

MEASUREMENTS AND MODELING OF NO_x OFFGASING FROM FEP TEFLON CHAMBERS

MAJOR OBJECTIVE OF THE NEW CHAMBER PROGRAM AT UCR IS TO CONDUCT MODEL EVALUATION EXPERIMENTS AT LOW NO_x

NO_x OFFGASING LIMITS HOW LOW NO_x CAN BE REDUCED, AND MAKES MECHANISM EVALUATION MORE UNCERTAIN

NO_x OFFGASING AS HONO COULD ACCOUNT FOR THE CHAMBER RADICAL SOURCE

RESULTS OF A PRELIMINARY ANALYSIS OF PREVIOUS AND NEW DATA CONCERNING THIS PROBLEM ARE SUMMARIZED

TYPES OF CHARACTERIZATION EXPERIMENTS

NO_x OFFGASING CAN BE EVALUATED BY

- MEASURING NO_x BUILDUP IN THE DARK
- MODELING PURE AIR IRRADIATIONS
- MODELING ALDEHYDE - AIR IRRADIATIONS
- MODELING CO - AIR IRRADIATIONS

CHAMBER RADICAL SOURCE CAN BE EVALUATED BY

- MODELING CO - NO_x OR N-BUTANE - NO_x EXPERIMENTS

WALL MODEL EMPLOYED

NO_x OFFGASING AND CHAMBER RADICAL SOURCE REPRESENTED BY CONTINUOUS HONO INPUT

INITIAL HONO OR NO₂ ADDED AS NEEDED TO FIT O₃ AND NO_x DATA

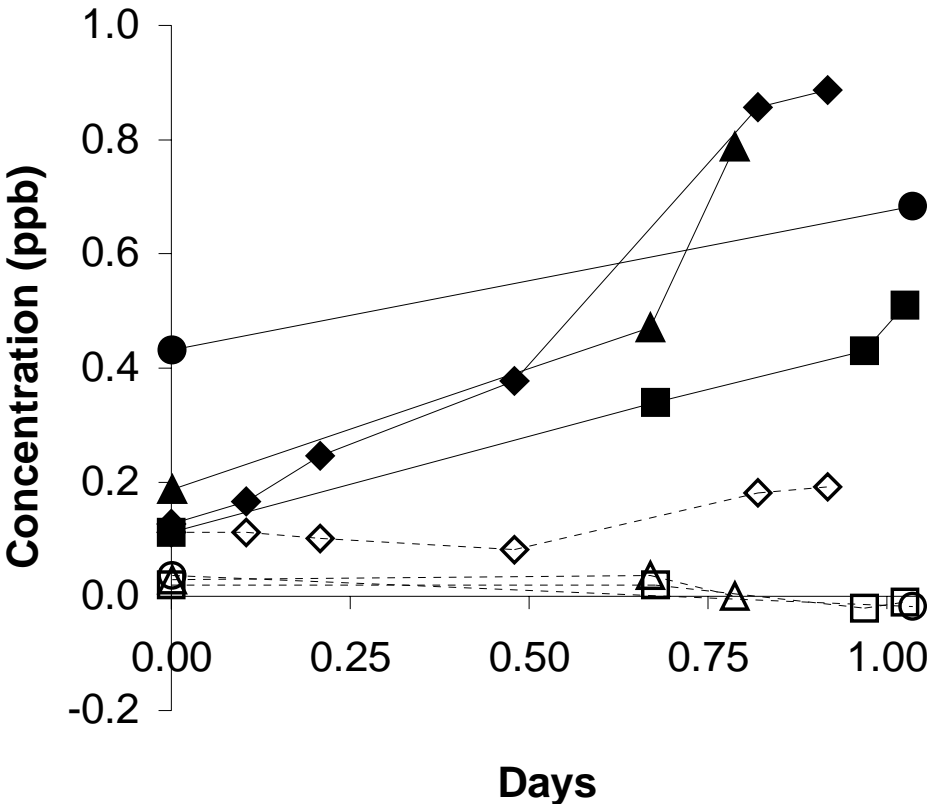
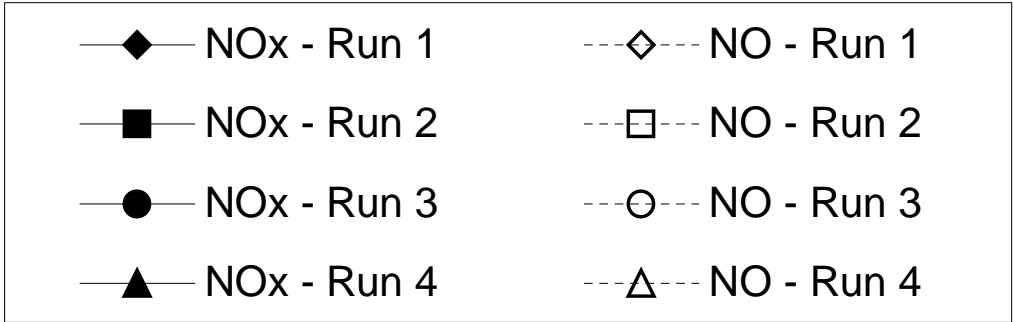
O₃ WALL DECAY RATES AS APPROPRIATE FOR TEFLON BAG CHAMBERS OR EC

