

**UPDATED CHEMICAL MECHANISMS
FOR AIRSHED MODEL APPLICATIONS**

**Research Proposal to the
California Air Resources Board**

by

**University of California, Riverside
Air Pollution Research Center**

October 27, 2003

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ABSTRACT

The College of Engineering-Center for Environmental Research and Technology (CE-CERT) at the University of California, Riverside (UCR) proposes to develop and comprehensively evaluate updated, detailed, and condensed mechanisms for use in photochemical airshed models for predicting formation of secondary gas-phase and PM pollutants. The mechanisms will incorporate the most recent laboratory and environmental chamber data, improve representations for aromatics, and reduce uncertainties in estimated mechanisms for species where no data are available. This project also includes obtaining environmental chamber data most needed to support this objective and developing more scientifically-supportable condensed mechanisms for model applications where use of CB4 is currently preferred. The results of this will provide the CARB, other regulatory agencies, and researchers with improved and more up-to-date models for gas-phase and secondary PM prediction that have been evaluated against environmental chamber data. The cost for this proposed one-year project is \$166,132.

CONTENTS

BACKGROUND	3
Recent Chemical Mechanisms for Airshed Models	4
Environmental Chamber Database and Evaluation Results	9
Existing Gas-Phase Chamber Database	9
Existing PM Chamber Database	10
New UCR EPA Chamber Data	11
OBJECTIVES	17
APPROACH	18
Task 1. Gas-Phase Mechanism Updates and Improvements	18
Task 1.1. General Gas-Phase Mechanism	18
Task 1.2 Aromatic Mechanisms	19
Task 1.3 Mechanism Evaluation	20
Task 2. Environmental Chamber Experiments	21
Task 3. Mechanism Condensation	22
Task 4. Chlorine Chemistry	23
Task 5. Model Implementation and Testing	24
SCHEDULE, REPORTING AND DELIVERABLES	26
BUDGET	27
QUALIFICATIONS OF THE INVESTIGATORS	28
RELATED PROGRAMS	29
REFERENCES	38
APPENDIX A. BUDGET FORMS AND DETAILS	44

BACKGROUND

Despite improvements in urban air quality in recent years, unacceptable levels of ground-level ozone and atmospheric particulate matter (PM) continues to be a persistent problem, and is not restricted to urban areas (NRC, 1991). To meet National Ambient Air Quality Standards, state and local agencies must implement additional regulations to control pollutant emissions. These should be as cost-effective and as least disruptive as possible. Because all the “easy” emissions control regulations have already been implemented, the additional regulations required to meet the air quality goals must necessarily be increasingly burdensome. However, failing to improve air quality may ultimately be even more costly, because of adverse public health effects and economic damage to crops and materials. Indeed, based primarily on health considerations, the EPA announced changes to the ozone and particulate standards that make them more difficult to attain, particularly in non-urban areas.

In view of the high cost of ozone and PM pollution and the regulations needed to abate them, knowledge of the most appropriate and effective regulatory approach has significant economic value. It is therefore necessary to understand the physical and chemical processes that form these pollutants, both in the present environment and in the future environment that we hope to achieve. With this knowledge, plans to attain the desired environment at a cost that is economically and politically acceptable may be developed.

For example, ground level ozone is not emitted directly, but is formed in a complex and incompletely understood series of light-induced chemical reactions involving oxides of nitrogen (NO_x) and volatile organic compounds (VOCs) which are emitted from a variety of sources (NRC, 1991; Atkinson, 1990). Developing appropriate control strategies for ozone is complicated by the fact that reducing NO_x and VOCs have quite different effects on the ozone produced. Different types of VOCs also have very different effects on ozone. For example, reducing NO_x emissions may actually cause ozone concentrations to become higher in some urban areas, but NO_x reductions are necessary to reduce secondary particulate matter and are probably the only means by which significant ozone improvement can be obtained in rural or downwind areas. VOC controls are often most effective in reducing ozone in urban areas, but VOC controls may have little effect on ozone in downwind areas where ozone is largely NO_x -limited. Furthermore, some VOCs have little effect on ozone even in urban areas, while the effects of others can vary significantly depending on the environment where they are emitted. The relative effects of different VOCs on ozone formation also depend on the environment where they are reacting, with the NO_x levels being an important, but not the only factor (Carter and Atkinson, 1989; Carter, 1994).

The formation of secondary PM is probably even more complex and incompletely understood than the formation of ozone. Secondary PM formation also depends on the nature of the VOC reacting as well as the levels of NO_x and other pollutants, as well as PM from other sources. The factors affecting PM formation from VOCs are quite different from those affecting ozone reactivity, and models designed to predict effects of VOCs on ozone are generally not designed to predict their effects on PM, except in a highly parameterized manner.

Ozone and secondary PM are not necessarily the only secondary pollutants of interest to regulators. The reactions of organics in the atmosphere form formaldehyde and higher aldehydes, PAN and higher peroxy nitrates, organic acids and other pollutants that can affect the environment and exposed populations and materials. Exposure to aldehyde and PAN pollutants in the atmosphere may have health effects that are not characterized, and formation of organic acid products can affect acid deposition processes. In addition, the secondary organic products undergo further reaction in the atmosphere, and

these reactions may significantly affect ozone, PM, and other measures of air quality in multi-day, long-range transport episodes.

Because of these complexities, those responsible for developing plans and regulations for achieving air quality standards must rely on computer airshed models to assess the effectiveness of the strategies they are considering. A critical component for predictions of pollutants such as ozone and other secondary pollutants is the gas-phase chemical mechanism, i.e., the portion of the model used to represent the gas-phase chemical reactions involved. This is because the chemistry is the source of much of the complexity and non-linearity involved. The gas-phase mechanism is also a critical component for the prediction of secondary PM, because this is formed from condensation of high molecular weight oxidized products formed in the gas-phase reactions. Because many of the chemical reactions are incompletely understood, these mechanisms cannot be relied upon to give accurate predictions of impacts on emissions on air quality until they have been shown to give accurate predictions of pollutant concentrations under realistic but controlled conditions.

The most cost-effective and reliable way to test the accuracy of the chemical mechanisms is to compare their predictions against results of environmental chamber experiments that simulate the range of conditions in the atmosphere. An extensive database to evaluate gas-phase mechanisms already exists, though as discussed below it has limitations that need to be addressed. The database of chamber experiments to evaluate secondary PM formation is considerably more limited, and most such experiments were not carried out with the degree of control or characterization that is important for reproducibility and comprehensive mechanism evaluation. Since accurately modeling gas-phase processes that form the PM precursors is critical to properly modeling secondary PM, it is important that conditions in such experiments be at least as well controlled and characterized as those used for gas-phase mechanism evaluation, if not more so. However, until recently most experiments have focused on measuring overall aerosol yields, and not obtaining data to evaluate models for the dynamic processes actually causing the PM formation.

Recent Chemical Mechanisms for Airshed Models

The most recently developed gas-phase mechanisms for use in airshed model applications include the detailed and condensed SAPRC-99 mechanisms (Carter, 2000a), the Regional Atmospheric Chemistry (RACM) mechanism (Stockwell et al., 1997), the Caltech Atmospheric Chemistry (CACM) mechanism (Griffin et al., 2002), and updates to the Carbon Bond IV (CB4) mechanism (Gery et al., 1989, 1989) by Jeffries et al (2002), and the European Master Chemical Mechanism developed by Derwent and co-workers (MCM, 2002). Each of these were developed for different purposes and represent different level of chemical detail and incorporate different assumptions and approximations concerning regarding uncertainties and complexity of atmospheric chemistry. The status and evaluation of each will be discussed briefly below.

The Detailed SAPRC-99 mechanism was developed in our laboratories primarily under CARB funding (Carter, 2000a). It was developed for the purpose of computing ozone reactivity scales for the many types of emitted VOCs, and to serve as a basis for deriving more condensed mechanisms for predictions of O₃ and other gas-phase species in airshed models. This mechanism includes the capability of representing the reactions of approximately 400 types of VOCs, either singly or in mixtures, making it the most detailed in terms of the number of different types of VOC species it can represent. It was used as the basis for calculating the Maximum Incremental Reactivity (MIR) scale for quantifying the effects of VOCs on ozone for regulatory applications in California (CARB, 2000). In addition to ozone, it can be used to predict the formation of a number of aldehyde, PAN, and organic acid species (see, for example, Carter, 2001), and as discussed below can potentially serve as the basis for developing mechanisms for predicting PM formation. This mechanism was evaluated against the full set of environmental chamber

experiments carried out at UCR through 1999 (Carter, 2000) and earlier versions of this mechanism were evaluated against a large number of relatively high NO_x chamber experiments carried out at UNC (Carter and Lurmann, 1991; Carter and Atkinson, 1996). This included experiments to test model predictions for over 80 types of individual VOCs, as well as experiments simulating more realistic mixtures of ambient VOCs.

This mechanism is also being evaluated against new experiments being carried out in our laboratory, and the preliminary results to date are discussed in more detail below as part of the discussion of the new UCR EPA chamber experiments. Briefly, they suggest that although the mechanism appears to perform reasonably well in simulating O₃ under low NO_x conditions, there appear to be significant problems with the aromatic mechanisms that were not evident previously that need further investigation. Since all mechanisms that have been evaluated against chamber data have generally similar aromatics mechanisms, these problems are probably applicable to the other mechanisms as well.

The SAPRC-99 mechanism uses a relatively condensed method to represent the peroxy + peroxy reactions that are not important when O₃ formation is occurring but become important under very low NO_x conditions. As part of our ongoing project to develop and evaluate mechanisms for low NO_x conditions for the CARB (see Related Programs, below), we are evaluating whether to develop a version that uses the more detailed treatment of peroxy reactions incorporated in the RADM-2, RACM, and CACM mechanisms. Since these reactions are not important when O₃ formation is occurring this modification wouldn't affect O₃ predictions, but it may affect predictions of peroxide species or the types of organic products formed when NO_x is very low. However it is unclear whether the differences in model predictions with the less approximate treatment of peroxy reactions would be sufficiently large to merit the considerable increase in mechanism size required to implement this¹.

Although the SAPRC-99 mechanism was not designed for PM predictions, other researchers have used it as a basis for developing mechanisms for PM prediction (e.g., Boylan et al., 2002). This can be readily done by adding new condensable product model species to the list of product species that the various types of individual VOCs can form when they react. In principle this can be used to derive models that take differences in PM formation potentials for all the ~400 types of represented VOCs, though presently the data are insufficient to implement this for most compounds. In practice, most adaptations of SAPRC-99 for PM predictions have utilized the condensed version of the mechanism, discussed below, as the starting point.

