^{-4}	27%
NO ₃ \rightarrow NO ₂ + O	9.25×10^{-3}	1.02×10^{-1}	167%

[a] SET AT 0.3 MIN^{-1} FOR BOTH.

EXAMPLES OF DATA FILES INCLUDED WITH SAPRC ENVIRONMENTAL CHAMBER DATA BASE

runid.CHA: INDIVIDUAL RUN FILE. RUN-SPECIFIC DATA, COMMENTS, MODEL INPUT, ETC.

chamid-USE.XLS, chamidK1.XLS: SPREADSHEETS CONTAINING SUMMARY DATA FOR ALL RUNS AND ACTINOMETRY EXPERIMENTS IN A CHAMBER.

cham-nn.CHR: CHAMBER-DEPENDENT MODEL INPUT PARAMETERS FOR A CHARACTERIZATION SET.

chamUSE.INS: SUMMARY OF ALL TYPES OF MEASUREMENT DATA FOR RUNS IN A CHAMBER.

instid.CAL: AVAILABLE RELEVANT CALIBRATION DATA FOR AN INSTRUMENT

PGMS*.EXE: PROGRAMS FOR DATA CONVERSION AND EXAMPLE MODEL SIMULATIONS.

MECH\SAPRC90*.*, \MECH\CB4*.*: MECHANISM FILES FOR SIMULATING RUNS USING THE SAPRC-90 OR THE UAM 6.21 VERSION OF THE CB4 MECHANISM.

INSTALL2.BAT: INSTALLS FILES AND PROGRAMS ON A PC-COMPATIBLE COMPUTER.

EXAMPLE2.BAT: DOES EXAMPLE MODEL SIMULATIONS.

EXAMPLE CONTENTS OF A RUN DATA FILE

```
FILE      ,DTC064
TITLE    , "HIGH NOx SURROGATE + ACETONE (B)      "
UPDATED  ,08/21/94 (20:32)
SIDES    2
((more run parameters))

INST     , 10
1140    , "D-1140 " , "DASIBI O3 MONITOR; ID:1140      "
((more instrument descriptions))
1540    , "TECO-42 " , "TECO MODEL 42 NO-NO2-NOX ANALYZER      "

CHAN     , 4
NAME    , "O3      " , "NO      " , "NO2-UNC " , "NOX-UNC " ,
INST    , , 1140    , , 1540    , , 1540    , , 1540    ,
SIDE    , , 1      , , 1      , , 1      , , 1      ,
PRIORY  , , 1      , , 1      , , 1      , , 1      ,
STATUS  , , OK     , , OK     , , OK     , , OK     ,
DATA    , 27, 1
815    , , -0.006622 , , 0.003596 , , -0.002085 , , -0.001534 ,
825    , , 0.002223  , , 0.002926 , , -0.002711 , , -0.002674 ,
845    , , 0.001176  , , 0.1277   , , -0.003413 , , 0.1213   ,
((more channel data))
1645   , , 0.3502   , , -0.001572 , , -0.002401 , , -0.002423 ,
CALFAC , , 1.032   , , 1.038   , , 1.038   , , 1.038   ,
ZERCOR , , 0.0     , , -0.006000 , , 0.0     , , 0.0     ,
((more channel parameters))
ENDCHAN
((data and parameters for additional channels))

AUX_DATA , "M-XYLENE" , 2600 , 1 , 4
INIT     , 0.07689 , COMPUT
I-CAL.F  , 5.515E-6 , ORIG
CAL.F    , 5.040E-6 , CALFIL
U-CAL.F  , 2.690E-7 , CALFIL
((more auxiliary channel data))

COMMENTS
((comments from log book))
ENDCOMMENTS

NOTES
.,O3 Calibration factors updated from .CAL files 2/15/94
.,NOx Calibration factors updated from .CAL files 2/17/94
.,Assign k1= 0.3880 Average w/o highest, lowest. 6/2/94.
((other notes))
```