RAPID HNO₃ WALL DECAY RATE (12% HOUR⁻¹) ASSUMED FOR ALL CHAMBERS (UNCERTAIN)

CHAMBERS EXAMINED

CHAM	SURFACE	CLEANING	RH
THIS WORK	NEW FEP TEFLON FILM. WIPED WITH H ₂ O	NO _x NEVER INJECTED. REACTOR INSIDE BAG FLUSHED WITH CLEAN AIR	DRY
TVA	WELL-USED FEP TEFLON PANELS	FLUSHED WITH LIGHTS ON FOR 2 DAYS BETWEEN LOW NO _x RUNS	20%
DTC	WELL-USED FEP TEFLON FILM	FLUSHED BETWEEN RUNS	DRY
EC	TEFLON COATED METAL, QUARTZ	EVACUATED BETWEEN RUNS	50%

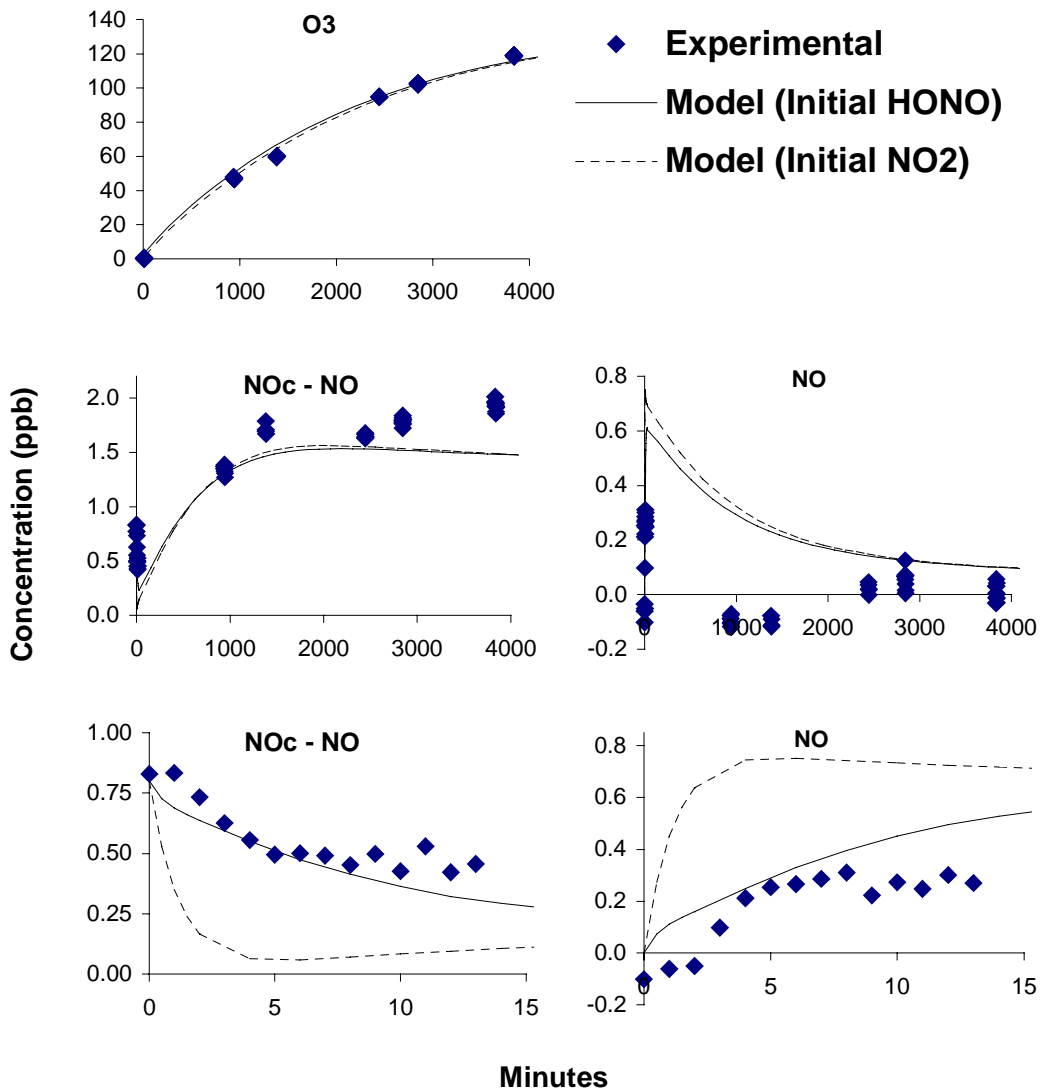
MEASUREMENTS OF DARK NO_x OFFGASING IN NEW TEFLON REACTOR