The Condensed SAPRC-99 mechanism (Carter, 2000b) is essentially the same as the detailed version except that a set of ~30 VOC model species is used to represent the complex mixtures of VOCs in ambient simulations, rather than representing all the ~400 types explicitly. The rate constants and product yields for some of these model species are adjusted based on those for the distribution of compounds they represent, using an assumed representative ambient emitted VOC profile and the rate constants and product yields for the individual species in the detailed mechanism (Carter, 1988a,b, 2000a,b). Therefore, although it uses a similar number of model species to represent the many emitted VOCs as do the RADM-2 (Stockwell et al, 1999) and RACM mechanisms, it utilizes the mechanistic information

¹ The approximation used in SAPRC-99 and also CB4 uses the same distribution of organic compounds to represent products of peroxy + peroxy reactions as used when the peroxy radicals react with NO, and use a limited number of “operator” species to represent the effects of the peroxy radical reactions on NO_x and other radicals. RADM-2, RACM, and CACM include separate model species for each type of peroxy radical, permitting their reactions to be represented separately. CACM uses a combination of operators and explicit reactions to represent these processes in a less approximate way than RADM-2 and RACM, and incorporates the general method that we are considering for modifying SAPRC for the current low NO_x mechanism program.

contained in the detailed version to derive the optimum parameters for the lumped species. Since it is directly derived from the detailed mechanism, the evaluation of the detailed mechanism is also applicable to this version.

The condensed SAPRC-99 mechanism can be implemented in models using either the adjustable or fixed parameter versions, depending on whether the kinetic and mechanistic parameters of the lumped model species are derived from the actual emissions being represented or whether a default set of parameters, based on a representative emissions profile, is used (Carter, 2000b). Because of limitations in current emissions processing systems most models use the latter, fixed parameter version, but work on improving emissions processing systems to permit use of the adjustable parameter version, which is necessary for assessing VOC reactivity effects, is underway (see Related Programs, below).

The Caltech Atmospheric Chemistry Mechanism (CACM) (Griffin et al, 2002, Seinfeld et al, 2002) was also developed primarily from CARB funding, but in this case the primary objective was for modeling PM formation in the atmosphere with a relatively high level of chemical detail. Its inorganic and base simple organic mechanism is based largely on that of SAPRC-99, though it uses the somewhat more detailed approach of RADM-2 and RACM when representing peroxy radical reactions. It employs a similar number of model species as condensed SAPRC-99 to represent emitted organics, but has a slightly different aggregation approach in some cases based on considerations of secondary PM formation characteristics, and uses a considerably larger number of model species to represent organic products. The very large number of organic product model species (~80 compared to ~30 for SAPRC-99) is used primarily to represent condensable product compounds with different PM forming characteristics to more accurately model secondary PM formation.

The discussion of the CACM mechanism in the Seinfeld et al (2002) report does not indicate that it was evaluated against any environmental chamber data. The only evaluation consisted of comparing modeled and observed predictions of O₃ in a SCAQS episode. Because of the uncertainties in model input and data in real episodes and the many other factors affecting O₃ predictions in such simulations, and the fact that the effects of changing VOC compositions are not examined, this cannot be considered to be an adequate evaluation of a mechanism of this level of detail. The performance of mechanisms in simulating aromatics experiments is very sensitive to how reactive aromatic products are represented and their assumed photolysis rates, yet there was no discussion of this in the mechanism documentation. If this is not adequately considered, the mechanism would not perform well simulating experiments containing aromatics, and would not accurately predict how formation of O₃, radicals, and thus formation rates of PM precursors would change as aromatic contents of emissions is changed. In order to accurately simulate PM formation, the mechanism must first be able to simulate the overall rates of the oxidation reactions that cause O₃ as well as secondary PM formation.

Although it has similar or greater level of chemical detail as condensed SAPRC-99, the CACM mechanism uses a somewhat different approach for deriving mechanisms for the lumped model species that represents many compounds. While the condensed SAPRC-99 uses weighed averages of parameters for the compounds the model species represent, CACM uses mechanisms of individual compounds chosen as representative of the groups. In the case of aromatics, the choice is made on the basis of secondary PM forming potential and not the effects of the compounds on O₃ and radical levels. This is probably the most practical approach for deriving detailed mechanisms for PM formation, especially given the limited information available and the amount of estimates required to predict PM forming behavior, and provides a reasonable basis for deriving chemically-detailed approximate mechanisms for this purpose. However, this level of approximation is not necessary and probably not optimum for models for predicting O₃ and radical levels, which as indicated above is also important for PM models.

Despite the deficiencies in its formulation and evaluation with regard to prediction of O₃ and radical levels, the CACM mechanism probably represents the state of the science in modeling precursors to PM formation in a chemically detailed manner. However, it needs to be evaluated against results of available chamber experiments with PM measurements as well as experiments used to evaluate mechanisms for O₃ predictions. This is discussed further later in this proposal.

Although condensed in terms of representing emitted VOCs, the CACM mechanism is probably more detailed than needed for practical model applications, as indicated by the fact that a significantly smaller number of species is used to represent PM precursors in the model in which it was implemented in practice (Seinfeld et al, 2002). However, developing and evaluating detailed mechanisms is appropriate since they serve as the most scientifically justifiable starting point for deriving condensed mechanisms for airshed model applications.

The Master Chemical Mechanism (MCM) is a fully explicit mechanism for the gas-phase reactions of approximately representative 125 VOC species, and is designed primarily simulations of O₃, PAN, and other gas-phase oxidant species in trajectory model calculations, and for deriving VOC reactivity scales for those species (Saunders et al, 2003; Jenkin et al., 2003; MCM, 2003). In this respect it is similar to the SAPRC-99 detailed mechanism, except that somewhat fewer types of primary VOC species and very many more organic product are represented. Although characterized as being fully explicit, it represents most of the complex sequences of competitive reactions by assuming that one or a few major routes represent all the competing processes². This is necessary because otherwise hundreds and even (in some cases) thousands of reactions would have to be included, which is not practical if all are to be represented explicitly, though they can be used as the basis for developing condensed mechanism³. However, this means that the mechanism is not strictly speaking explicit, since in effect some reactions and product species are being used to represent others. In some ways this is analogous to the condensation approach used in the CACM mechanism, though in this case the condensation is used only for the products and intermediates, not the primary emitted VOCs.

The MCM has not been systematically evaluated against the large body of available chamber data, though there are studies where selected portions are evaluated using results of experiments in the Euphore outdoor chamber. Even though the mechanism is designed to be explicit, almost all of the rate constants or rate constant ratios are estimated and many of the reactions (particularly for compounds with incompletely characterized mechanisms, such as aromatics) are entirely speculative. Therefore, its predictions may be no more accurate than highly condensed mechanisms that are based on the same body of theory and knowledge, and are probably in most cases less accurate than mechanisms that have been more comprehensively evaluated and, where necessary modified, using chamber data.

In principle the MCM is well suited to serve as a basis for predicting PM precursor formation, since it can predict the formation of at least a large representative subset of individual PM precursor species. However, since the uncertainty in mechanisms generally increases with the size of the molecule, the reactions forming the PM precursors would almost certainly be the most speculative and uncertain

² For example, the reaction of OH with n-undecane is assumed to form only 2-peroxy undecyl radicals, whose subsequent reactions and products represent those from the reactions at the 5 other positions.

³ The SAPRC-99 mechanism generation system generates all the reactions estimated to occur over 1% of the time relative to the competing reactions of the same species or radical, resulting in some cases mechanisms with thousands of reactions and products. However, the system outputs condensed reactions that represent the overall processes, with the many products represented by the limited number of product model species according to specified “lumping rules”. Thus, these many processes are taken into account but are not represented explicitly.

part of the mechanism. But the PM precursor mechanisms would be no more uncertain or speculative than those already incorporated in CACM.

Although the MCM represents a useful approach for developing detailed mechanisms, it is not widely used in ambient modeling in the United States since it has not to our knowledge been implemented in the types of 3-D urban and regional models that are required for regulatory applications. However, it could be used as a basis for developing condensed mechanisms for such models, and in principle could provide an alternative to SAPRC-99 that is worth investigating.

The Regional Atmospheric Chemistry (RACM) mechanism was developed as an updated and somewhat expanded version of the RADM-2 mechanism for the purpose of predicting O₃ and other oxidants and acid deposition in regional models (Stockwell et al., 1990, 1997). The RADM-2 mechanism is widely used in regional models in the United States and the RACM mechanism is becoming relatively widely used by researchers in Europe. It has a similar level of detail as condensed SAPRC-99 in terms of representing emitted VOC species and a similar approach for representing the low NO_x peroxy + peroxy reactions as CACM. It has been evaluated against a subset of the experiments used to evaluate SAPRC-99 and found to give similar model performance in simulating O₃ and other species. The aromatics mechanism is based largely on that used in RADM-2 (Stockwell et al, 1990), and are generally similar to those used in the more recent SAPRC mechanisms because they were derived using similar procedures (Carter et al, 1990). Although SAPRC-99 rather than this mechanism will be used as the primary basis for mechanism development discussed in this proposal, it provides a valuable alternative for insights and alternatives to consider during the mechanism development process and mechanism intercomparison studies.

The Carbon Bond 4 (CB4) mechanism (Gery et al., 1988, 1989), though out of date, is still widely used in urban and regional airshed model applications because of its computational efficiency and because it has been widely used for a long time and limitations in current emissions procedures make use of changing mechanisms difficult⁴. To address the need for a more up-to-date version with the same computational advantages and that is consistent with existing CB4 emissions databases, Jeffries et al (2002) recently developed an updated version of this mechanism and tested it against a large body of UNC outdoor chamber data. However, to our knowledge this version has not yet been widely implemented in airshed models.

The Carbon Bond approach, which assumes that parts of molecules can be represented as reacting is inappropriate for predicting formation of PM precursors because it is molecules that *stay together* that are of primary interest. Nevertheless, PM formation modules have been appended to the CB4 mechanism in a number of models. Although use of appropriate parameters may provide best estimates of PM precursor rates for an assumed set of emitted VOCs, such models by their formulation could not predict effects of changing compositions on PM precursor formation. In addition, many gas-phase processes are believed to involve isomerization and other reactions involving one part of the molecule or radical reacting or interacting with the other (Atkinson, 1990, 2000 and references therein, Carter, 2000a). Although laboratory studies of aromatic reactions are insufficient to directly assess this, the fact that the reactivity of ethylbenzene is considerably different than that of toluene suggests that the assumption that the aromatic ring reacts independently of the size of the side chains is also probably incorrect. Therefore, we do not believe that updating the Carbon Bond mechanism is the appropriate approach for developing improved condensed mechanisms for airshed models. This is discussed further later in this proposal.

