EXPERIMENTAL EVALUATION OF OZONE FORMING POTENTIALS OF MOTOR VEHICLE EMISSIONS

W. P. L. Carter, M. Smith, T. J. Truex
and J. M. Norbeck

College of Engineering, Center for Environmental Research and Technology
University of California, Riverside, CA 92521

OUTLINE

BACKGROUND AND OBJECTIVES

APPROACH AND RATIONALE

METHODS

VEHICLES AND FUELS STUDIED

RESULTS

CONCLUSIONS

BACKGROUND AND OBJECTIVES

THE OZONE IMPACTS OF VEHICLE EXHAUSTS CAN VARY DEPENDING ON THE FUEL, VEHICLE, AND OTHER FACTORS.

THE IMPACTS OF DIFFERENT EXHAUSTS ARE ASSESSED USING MODELS. THIS REQUIRES KNOWLEDGE OF:

- HOW MUCH NO_x AND VOCs ARE IN THE EXHAUST
- THE TYPES AND RELATIVE AMOUNTS OF VOC SPECIES IN THE EXHAUST
- THE RELEVANT ATMOSPHERIC REACTIONS OF THESE SPECIES.

RELYING ON THESE ASSESSMENTS REQUIRE ASSUMING THAT

- ALL THE RELEVANT SPECIES HAVE BEEN IDENTIFIED AND QUANTIFIED
- THE MODEL CAN ACCURATELY PREDICT HOW THESE SPECIES AFFECT OZONE.

THE OBJECTIVES OF THIS PROJECT IS TO TEST THESE ASSUMPTIONS

OVERALL APPROACH

ENVIRONMENTAL CHAMBER EXPERIMENTS CARRIED OUT USING EXHAUSTS FROM VARIOUS FUEL-VEHICLE COMBINATIONS.

SPECIATION ANALYSES WERE CARRIED OUT FOR ALL EXHAUSTS STUDIED.

EXHAUST “SURROGATES” WERE PREPARED BASED ON RESULTS OF THESE ANALYSES.

“SURROGATE EXHAUST” EXPERIMENTS CARRIED OUT TO DUPLICATE THE ACTUAL EXHAUST EXPERIMENTS.

CONTROL AND CHARACTERIZATION EXPERIMENTS CARRIED OUT SO EXHAUST EXPERIMENTS COULD BE MODELED.

EXPERIMENTS MODELED USING THE SAPRC-97 AND SAPRC-99 MECHANISMS.

SEPARATE FTP TESTS PERFORMED ON MOST VEHICLES STUDIED.

RATIONALE FOR APPROACH

TESTS OF ACCURACY AND COMPLETENESS OF SPECIATION ANALYSIS PROVIDED BY

- COMPARISON OF “SURROGATE” AND ACTUAL EXHAUST EXPERIMENTS.
- ABILITY OF MODEL TO SIMULATE ACTUAL EXHAUST EXPERIMENTS

TESTS OF ABILITY OF MECHANISM TO SIMULATE O_3 IMPACTS OF EXHAUST COMPONENTS PROVIDED BY:

- ABILITY OF MODEL TO SIMULATE SURROGATE EXHAUST RUNS
- ABILITY OF MODEL TO SIMULATE ACTUAL EXHAUST RUNS

THIS APPROACH ALLOWS FOR SEPARATE TESTS OF THESE TWO FACTORS

METHODS

EXHAUST SAMPLING

VEHICLES PLACED ON CE-CERT 48” SINGLE-ROLL CHASSIS DYNAMOMETER WITH PIERBURG CVS AND ANALYTICAL SYSTEM

MOST SAMPLES TAKEN DURING COLD START MODE TO GET MOST SUFFICIENT QUANTITY OF VOC FOR CHAMBER TESTING

TYPICAL PROCEDURE:

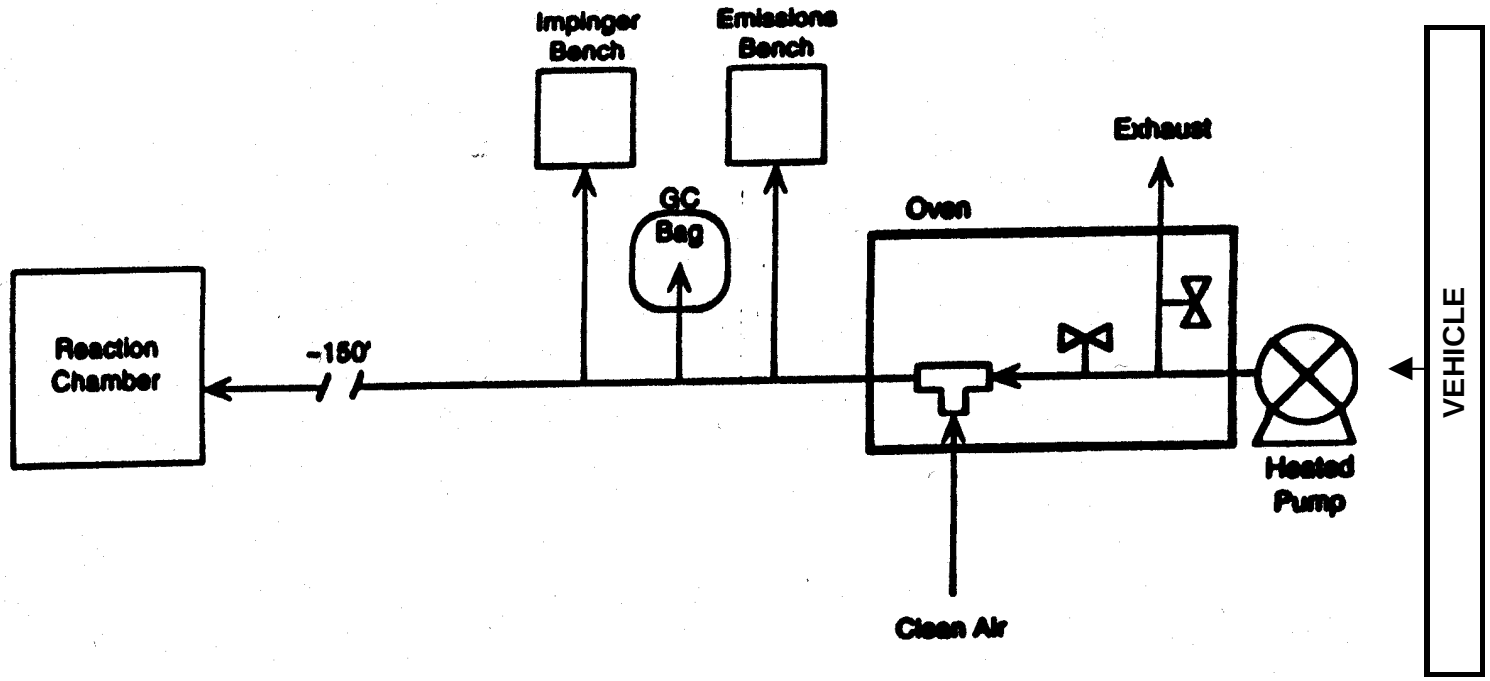
- ACCELERATE COLD TO 40 MPH
- SAMPLE FOR ~30 SECONDS ONCE STEADY-STATE OPERATION ACHIEVED.