**EXPERIMENTS USED IN ASSESSMENT OF
EFFECTS OF CHAMBER AND LIGHT SOURCE
ON MECHANISM EVALUATION RESULTS**

RUN TYPE	EC	ITC	ITC2¹	XTC	OTC²
N-BUTANE	7	4	4	2	6
FORMALDEHYDE	4		2	3	2
ACETALDEHYDE	2		2	2	4
ETHENE	6	3	17 ³	3	7
PROPENE	5	13 ⁴	10 ⁴	4 ⁴	6 ⁴
TOLUENE	9 ⁵	2 ⁵	2	1	6
M-XYLENE	2 ⁵	1 ⁵	3	1	4
1,3,4-TM BENZENE	2 ⁵	3 ⁵		1	
MINI-SURROGATES			27 ³	1	
FULL SURROGATES	10	18	33 ³	1	7

¹ ETC and XTC (DRY TEFLON CHAMBERS, BLACKLIGHTS)

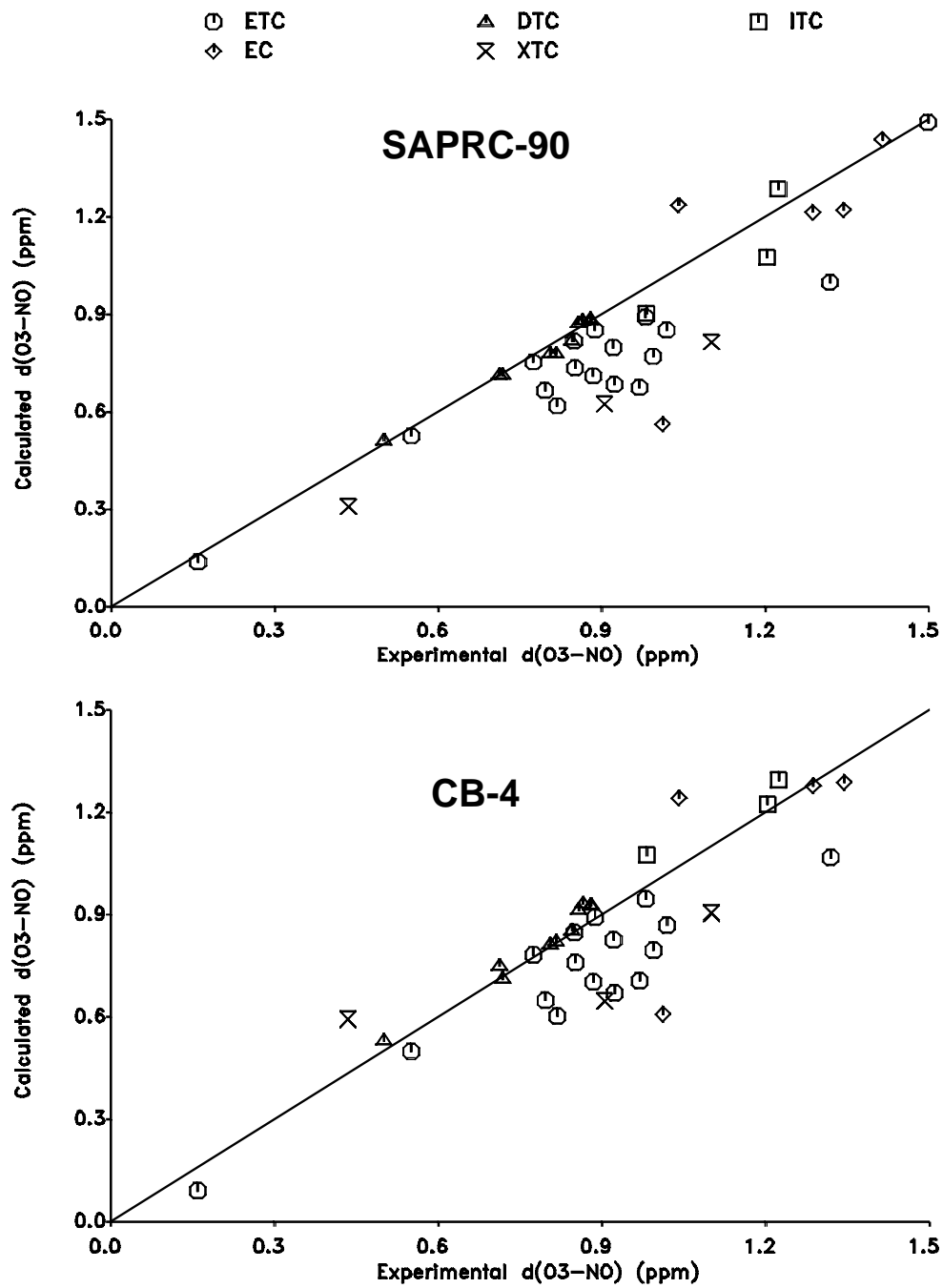
² NEW OTC. NOT CURRENTLY IN DISTRIBUTED DATA BASE.