⁴ See Related Programs for a discussion ongoing work to address this problem.

Environmental Chamber Database and Evaluation Results

Existing Gas-Phase Chamber Database

The available environmental chamber data base up to the late 1990's for evaluating ozone mechanisms has been reviewed by Dodge (2000) as part of the 1998 NARSTO ozone assessment. A fairly extensive set of quality-assured data exist for experiments carried out at our facilities at UCR (Carter et al, 1995, 1997, others⁵) and at the University of North Carolina (UNC) (Jeffries et al, 1982, 1985a-c, 1990; Jeffries, private communication, 1995). These experiments have used a variety of compounds and mixtures, and have been used as the basis for the development and evaluation of the three major oxidant mechanisms currently used in the United States (Dodge, 2000; Carter and Lurmann, 1990, 1991; Gery et al, 1989; Stockwell et al, 1990). A smaller set of data are available at other facilities, but except for the very limited number of experiments at the Tennessee Valley Authority (TVA) facility (Simonaitis and Bailey, 1995; Bailey et al, 1996) and perhaps the Commonwealth Scientific and Industrial Research Organization (CSIRO) chamber in Australia (Johnson et al, 1997) the experiments were designed more for empirical reactivity assessment than for mechanism evaluation (Dodge, 2000). Several new facilities are being developed in Europe (Becker, 1996; Mentel et al, 1996; Wahner, 1998; Wahner et al, 1998; Dodge, 2000, and references therein), though the available data primarily involve specialized studies of specific chemical systems rather than general mechanism evaluation.

As discussed by Dodge (2000), the then-current chamber data base has a number of serious limitations and data gaps that could be limiting the accuracy of the mechanisms used in the models to predict control strategies. Uncertainties exist concerning characterization of chamber conditions, particularly how wall artifacts affect the gas-phase reactions (Carter and Lurmann, 1990, 1991), and inappropriate treatment of these effects could cause compensating errors in the gas-phase mechanism (Jeffries et al, 1992). Most chamber experiments lack measurement data for important intermediate and product species, limiting the level of detail to which the mechanisms can be evaluated, and limiting the types of air quality impact predictions that can be assessed. Furthermore, because of chamber background and wall effects, and because of inadequate analytical equipment currently available at environmental chamber facilities, the current environmental chamber data base is not suitable for evaluating chemical mechanisms under the lower NO_x conditions⁶ found in rural and urban areas with lower pollutant burdens.

There has been a limited database of environmental chamber experiments carried out under relatively low NO_x conditions that has not been adequately utilized for mechanism evaluation. Until recently (see below), the effort in the United States has been limited to work with the TVA chamber in 1993-1996. In 1995 and 1996, Graham Johnson of the Commonwealth Scientific and Industrial Research Organization (CSIRO) in Australia used outdoor smog chambers to perform a series of chamber experiments at low NO_x and VOC concentrations under sponsorship of the US EPA (Johnson et al, 1997). Jeffries et al. (2000b) prepared these data in a format suitable for modeling, though to our knowledge they have not been used for evaluation of a state-of-the art mechanism.

The SAPRC-99 gas-phase mechanism was evaluated against the results of most of the suitable UCR chamber experiments and selected experiments carried out at UNC and (more recently) TVA. (Carter, 2000a, 2003). Carter (2000) considered the performance against the UCR and selected UNC chamber experiments to be generally satisfactory, though there was run-to-run variability in the quality of the fits and there were some discrepancies that suggested probable mechanism problems. As part of our

⁵ See downloadable documents at <http://cert.ucr.edu/~carter/bycarter.htm>.

⁶ In this proposal, the term "low NO_x conditions" will refer to conditions where total NO_x concentrations are less than about 25 ppb, and "very low NO_x conditions" will refer to conditions where NO_x is sufficiently low that peroxy + peroxy reactions dominate over reactions of peroxy radicals with NO.

current program to evaluate the mechanism under low NO_x conditions, the mechanism was evaluated against results of TVA experiments carried out at lower NO_x than the experiments used in the previous evaluations, and the results also indicted generally satisfactory performance of the mechanism (Carter, 2003). However, simulations of new UCR EPA chamber experiments, discussed in the following section, indicated problems with the aromatics mechanisms and the general mechanism under low ROG/NO_x conditions that were not noted in the previous evaluations of this mechanism.

Existing PM Chamber Database

A number of studies have been performed that measure the aerosol formation potential from a number of gas-phase hydrocarbons. SOA formation is typically presented as aerosol mass produced per parent hydrocarbon reacted. Secondary organic aerosol formation studies have been performed in a environmental chambers at UC Riverside (Ziemann, 2002), Caltech (Bowman et al, 1995; Cocker et al, 2001a,b; Griffin et al, 1999; Hoffman et al, 1997; Odem et al, 1997; Yu et al., 1999), UNC (Jang et al, 2001; Jaoui et al, 2001, 2002, 2003a,b), EPA (Kleindienst et al, 1999; Smith et al, 1999), EUPHORE (Hallquist et al, 1999; Virkkula et al, 1999), and CSIRO (unpublished results). However, little inter-laboratory comparison has been performed and those comparisons typically lead to significant discrepancies due to differences in temperature, light source, hydrocarbon/NO_x ratios, aerosol wall loss correction, etc. The most comprehensive database on SOA formation potential from a suite of hydrocarbons has been produced at Caltech in their outdoor environmental reactor. (Hoffman et al., 1997; Bowman et al., 1995 Odum et al., 1996,1997; Griffin et al., 1999) A database for aerosol formation potential in terms of partitioning parameters is available for 17 aromatic compounds and 14 biogenic compounds. The UNC chamber has focused on the development of explicit mechanisms for a few specific compounds. Recently, Seinfeld and Pankow (2003) published a review on organic atmospheric particulate matter where they provided a summary of laboratory studies on SOA. In addition, Calvert et al. (2002) provides a survey of available results on product identification and photooxidation mechanisms for SOA from aromatic hydrocarbons. Due to limitations in analytical techniques for identification of highly polar organic compounds, a majority of SOA products from aromatic photooxidation is not known.

The data sets currently available have a number of serious limitations and data gaps that may limit the accuracy of a model using these data. Variability in the accounting of wall effects, temperature changes, the role of relative humidity, HC/NO_x, limit the ability of these data sets to be used in current models. The ability to control temperature, a critical parameter in gas-particle partitioning, in outdoor chambers makes it difficult to assess the appropriate temperature that the aerosol yield is valid for. (Typically, the average temperature of the experiment is used). An additional limitation to the model is that relatively little work has been performed on measuring SOA formation from a mixture of hydrocarbons. Little is known about potential interactions of these hydrocarbons (by altering the gas-phase production of radical species). A paper by Odum et al. is the only experiment assessing the effects of mixtures; in his study it appeared that the presence of multiple hydrocarbons did not affect the parameterization of aerosol formation. However, further investigation is needed to confirm these findings in lieu of more recent work by Griffin et al. (1999) that demonstrated that for biogenic compounds the oxidant reacting with the parent hydrocarbon was critical in determining the aerosol formation parameters of a given reaction.

A smaller subset of experiments is available with experiments that focused on evaluation of explicit mechanisms for specific compounds. These experiments have been primarily conducted at UNC by the Kamens group; (for ex: Jang and Kamens, 2001; Jaoui et al., 2001; Jaoui and Kamens 2001, 2002, 2003); experiments focusing on detailed SOA composition for cyclohexene, m-xylene, a-pinene, b-pinene, sabinene, and Δ^3 -carene have also been performed by the Seinfeld group (Yu et al., 1999; Cocker et al., 2001; Kalberer et al., 2000) at Caltech. These experiments provide details of the chemical composition of the SOA and allow for estimation of the vapor pressures of these condensable products.

Pankow et al. (2001) compared observed and predicted yield values for SOA formed from cyclohexene ozonolysis and monoterpene ozonolysis and found generally good agreement between predicted and measured SOA formation.

A vast majority of these experiments have been performed in the absence of gas-phase water. Little is currently understood about the potential role of RH on SOA formation. It is expected that aerosol produced from organic oxidation reactions will have some polarity and will therefore uptake water. Recently some researchers (Cocker et al., 2001a,b; Edney et al., (2000); Virkkula et al., 1999) have begun to investigate the role of RH but little can be concluded from these initial experiments.

New UCR EPA Chamber Data

Under funding from the U.S. EPA, we have developed a “Next Generation” environmental chamber facility for mechanism evaluation and VOC reactivity assessment research. The objectives and current status of this project is briefly summarized in the “Related Programs” section of this proposal. As indicated there, a major objective of the project is mechanism evaluation under low NO_x conditions, which clearly is highly relevant to this project. The chamber consists of a 16,000 cubic ft temperature-controlled “clean room” enclosure fitted with a 200 KW argon arc light source, with space for two up to 8,000 cubic ft reactors where the reactions are monitored. A blacklight light source was also installed in the enclosure for experiments where the argon arc light is not needed or for assessing effects of varying light source. The dual reactors are constructed of Teflon® film fitted on specially designed moveable frameworks, with an associated high volume mixing system suitable for injecting low volatility materials, and a computer-controlled sampling and calibration system for the analyses. A high capacity air purification system is used to keep the enclosure clean and provide highly purified air for the experiments. A diagram of the reactor is shown on Figure 1.

Instrumentation is available to measure the range of gas-phase species needed for comprehensive evaluations, including tunable diode laser absorption spectroscopy instruments for sensitive and specific analysis of NO₂, HNO₃, H₂O₂, and formaldehyde, GC's for speciated analysis for organic reactants and toxic products, and extensive instrumentation for characterizing experimental conditions. There are also two Scanning Electrical Mobility Spectrometers (SEMS) for measuring aerosol size and number distribution and a Tandem Differential Mobility Analyzer (TDMA) for measuring aerosol responses to changes in temperature and humidity has been constructed and will be available for this project.

The new environmental chamber has significant advantages for chemical mechanism evaluation. Because of the more sensitive analytical instrumentation and the steps taken to minimize background effects, the chamber can be used to carry out useful mechanism evaluation experiments using initial NO_x levels as low as ~10 ppb and possibly lower – considerably lower than used in the previous database, and lower than experiments in the TVA and CSIRO chambers. The chamber also provides the ability to conduct experiments at a wide range of temperatures (~5-45°C) and humidities, which is needed for evaluating temperature effects predictions of uncertain gas-phase mechanisms, and is essential for systematic studies of PM formation. The availability of advanced instrumentation for PM measurements along with gas-phase species PM provides a means for testing mechanisms for PM formation as well as gas-phase mechanisms. This will permit PM formation mechanisms to be evaluated at lower pollutant concentrations and under far more controlled conditions than used for most of the previous PM evaluation experiments discussed above. The ability to provide PM evaluation data using procedures and high characterization standards developed for gas-phase mechanism evaluation is a unique advantage of this facility.