TWO DIFFERENT PROCEDURES USED TO TRANSFER EXHAUST TO CHAMBER

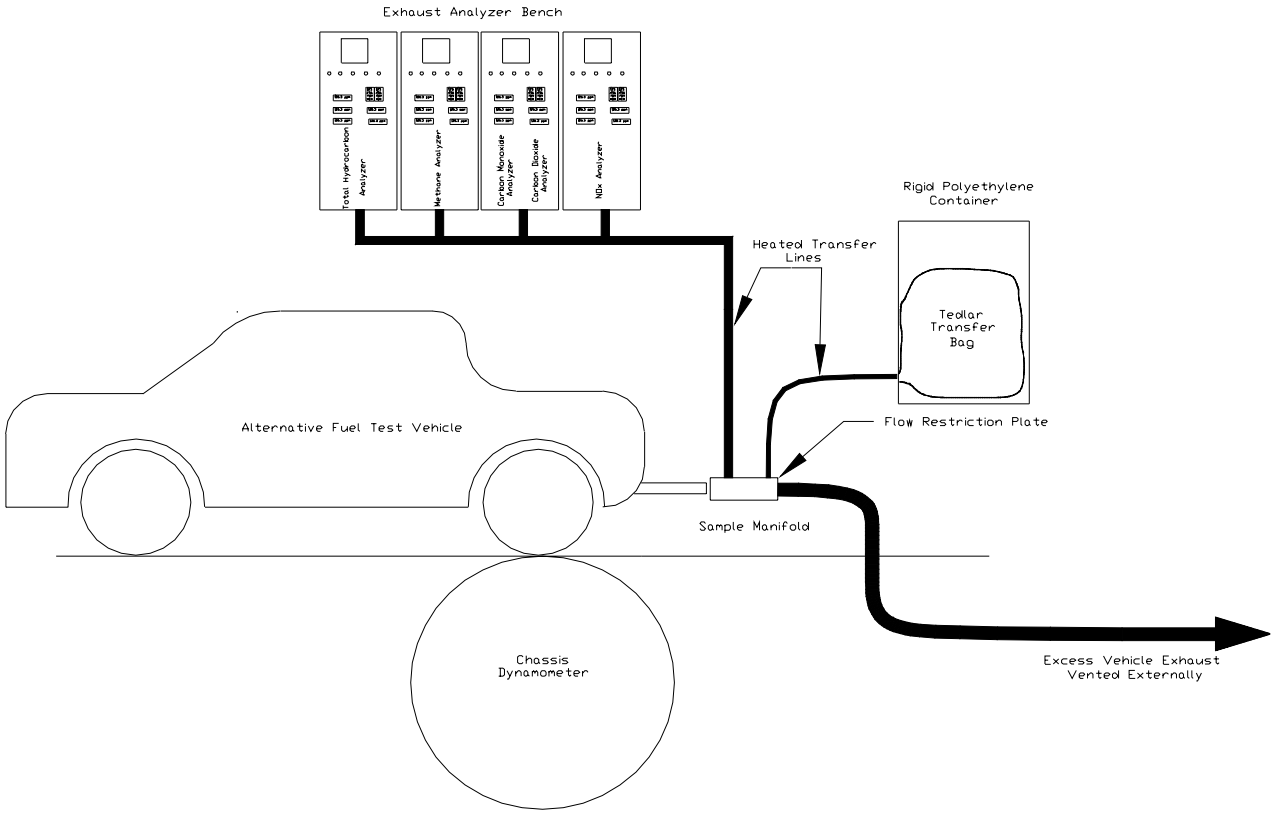
- INITIAL EXPERIMENTS: MINI-DILUTION SYSTEM USED TO DILUTE EXHAUST FOR TRANSFER VIA 0.5” TEFLON LINE
- MOST EXPERIMENTS: TRANSFER BAG USED BECAUSE OF EVIDENCE FOR HCHO LOSS IN TRANSFER LINES.

