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Project Summary

Protocols for Evaluating Oxidant Mechanisms for Urban and Regional Models

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A task force of chamber operators and modelers was assembled to address needs raised at a prior workshop on the procedures and practices that should be followed when evaluating photochemical reaction mechanisms for their suitability for use in EPA's urban and regional air quality models. In addition to the task force, two workshops were held that were attended by researchers in the field and at which issues raised by the task force were discussed and guidance was sought. Based on our work and the community input, we describe how to create a protocol for the evaluation of photochemical reaction mechanisms. Rather than prescribe a set of actions, we present instead criteria that influence decisions without specifying what those decisions must be. These specify what the evaluator must consider, what is and is not relevant, and what must be reported as the basis of decisions made.

Based on general scientific principles, we describe five characteristics that reaction mechanisms must have if they are acceptable. Our approach is based on a complex argument in the form of a cascaded inference chain showing how to proceed to establish that a candidate mechanism might exhibit all five characteristics. The evidence in this argument is chamber data. The report details the elements that must be considered and describes the general content of reports the evaluator must produce. We conclude that, because of data incompleteness problems, it is not presently possible to make a compelling case for accepting a mechanism for ambient air use, only to vindicate its use as having been evaluated the best that can be currently done, given the available data.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment 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

The EPA must be able to defend its control policies and regulations. For ozone and other oxidants these policies depend upon the application of mathematical models of emissions, atmospheric transport, and chemical transformations to forecast the effects of proposed controls. An important element in this defense is the evaluation of the accuracy and reliability of these models. Because the models are large and complex, the first approach to establishing their overall accuracy is to assess independently the accuracy of each major component in the models, i.e., emissions, transport, and chemistry. Not only can the accuracy of the atmospheric chemical transformation component of these models be evaluated independently of the emissions and transport terms, such independent testing is the least ambiguous method. The need for such testing raises the need for standards to compare with the model and for a method by which the comparisons can best be done. Previous work sponsored by EPA (see, "Workshop on Evaluation/Documentation of Chemical Mechanisms," EPA/600/9-87/024, 1987) established that both standards and methods acceptable to the scientific community exist. Provided it was of high quality, smog chamber data was recommended as the best standard. Provided that efforts were made to treat the problems caused by the influence of the chamber and for coping with the scarcity and quality of measurement data, and even though it varied significantly from modeler to modeler, the then-existing mechanism evaluation practice was recommended as the best comparison process. The workshop recommended that a task force of chamber operators and modelers be assembled to address these problems. The work described in this summary is part of the effort of this task force. During the project, the task force held two workshops which were attended by researchers in the field. In these, issues raised by the task force were discussed and guidance was sought. Based on our work and community input, we describe how to create a protocol for the evaluation of photochemical reaction mechanisms that are candidates for use in EPA urban and regional oxidant models.

Based on general scientific principles, we present a set of characteristics that reaction mechanisms must have if they are to be acceptable. A central assertion here is that mechanism acceptance is more than just establishing agreement of the model's predictions with observations. We also recognize that any set of objective criteria may be insufficient to determine in full any algorithm for mechanism choice. Therefore, rather than prescribe a detailed set of actions (i.e., a cookbook), we present instead criteria that influence decisions without specifying what those decisions must be. Such criteria specify: (1) what each evaluator must consider in reaching his decisions, (2) what he may and may not consider relevant, and (3) what he can legitimately be required to report as the basis for his choices. Our goal is to have the evaluation be a complete and persuasive argument and this requires a clear chain of reasoning based on credible and complete evidence.

Our approach is based on a complex argument in the form of a cascaded inference chain showing how to proceed from kinetics data and chamber data to the necessary claims that allow use of the mechanism in EPA models. A second part of the inference chain addresses credibility issues for the kinetics and chamber data. Further, we provide general warrants for why this reasoning chain is legitimate.

Our argument is structured around establishing that an acceptable mechanism has five general characteristics: (1) consistency with currently accepted theories and facts applicable to these theories; (2) accuracy, that is, its predictions are in demonstrated agreement with observations from experiments and such agreement does not arise from compensating errors; (3) simplicity, that is, the mechanism should explain events in terms of necessary causal forces rather than empirical generalizations; (4) scope, that is, the mechanism's predictions should extend beyond the particular observations it was initially designed to explain; and (5) fertility, that is, the mechanism is expected to predict novel phenomena that were not part of the set to be originally explained. In an evaluation, data that are relevant to each of these characteristics are assembled to construct lower-order claims (e.g., the mechanism is well-formulated) which in turn are assembled into higher-order and more abstract claims that lead to acceptance or rejection of the mechanism.