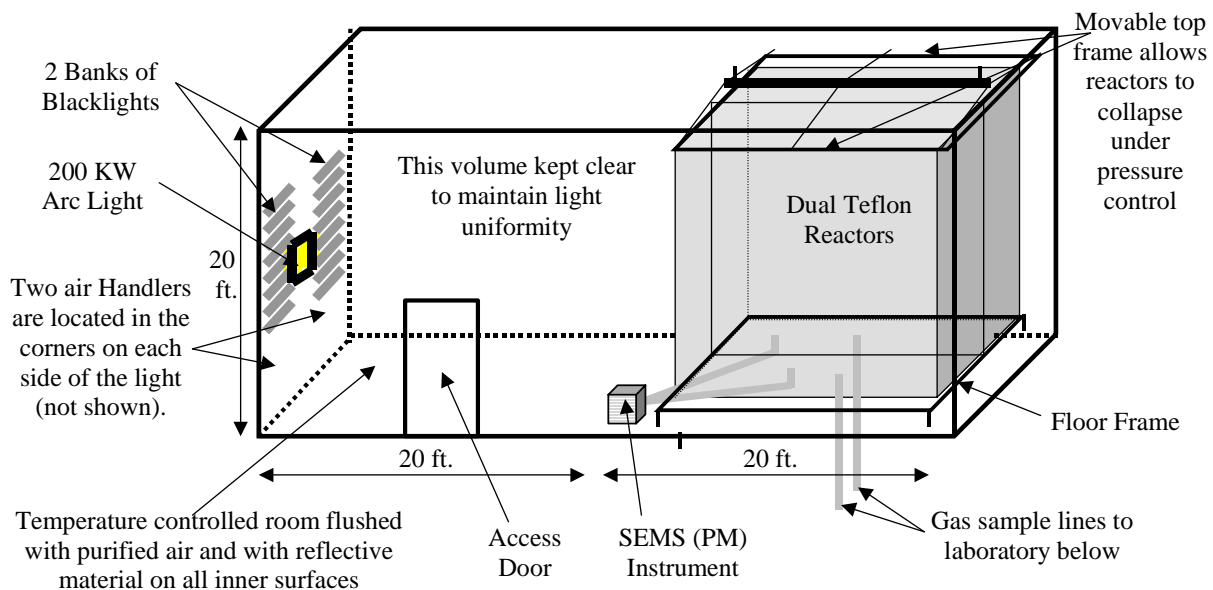


Figure 1. Schematic of the temperature-controlled enclosure housing the reactor.

The first experiment in the new facility, using a preliminary light source and reactor configuration, was carried out in February of 2002 (Carter et al, 2002). The first experiment with the arc lights and the near-final configuration for a single reactor was conducted in July. The second reactor and the final mixing and sampling system were completed in late 2002 and the first successful experiment with the dual reactor system in its current configuration was completed in early 2003. The initial experiments included evaluations of background effects, the performance of the light source, temperature control system, and analytical instrumentation in the current configuration. The initial characterization results are discussed in a previous interim report to the CARB (Carter, 2003b). Briefly, the results indicated that chamber effects are as low as can be feasibly obtained in Teflon film reactors. In particular, the background effects were sufficiently low that useful mechanism evaluation experiments could be carried out experiments with NO_x levels as low as 2 ppb and perhaps lower.

Experiments useful for model evaluation began in early 2003. Although the data are not completely analyzed and experiments are continuing, a discussion of the major types of experiments carried out for which preliminary findings have been obtained from them can be summarized as discussed below.

Low NO_x Mechanism Evaluation

Experiments with simple chemical systems were conducted with NO_x levels down to ~5 ppb and with ambient surrogate mixtures with NO_x levels down to ~2 ppb. These are the lowest NO_x chamber experiments carried out to date for the purpose of mechanism evaluation. It was found that the SAPRC-99 simulated the results of these experiments approximately as well as it simulated the existing chamber base at higher NO_x levels. Thus the results to date indicate no apparent deterioration in mechanism performance in simulating O_3 formation at the lower NO_x levels. This is a significant finding because mechanisms have not been evaluated previously by as well characterized experiments at these NO_x levels, and there was a concern about this because of the nonlinearity of the chemical system involved. However, the number of experiments is relatively limited and additional data are needed to confirm this.

Aromatic Mechanism Evaluation

The SAPRC-99 mechanism simulated the results of the limited number of aromatic (toluene and m-xylene) experiments carried out in this chamber reasonably well, including the experiments with NO_x levels as low as ~5 ppb. This is consistent with results of simulations of previous runs. However, experiments with relatively high concentrations (\geq ~50 ppm) of CO added to the aromatics - NO_x system, which have not been carried out previously, were not successfully simulated by the model. The results were consistent with model predictions in that the addition of CO caused a significant increase in O₃ formation, but the observed additional O₃ formation was about twice the amount predicted by the model. This suggests that the mechanism may be underpredicting the radical initiation in the aromatics mechanisms, which is being compensated for in simulations of aromatics - NO_x and aromatics incremental reactivity experiments by the model overpredicting NO to NO₂ conversions in the mechanism. Additional evidence for this is preliminary results indicating that mechanisms underpredict the “direct reactivity” of aromatics, which measures NO to NO₂ conversions caused by their reactions (Carter and Malkina, 2002). Thus, the new data from this facility indicate significant problems with aromatics mechanisms that have not been evident previously.

Evaluation of Base Case Surrogate - NO_x Experiments

Base case surrogate - NO_x experiments designed to simulate ambient pollution at different ROG and NO_x levels, and are important for mechanism evaluation and to characterize as base case experiments for incremental reactivity studies. In the latter case, it is important that the model appropriately simulate the base case before its ability to simulate the effects of added VOCs is evaluated. To support the use of the chamber for reactivity studies, base case experiments were carried out at various ROG and NO_x levels, as indicated on Figure 2. Symbols on the figure indicate ROG and NO_x levels where the base case experiments were carried out, and also indicate those for reactivity experiments discussed below. Figure 3 shows the same matrix except with superimposed experimental and SAPRC-99 calculated concentration-time plots for O₃ formed selected experiments at positions indicating the initial ROG and NO_x levels. It can be seen that there is a consistent pattern in terms of the model being able to simulate the results, with the data being fit reasonably well at MOIR or lower NO_x conditions, but with the model having an increasing large bias for underprediction of O₃ as NO_x levels are increased to MIR or higher levels⁷. This bias also appears to increase as the absolute pollutant levels increase along lines of constant ROG/NO_x ratios. This “high NO_x” bias, which has not been evident before perhaps because of the focus on experiments where “true” O₃ maxima are reached, indicates a serious problem with the mechanism that needs to be evaluated. The problem may be related to the apparent radical initiation problem with the aromatics mechanism discussed above; this needs to be investigated.

Figure 2 also indicates the ROG and NO_x levels where incremental reactivity experiments for n-octane and m-xylene were conducted. These were chosen as relatively well-studied representative compounds with significantly different types of reactivity characteristics that are representative of the major types of compounds in coatings VOCs. As such these are useful for evaluating the utility of experiments at the different ROG and NO_x levels for reactivity assessment purposes for our coatings VOC and related projects. Points “A” and “B” indicate the ROG and NO_x levels of the base case experiments being used in our current experiments for the coatings reactivity project. These were chosen based on input from the CARB staff that experiments with 1-50 ppb NO_x should be the focus of the experiments for this project (Luo, 2003), with the middle of this range, ~20-30 ppb, being chosen for the initial experiments, with the ROG levels being chosen to represent MIR and relatively low NO_x, ½ MOIR

⁷ MIR conditions indicate ROG and NO_x levels where O₃ formation is most sensitive to added VOCs, while MOIR conditions are those where the highest O₃ concentrations are formed, i.e., the “ridgeline” on O₃ isopleth plots (Carter, 1994).

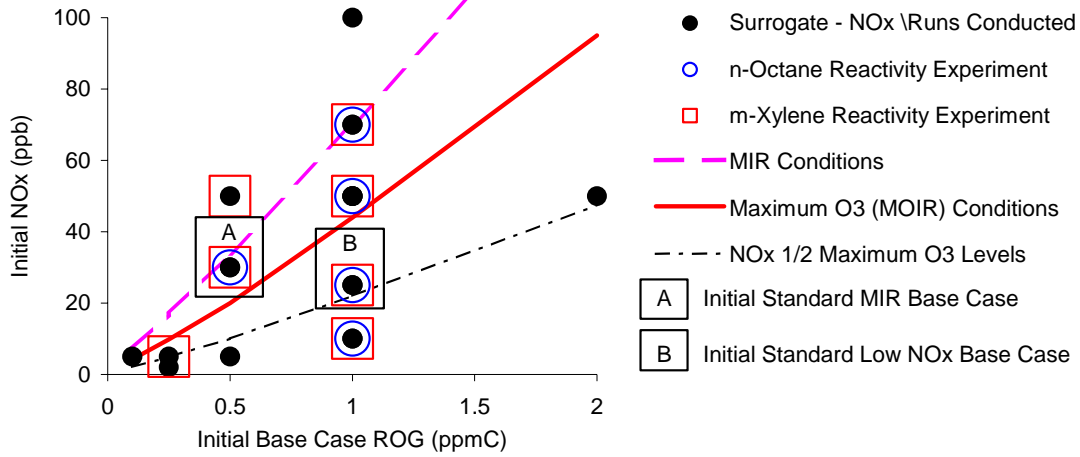


Figure 2. Matrix of Surrogate - NO_x experiments carried out for base case surrogate and low NO_x mechanism evaluation.