³ MOST ARE REPLICATE "BASE CASE" REACTIVITY RUNS.

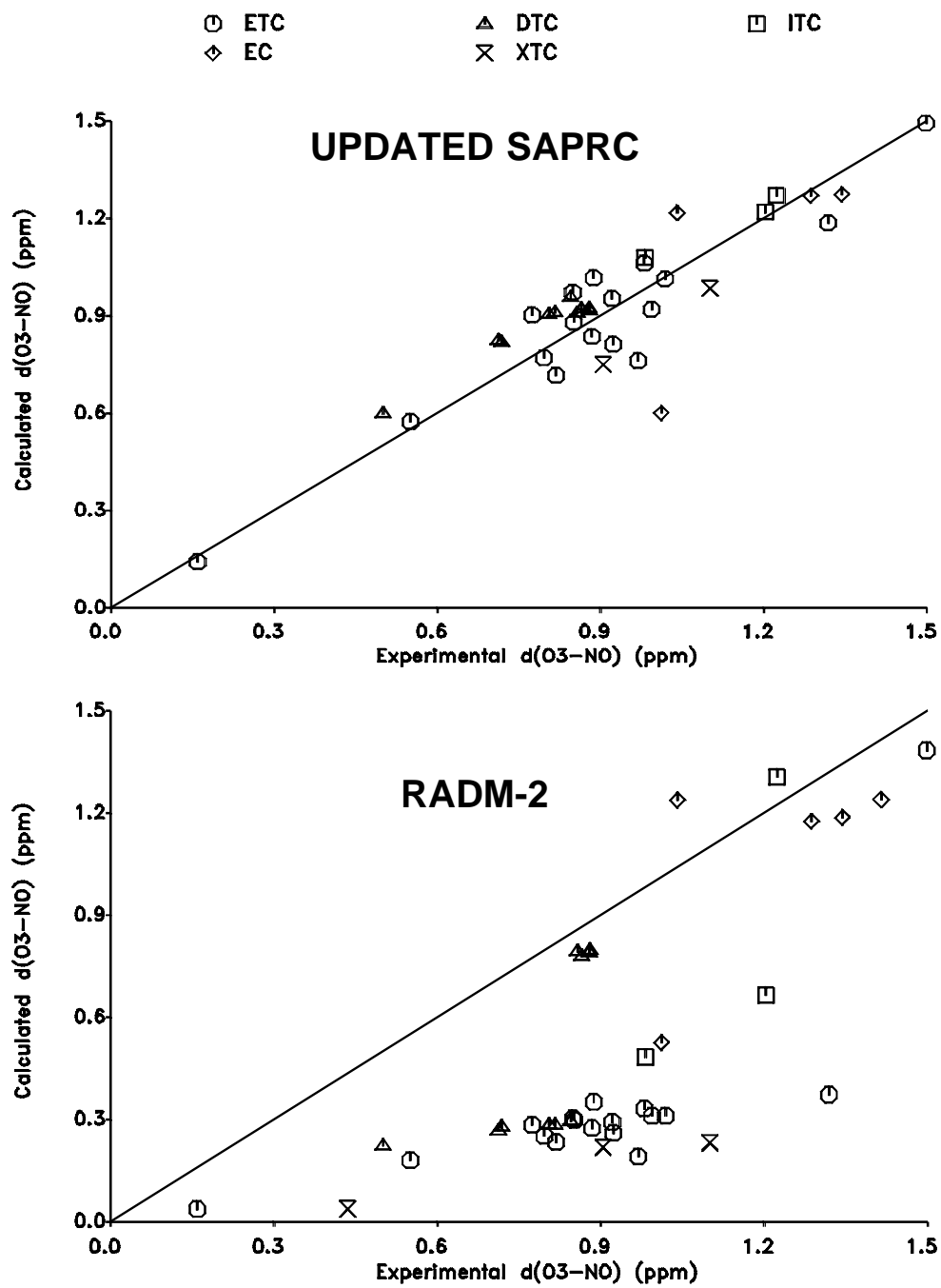
⁴ MOST ARE REPLICATE "STANDARD PROPENE" RUNS.