AVG. NO_x INPUT RATE IS 0.02 PPB HOUR⁻¹

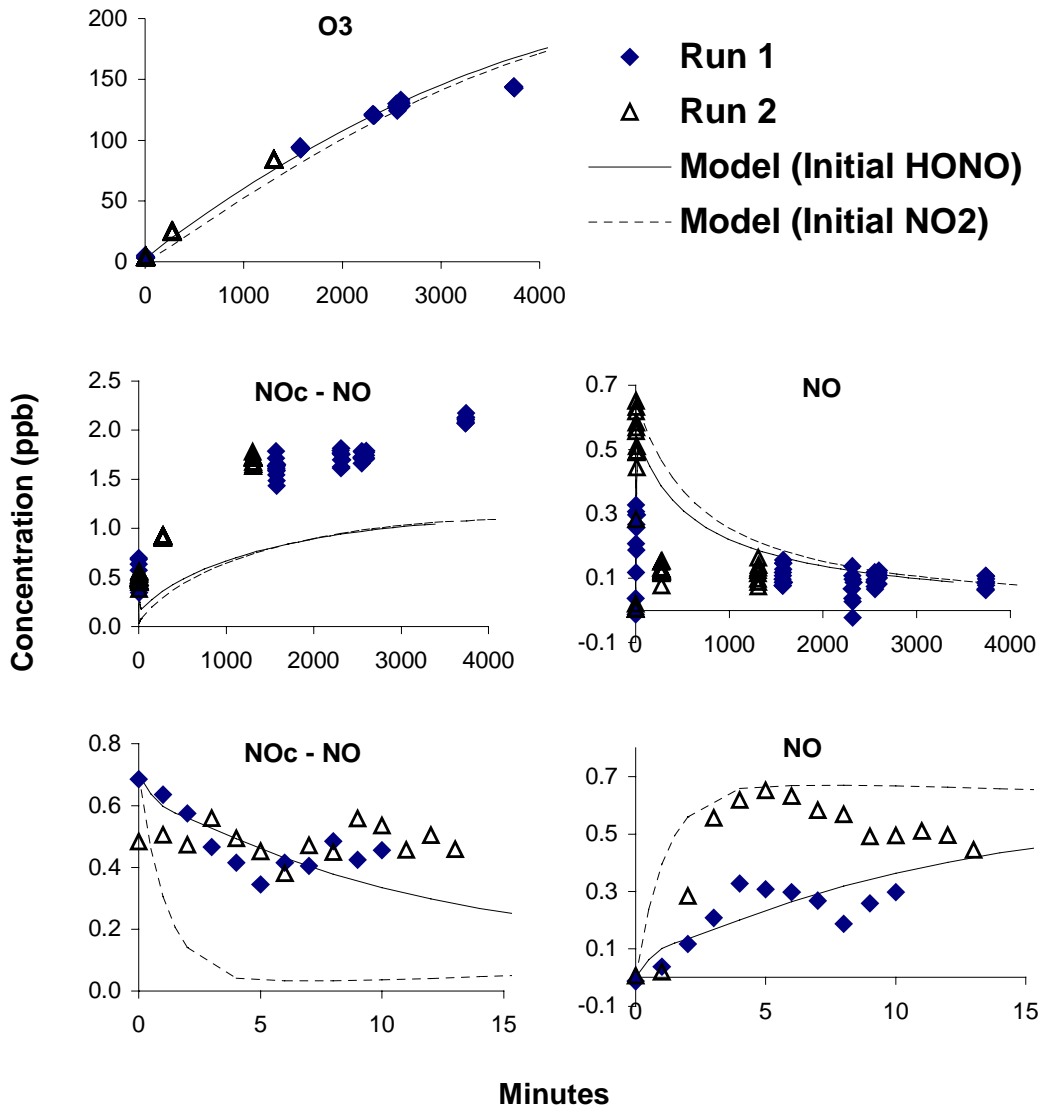
PURE AIR IRRADIATION IN NEW REACTOR

FIT USING INITIAL HONO OR NO₂ = 0.8 PPB,
HONO INPUT = 0.1 PPB HOUR⁻¹

