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Project Summary

The University of California, Riverside Environmental Chamber Data Base for Evaluating Oxidant Mechanisms: Indoor Chamber Experiments Through 1993

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Data collected in the environmental chambers operated by the University of California, Riverside, have been documented and are now available for use by the scientific community for evaluating photochemical mechanisms for urban and regional airshed models. The compiled data include experiments performed in the Statewide Air Pollution Research Center (SAPRC) Evacuable Chamber (EC), Indoor Teflon Chamber #1 (ITC), Indoor Teflon Chamber #2 (ETC), Dividable Teflon Chamber (DTC), and Xenon arc Teflon Chamber (XTC) between September of 1975 through November of 1993. The experiments contained in this data base are listed and summarized, the facility and procedures employed are described, and the analytical and monitoring methods and their calibration data and associated uncertainties are documented. In addition, input data needed to conduct model simulations of the experiments in the data base are included, and the format of the data sets, which are available on the Internet by anonymous FTP, are described. Also available on the Internet are files that permit modeling of the experiments in the data base using the SAPRC-90 and the Carbon Bond IV chemical mechanisms. Recommendations are made concerning the steps that need to be taken before using these data to evaluate chemical mechanisms.

This Project Summary was developed by EPA's National Exposure 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

Urban and regional oxidant models are important tools in the development and assessment of regulatory strategies aimed at reducing ground-level ozone formation. The gas-phase photochemical mechanism is an important component of such models because ozone is not emitted directly, but is formed from the gas-phase photochemical reactions of the emitted volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) in air. The chemistry of ground level ozone formation is highly complex and nonlinear and has many uncertainties. Because of this, no chemical model can be relied upon to give even approximately accurate predictions unless it has been evaluated by comparing its predictions with experimental data.

There are essentially two ways a photochemical oxidant model can be evaluated. The first is to compare the predictions of the complete model against data taken during an historic ozone pollution episode. However, this is rarely definitive because of the many uncertainties in the input data needed to represent any historic episode. Furthermore, it is rarely clear which component of the many components of comprehensive airshed models is the source of any discrepancy observed, or, if the model agrees with the data, whether there may be compensating errors among the different components.

The other approach for evaluating models is to evaluate each of the components separately. In the case of the gas-phase chemical mechanism, this means evaluating the predictions of the mechanism against results of environmental chamber experiments. If the model can successfully predict the transformations under a range of chemical conditions which encompass the range of variability in the atmosphere, one has at least some basis to conclude that the model may give reasonably accurate predictions of chemical transformations in the atmosphere, if provided with the appropriate input data.

However, modeling environmental chamber data is not without significant uncertainties. Analytical methods for the reactants and products have inaccuracies and imprecisions which might introduce errors in the amount of initial or injected reactants assumed in the model, or in evaluating the extent to which the model can predict pollutant concentrations. Simulating a chamber experiment also requires knowledge of the temperature, light intensity, and spectrum of the photolyzing light, and how they vary with time. All of these have uncertainties that can result in errors in reaction rates when simulating the experiments. Characterizing the light intensity and spectra is particularly difficult in outdoor chamber experiments. Because of this, it is important that chamber experiments used to evaluate mechanisms have as high quality analytical data and as well characterized experimental conditions as possible, and that the sources of the uncertainties in these data are identified and quantified. With a knowledge of the range of uncertainty in the input or evaluation data, one can assess the extent to which a model agrees with the data.

Perhaps the most serious problem is the existence of chamber wall effects (heterogeneous processes involving the walls) which are known to be non-negligible in all current-generation chamber experiments and can dominate the results of certain types of experiments. Because of this, one should not rely on data from a single chamber for evaluating mechanisms; the use of data from a variety of chambers is necessary to minimize the chance for errors in the chamber model causing errors in model simulations of experiments where the gas-phase chemistry is being evaluated.