SAMPLES TAKEN FOR ANALYSIS IN VEHICLE EMISSIONS ANALYTICAL LABORATORY

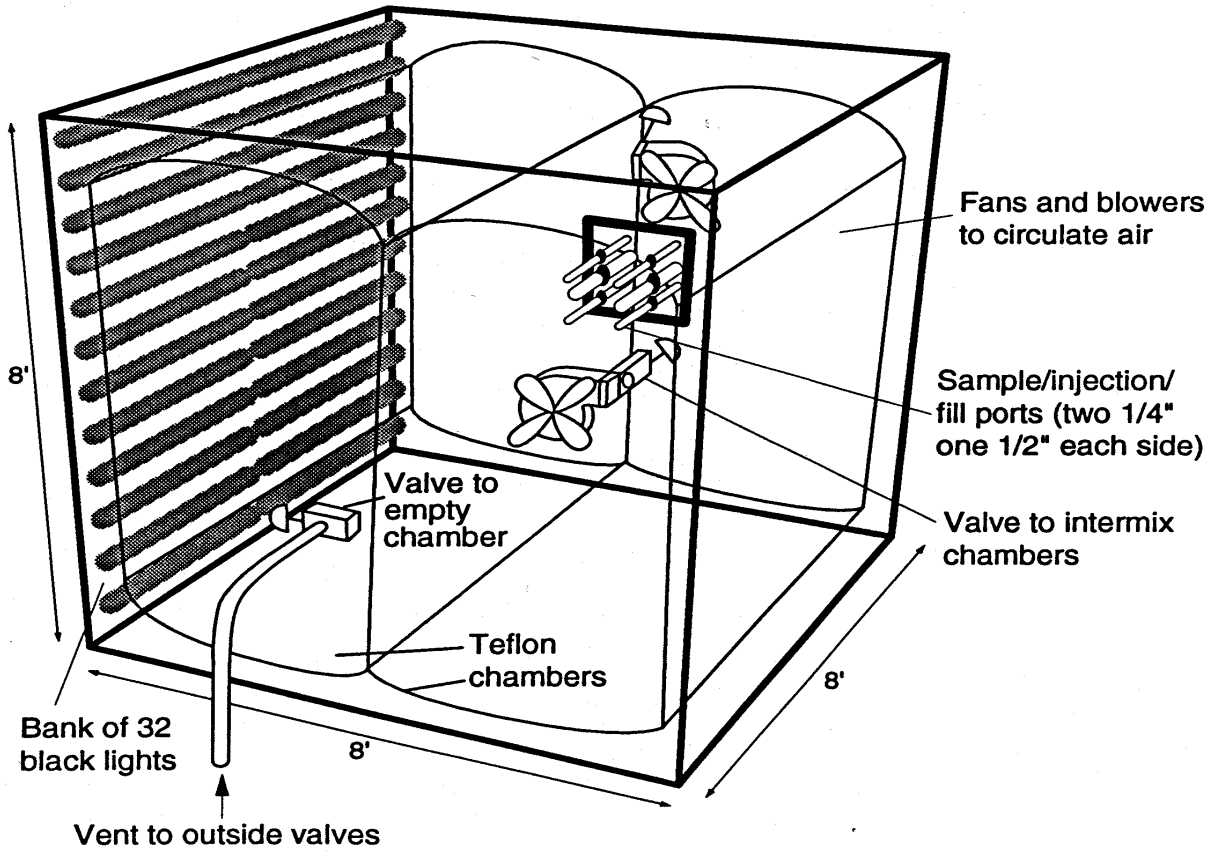
PHASE 1 SAMPLING SYSTEM



PHASE 2 SAMPLING SYSTEM



ENVIRONMENTAL CHAMBER



TYPES OF ENVIRONMENTAL CHAMBER EXPERIMENTS

EXHAUST ONLY EXPERIMENTS

- SIMPLEST TEST OF MODEL AND MOST STRAIGHTFORWARD PROCEDURE
- BUT VERY LITTLE O_3 FORMED FOR "CLEANER" VEHICLES

INCREMENTAL REACTIVITY EXPERIMENTS

- EXHAUST ADDED "ROG SURROGATE" - NO_x MIXTURES SIMULATING SMOG
- MORE REPRESENTATIVE OF AMBIENT CONDITIONS
- GET MEASURABLE O_3 IMPACTS EVEN FOR RELATIVELY "CLEAN" EXHAUSTS
- TWO DIFFERENT "ROG SURROGATES" USED FOR MECHANISM TESTING

EXHAUST + FORMALDEHYDE EXPERIMENTS

- USED IN SOME LPG EXPERIMENTS TO INCREASE REACTIVITY OF MIXTURE WITH CHEMICALLY SIMPLE SYSTEM

PROCEDURES FOR CHAMBER EXPERIMENTS

DUAL CHAMBER USED TO IRRADIATE TWO MIXTURES AT THE SAME TIME

EXHAUST-ONLY EXPERIMENTS:

- COMPLEX EXHAUSTS (E.G., RFG) ADDED TO BOTH REACTORS ("SIDES")
- SIMPLE EXHAUSTS (E.G., M100, CNG) ADDED TO ONE SIDE, SURROGATE EXHAUST TO OTHER

INCREMENTAL REACTIVITY EXPERIMENTS:

1. ROG SURROGATE MIXTURE ADDED TO BOTH SIDES
2. EXHAUST ADDED TO ONE SIDE
3. NO_x INJECTED SEPARATELY TO EACH SIDE SO NO_x ON EACH ARE THE SAME

SIX HOUR BLACKLIGHT IRRADIATIONS. NO_2 PHOTOLYSIS RATE ~0.2 - 0.25 MIN^{-1}

ANALYTICAL METHODS

VEHICLE EMISSIONS RESEARCH ANALYTICAL LABORATORY

PIERBURG CVS AND ANALYTICAL SYSTEM USED TO MEASURE NO_x, CO, CH_4, CO_2, AND THC DURING EXHAUST COLLECTION

IMPINGER SAMPLING WITH HPLC ANALYSIS USED FOR ALCOHOLS AND CARBONYLS

SPECIATED HYDROCARBON ANALYSES BY GC USING AUTO/OIL PHASE II PROTOCOL

ENVIRONMENTAL CHAMBER LABORATORY

COMMERCIAL NO_x, O_3, CO, THC MONITORS

HYDROCARBONS, ALCOHOLS, HIGHER ALDEHYDES MEASURED BY GC/FID

FORMALDEHYDE MONITORED BY DASGUPTA DIFFUSION SCRUBBER METHOD.

VEHICLES AND FUELS STUDIED

VEHICLE	FUEL	FTP G / MILE	
		NMOG	NO_x
1989 Plymouth Reliant	LPG	1.1	0.2
1992 Ford Taurus FFV	M100	0.5	0.2
1997 Ford Taurus FFV	M85	0.3	0.1
1997 Ford Ranger Pickup Dedicated retrofit	CNG	0.04	0.5
1997 Ford Taurus FFV	RFG	(not tested - low)	
1991 Dodge Spirit	RFG	0.1	0.2
1994 Chevrolet Suburban	RFG	0.4	0.5
1984 Toyota Pickup (227K miles)	RFG	2.1	1.7
1988 Honda Accord (150K miles)	RFG	0.2	0.7
1984 Mersedes 300D Diesel (170K miles)	Diesel	(not tested)	