After the first chapter that presents the mechanism characteristics, the argument, and a general description of the process, the report is divided into five substantive chapters and a conclusions chapter. One chapter defines the terminology and methods used and presents an overview of the operations. Four chapters describe the elements that must be considered in an evaluation and provide specification of the content of reports that must be produced by the evaluator. These are: (a) reports on the mechanism, (b) reports on the chamber data, (c) reports on the simulations, and (d) reports on the evaluation process.

Names and Definitions

In such a complex procedure involving models, data, and operations, it is necessary to agree on formal terms and to have formal definitions. For example, the first part of the definition of a principal mechanism is "a complete mechanism for an organic compound or mixtures of organic compounds combined with oxides of nitrogen and air that all chambers and the ambient air are thought to have in common at present." The rest of the definition describes what is included in and what is not included in a mechanism. Unfortunately, principal mechanisms are not what are tested with chamber data. This is because each chamber has a perhaps unique set of wall-mediated reactions with reactants and products in common with the principal mechanism, and thus, these wall reactions influence the chemistry; their effects must be included in any simulation if it is to describe accurately the chamber observations. Thus, auxiliary reaction mechanisms, one for each chamber, must be added to the principal mechanism and it is this combined mechanism that is tested with chamber data. Other terms and definitions given in this chapter are related to the chamber operations models and the comparison of observations and predictions.

Reporting Mechanisms

For an evaluator to test a principal mechanism using our procedures, certain information about the principal mechanism must be known and reported. First, the evaluator must report that he has an executing version of the mechanism and that he can operate the mechanism as intended by the developer. Next, he must report that he has assured that the mechanism is "well-formed." Thus, he must have knowledge of the development protocol, knowledge of the supporting data used in formulating the mechanism, and he must document that he understands the formulation and condensation rationale used by the developer. Further, he must determine the basis for believing that the principal mechanism's formulation is independent of the chamber data used in its development. If the evaluator determines that the mechanism suffers from flaws in its formulation, he must decide and report (justify) one of three courses of action: (1) decide to act as if the problem would not influence the mechanism's predictions and proceed; (2) decide that the mechanism needs to be "fixed" before proceeding, deviate from the protocol to fix the mechanism's formulation, and then proceed; or (3) decide that the mechanism's flaws are so bad that it cannot be fixed and, therefore, stop the evaluation because any exhibited accuracy by a fundamentally flawed mechanism is meaningless.

Assuming that he chooses to proceed, the evaluator must select chamber-dependent auxiliary mechanisms for each chamber that will be used and he must assure (and document) that these mechanisms are also as well-formed as we know how to make them.

Reporting Chamber Data

The primary evidence that would support the claims leading to mechanism acceptance are chamber data. For chamber data to be evidence in these matters, they must exist and they must be relevant to the claims being made, i.e., the chamber data must be capable of causing the evaluator to change his mind about the validity of the claims.

Thus, the evaluator must first report the chamber data needed to conduct a compelling evaluation. That is, one in which the evidence (if it existed) would permit only one reasonable interpretation about the acceptability of the mechanism. The second condition to be reported is the existence of the needed data; and the third condition is the relevance of any existing data to the case being made. The foundations of these arguments rest on the credibility of the chamber data used, and if the evaluator is to produce a successful evaluation, a reviewer of the evaluation must be convinced that the chamber data used in the comparisons are believable. Therefore, the fourth condition the evaluator must report is chamber data credibility and why he believes it has this quality. The evaluator then must report the extent to which the available, relevant, credible chamber data meet the data need. Where there is a significant shortfall in available data, the evaluator must report on how he will continue to conduct an evaluation when only part of the chamber data that is needed is available.

Once the chamber data are selected, the evaluator must prepare the appropriate summary observations for comparison with simulation predictions in subsequent work.