With these problems in mind, the University of North Carolina (UNC), the Statewide Air Pollution Research Center (SAPRC) at the University of California at Riverside (UCR), and several other research institutions initiated an effort that was sponsored by the U.S. Environmental Protection Agency to develop a data base and protocol for evaluating photochemical mechanisms for air quality simulation models. An overview of the many factors which must be considered when developing such a protocol is discussed in the document entitled “Protocols for Evaluating Oxidant Mechanisms for Urban and Regional Models” (Jeffries et al., 1992), which was prepared under this program. As discussed there, the specifics of the evaluation protocol will depend on the nature of the model being evaluated and the uses to which it will be put. However, regardless of these application-specific considerations, the data base of chamber experiments, and the comprehensiveness of its associated documentation, are critical to any evaluation. Sufficient information must be given concerning the experiments so the evaluator can represent them in the model appropriately and can understand and document their uncertainties and variabilities. The report of Jeffries et al. (1992) gives standards for the necessary documentation of the data base.

The report described in this Project Summary documents the results of SAPRC efforts to develop a data base of environmental chamber experiments for mechanism evaluation. The Project Report is composed of two volumes. The first volume serves as the backing document for the SAPRC environmental chamber data base. That volume describes the procedures employed in the experiments and the analytical methods used to generate the data and the calibration and other data which can be used to estimate their uncertainties. It also contains a comprehensive discussion of the light intensity and light spectrum information, discusses and evaluates the temperature and other characterization data necessary to establish run conditions for modeling, discusses corrections made to the data as a result of reevaluations under this program, gives recommendations for modeling these runs, and describes the formats of the distributed data sets. The second volume contains the data sets themselves. In addition to the environmental chamber data, this includes spreadsheets giving run condition and data summaries, data sets giving supporting information relevant to data quality, and programs and data which can be employed for mechanism evaluation.

Scope

Coverage

To date, six different environmental chambers at SAPRC have provided data which are potentially useful for mechanism evaluation. These include the Evacuable Chamber (EC), the Indoor Teflon Chamber #1 (ITC), the Indoor Teflon Chamber #2 (ETC), the Dividable Teflon Chamber (DTC), the Xenon Teflon Chamber (XTC), and the Outdoor Teflon Chamber (OTC). These chambers are described in the backing documentation and are summarized in Table 1. Data from the indoor chambers are included in this release of the data base, and data from the outdoor chamber will be included in a later release. The DTC and XTC have since been moved to another location and are currently generating additional data. The data base will be updated to include these re-

Although the presently distributed data base only includes indoor chamber data, the backing documentation contains a description of all six chambers and their operating procedures, and discusses the analytical methods and calibration data applicable for all groups of runs listed in Table 1.

Not all environmental chamber experiments carried out in the chambers listed in Table 1 are considered appropriate for this data base. The main criteria used when determining whether to include a run in the data base were as follows: (1) the data from the experiment must be in our computer data base; (2) the experiments should either have been carried out for the purposes of mechanism evaluation or characterization of chamber effects for mechanism evaluation, or they should be judged to be potentially useful for such purposes; and (3) the experiments were carried out under conditions which are sufficiently well characterized for modeling. A number of experiments which passed the initial screening and thus were included in the data base were subsequently found to have problems which limit or prevent their use for mechanism evaluation. Therefore, not all runs in the data base are considered useful for mechanism evaluation.

The total number of experiments from each chamber in the current data base and the number of experiments considered to be potentially useful for mechanism evaluation are indicated in Table 1. Some of these experiments have higher data quality than others, and the summaries distributed with the data base indicate runs which have problems and include estimates of uncertainties in reactant concentrations and run conditions.

The run-specific data which were evaluated and documented in this project are sufficient for using them to evaluate a mechanism's performance in predicting ozone formation. The data that were evaluated most comprehensively include the NO and NO_2 data; organic reactant data; ozone data; the light intensity and spectral distribution; the temperature and humidity conditions, and information concerning special run conditions. In addition, data for PAN, formaldehyde, and other organic products were evaluated to some extent, but not as comprehensively as for those listed below. Mechanism evaluators can utilize the calibration summaries and other information contained in the Project Report and the data sets to make conclusions concerning the data for individual runs of interest.