REACTIVE COMPONENTS USED TO MAKE EXHAUST SURROGATES

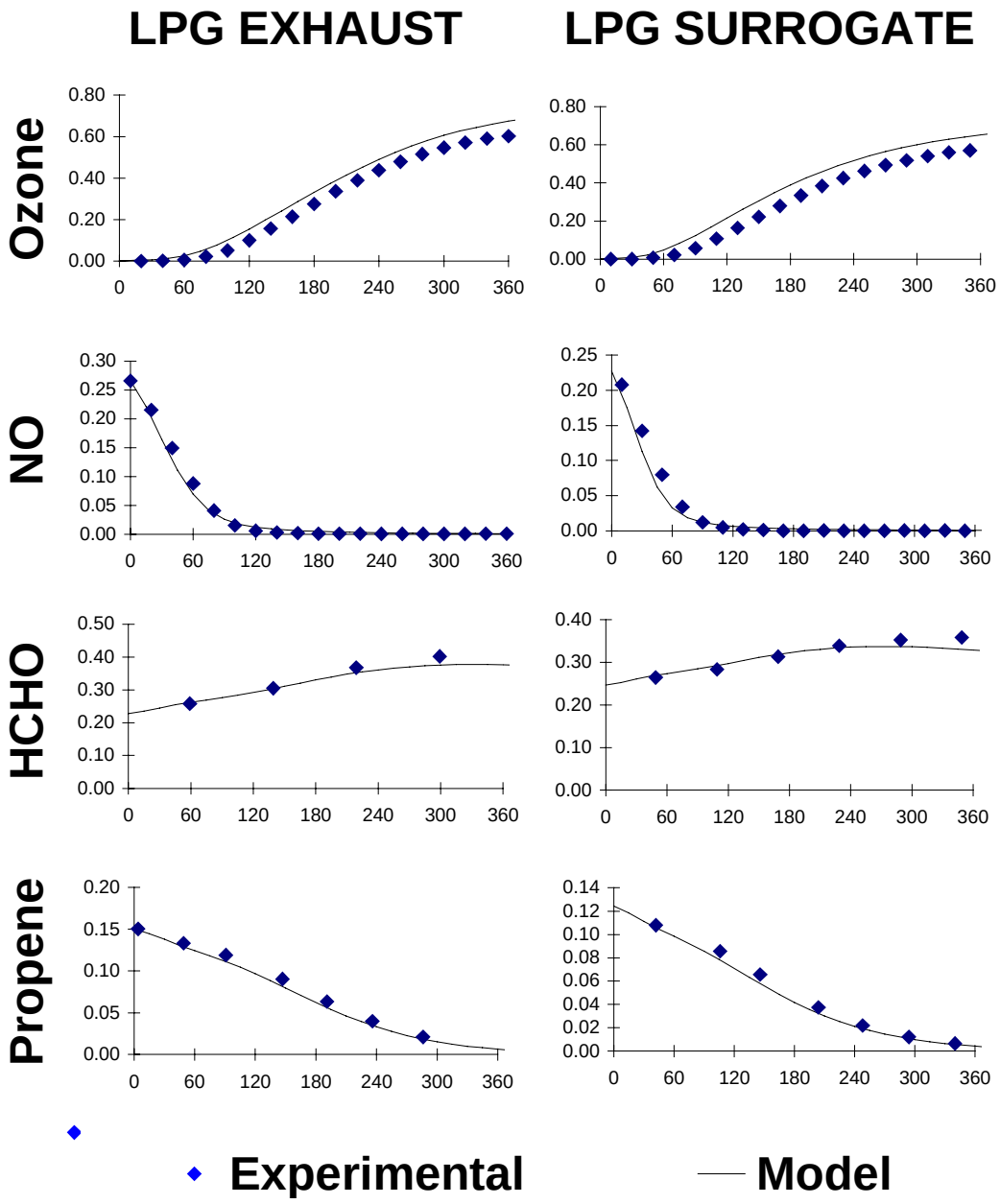
EXHAUST	SURROGATE COMPOSITION
LPG	CO, Propane, isobutane, n-butane, ethylene, and propene
M100	Methanol and Formaldehyde
M85	Methanol and Formaldehyde
CNG	CO and Formaldehyde
RFG	CO, 8 hydrocarbons representing a lumped the HC classes used in airshed models, and formaldehyde
Diesel	No surrogate made. Only CO, formaldehyde, and only low levels of hydrocarbons detected.

COMPOUNDS USED TO MAKE SURROGATE RFG EXHAUSTS

COMPOUND	USED TO REPRESENT
n-Butane	Alkanes ($kOH < 10^4$ ppm^{-1} min^{-1})
n-Octane	Alkanes ($kOH \geq 10^4$ ppm^{-1} min^{-1})
Ethene	Ethene
Propene	Terminal Alkenes
trans-2-Butene	Internal and Iso-Alkenes
Toluene	Monoalkyl Benzenes and Naphthalenes
m-Xylene	Dialkyl Benzenes
1,2,3-Trimethyl benzene	Tri- and Polyalkyl Benzenes
Formaldehyde	Formaldehyde
(Other Oxygenates Negligible)	

COMPOUNDS WEIGHTED WITHIN EACH CLASS BY THE RATIO OF THEIR MIR TO THE MIR OF THE REPRESENTATIVE COMPOUND.

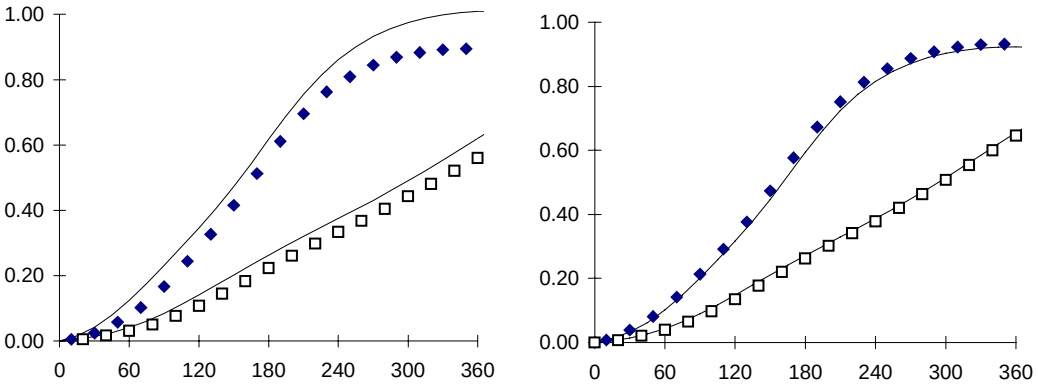
LPG EXHAUST EXPERIMENTS



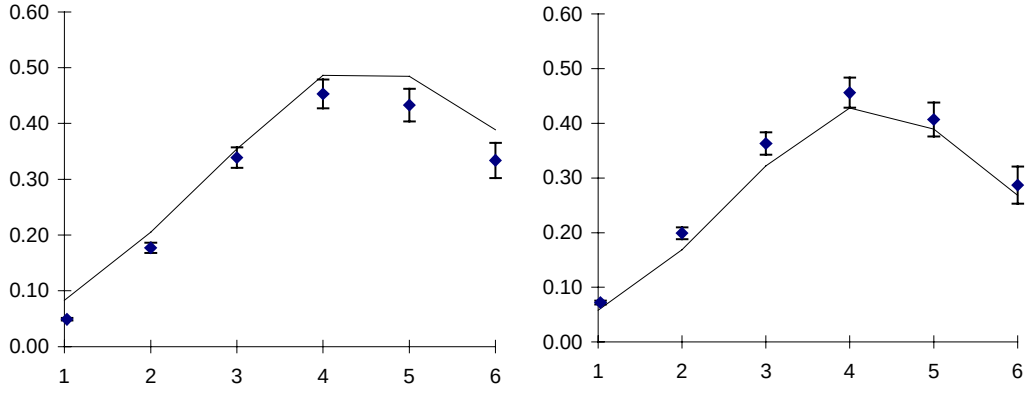
INCREMENTAL REACTIVITY EXPERIMENT WITH LPG EXHAUST

LPG EXHAUST LPG SURROGATE

Δ([O3]-[NO]) (ppm)