⁵ USED IN DEVELOPMENT OF SAPRC-90 MECHANISM.

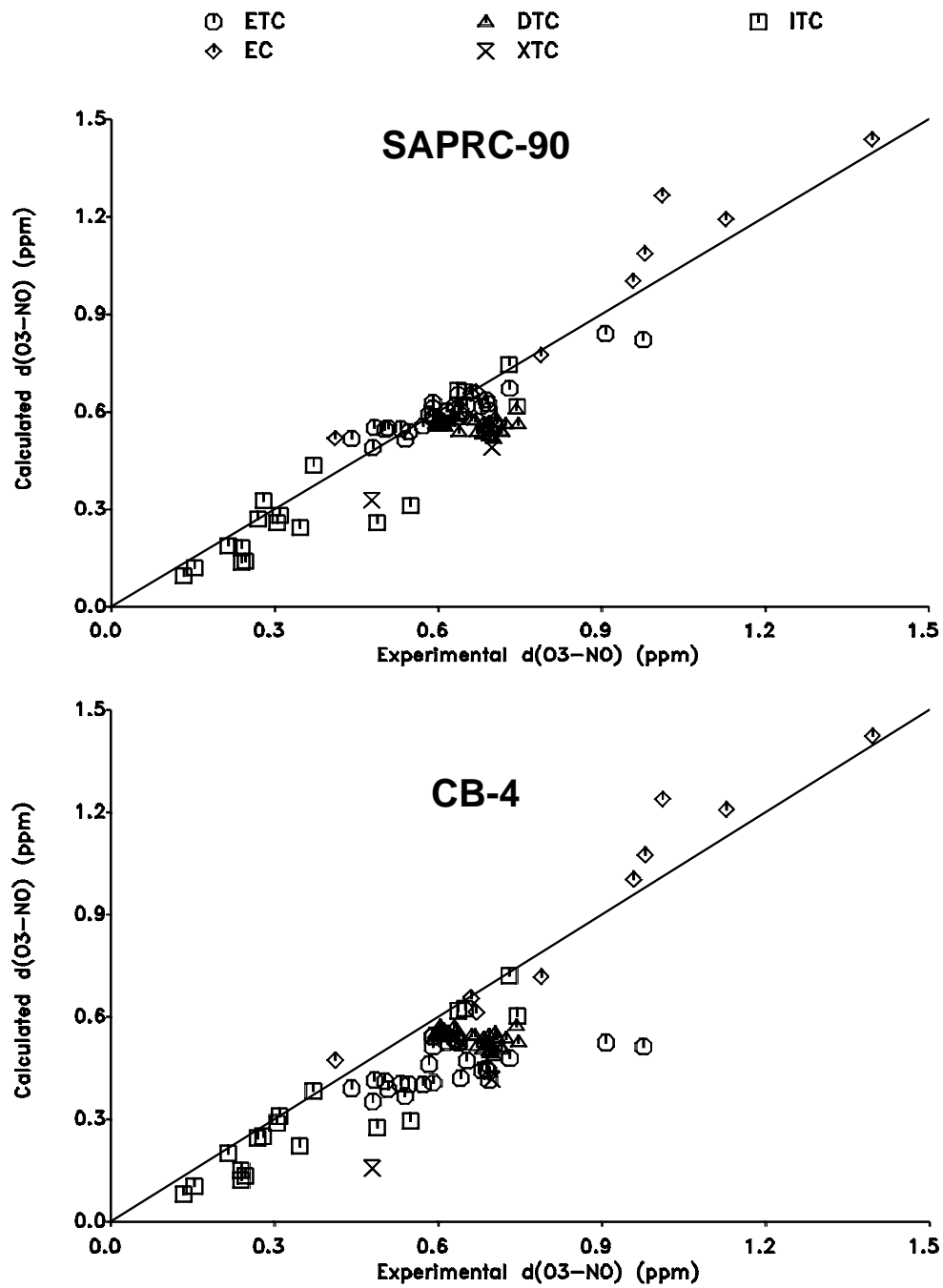
RESULTS OF MODEL SIMULATIONS OF MAXIMUM OZONE IN ETHENE - NO_x CHAMBER EXPERIMENTS