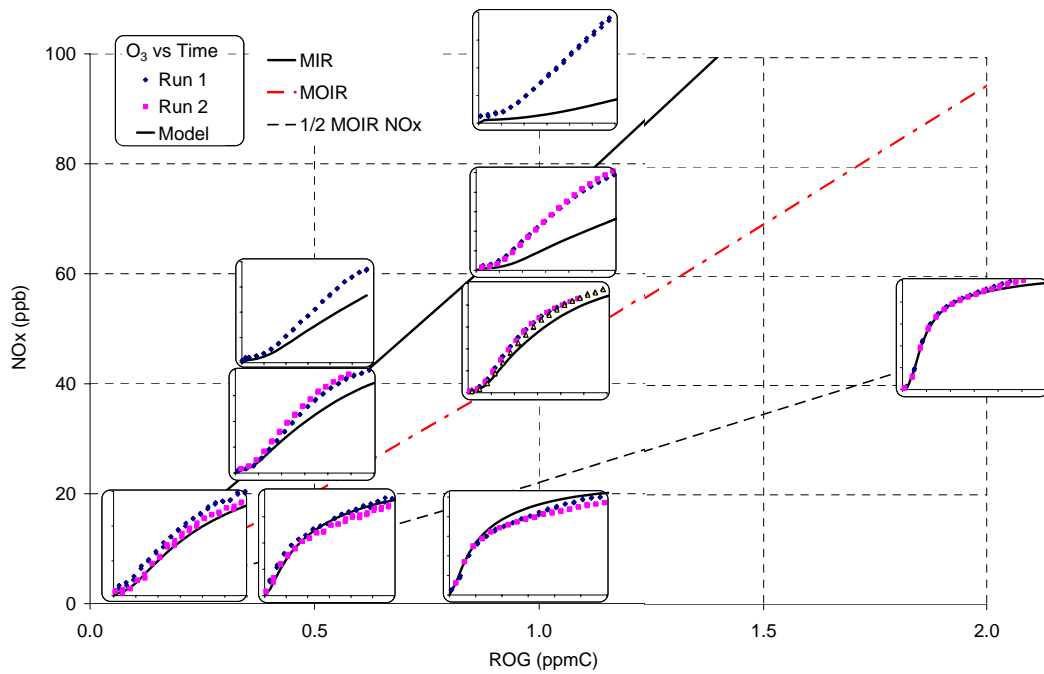


Figure 3. Plots of experimental and calculated concentration-time plots for O₃ for selected surrogate - NO_x experiments at various ROG and NO_x levels. The positions of the plots on the larger matrix plot indicate the ROG and NO_x levels employed.

conditions. The results of the incremental reactivity experiments, and their consistency with model predictions, are currently being evaluated.

Initial PM Studies

Our research group has recently performed a set of characterization runs to demonstrate the ability of the new UCR chamber facility to perform SOA formation experiments. *m*-Xylene was chosen as the initial test compound. A side-by-side repeatability experiment with *m*-xylene and NO initial concentrations of 75 ppb and 50 ppb, respectively, is shown in Figure x below. This experiment had no initial aerosol present; the number and the volume shown have been corrected for wall losses assuming first order kinetics for wall loss, and was performed using blacklights as an irradiation source. Table 1 summarizes the results of four replicate experiments.

Table 1 and Figure 4 demonstrate the excellent reproducibility of SOA formation studies within our chamber. In particular, four experiments were performed under similar conditions with the net measured SOA formation nearly identical. The experimentally determined SOA formation was then compared to experimental results obtained by other researchers. The yield data is most easily compared to (Figure y) recent *m*-xylene irradiations at Caltech at comparable experimental conditions (indoors, blacklight source, temperature similar) (Cocker et al., 2001). Some possible reasons for the slightly different yield include slightly differences in temperatures and HC/NO_x ratios. The overall agreement between the UCR chamber and the Caltech chamber demonstrates that our chamber can reproduce literature values under similar lighting conditions. .

Next, the data are compared with other experiments performed outdoors (Odum et al., 1997) at higher temperatures, and different NO_x levels (Figure 5). A significant difference is seen in the predicted SOA formation between our indoor experiments and the earlier outdoor experiments. Figure 5 clearly demonstrates the need for an improved understanding in the mechanisms leading to SOA formation. This work will elucidate the differences in the mechanisms that led to these differences including temperature effects, HC/NO_x ratios, and different lighting conditions.

Table 1. Summary of results for four replicate *m*-xylene photooxidations carried out in the UCR EPA chamber. All experiments carried out at 301°K and used the blacklight light source.

<i>m</i> -Xylene reacted (ppb)	Initial NO (ppb)	Aerosol Produced (corrected for wall loss, $\mu\text{g m}^{-3}$)
319	50	21.7
324	50	21.2
307	49	21.0
306	49	21.3

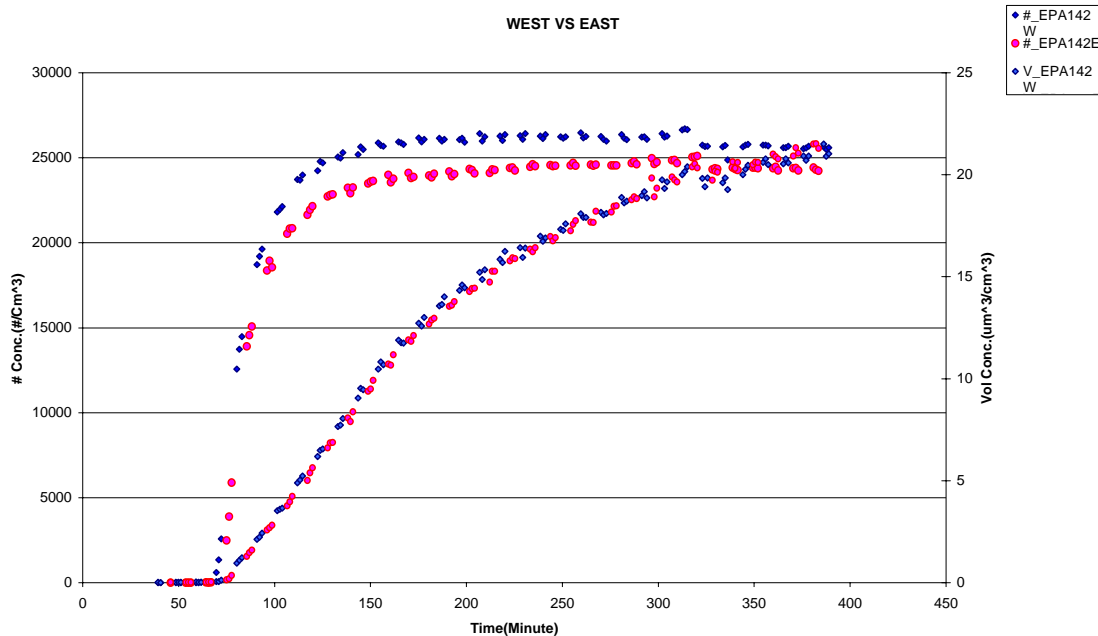


Figure 4. Comparison of side by side m-xylene experiments. Top two curves are the number concentration of SOA corrected for wall losses, Bottom two curves (nearly indistinguishable from each other) are for the aerosol volume concentration produced corrected for wall loss.

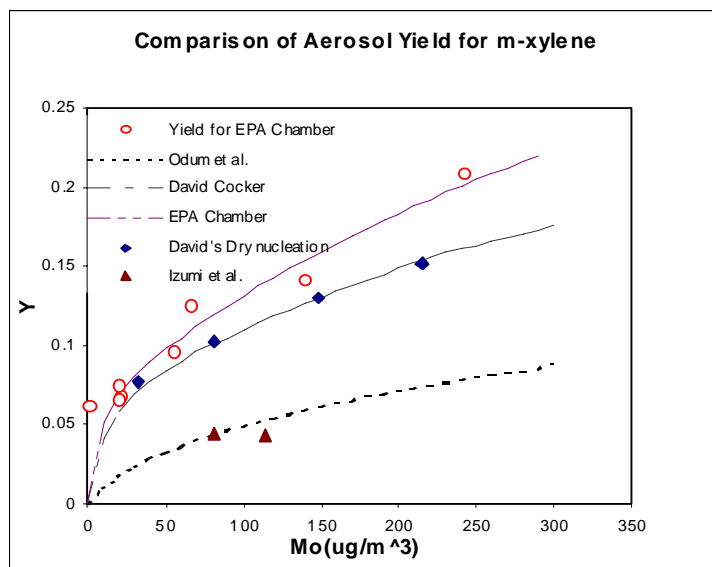


Figure 5. Comparison of SOA formation for our chamber (top curve), Caltech indoor (2nd from top curve (Cocker et al., 2001), Caltech outdoor (lower curve, (Odum et al., 1997)), and (Izumi and Fukiyama, 1990)) triangles.

OBJECTIVES

The overall objective of this project is to develop and comprehensively evaluate updated detailed and condensed mechanisms for use in photochemical airshed models for predicting formation of secondary gas-phase and PM pollutants. The mechanisms should incorporate the most recent laboratory and environmental chamber data, improve representations for aromatics and PM precursors, and reduce uncertainties in estimated mechanisms for species where no data are available. Specific objectives include the following:

- Update the detailed SAPRC-99 mechanism and mechanism generation system to be consistent with the most recent data, theoretical assessments and estimation methods, and review and as appropriate revise the assumptions, approximations, and lumping approaches incorporated in the mechanism to optimize it for predictions of PM precursors and toxics as well as ozone reactivity.
- Improve the representation of the aromatics in the mechanism so its predictions are consistent with available current environmental chamber data and so it incorporates most recent laboratory results.
- Carry out environmental chamber experiments most needed to develop, evaluate, and reduce uncertainties in the updated gas-phase mechanism. Although carrying out experiments solely for PM mechanism evaluation is beyond the scope of this project, PM data will be collected during the experiments so the data should also be useful for PM mechanism evaluation as well.
- Develop and evaluate systematic procedures for deriving condensed mechanisms from the more detailed mechanisms developed for this project, with the goal of deriving a mechanism with computational efficiency comparable to that of CB4, but with the scientific basis of the more detailed mechanism.
- Develop an up-to-date capability of representing chlorine chemistry in the mechanisms developed for this project, including the reactions of Cl with the VOC species as well as the inorganic reactions.
- Incorporate the updated mechanisms into an appropriate selected regional model, and conduct simulations to test the implementation and to compare predictions of the same model and other mechanisms.

The results of this will provide the CARB, other regulatory agencies, and researchers with improved and more up-to-date models for gas-phase prediction. Although uncertainties and approximations will no doubt remain, this project should provide a basis for reducing uncertainties in future mechanisms, and establish standards and procedures for future mechanism updates.

APPROACH

Task 1. Gas-Phase Mechanism Updates and Improvements

Task 1.1. General Gas-Phase Mechanism

The general SAPRC-99 mechanism consists of several components, and each of these will be examined and as appropriate updated and improved as part of this project. Work on each of these is briefly summarized below.

Base Mechanism. The base mechanism consists of the representation of the inorganic reactions and the reactions of the explicitly represented VOCs and organic product species that are represented explicitly in both the detailed and the more condensed version of the mechanisms. All the reactions in the base SAPRC-99 mechanism will be examined in light of results of the most recent available evaluations and their rate constants or mechanisms will be updated or modified as appropriate. Although the focus of the updates will be on the existing gas-phase mechanism, they will be made with the thought of adapting this mechanism for PM predictions in mind.