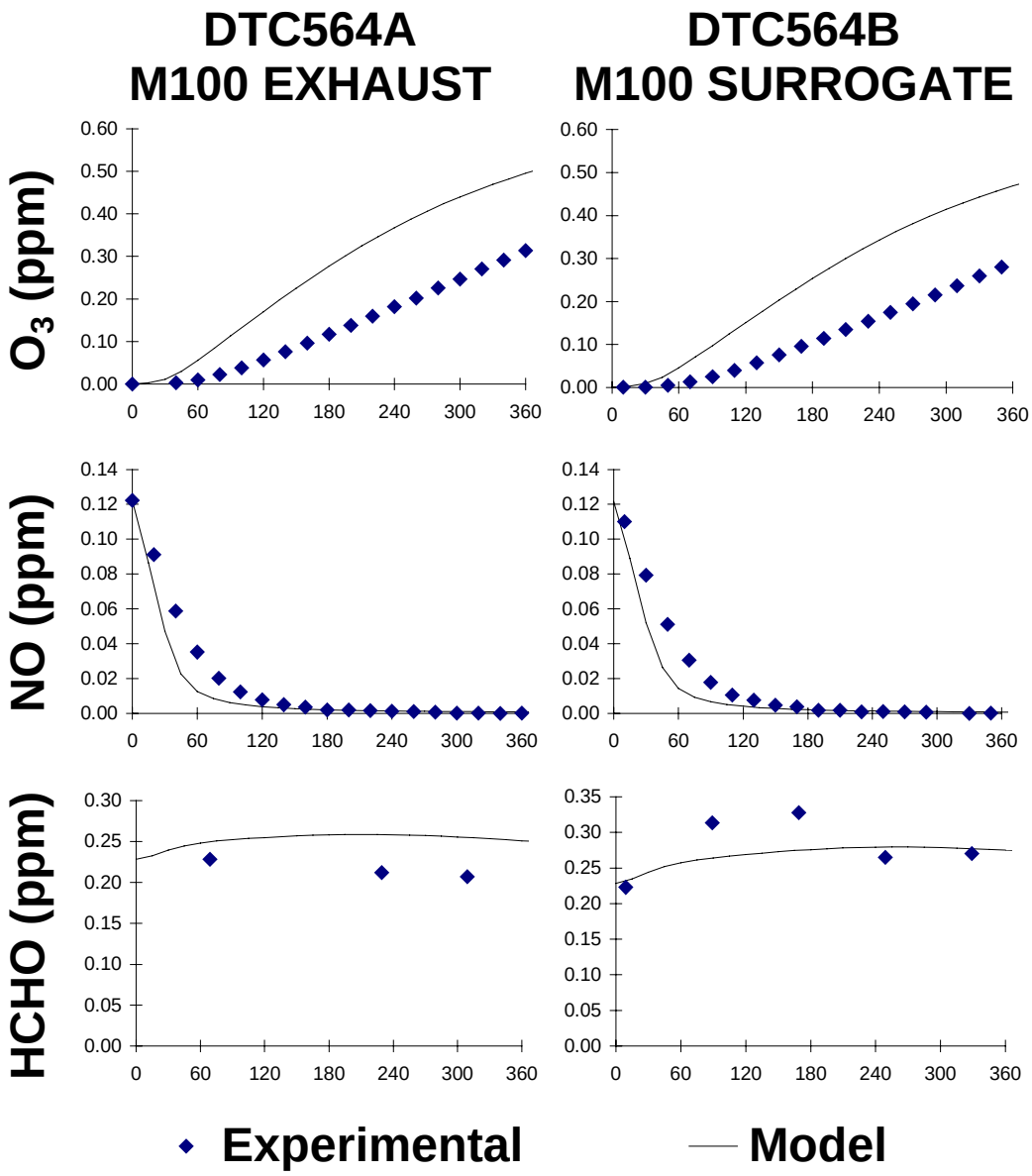


Change in Δ([O3]-[NO]) (ppm)



◆ **Added Test Mixture** ▫ **Base Case** — **Model**

M100 EXHAUST EXPERIMENTS

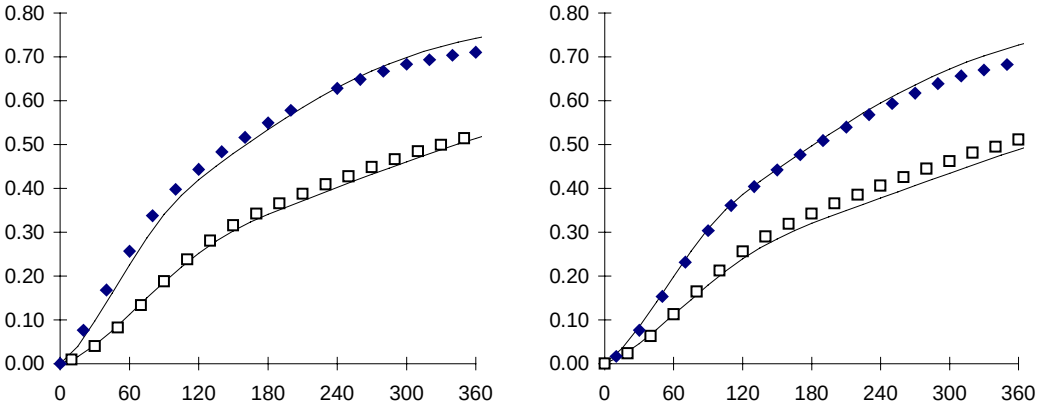


INCREMENTAL REACTIVITY EXPERIMENTS WITH M100 EXHAUST

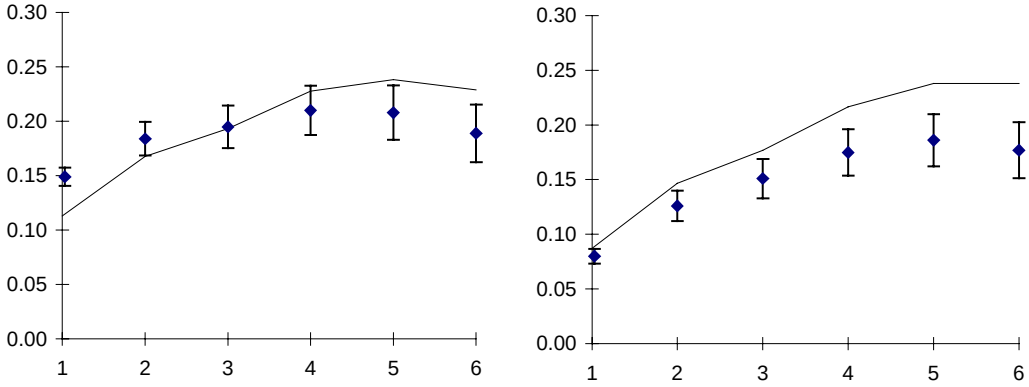
Full Surrogate + M100 Exhaust

Full Surrogate + Synthetic M100

Δ([O3]-[NO]) (ppm)