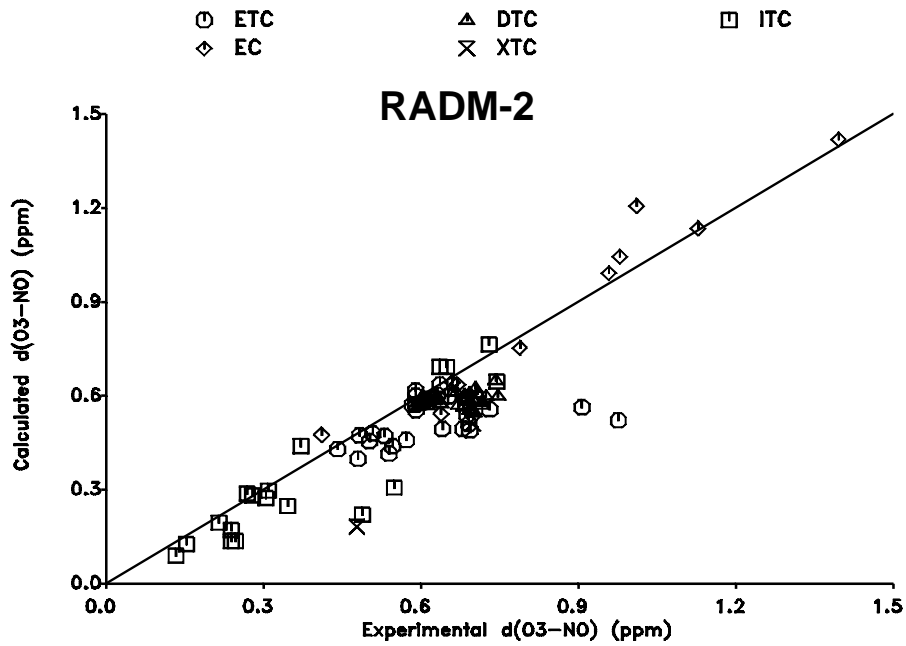
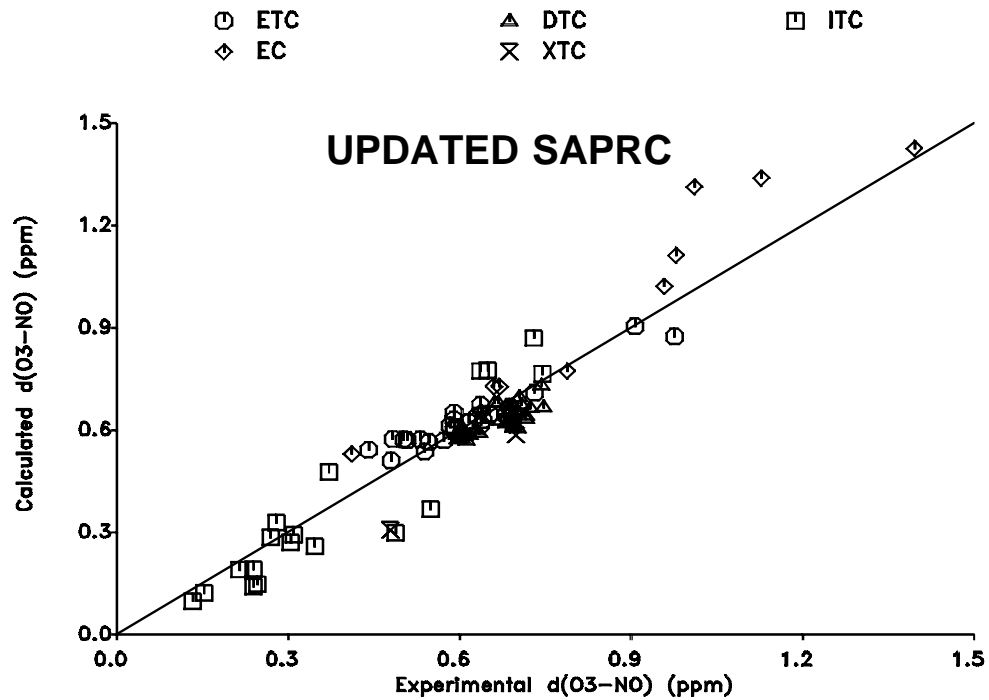
RESULTS OF MODEL SIMULATIONS OF MAXIMUM OZONE IN ETHENE - NO_x CHAMBER EXPERIMENTS