Computer Data Sets

The computer data sets prepared for this program are available on the Internet for anonymous FTP at carterpc.ucr.edu in the directory "/chdata", and also at cert.ucr.edu in the directory "pub/carter/chdata". The format of the data sets and instructions on how to install them on PC-compatible computers are discussed in the Project Report. The distributed data sets include the following.

Master Run Summary Spreadsheets

For each chamber whose data are included in this distribution, there is a series of Excel 5 (and ASCII CSV) spreadsheet files giving important summary information for each run in the data base. This includes, for each run in the data base, the run descriptions and classification, initial reactant concentrations and their estimated uncertainties, notations where applicable of special run conditions or problems, notations where applicable of special problems with the run data, notations where applicable indicating runs judged not suitable for modeling, information concerning light intensity and spectral distribution assignments, and other data that might be of significance to the modeler.

Individual Experiments Data Sets

For each experiment, there is an ASCII file containing all the run-specific data. In addition to the experimental measurements as a function of time, it includes (where available) identifications of instruments and calibration and zero corrections, uncertainty estimates, recommended input data for modeling the runs, comments from the log book and comments documenting data corrections and special run conditions and input data to use when modeling. These contain all the run-specific information needed for conducting model simulations and evaluating model performance for all runs which are sufficiently well characterized for modeling.

Calibration Data Summary Files.

For most of the instruments used to monitor O_3, NO_x or organics, there are calibration data files giving the calibration data and the times the instruments were calibrated, codes indicating how recommended calibration factors are to be computed, and relevant comments. Computer programs to read these files and produce output summary files are also included.

Table 1. *Summary of SAPRC Environmental Chambers*

Chamber	Runs [a] Tot	Model	Description
EC	*216*	*160*	*5800-liter evacuable, thermostatted cylindrical chamber. Teflon-coated aluminum walls. Quartz windows on both ends. 25 KW Xenon arc light "solar simulator" light source with pyrex filters to remove UV below~290 nm. Generally operated at ~303 K and 50% RH. Experiments carried out between 9/29/75 and 11/18/83 are on the present data base.*
ITC	*346*	*329*	*Replaceable~6000-liter FEP Teflon bag in aluminum frame banks of blacklights on either side. Generally operated at room terperature and 50% RH. Experiments carried out in the periods 1/29/82-8/29/86 and 10/2/89-10/16/89 are on the present data base.*
ETC	*413*	*384*	*Replaceable~4000-liter FEP Teflon bag in an aluminum frame with banks of blacklights on the top and bottom. All runs at room temperature re and ~5% RH. Experiments carried out between 10/25/89 and 2/25/93 are on the present data base.*
DTC	*132*	*128*	*Dual Replaceable~5000-liter FEP teflon bags located next to each other, between banks of blacklights on either side. Allows for simultaneous irradiation of two mixtures. All runs at room temperature and all but 2 at ~5% RH. Experiments between 3/5/93 through 8/4/94 are on the present data base.*
XTC	*31*	*31*	*Replaceable~50,000-liter pillow-shaped FEP teflon reaction bag located in a room with reflective walls and with 4 6.5 KW xenon arc lights on a wall 4' from the bag. Uses same enclosure as DTC, and run numbering continues from that of DTC runs. All runs at room temperature and ~5% RH. Experiments between 8/23/93 and 11/17/93 are on the present data base.*
OTC	*(not incl.)*		*Replaceable~50,000-liter pillow-shaped FEP teflon reaction bag located outdoors and irradiated with sunlight. No OTC experiments are on the present data base, though the backing document discusses most of the analytical procedures employed. Experiments from the periods 6/22/83-10/14/83, 5/13/85-11/27/85 and 6/10/92-10/26/93 may be included in future releases of the data base.*

[a] "Tot" = total number of experiments whose data are in the distribution. "Model" = number of experiments with sufficiently well characterized conditions to be potentially useful for modeling.

