



## Project Summary

# Outdoor Smog Chamber Experiments to Test Photochemical Models: Phase II

H. E. Jeffries, K. G. Sexton, R. M. Kamens, and M. S. Holleman

The smog chamber facility of the University of North Carolina at Chapel Hill (UNC) was used in a study to provide experimental data for developing and testing kinetic mechanisms of photochemical smog formation. The smog chamber, located outdoors in rural North Carolina, is an A-frame structure supporting Teflon film. Because the chamber is partitioned into two sections, each with a volume of 156 m<sup>3</sup>, two experiments can be conducted simultaneously. The dual chamber is operated under natural conditions of solar radiation, temperature, and relative humidity.

In this study, 128 dual-experiments were performed using NO<sub>x</sub> and various hydrocarbons and hydrocarbon mixtures. The experiments performed during this three-year project have been added to the existing UNC database for model validation testing, bringing the total number of dual-experiments to 346.

This report presents an organizational scheme for these 346 experiments. Six attributes of each experiment were used for classification. These are class of experiment, experimental conditions, quality, processing status, project that produced the data, and membership in a run series. Run series, a collection of experiments performed in a certain manner or addressing a particular question, formed a major organizational basis. Forty series were used, including seven types of side-by-side series, four types of chemical issues series, and five

types of characterization series. All dual experiments, or runs, were classified into one of the side-by-side series. Each run could also appear in up to two additional series.

The report also discusses three examples of selecting runs to test mechanisms. The examples are: runs to test an explicit toluene chemistry mechanism; runs to test mechanisms under dynamic operating conditions; and runs to test EKMA-type mechanisms for air quality modeling. Recommendations for how best to take advantage of the side-by-side nature of the UNC runs in testing mechanisms are given throughout the discussion.

*This Project Summary was developed by EPA's Atmospheric Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

## Introduction

Photochemical kinetics reaction models are central components in EPA's method for computing control requirements for organic emissions needed to meet the National Air Quality Standard for ozone. State and local control officials are expected to use these models to estimate control requirements. However, different kinetic models apply different methods, often resulting in different descriptions of the same situation. Smog

chamber data must be used to test photochemical mechanisms to determine the adequacy of the chemical representation. Presently, mechanism testing has not used a large enough range of test data encompassing the range of conditions likely to occur in an urban control situation. This is because, in part, an organized database containing the range of conditions needed was not available before now.

This report uses a hierarchy of chemical species, based on the number of hydrocarbon and oxides of nitrogen (HC/NO<sub>x</sub>) systems in which the species occur, to determine the type of smog chamber experiments needed for ideal mechanism validation. This species hierarchy included a hierarchy of operating conditions. These four sets of conditions, which include large dilution and continuous injection, are ordered to proceed from the standard smog chamber type experiment to conditions that simulate the urban environment. All experiments took place under natural sunlight and ambient temperature. An example of this hierarchy of experimental conditions is shown in Figure 1, in which a similar photochemical system was performed under four different physical conditions. Two of these experiments also show the unique side-to-side nature of the UNC chambers.

Three other projects using the UNC Outdoor Smog Chamber have contributed data for model testing. The types of data provided by these projects are described briefly in this report, and the project identifications are used in the classification scheme.

## Purpose

The purpose of this research project was to: (1) measure reactant and product concentrations as functions of time in selected photochemical smog systems; (2) process these data into a form readily distributable to model developers and testers; and (3) provide auxiliary information needed to create mathematical model descriptions of the systems. The 128 dual-experiments, when added to the other experiments in the database, encompass a range of complexity from single HC species in totally static situations to complex urban mixtures in fully dynamic conditions. As a whole, the data set is well suited to develop and test models of chemical transformations in polluted atmospheres.