RESULTS OF MODEL SIMULATIONS OF MAXIMUM OZONE IN MIXTURE - NO_x CHAMBER EXPERIMENTS

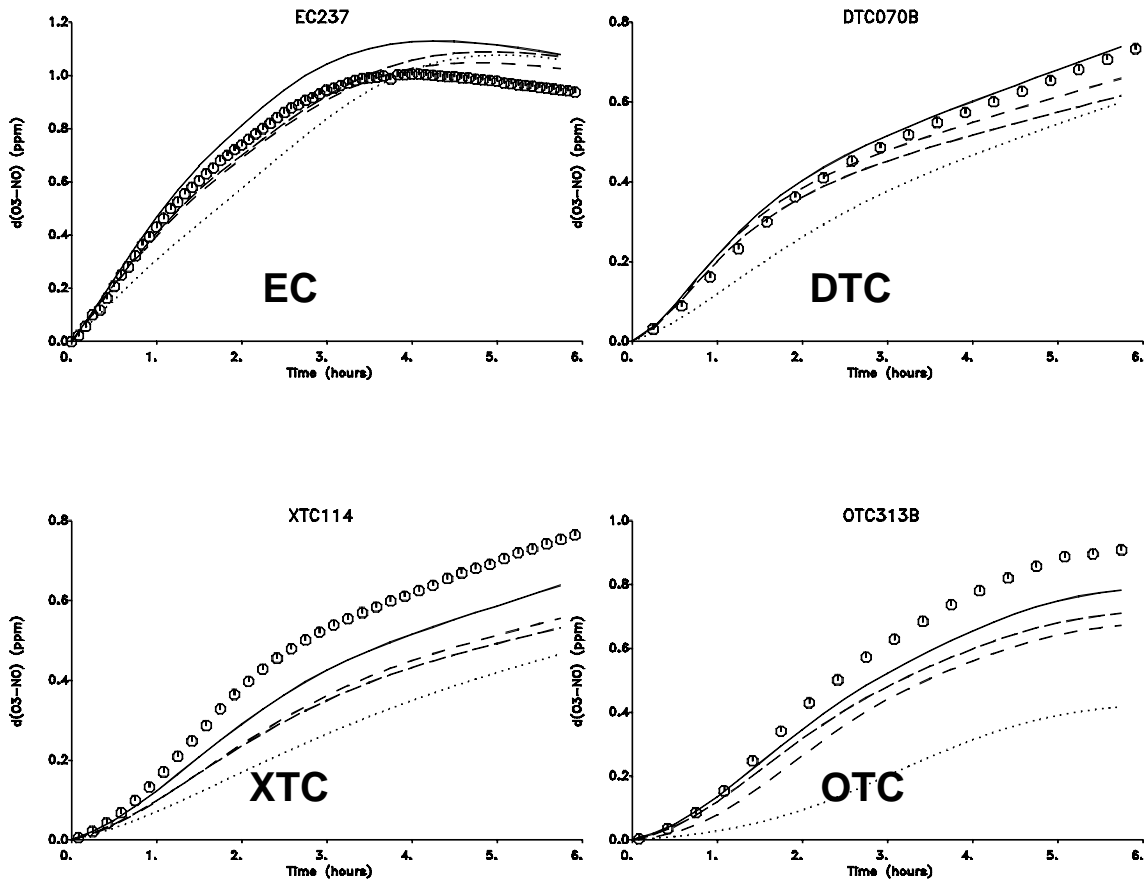


RESULTS OF MODEL SIMULATIONS OF MAXIMUM OZONE IN MIXTURE - NO_x CHAMBER EXPERIMENTS