Change in Δ([O3]-[NO]) (ppm)



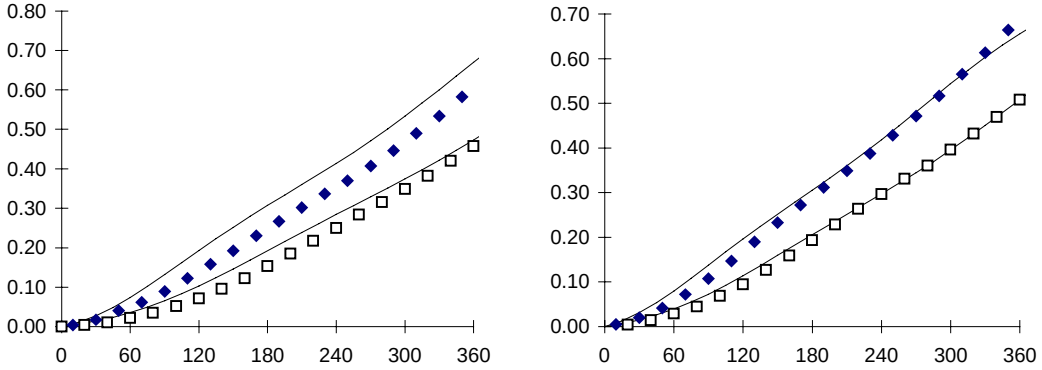
◆ **Added Test Mixture** ▫ **Base Case** — **Model**

INCREMENTAL REACTIVITY EXPERIMENTS WITH CNG EXHAUST

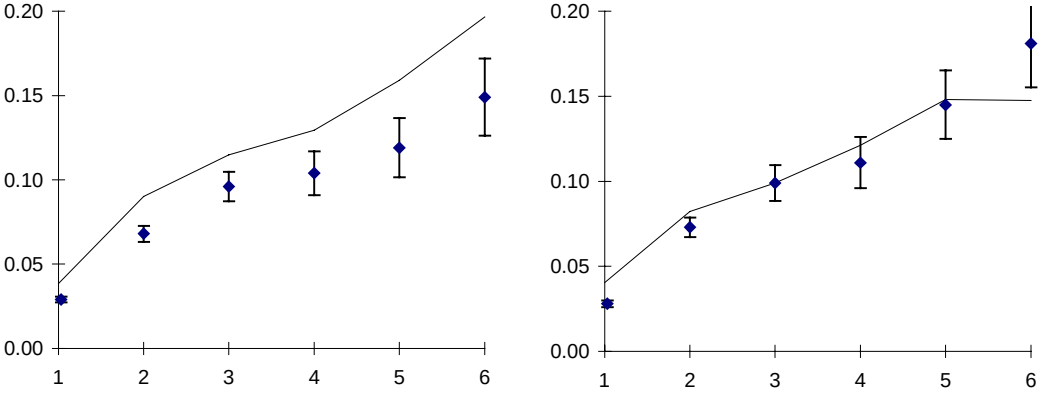
MINI-SURROGATE + CNG EXHAUST

MINI-SURROGATE + SYNTHETIC CNG

Δ([O3]-[NO]) (ppm)

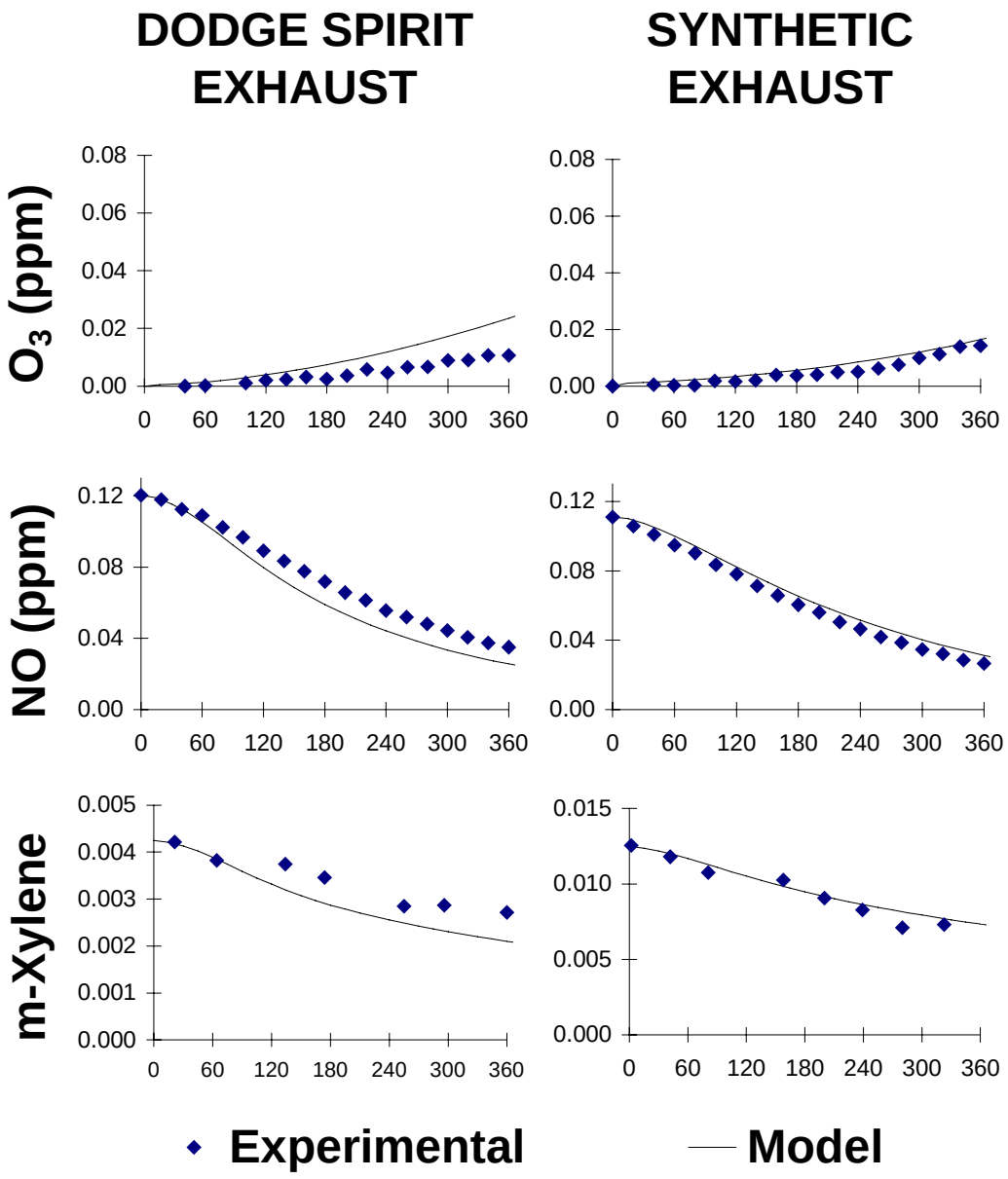


Change in Δ([O3]-[NO]) (ppm)