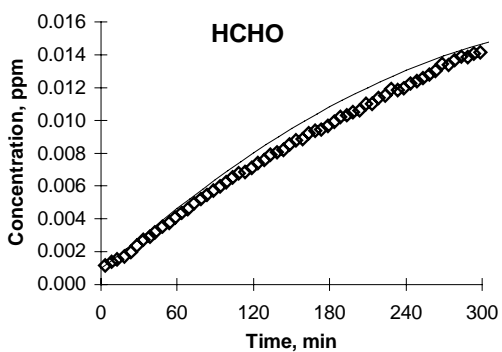
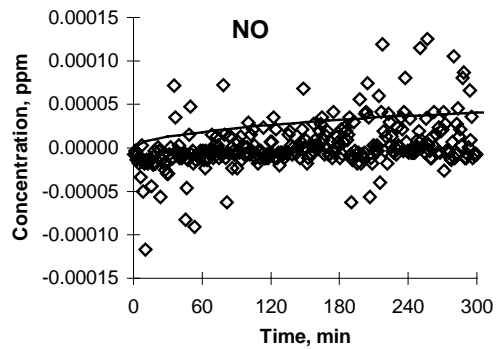
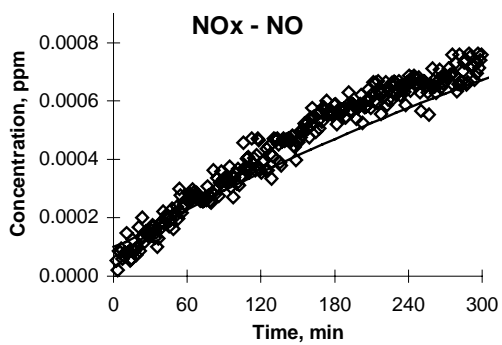
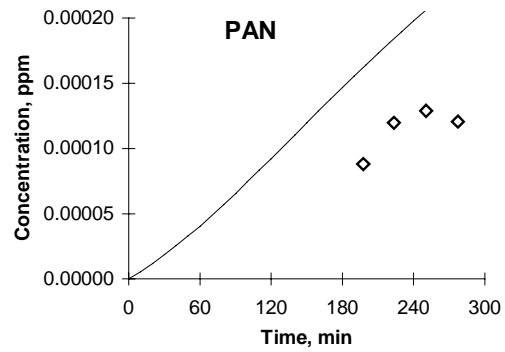
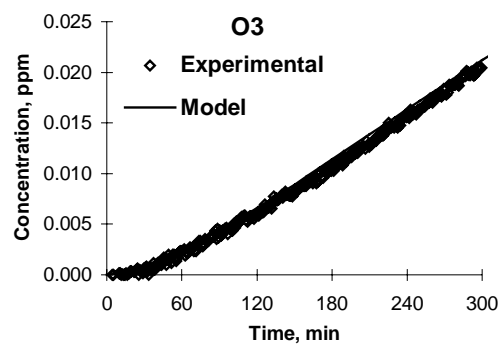