## Organizing Principles

The 346 runs were classified by "keys" to allow easy selection. Six kinds of

attributes were used to organize the runs in the data set. The *Class* of a run was either a characterization run that addressed unique aspects of the UNC chamber or organic/NO<sub>x</sub> runs to test mechanism design. Further, either of these types could be one-day or multi-day runs. *Experimental Conditions* were based on four major types of run conditions. These conditions were: dilution (large or normal), injection (initial or continuous), and type of HC system used, i.e., single HC species or mixture, and, if a mixture, whether the composition was constant or varying over time. *Initial Conditions* included the exact NO<sub>x</sub> and HC concentrations that occurred on both sides, as well as the identity of the HC for up to three HC species. For runs that had more than three species, HC mixture names were used. The *Quality* of a run was rated on a scale of 0 to 9. The major determining factors for quality were the weather conditions and the number and performance of the analytical instruments. The *Processing Status* of a run indicated the availability of validated data on tape or in other forms such as plots. All runs were included in the database, but not all have yet been completely processed to the final validated form. The *Project Name* identified the runs by the project that produced the experiment.

## Data Set

The report describes how the runs were distributed across the organization keys set forth. The majority of the experiments were one day, normal dilution, initial injection runs performed between June and October. The experiments were summarized by HC type. All the species and named mixtures used are listed. The grading of experiments is explained: important factors are sunlight, initial conditions, analytical support, chamber conditions, and need/usefulness. Most runs were graded at 7 or 8.

All experiments in the data base are listed two ways: sorted by series and by species. The seven types of series lists are characterization, matched conditions, relative reactivity between sides, carbon substitution, carbon addition, delta concentration of HC or NO<sub>x</sub>, and static-to-dynamic transition experiments. The five species lists are: formaldehyde, acetaldehyde, ethylene, propylene (other than matched propylene) and toluene. These lists include all experiments in which the species appeared, alone or in mixtures, on either side of the chamber. Within each series and species list, the runs are

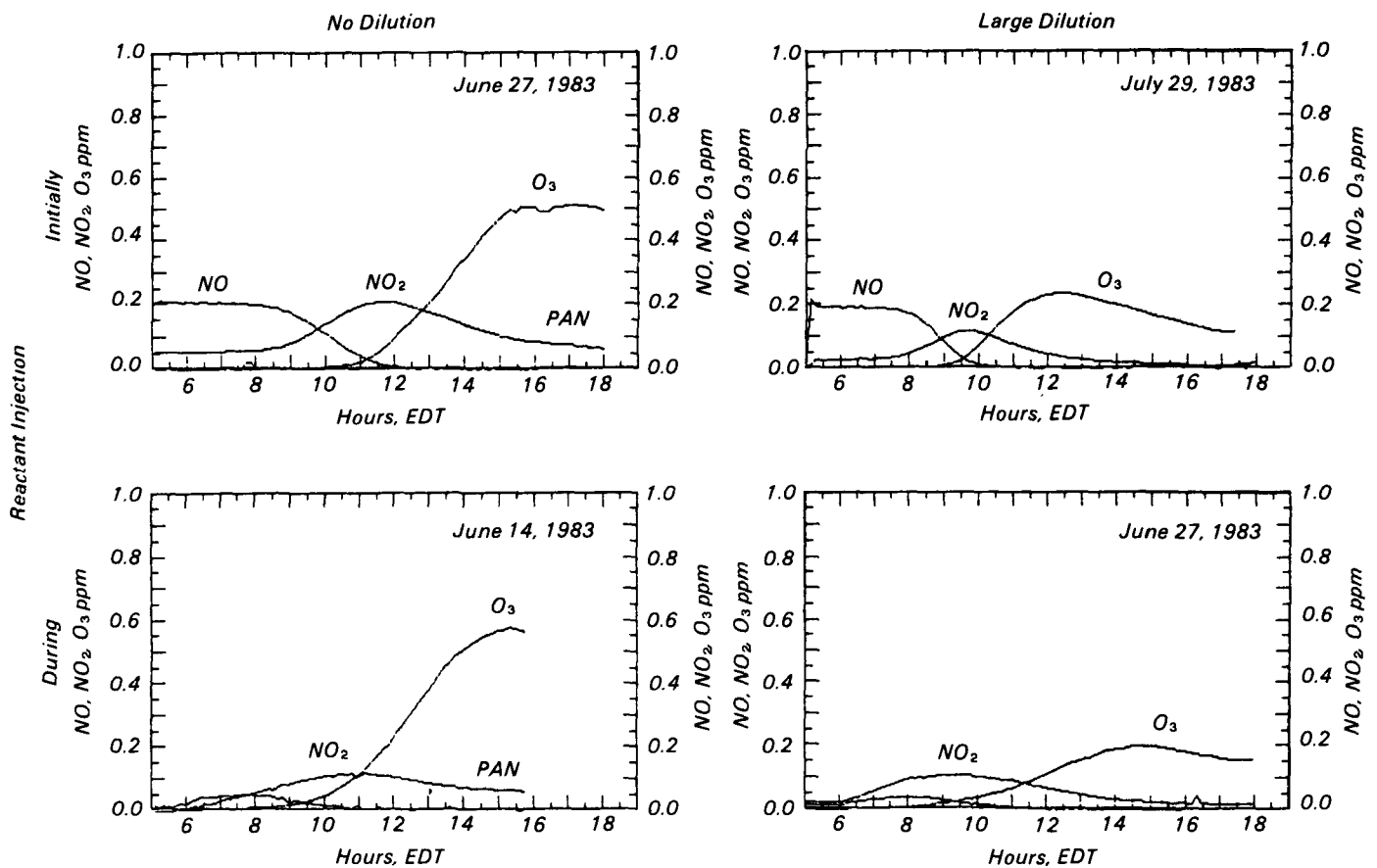
grouped by HC type beginning with the simplest type that appears in the series. Within the HC type, the runs are in chronological order. Guidance for the usefulness of a specific run for the purpose of model testing is also given in terms of general ranking categories.