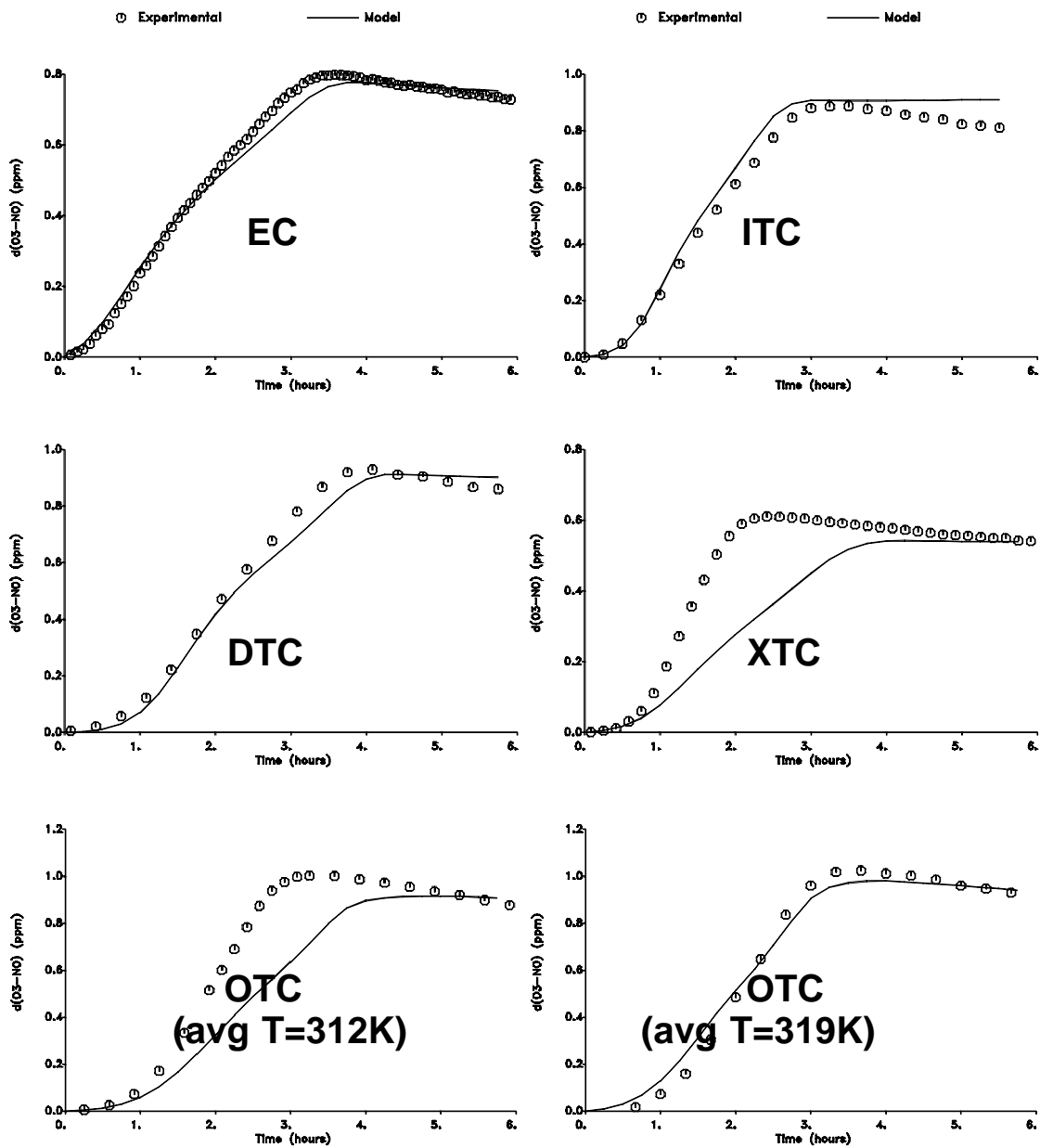


MODEL SIMULATIONS OF $\Delta([O_3]-[NO])$ FOR SELECTED SAPRC MIXTURE RUNS

- Experimental
- Updated SAPRC
- - - SAPRC-90 Calc
- · - · - · RADM Calc
- CB4 Calc