The current SAPRC mechanisms from SAPRC-90 through SAPRC-99 all represented peroxy + peroxy reactions using an approximate “operator” method that eliminates the need to represent all peroxy radical species explicitly, while still representing their effects on NO to NO₂ conversions under various NO_x conditions. Although this approximation is probably satisfactory for O₃ predictions, it doesn't represent how organic product distributions may change as when peroxy + peroxy reactions become important. We are currently investigating whether use of less approximate representations of peroxy + peroxy reactions, such as that used in RACM or CACM, give sufficiently different model predictions of species of interest to be worth the increased number of reactions and model species that they require. We know already that the current mechanism gives satisfactory predictions of O₃ under low NO_x conditions, so mechanism changes will probably not be needed for this reason. However, other considerations, such as prediction of PM precursors from organics who are expected to form different types of products under low NO_x conditions, may indicate that a mechanism with a less approximate representation should be maintained at least for comparative purposes. A decision on whether to do this will be made as part of this project.

Mechanism Generation System and Estimation Methods. The mechanism generation system is an important part of the overall SAPRC-99 mechanism because it is used to derive mechanisms for many of the individual VOCs, and also for some of the lumped organic product species used in the base mechanism (Carter, 2000a). The various structure-reactivity estimation methods and other estimates of branching ratios will be updated as part of this project to be consistent with more recent evaluations and relevant new laboratory data on branching ratios as applicable. A discussion of the various considerations involved and how laboratory data and structure-reactivity estimates are incorporated into the system is given by Carter (2000a). Attempts will be made to add representations of other classes of compounds, though the scope of this project is probably insufficient to expend a major effort in this regard unless a new approach becomes evident based on new information or theories.

Individual VOC Mechanisms. The rate constants assigned for the OH, O₃, NO₃ and other applicable reactions of individual VOCs in the mechanism will be updated based on new evaluations and discussions with Roger Atkinson. The mechanistic parameters assigned to them will also be re-evaluated and updated as appropriate. Mechanisms for VOCs that are derived using the mechanism generation

system will be re-derived using the updated mechanism generation system. Considerations used in developing mechanisms for VOCs that are not derived in this way, such as terpenes, will be re-evaluated and updated mechanisms will be re-derived. Note that more detailed terpene mechanisms will almost certainly be needed for PM predictions, and these needs will be taken into account when formulating how they are represented in the gas-phase mechanisms. Updates and modifications to the aromatic mechanisms are discussed below in Task 1.2.

Lumped VOC Mechanisms. For airshed modeling applications, it is necessary to lump the many hundreds of individual VOCs into a more limited number of model species. The lumping approach developed previously (Carter, 2000b) is probably sufficient for prediction of O₃ formation, though the addition of more VOC classes may be necessary for PM modeling. For this project, we will probably derive at least two versions of the VOC lumping, excluding the lumping that may be employed the more extreme condensations investigated under Task 3), one based on or similar to that developed previously (Carter, 2000b). In both cases, the parameters for the major lumped model species are derived from those for the compounds they represent, based on an assumed distribution of compounds. These can be derived based on emissions data as discussed below (see also Carter, 1988a, 2000b), and a “fixed parameter” version can be derived based on a representative emission profile. The fixed parameter version will be updated using updated emissions data based on discussions with the CARB and the EPA. Note that the parameters used for the adjustable parameter version will have been updated as part of the update of the individual VOC mechanisms, discussed above.

Emissions Processing Support. An important component of mechanism development is its incorporation into emissions processing systems. Under funding from the American Chemistry Council we are developing an emissions speciation database that incorporates emissions profile assignments for the SAPRC-99 and other mechanisms that can be used by SMOKE and other emissions processing systems (see Related Programs, below). These assignments will be updated to be consistent with the mechanisms updates and the lumping modifications they may incorporate. Note that if different lumping is used for mechanism for more detailed PM predictions, the assignments for this mechanism will be added to the system so emissions data can be processed for it as readily as for other mechanisms. Appropriate software updates to the emissions processing system may be made as part of this effort if they are deemed to be useful to the implementations of the mechanisms developed in this work to the models used by the CARB.

Toxics Modeling Support. Note that as part of this system, provision will be included so selected individual compounds that are usually lumped in O₃ or even O₃ and PM models can be represented explicitly. This is important for predictions of individual toxic VOCs as part of assessments of toxic impacts. This can be incorporated using the emissions processing system being developed for the ACC if the toxic VOC is already among the ~400 VOCs for which assignments have been made. It may be appropriate to add other VOCs to the list of detailed model species if they are particularly important to toxics modeling applications because of low emissions or low reactivity. It also may be necessary to add more lumped product species, at least as an option for the mechanism, if the toxic product of concern is a secondary organic product that is presently not represented explicitly. We will consult with the CARB staff with regard to the level of effort that may be appropriate in this regard.

Task 1.2 Aromatic Mechanisms

As discussed above, there are significant problems with the current aromatics mechanism in terms of consistency with the current chamber database and recent measurements of direct reactivity. At a minimum, the mechanism needs to be re-parameterized and re-adjusted so its overall reactivity predictions are consistent with the available mechanism evaluation data. Some of this work may be done as part of the current “low NO_x” mechanism project, but it is uncertain whether this can be completed

within the scope of that project given the other work that needs to be completed. It is also important that any updates to the aromatics mechanism take into account more recent laboratory data (e.g., Calvert et al, 2002 and references therein), including new data that are to be obtained by Atkinson as part of his proposed work for the CARB, as well as ongoing and proposed work for other projects. We will conduct a review of available relevant data and work with Atkinson with regard to information he is obtaining, and providing input concerning the types of data potentially most useful for mechanism development for modeling applications. This new information will either be incorporated in the updated mechanism or used to guide the parameterization or representation employed.

In this regard, it should be noted that unless unanticipated breakthroughs are made in the upcoming year, a parameterized or lumped mechanism approach will almost certainly continue to be used the representation of aromatics in an updated SAPRC mechanism. The primary utility of the new mechanistic and product data will probably be to guide how to derive mechanisms for the lumped model species that represent the reactive aromatic ring-opening products. The actual product compounds formed are probably a distribution of compounds and no single compound is probably representative of all of them. However, a set of model species with appropriate mechanisms may be sufficient to represent the overall effects of their reactions, though probably more than one species would be required. It is also important to assess which of the many aromatic ring-opening species are likely to be SOA precursors, so PM mechanisms can be appropriately added to this mechanism.

One of the problems with representing aromatics is that mechanism evaluation data are only available for the C₆ through C₉ alkylbenzenes, and the mechanisms for the higher aromatics have to be represented by the lower molecular weight aromatic assumed to have the most similar structure about the aromatic ring. If this approach were valid, then the ring-opening products formed from ethylbenzene should be representable by those formed by toluene. In fact this is not the case, since less reactive products need to be assumed to fit the environmental chamber data for ethylbenzene. Further tests of this should come when we attempt to model the chamber data for Aromatic-100 that we are generating for the CARB coatings project. Aromatic-100 contains significant amounts of ethyltoluenes and C₁₀ or higher aromatics for which no data are available, and such "lumped molecule" estimates have to be made. If the results of modeling experiments with those compounds are unsatisfactory, we will have to develop new ways to estimate mechanisms for aromatics for which no data are available. Basic laboratory data, theoretical considerations, and discussions with Atkinson and others may be helpful in this regard. This will be examined as part of this project.

Comparisons of model predictions against chamber data (discussed further in Task 1.3, below) is an essential part of developing aromatic mechanisms given that uncharacterized highly reactive species have major impacts in their overall reactivity characteristics. The available chamber data will be utilized in this regard, as well as any new data that becomes available, including data from Euphore or new data from our chamber from this and other projects. In this regard, part of this task will be to determine the chamber experiments that are most needed for mechanism evaluation. Note that this may well include experiments with ethylbenzenes or other compounds for which no data are currently available, in order to evaluate alternative estimation methods for higher compounds.

Task 1.3 Mechanism Evaluation

The updated and modified mechanisms developed in the above tasks will be evaluated by comparing their predictions against the full body of environmental chamber data used to evaluate SAPRC-99, as well as data from the TVA chamber, new data obtained in our chamber, and any new data that become available to us. Note that the comparisons of model predictions to the chamber data is an essential part of development of current aromatic mechanisms as discussed below, and it is also part of the derivation of uncertain but sensitive mechanistic parameters for other VOCs, such as overall nitrate

yields. Any SAPRC-99 mechanistic parameters for individual VOCs that were derived by fits to chamber data will be re-derived as part of this work, since changes to the base mechanism may affect such simulations.

An evaluation against the ambient surrogate chamber data will be an important component of this task, given the results with the new chamber as above in Figure 3. An even larger body of ambient surrogate chamber data at various ROG and NO_x levels, which include measurements of OH and HO₂ radicals, H₂O₂, and HNO₃ as well as the other species we now routinely measure in the UCR EPA chamber is being generated as part of the ongoing EPA OBM project. These data will be available by the time this project begins and will be used to evaluate the full mechanism to see if the biases noted above have been removed, or if other problems are evident. It is hoped that the improvements to the aromatics mechanism will resolve this “high NO_x” bias, but if not then other possible problems will be investigated, such as uncertain rate constants in the base mechanism.

As part of this task, we will review the applicable chamber database from other laboratories to determine if additional data are available that would be useful for mechanism evaluation. For data to be useful they would have to be sufficiently well characterized so that uncertainties in chamber or light conditions cannot be used to explain model discrepancies, and would need to complement the extensive database we already have, and the investigators who generated the data would need to make it available for our use. Data from the Euphore chamber present a promising possibility, since advanced instrumentation that is not generally available for chamber experiments are often employed. This will be investigated as part of this project. However, there is not a single database for Euphore data, since separate investigators maintain the data for the various “campaigns” in the chamber. Thus, obtaining the full database may not be feasible within the scope of this project, especially for experiments for which the investigators intend to write up for publication, but have not yet done so.

The results of the evaluation will be summarized to assess overall model performance and determine whether any significant biases are present. If such biases are found, then possible sources for the problems in the underlying mechanisms will be investigated as part of the tasks discussed above.

Task 2. Environmental Chamber Experiments

The tasks discussed above are the minimum we feel are necessary to the development of updated mechanisms for modeling gas-phase processes in the atmosphere. Because the mechanisms have many uncertainties and semi-empirical parameterized mechanisms need to be used in some important cases (e.g., aromatics ring opening), environmental chamber data are essential to mechanism development and evaluation. Although as discussed above there is a large body of environmental chamber already available for gas-phase mechanism evaluation, as discussed below we feel that additional data are essential to reduce significant uncertainties, evaluate assumptions and parameterization methods, and where necessary derive parameter values needed for predictive modeling. The specific types of experiments are briefly discussed below.