NO_2 Actinometry Results Data Files

The results of all the NO_2 actinometry experiments, the primary method used to measure light intensity, are included. The modeler can use these to recompute the light intensities if it is judged that the method or rate constants used in this work are inappropriate.

Recommended Spectral Distributions

Data files are included giving spectral distributions we recommend using for calculating photolysis rates when modeling these experiments.

Computer Programs

A number of FORTRAN computer programs that can read and process these files are included to assist the modeler in using these data. These include programs which can be used to conduct model simulations of the experiments and plot and summarize the results. The source files for these programs are available on a separate distribution that can be found on the Internet for anonymous FTP at carterpc.ucr.edu in the directory "/model" or at cert.ucr.edu in the directory "/pub/carter/model". All executable files require a 386 PC-compatible computer with a math co-processor or a 486DX or better. The programs are not fully documented, but sample input files with comments and batch files giving examples of these are included.

Chemical Mechanism Implementation Files and Software

Computer files implementing the SAPRC-90 and Carbon Bond IV mechanisms are included so example model simulations of the experiments can be carried out. Batch files showing examples of their use are included. The evaluator can use these as guidelines as how these data can be used for mechanism evaluation.

Discussion and Recommendations

This project has provided important input data for the evaluation of chemical mechanisms for use in urban and regional oxidant models. Although many of the chamber experiments whose data have been compiled under this project have been used in previous mechanism evaluations, a number of potentially significant corrections have been made to these data, and many other potentially important experiments whose results have not been available previously have been included in this data base.

However, it is essential that the modeler recognize the limitations of this data base. In the first place, the present distribution includes data only from SAPRC experiments carried out through the end of 1993 and does not include the extensive body of SAPRC outdoor chamber experiments, nor the experiments we are currently carrying out for mechanism evaluation and VOC ozone reactivity assessment. We expect to include these in future distributions, to be prepared as a part of our ongoing environmental chamber programs. In addition, UCR is not the only laboratory where environmental chamber experiments useful for mechanism evaluation have been carried out. A large data base of University of North Carolina (UNC) outdoor chamber experiments is now being compiled by the UNC researchers as part of the overall effort of preparing an environmental chamber data base for the EPA. Environmental chamber experiments that are potential candidates for this data base have also been or are being carried out at other laboratories. As discussed by Jeffries et al. (1992), a comprehensive and complete mechanism evaluation requires the use of data not only from different environmental chambers, but also from different research groups.

It is important that users of environmental chamber data recognize the many problems that can be associated with chamber experiments which might affect the accuracy of the results or the modeler's ability to accurately characterize the conditions of the experiment. When preparing this data base, we attempted to identify and note all problems which might affect the use of the experiment (or particular measurements associated with it) for mechanism evaluations. However, because of the large number of runs involved, combined with the number of things that can go wrong, we cannot guarantee that all problems have been detected and noted. Therefore, if the model simulation is in gross disagreement with the results of an experiment, the possibility that the problem exists with the data and not the model cannot be totally ruled out. In this case, it is important that the modeler has some understanding of the limitations associated with the data or run conditions. One of the objectives in preparing the backing documentation is to help the modeler obtain this understanding.

References

Jeffries, H.E., M.W. Gery, and W.P.L. Carter. Protocols for Evaluating Oxidant Mechanisms for Urban and Regional Models. EPA/600/R-92/112, U.S. Environmental Protection Agency, Research Triangle Park, NC 1992. 89pp.

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The complete report consists of two volumes entitled "The University of California, Riverside Environmental Chamber Data Base for Evaluating Oxidant Mechanisms: Indoor Chamber Experiments Through 1993"
"Volume I. Backing Document and Data Base Description " (Order No. PB96-190 673; Cost: $44.00, subject to change)
"Volume II. Appendices" (Order No. PB96-190 681; Cost: $31.00, subject to change)
The above reports will be available only from:
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