Added Test Mixture **Base Case** **Model**

EXPERIMENTS WITH 1991 DODGE SPIRIT EXHAUST

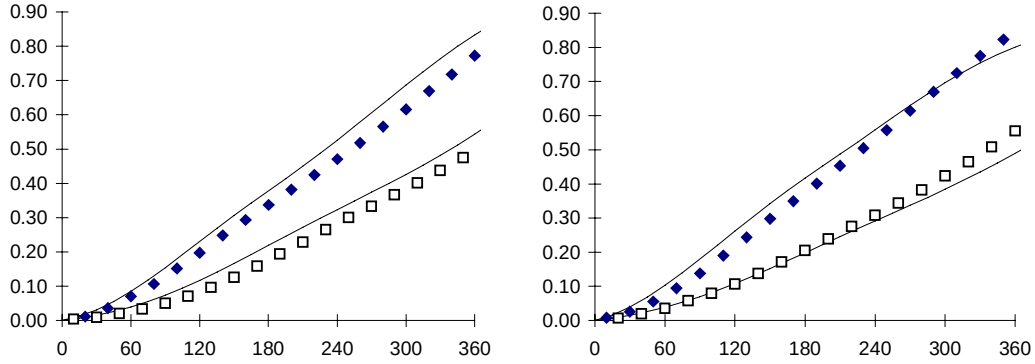


INCREMENTAL REACTIVITY EXPERIMENTS WITH DODGE SPIRIT EXHAUST

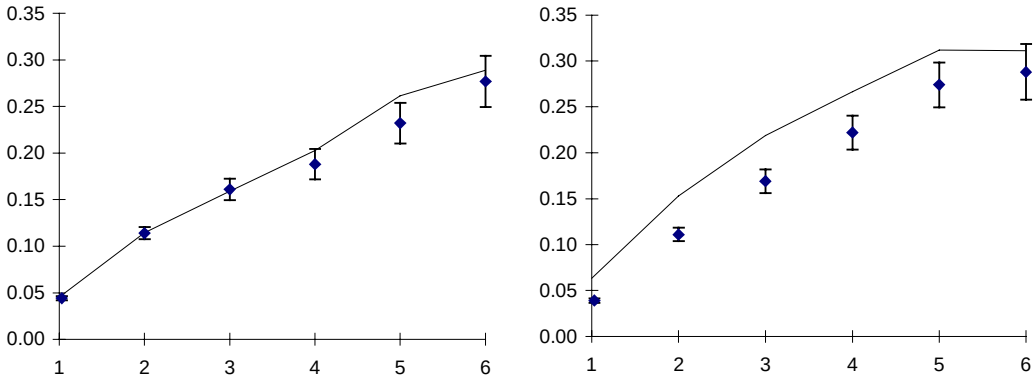
MINI-SURROGATE + DODGE SPIRIT EXHAUST

MINI-SURROGATE + SYNTHETIC EXHAUST

Δ([O3]-[NO]) (ppm)



Change in Δ([O3]-[NO]) (ppm)



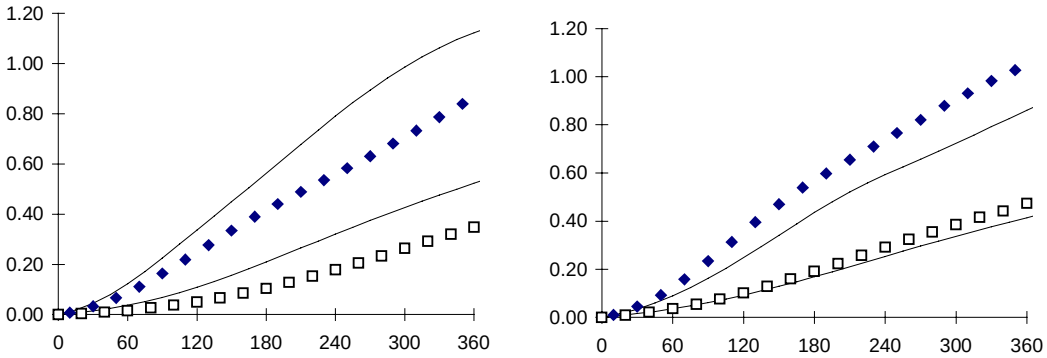
◆ **Added Test Mixture** ▫ **Base Case** — **Model**

INCREMENTAL REACTIVITY EXPERIMENTS WITH CHEVROLET SUBURBAN EXHAUST

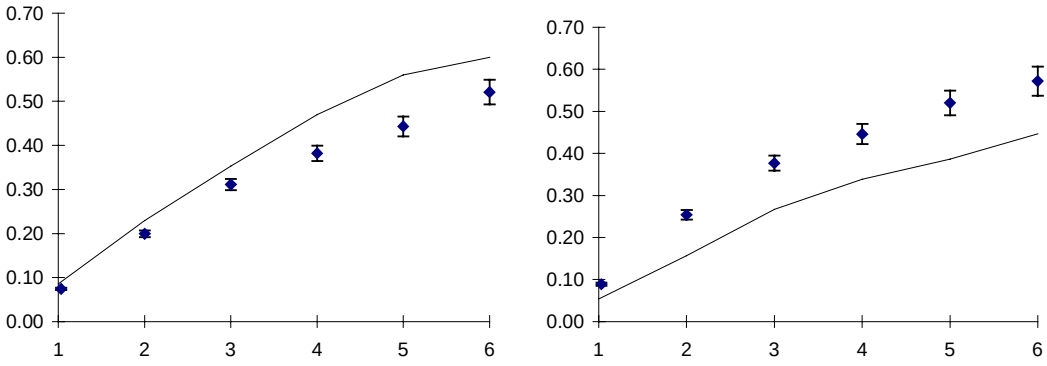
MINI-SURROGATE + SUBURBAN RFG EXHAUST

MINI-SURROGATE + SYNTHETIC EXHAUST

Δ([O3]-[NO]) (ppm)



Change in Δ([O3]-[NO]) (ppm)