All the experiments will be carried out in the UCR EPA chamber using the procedures and gas-phase and PM instrumentation currently available. More detailed descriptions of the chamber and instrumentation are given in reports and proposals posted at the UCR EPA chamber web site at <http://www.cert.ucr.edu/~carter/epacham>. That web site also has the draft quality assurance project plan (QAPP) and data processing procedure that can be downloaded. Note that the QAPP and data processing procedures are evolving and undergoing revision as part of the ongoing project, and are expected to be updated prior to or during the course of the proposed project.

Although there is already a large body of gas-phase mechanism evaluation experiments, it is expected that during the course of conducting Task 1.1 and especially Task 1.2 there will be a need for additional chamber experiments to resolve specific uncertainties or test assumptions that may arise during the mechanism update or revised aromatic mechanism development process. If nothing else, there is a need for data to evaluate assumptions concerning aromatic product yields assigned to important aromatic hydrocarbons for which there are no data, such as ethyltoluenes.

Note that PM measurements can be made at relatively little added cost during the experiments, since the instrumentation is available and is being routinely operated for other projects. Therefore, although the primary purpose of the experiments for this option is reducing uncertainties in the gas-phase portion of the mechanism, the experiments for this option would also benefit PM mechanism evaluation. Although analyzing the PM measurements is beyond the scope of this proposal, such analyses will be carried out for other projects and the results will be made available to researchers funded by the CARB to evaluate PM mechanisms. The relatively low added cost of making PM measurements with these experiments greatly enhances the value of the data and provides potentially valuable database for PM mechanism evaluation under conditions where the gas-phase system is better characterized than most previous PM experiments.

The budget for the current project covers the cost for carrying out at least 10 UCR EPA chamber experiments. The specific experiments will be determined as part of Task 1.1 and Task 1.2.

Task 3. Mechanism Condensation

Despite the fact that it is out-of-date and by its formulation unsuitable for secondary PM predictions, the Carbon Bond 4 (CB4) mechanism continues to be widely used in airshed models. This is in part because there is a large database of CB4-processed emissions and deficiencies in current emissions processing systems make processing for other mechanisms difficult, but primarily because the condensed nature of the CB4 mechanism makes its use highly computationally efficient. Although computers are getting more powerful, for many types of applications modelers would prefer to use the extra power for other purposes, such as improving resolution or representing other processes better, rather than using a more computationally expensive mechanism. Therefore, CB4 continues to be widely used despite its underlying problems because there is really no real alternative if computational efficiency for the chemistry model is the priority.

As discussed in my peer review of the CARB ozone modeling work (Carter, 2001) what needs to be developed is a new highly condensed mechanism that has the scientific basis of the state-of-the-art detailed mechanisms, yet with the degree of condensation needed for applications requiring computational efficiency. Obviously compromises need to be made whenever condensations are employed, and these compromises would necessarily affect accuracy in some way. However, as it is now, one does not really know the impacts of the necessary compromises, and unnecessary compromises, such as using out-of-date rate constants or inappropriate parameterization and formulation, are now being made. If a condensed mechanism were derived from a detailed one that is used in model applications where chemical resolution and accuracy is of higher priority, (and the emissions were processed in a consistent manner⁸), then one could determine in a relatively unambiguous manner what is the effect of the condensations, and based on that decide whether the computational efficiency gained is worth the cost in accuracy.

⁸ Emissions for CB4 and SAPRC are not currently being processed in a consistent manner, since each are based on independent assessments of what chemical compounds various mixture categories in emissions profiles represent. However, this is currently being addressed (see Related Programs), and should be less of a problem in future models.

Another problem with the current situation is that condensed mechanism are developed independently of detailed ones, and even if a new version were developed that is consistent with a current detailed mechanism, it would eventually become out of date and inconsistent if the detailed version when the latter mechanism is updated. Rather than having to have a parallel track in updating condensed mechanisms as well as detailed ones (making them have a different scientific basis as the detailed ones if done by different developers), it would be more efficient if there were as standard procedure to derive a condensed mechanism from the detailed version that would result in both versions being updated simultaneously. It would be similar to the relationship between the current detailed and condensed version of SAPRC-99, though for this application the level of condensation would be much greater.

Therefore, for this optional task we propose developing procedures and condensation approaches that can be applied to the updated detailed mechanism developed under Task 1.1 to produce a mechanism with the level of condensation similar to that of CB4. Test calculations will be employed to assess the effects of various condensation approaches. Condensation procedures to be examined will obviously include using fewer model species to represent primary emitted VOCs and reactive VOC products, but other possibilities will also be examined. The priority will be in reproducing predictions of the detailed mechanism of O₃, NO_x, HO_x, NO_y, total PANs, and total PM formation under as wide a set of conditions as possible. The VOC compositions used will be derived based on the typical emissions profile used to derive the fixed parameter version in Task 1.1. We will work with the CARB modeling staff in prioritizing the predictions that are considered to be important for model applications where use of CB4 is now preferred.

An important part of this task would be to set up a set of box model scenarios that represent the range of chemical conditions where the model may be applied that can be used as the basis for assessing the effects of the various condensation approaches on model predictions. A single scenario will not do – multiple scenarios representing different concentration regimes, levels of NO_x availability, sensitivities to radical inputs, and overall PM levels would be needed to satisfactorily serve this function. These scenarios could also serve as a basis for other mechanism intercomparison and sensitivity studies, and benefit other research objectives besides this one. We will work with the modeling group at CARB to assure that the set chosen adequately represent the range of conditions of importance in California. However, we will not restrict ourselves to California conditions, since if this project is successful any mechanism we develop will also be used outside of California. The choice of scenarios is important since it will ultimately determine which condensations are considered acceptable and thus adopted in the condensed mechanism we develop.

The condensations will be done in such a way that new versions of the condensed mechanism can be derived from new versions of detailed mechanism, so the condensed mechanism shares the same scientific basis as the detailed version from which it is derived. Thus the condensation will not really be a new *mechanism*, it will be a *set of procedures* that is used to condense more detailed or explicit mechanisms. Thus, it may even be applicable to developing more condensed versions of other detailed mechanisms such as MCM or other less condensed mechanisms such as RACM or CACM.

Emissions processing assignments needed to support use of the condensed mechanisms will be developed as part of this task, and implemented so they can be used with the emission speciation software and databases developed for other projects (see Related Programs and Task 1.1).

Task 4. Chlorine Chemistry

Chlorine chemistry is not incorporated in most urban regulatory models, though it is known to be important in many non-urban atmospheres, and its role in urban atmospheres is uncertain. Chlorine gas or HOCl is emitted from urban sources such as some manufacturing processes, cooling towers and

swimming pools a number of chlorine-containing VOCs are in current emissions inventories, and there are a number of other sources of reactive chlorine species that may be non-negligible in airsheds of interest to the CARB (Wan et al, 1996, Finlayson-Pitts and Pitts, 1997; Tanaka et al, 2000, Chang et al, 2002). Although its importance to regulatory importance has not been established, at a minimum it is necessary to incorporate these reactions in research models to investigate their effects and the importance of representing these reactions, before deciding whether they need to be considered or not. Models using such chemistry are employed from time-to-time, but there is no established standard mechanism or set of procedures that have been established and documented for implementing this with the current models and mechanisms.

For this optional task, we will develop a chlorine chemistry module that can be added to the detailed mechanism developed under Task 1.1 for this project, for use for research or regulatory applications where effects of chlorine chemistry need to be investigated. The chlorine chemistry mechanism we have used previously in studies of various chlorine-containing VOCs (1996, 1997b) will be used at the starting point. We will review the evaluations and literature data and previous mechanism representing ClO_x and BrO_x reactions and implement such reactions as an option into the updated mechanism developed under Task 1. Sensitivity calculations will be conducted using the scenarios developed under Task 3 (with some chlorine emissions added) to determine what reactions may not need to be needed, and key uncertainties if applicable.

Note that this will also require developing mechanisms for the reactions of Cl atoms with all the VOC species in the mechanisms. The mechanism generation system will be expanded to include reactions of Cl with the various represented VOCs, utilizing published structure-reactivity methods and our own estimates to derive the necessary rate constants and branching ratios. Note that for species without double bonds most of the subsequent reactions will involve the same intermediates as formed in the OH reaction, so the system will automatically generate the subsequent products. Adaptations will probably have to be made for the system to handle the chlorine-substituted radicals formed when they react with alkenes, and this will be investigated as part of this task. Estimates will be made concerning mechanisms with reactions with aromatics and other species not presently processed using the mechanism generation system. The degree of estimation that is employed may depend on the resources and time available for this project and difficulties encountered, but at a minimum a framework will be developed into which new information can be incorporated, and probably a less approximate representation than those used previously will be developed.

Task 5. Model Implementation and Testing

The detailed gas-phase and secondary PM mechanisms and the condensed mechanism developed for this project will be implemented into a state of the science, photochemical grid model (e.g., Models-3/CMAQ or CAMx). There are several advantages to implementing the new mechanisms in CMAQ for testing. CMAQ already includes CB4 and SAPRC99 chemistry, and we have recently implemented an updated version of CB4 (Jeffries et al., 2002) in CMAQ. Moreover, CMAQ offers a variety of options for representing PM species including the original modal algorithm (Binkowski and Shankar, 1999) and two sectional algorithms, CMAQ-AIM developed by Wexler group at UC Davis (Zhang and Wexler, 2002), and CMAQ-MADRID developed by Seigneur et al. (2002). CE-CERT also has a large data base of CMAQ model scenarios that can be used to test the new mechanisms. If CMAQ is selected as the test model we would propose to test the new mechanism using the following modeling scenarios:

- Gas phase chemistry for the CCOS 2000 July 30-August 2 episode.
- Gas phase chemistry for the SCOS 1997 August 3-7 episode.
- Gas phase chemistry for the TEXAQS 2000 field study.

- PM and gas chemistry for the Western Regional Air Partnership (WRAP) Model scenarios for January and July in 2002, using a 36 km coarse grid domain, and a 12 km high resolution domain for the western states, including CA.
- PM and gas chemistry for the eastern US using model scenarios for January 2002 and July in 1999, using a 36 km coarse grid domain, and a 12 km high resolution domain.