## Selecting Runs and Obtaining Data

Using three examples, the report illustrates how experiments from the UNC Smog Chamber Database might be selected to test mechanisms. General recommendations and assumptions are defined to guide modelers in general selection. The examples discussed involved the testing of an explicit toluene reaction mechanism, a mechanism under dynamic conditions, and an EKMA-type mechanism for urban conditions.

The data set described in this report is neither complete nor static. New projects are adding to this data set, and the existing runs are under constant review and analysis. The possibility for, and the means of, future revisions are explained.

This data set has been supplied to modelers for analysis under EPA Contract Nos. 68-02-3738 and 68-02-4104. The purpose of this report is to describe the data set and to provide guidance so others in the scientific community can use it. Fully processed runs and the experimental conditions database are available on an ANSI formatted magnetic tape. Copies of the tape and other supporting information are available through the authors.



**Figure 1.** Outdoor smog chamber runs as examples of hierarchical experimental conditions. The NO<sub>x</sub> concentration was  $\approx 0.25$  ppm, HC concentration  $\approx 2.6$  ppmC of propylene/n-butane/toluene mixture. Large dilution means that 20% of initial mass is left after 10 hours of dilution (equivalent to mixing height rise from 250 m to 1250 m).

H. E. Jeffries, K. G. Sexton, R. M. Kamens, and M. S. Holleman are with the University of North Carolina, Chapel Hill, NC 27514.

**Marcia C. Dodge** is the EPA Project Officer (see below).

The complete report, entitled "Outdoor Smog Chamber Experiments to Test Photochemical Models: Phase II," (Order No. PB 85-191 542/AS; Cost: \$19.00, subject to change) will be available only from:

National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:  
Atmospheric Sciences Research Laboratory  
U.S. Environmental Protection Agency  
Research Triangle Park, NC 27711

PS

United States  
Environmental Protection  
Agency

Center for Environmental Research  
Information  
Cincinnati OH 45268

Official Business  
Penalty for Private Use \$300

RECEIVED  
JUN 14 1975  
FBI  
622  
6250347

• 0000329 PS •

U S ENVIR PROTECTION AGENCY  
REGION 5 LIBRARY  
230 S DEARBORN STREET  
CHICAGO IL 60604