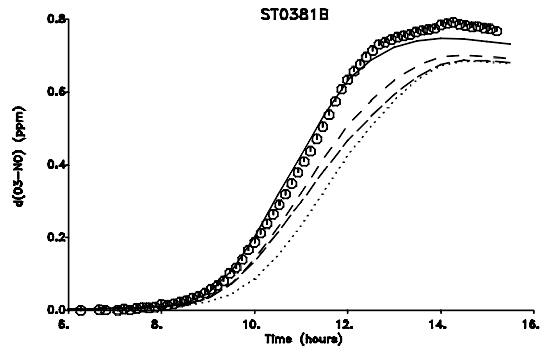
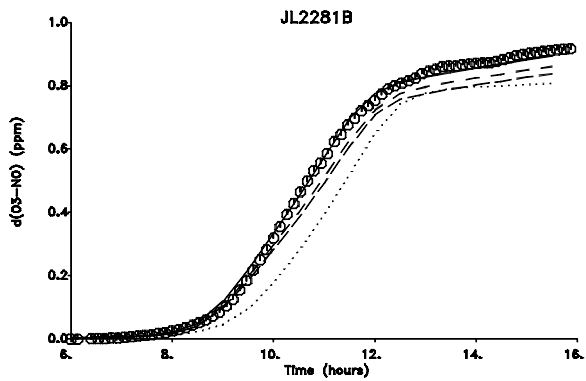
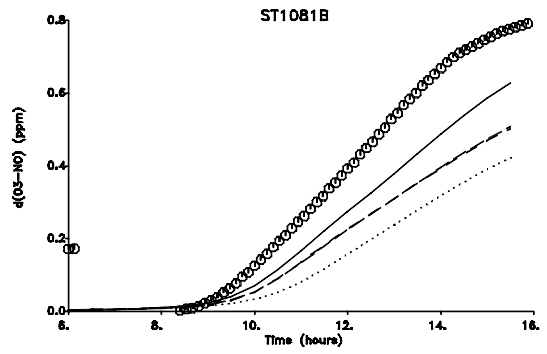
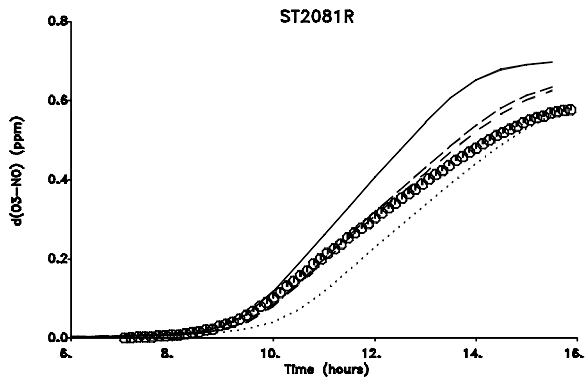


EFFECT OF CHAMBER ON SIMULATIONS OF TOLUENE - NO_x EXPERIMENTS USING THE UPDATED MECHANISM



MODEL SIMULATIONS OF $\Delta([O_3]-[NO])$ FOR SELECTED UNC MIXTURE RUNS

- Experimental
- Updated SAPRC
- - - SAPRC-90 Calc
- - - RADM Calc
- CB4 Calc



HOW TO GET SAPRC CHAMBER DATA BASE

CHAMBER DOCUMENTATION

- LIMITED NUMBER OF COPIES AVAILABLE FROM WILLIAM P. L. CARTER, CE-CERT, UCR
- COPIES AVAILABLE FROM EPA/AREAL UPON REQUEST
- WILL BE AVAILABLE FROM NTIS AS EPA REPORT
- DOCUMENTATION FILES (IN PORTABLE DOCUMENT FORMAT) INCLUDED WITH CHAMBER DATA ON INTERNET (SEE BELOW)

CHAMBER DATA AND EXAMPLE PROGRAMS AND FILES

- AVAILABLE VIA ANONYMOUS FTP ON INTERNET
- | <u>INTERNET ADDRESS</u> | <u>DIRECTORY</u> |
|-------------------------|-------------------|
| CERT.UCR.EDU | pub/carter/chdata |
| CARTERPC.UCR.EDU | chdata |
- DISKETTES AVAILABLE FROM EPA UPON REQUEST

PROGRAM SOURCE FILES, OTHER SAPRC MODELING SOFTWARE AND MECHANISM FILES

- AVAILABLE VIA ANONYMOUS FTP ON INTERNET
- | <u>INTERNET ADDRESS</u> | <u>DIRECTORY</u> |
|-------------------------|------------------|
| CERT.UCR.EDU | pub/carter/model |
| CARTERPC.UCR.EDU | model |
- DISKETTES AVAILABLE FROM EPA UPON REQUEST