Reporting Simulations

For each selected experiment to be simulated, the evaluator must build a simulation solver input file containing the model's representations of the chamber conditions. First, species present in the chamber experiment must be represented in the simulation input file. For explicit species in the model and in the chamber this is no problem. For chamber species that are represented as some type of generalized model species, the appropriate transformations must be applied. For species thought to be present in the chamber, but that were not measured, the evaluator must report his algorithms for estimating these values. Data on light intensity must also be converted into actinic flux for each experiment. The evaluator must report the algorithms he uses for this calculation. Next, photolysis rates for the photolyzing species in the mechanism must be calculated from the actinic flux, and these algorithms must be reported. Finally, the simulation's representation of chamber temperature, dilution, and water vapor must be created and again the evaluator must report the algorithms used to produce these representations from the observed chamber data. The simulation solver input files must have internal documentation for their values and the files must be available for distribution to interested parties.

After the simulations are run, the evaluator must compute and report the corresponding summary measures for the predictions as was done for the observations. He then must calculate the absolute and relative errors in amplitudes and in times to events. Next, he must display these errors on plots that show results on a chamber by chamber basis. Other requirements for these plots are described that help detect internal compensating errors among the parts of the principal mechanism. All simulations with large errors must be plotted as concentration time profile plots of observations and predictions and the evaluator must offer explanations for why the agreements were so poor.

Reporting the Evaluation

The evaluator would now have all the raw evidence at hand and he must build a case to accept or reject the mechanism. Three major obstacles stand in the way of making compelling cases: (1) Because the theories to support a chamber-auxiliary mechanism are much weaker than those for a principal mechanism and because there are too few chamber characterization data, the evaluator may have found it necessary to use an auxiliary mechanism that was more "tuned" than it was formulated. Thus, there is the real possibility that any demonstrated accuracy of the combined mechanism is caused by compensation between inaccurate components in both the auxiliary mechanism and the principal mechanism. (2) The chamber data are incomplete in the necessary inputs to simulate accurately an experiment and these inputs must be estimated by the evaluator. If there is bias in the choice of unmeasured but necessary simulation inputs, then again there is the real possibility any demonstrated accuracy of the combined mechanism is caused by compensating errors between the principal mechanism and the simulation inputs. (3) The chamber data are incomplete in their coverage of single species and simple mixtures. Thus, the accuracy of mechanisms for some reacting species in the principal mechanism cannot be tested at all. Strategies for treating these difficulties are discussed. The evaluator must report his choices and procedures for addressing these problems.

The evaluator must make judgments about each experiment he simulated and must record these judgments in a table form described in the text. He must report these judgments by chamber and by experimental class. Finally, he must make summary statements about the five characteristics that acceptable mechanisms must have.

Conclusions

We have presented criteria that influence decisions without specifying what those decisions must be; we have completely described all the elements the evaluator must consider in performing an evaluation; we have made clear those issues that are relevant to an evaluation; and we have been explicit about what the evaluator must report as the basis of the decisions he makes. We have presented a process for evaluating reaction mechanisms that is based on sound scientific principles, draws on classical logic and formal arguments, and considers practical difficulties. It is based upon evolving current practice, but represents a significant improvement over existing evaluations.

Using this report, an evaluator and a sponsor can produce a specific set of agreements—a protocol—for an evaluation of a mechanism using a set of chamber data. As an aid in this process, the Appendix contains a summary of all the necessary reports.

Chamber data from UNC and from UCR that meet the criteria given in this report will be available as part of this project later in 1992. Additional chamber data from the chambers operated by the Commonwealth Scientific and Industrial Research Organization in Sydney, Australia, are being documented and quality assured now and should be available by the end of 1993.

Because of the data incompleteness problem that is described in Chapter 6, however, it is presently not possible to make a compelling case to accept a chemical reaction mechanism as accurately describing urban chemical transformations. In fact, the chamber evidence may not allow even a presumptive standard to be used. For many species of interest, there is only missing evidence. Therefore, until relevant chamber data are made available, the evaluator and the sponsor must be satisfied with vindicating the use of a mechanism, that is, to claim that the mechanism has been evaluated the best we can currently do given the available data.

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The complete report, entitled "Protocols for Evaluating Oxidant Mechanisms for Urban and Regional Models," (Order No. PB92-205 848/AS; Cost: $26.00; subject to change) will be available only from:
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