CO - AIR RUNS IN NEW REACTOR

CALCULATION USES INITIAL HONO OR NO₂ = 0.7 PPB, HONO INPUT = 0.02 PPB HOUR⁻¹



**EXPERIMENTAL AND MODEL SIMULATION RESULTS OF
TVA ACETALDEHYDE - AIR RUN 6/11/96
Model Uses HONO Input Rate = 0.26 ppb / hour**



SUMMARY OF MODELING RESULTS OF NO_x
OFFGASING AND RADICAL SOURCE RUNS

Run	Type	Light Intensity (k ₁ , min ⁻¹)	HONO Input (ppb/hr)
<u>Clean, Unused Reactor (FEP Teflon film)</u>			
Average for Dark Experiments (NO _x input)			0.02
9/13 - 9/17	Pure Air	0.8	0.10
9/17 - 9/21	CO - Air	0.8	0.02
9/28 - 9/30	CO - Air	0.8	0.02
<u>TVA Chamber (Low NO_x Studies) (FEP Teflon film)</u>			
9/22/95	Acetald - Air	0.4	0.09
6/11/96	Acetald - Air	0.4	0.16
6/19/96	n-Butane - NO _x	0.4	0.9
<u>DTC (Well-used chamber) (FEP Teflon film)</u>			
DTC764	Acetald - Air	0.2	0.4
Various	n-Butane - NO _x	0.2	0.4 - 1.0
<u>EC (Teflon coated aluminum with Quartz Windows)</u>			
EC253	Acetald - Air	0.3	5
Various	n-Butane - NO _x	Consistent with above.	