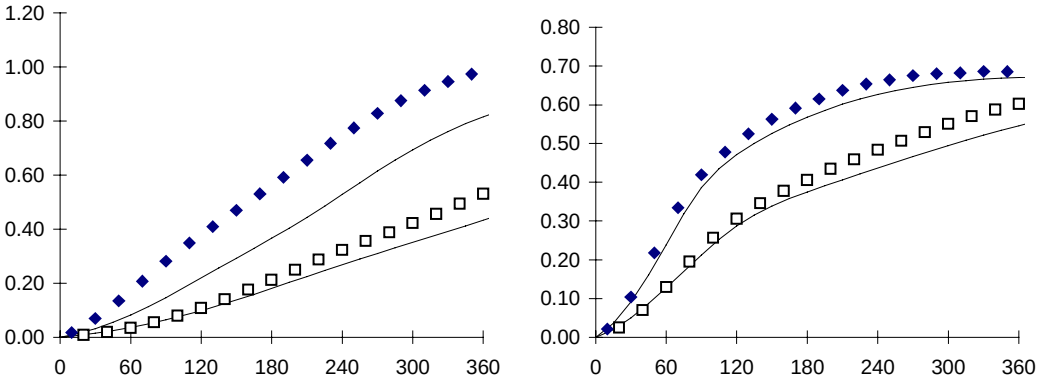


◆ **Added Test Mixture** ▫ **Base Case** — **Model**

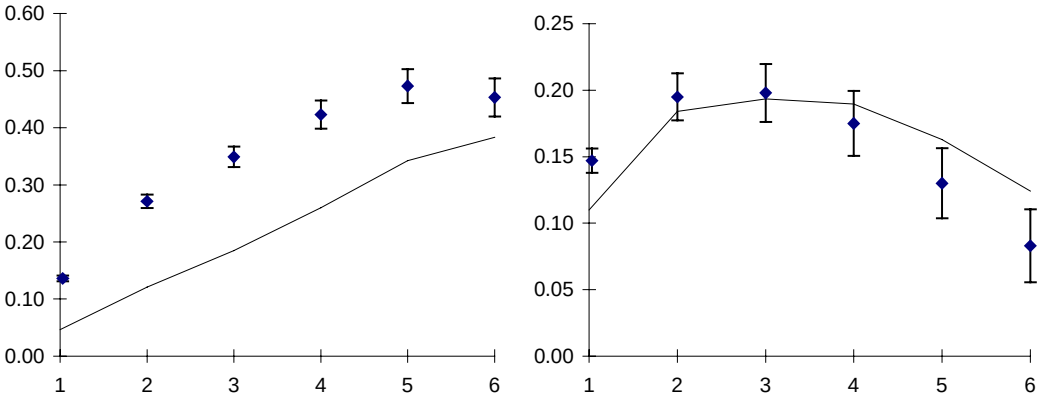
INCREMENTAL REACTIVITY EXPERIMENTS WITH EXHAUST FROM HIGH-MILEAGE 1984 TOYOTA PICKUP

MINI-SURROGATE + TOYOTA EXHAUST | **FULL SURROGATE + TOYOTA EXHAUST**

Δ([O3]-[NO]) (ppm)



Change in Δ([O3]-[NO]) (ppm)

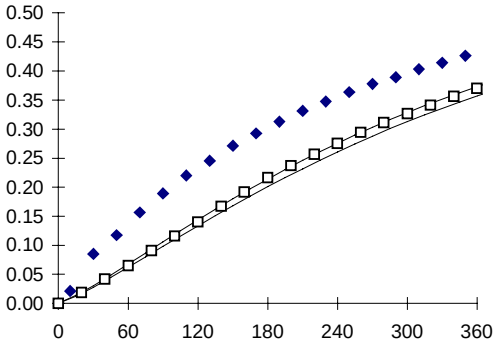


◆ **Added Test Mixture** ▫ **Base Case** — **Model**

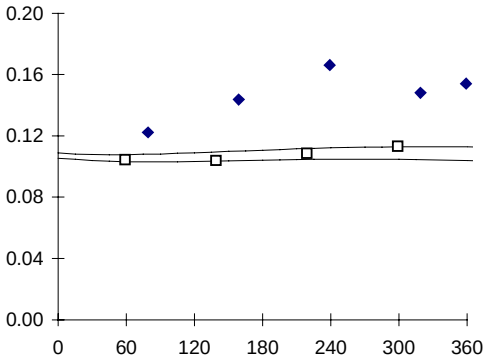
INCREMENTAL REACTIVITY EXPERIMENT WITH DIESEL EXHAUST

FULL SURROGATE + DIESEL EXHAUST

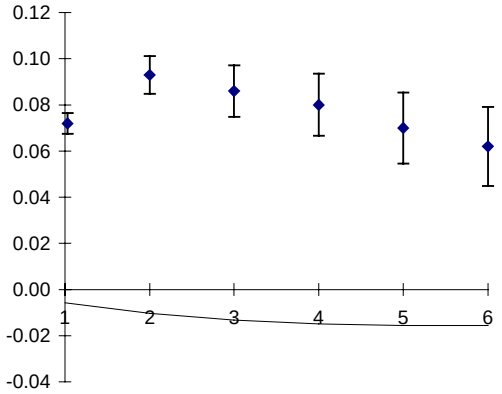
Δ([O3]-[NO]) (ppm)



FORMALDEHYDE (ppm)



Change in Δ([O3]-[NO]) (ppm)



◆ Added Test Mixture ▫ Base Case — Model

CONCLUSIONS

DATA OBTAINED TO TEST OZONE IMPACTS OF A NUMBER OF REPRESENTATIVE FUELS AND VEHICLE TYPES

THE COMPOUNDS CONTRIBUTING TO THE REACTIVITIES OF LPG, M100, M85, CNG, AND RFG FUELS HAVE BEEN IDENTIFIED:

- LPG $C_{\leq 4}$ ALKENES
- M85+ METHANOL, FORMALDEHYDE
- CNG CO, FORMALDEHYDE
- RFG HYDROCARBONS THAT CAN BE MONITORED USING GC-FID

THIS CONFIRMED BY OBSERVATIONS OF ONLY SMALL DIFFERENCES BETWEEN RUNS WITH ACTUAL AND SYNTHETIC EXHAUSTS

SAPRC-97 AND SAPRC-99 MECHANISMS ABLE TO SIMULATE RESULTS OF MOST EXPERIMENTS WITH THESE EXHAUSTS

THE COMPOUNDS CONTRIBUTING TO THE OZONE REACTIVITY OF DIESEL EXHAUST HAVE NOT BEEN IDENTIFIED

ACKNOWLEDGEMENTS

THIS WORK FUNDED BY

- CALIFORNIA AIR RESOURCES BOARD
- CALIFORNIA SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

VEHICLE EMISSIONS TESTING

- MATT SMITH
- VINH NGUYEN
- OTHERS ON CE-CERT VERL STAFF

ENVIRONMENTAL CHAMBER EXPERIMENTS

- DONGMIN LUO
- IRINA MALKINA
- KURT BUMILLER

ASSISTANCE IN ADMINISTRATION AND OVERSIGHT

- JOE NORBECK
- DENNIS FITZ