CONCLUSIONS

NEW TEFLON FILM HAS NON-NEGLIGIBLE
NO_x OFFGASING

MINIMUM OFFGASING RATE IS 0.5 PPB/DAY

NO_x OFFGASING RATE IN LIGHT NOT
ALWAYS HIGHER THAN IN DARK

INDIRECT EVIDENCE THAT MOST OF THE
OFFGASED NO_x IS HONO

OFFGASING RATES HIGHER IN WELL-USED
CHAMBERS

FLUSHING PROCEDURE USED WITH TVA
CHAMBER REDUCES OFFGASING, BUT NOT
TO NEW REACTOR LEVELS

NO_x OFFGASING IN SAPRC EC MUCH
HIGHER THAN IN TEFLON CHAMBERS

NEAR TERM WORK PLANNED

LUMINOL NO₂ ANALYZERS WILL BE USED TO MEASURE NO₂ DURING EXPERIMENTS

REPRODUCIBILITY AND POSSIBLE DECLINE OF NO_x OFFGASING WITH TIME BEING ASSESSED

HAVING DISCUSSIONS WITH DUPONT CO. ABOUT TEFLON FILM CHARACTERISTICS AND ALTERNATIVES

USE OF OTHER TYPES OF FILM BEING INVESTIGATED

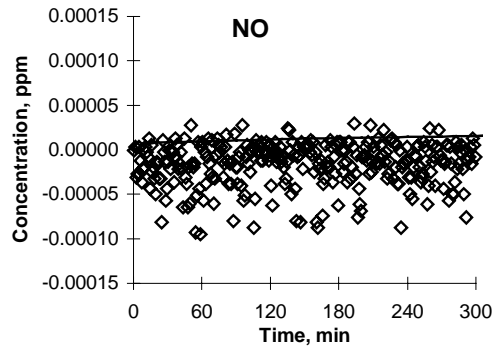
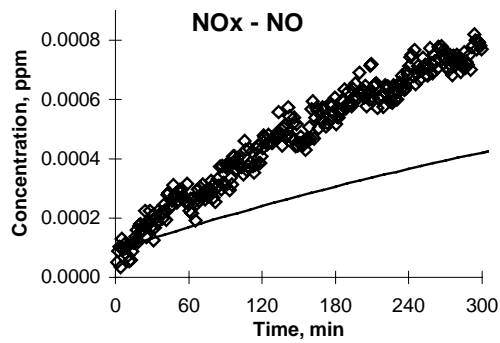
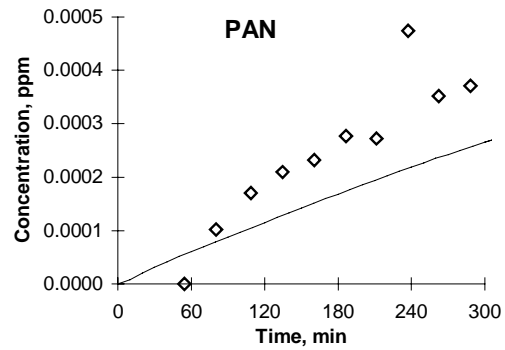
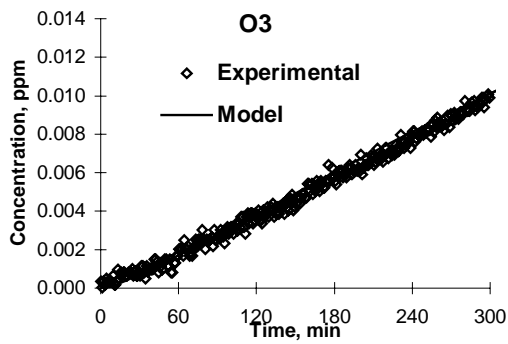
EFFECTS OF HEATING, OTHER TREATMENTS TO REMOVE NO_x SPECIES WILL BE INVESTIGATED

WILL ALSO STUDY EFFECTS OF VARYING:

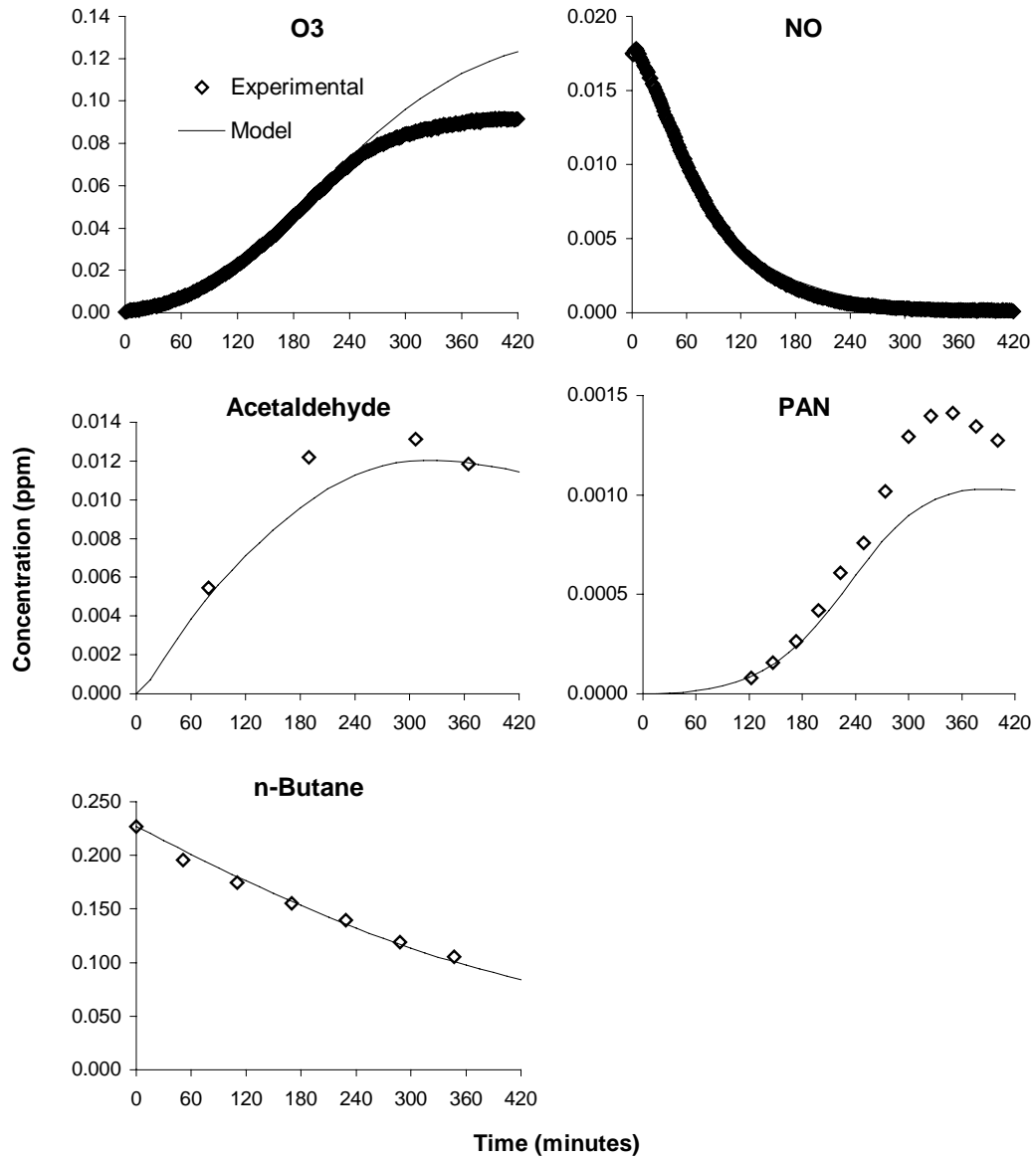
LIGHT INTENSITY	TEMPERATURE
HUMIDITY	EXPOSURE TO NO, NO ₂ , HNO ₃ , HONO

SUGGESTIONS ON **NEAR TERM** RESEARCH TO MINIMIZE OR CHARACTERIZE NO_x OFFGASING IS WELCOME!

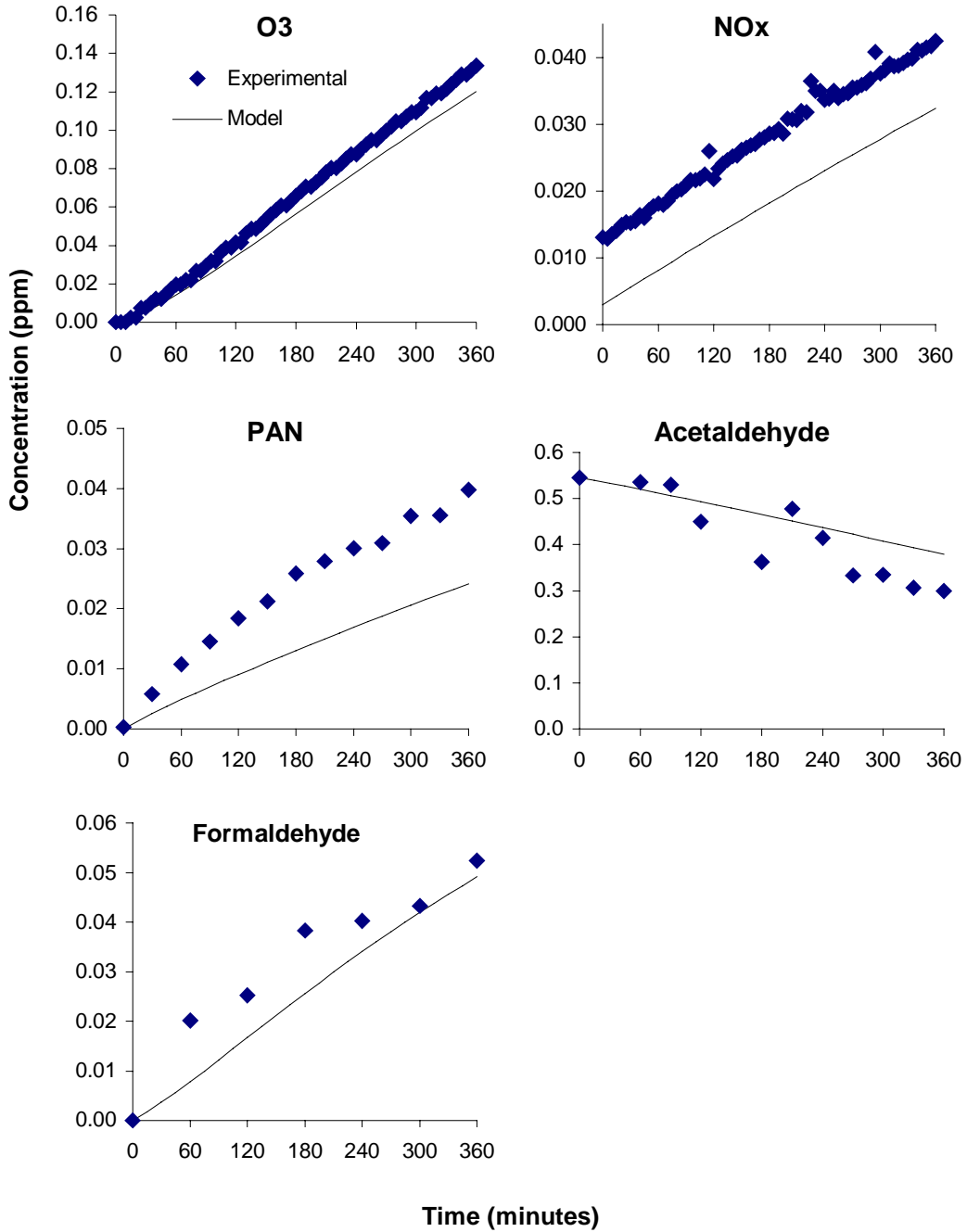
**EXPERIMENTAL AND MODEL SIMULATION RESULTS OF
TVA ACETALDEHYDE - AIR RUN 9/22/95
Model Uses HONO Input Rate = 0.09 ppb / hour**



**EXPERIMENTAL AND MODEL SIMULATION RESULTS OF
TVA N-BUTANE - NO_x RUN 6/19/95
Model Uses Radical Input Rate = 1 ppb / hour**



Acetaldehyde - Air Experiment EC253 Model Uses HONO Input Rate = 5.3 ppb / hour



ACETALDEHYDE - AIR EXPERIMENT DTC764

Fit with HONO Input Rate = $0.39 \text{ ppb hour}^{-1}$