If CRAPQS PM scenarios are available for the 2000 field study, we would propose to use this data set for evaluation of the new mechanisms. We note that there are advantages to testing the new mechanisms in several different model scenarios to evaluate the performance for a variety of meteorological conditions and photochemical regimes, and to verify that the mechanisms have not been tuned to fit a particular set of ambient conditions. We believe that choosing CMAQ as the test model for the new mechanisms will provide a thorough evaluation and testing effort that can be completed within the limits of the funding available for this project. This is because CE-CERT has previous experience in implementing new chemistry mechanisms in CMAQ, and because we have a large set of CMAQ scenarios that can be readily tested using the new mechanism,

For the model performance evaluation using the new mechanisms, we will compare model predictions to ambient monitoring data for several observation networks, including AQS and NAMS/SLAMS for gas phase species, and IMPROVE, CASTNet, NADP and STN networks for PM species. CE-CERT has developed model performance evaluation tools and has the ambient data available for each of these monitoring networks, and CE-CERT has already completed model performance evaluations using the currently available gas and PM species in CMAQ and CAMx. Thus, we can efficiently and rapidly compare model performance of the new mechanism to the existing mechanisms. The model performance evaluation tool produces a variety of time-series and analysis plots and also computes a comprehensive set of model performance metrics including mean fractionalized error and bias and normalized mean error and bias which are useful for evaluation of PM species

We would propose to meet with ARB staff early in the project to develop a protocol for testing and evaluation of the new mechanisms. We expect that collaboration with ARB staff would allow the mechanisms to be tested for a larger variety of model scenarios. Depending on the results of model performance evaluations in the test scenarios, and by comparing grid model predictions for the full mechanisms and the condensed mechanism, we would determine whether additional adjustments are needed for the condensed mechanism. Documentation of data sets and results will be provided through a project webpage, meetings with ARB staff, a final report, and manuscript to be submitted to a peer reviewed journal. All model source code will be provided to ARB upon completing the project.

We will then conduct simulations of a test case with the mechanisms and compare the results with each other and with results of previous simulations with other mechanisms.

SCHEDULE, REPORTING AND DELIVERABLES

A target schedule for the tasks in this project is given in Table 2. Note that this is highly approximate and subject to change depending on the progress of this program and the other demands on the investigator's time and the chamber facility.

Quarterly reports will be submitted to the CARB giving brief summaries of the progress and status of the program, problems encountered, and anticipated future schedules. Six months before the end of the project a draft final report will be prepared documenting the work carried out during the second year and discussing the conclusions and recommendations resulting from the program as a whole. The final report will be independent of the quarterly reports and will not contain citations to them. Final versions of the draft annual reports or final report will be submitted within 30 days following receipt of comments from the CARB.

Environmental chamber data obtained for this program will be added to the UCR environmental chamber database for mechanism evaluation, and documented and made available to modelers through the Internet as described by Carter et al. (1995). Mechanism files and supporting data, documentation and software developed for implementing the mechanism in airshed models will also be made available on the Internet.

Table 2. Target schedule for proposed tasks.

Task	Program Month												
	1	2	3	4	5	6	7	8	9	10	11	12	
1 Gas-phase mechanism updates and improvements													
1.1 Base mechanism	XX	XX	XX	XX									
1.2 Aromatic mechanism improvements	XX	XX	XX	XX									
1.3 Evaluation against chamber database		XX		XX	XX	XX	XX	XX	XX	XX	XX		
3 Environmental chamber experiments				XX	XX	XX	XX	XX	XX	XX			
4 Condensed mechanism development						XX	XX	XX	XX	XX			
5 Chlorine mechanism development		XX	XX					XX	XX				
6 Implement mechanisms in regional model and run test simulation								XX	XX	XX			
Periodic Reports			X			X			X				
Draft Final Report											X		
Final Report													X

BUDGET

The total cost of this one-year project is \$166,132. This consists of personnel costs for the mechanism development and evaluation and model implementation tasks, and the cost for carrying out the 10 chamber experiments in Task 2. A breakdown of the level of effort in terms of person-hours of the key personnel and chamber experiments is given in Table 3. The cost of carrying out UCR EPA chamber experiments consists of costs of personnel required to operate the chamber and process and QA the data, consumable supplies and expenses, maintenance costs, and an estimated productivity of approximately two working days per experiment useful for mechanism evaluation. Budget details and justifications for budget items are given in Appendix A.

Table 3. Breakdown of level of effort by task.

Task	Person-Months			Chamber Runs
	Carter	Tonnesen	Jung Chien	
1 Gas-phase mechanism updates and improvements				
1.1 Base mechanism	2			
1.2 Aromatic mechanism improvements	1			
1.3 Evaluation against chamber database	1			
3 Environmental chamber experiments	0.25			10
4 Condensed mechanism development	1.5		1.5	
5 Chlorine mechanism development	1			
6 Model implementation				
6.1 Implement updated gas-phase and PM mechanism in regional model and run test simulation		0.5	1	
6.2 Implement new condensed mechanism in regional model and test		0.5	0.5	
<u>Total</u>	6.75	1	3	10

QUALIFICATIONS OF THE INVESTIGATORS

The Principal Investigator of this project is Dr. William P. L. Carter. He will be responsible for most of the mechanism development work on this project, as indicated on Table 3 above. Dr. Carter is responsible for the development and evaluation of the SAPRC-99 mechanism and has extensive experience in chemical mechanism development, VOC reactivity assessment, and overseeing and utilizing data from environmental chamber experiments for mechanism development and evaluation. He is Principal Investigator for the EPA projects to develop and utilize the UCR EPA chamber and is Principal Investigator or co-Principal Investigator on several projects to utilize it for mechanism evaluation, reactivity assessment, and other purposes (see Related Programs, below). The SAPRC-99 mechanism and earlier or condensed versions of it have been implemented in various urban and regional models, and was utilized to calculate the MIR and other reactivity scales used by the CARB and others for VOC reactivity assessment. Details about his research and additional information and downloadable data and documents are available at his web site at <http://www.cert.ucr.edu/~carter>. His biographical sketch is attached.

Dr. Gail S. Tonnesen will be a co-investigator on this project. She will be primarily responsible for the model implementation, but she will also provide input on the mechanism development, evaluation, and condensation. She founded and directs the air quality modeling group at the University of California Riverside. Dr. Tonnesen is the Principal Investigator of a number of modeling projects as indicated in the Related Programs section, below. Dr. Tonnesen's primary area of research is numerical modeling of the chemistry and transport of trace gasses in the troposphere. Specific areas of interest include: development of process analysis methods to evaluate model simulations; development and evaluation of observation based methods for assessing ozone sensitivity to precursor reductions; evaluation of photochemical reactivity scales; and investigation of the effects of choice of algorithms, grid-structure and model formulation on the interaction of chemical and transport processes. Dr. Tonnesen's modeling group is currently developing GIS based tools for modeling emissions of atmospheric pollutants and for evaluating population exposure to air pollutants. Dr. Tonnesen has also organized a campus-wide group of faculty that meets regularly to develop interdisciplinary proposals for environmental research and education. Her biographical sketch is attached.

Dr. Chao-Jung Chien will contribute significantly to this project in the condensed mechanism development and model implementation, as indicated on Table 3, above. Dr. Chien received a B.S. degree in Chemistry from National Cheng Kung University, Taiwan, in 1989 and a PhD degree in Environmental Sciences and Engineering from University of North Carolina at Chapel Hill in 2001. Dr. Chien's research interests and specialties have been in atmospheric chemistry, organic analytical chemistry, smog chamber experiments and modeling, and urban air quality modeling. He joined CE-CERT's environmental modeling group in October, 2001 and has since been involved in research projects including development and implementation of new chemical mechanisms to represent particular matter (PM) formation and transport in urban air quality models. His involvement with Western Regional Air Partnership (WRAP) Regional Modeling Center (RMC) project includes analysis of air quality models on PMs and participating in applied modeling training seminars. His biographical sketch is attached.

RELATED PROGRAMS

The objectives and current status of ongoing and proposed projects at our laboratories that are relevant to this proposal are summarized below.

Development of a Next-Generation Environmental Chamber Facility for Chemical Mechanism and VOC Reactivity Research

United States Environmental Protection Agency Agreement CR 827331. William P. L. Carter, Principal Investigator.

Objectives

The objectives of this four-year, \$2.9 million project are to develop the next-generation environmental chamber facility needed for evaluating gas-phase and gas-to-particle atmospheric reaction mechanisms, for determining secondary aerosol yields, and for measuring VOC reaction products and radical and NO_x indicator species under more realistic and varied environmental conditions than previously has been possible. The facility is then to be employed to provide data that are most relevant to today's pollution problems and control strategy issues. The types of studies that this facility was designed to address include the following:

- Determining whether current predictions of effects of VOC and NO_x changes on ozone and secondary aerosol formation are applicable to lower pollutant concentrations.
- Assessing differences among VOCs in terms of effects on ozone, secondary aerosol formation, and other pollutants under low-NO_x conditions. Current ozone reactivity scales (e.g., Carter, 1994) for VOCs were developed for more polluted urban conditions and may not be appropriate for lower NO_x environments.
- Providing information needed to evaluate whether control strategies aimed at replacing reactive VOCs with less reactive but more persistent compounds may adversely affect ozone or other pollutants when they are transported downwind.
- Determining major oxidation products formed by organics when they react under low-NO_x conditions. This is important to developing scientifically-based models for low-NO_x reactions of VOCs, as well as to understanding the ultimate environmental fates and impacts of these compounds, which in some cases may affect global climate change.
- Determining the effects of temperature on secondary pollutant formation and VOC reactivity. Current environmental chamber facilities are not adequate to evaluate these effects, but limited studies of temperature effects indicate that temperature effects are probably significant.
- Determining the effects of temperature and humidity on secondary organic aerosol formation from various VOCs. The results will be compared with data obtained using outdoor chamber systems to evaluate the range of applicability of those data.
- Evaluating the budgets of HO_x and NO_y, and evaluating the usefulness of indicators of O₃ and P(O_x) sensitivity to precursors for conditions typical of ambient atmospheres.
- Evaluating impacts of various types of VOC sources, such as architectural coatings, on formation of ozone, secondary PM, and other pollutants in various environments.

- Utilizing the facility to test equipment to be used for monitoring trace pollutants in ambient air under controlled conditions where the actual pollutant concentrations, and the history and source of the air mass being monitored, are known.

The specific studies to be carried out will depend on the results of the initial experiments, discussions with a technical advisory group consisting of representatives of the EPA and other regulatory agencies, industry groups, and atmospheric chemistry researchers, and availability of funding.

Current Status

The project was initiated in late 1999, the design and construction of the facility was completed in early 2003, initial characterization and mechanism evaluation experiments are now complete, and experiments are underway under funding for other projects, discussed below. A detailed report describing progress through October of 2001 was submitted to the EPA, and a summary report summarizing progress through August 20, 2002 was submitted to the EPA and the RRWG Advisory Committee for this project. The status of the project and funding situation was also summarized in that report. The latest report provides an update on the progress on this project through February 20, 2003, and also provides an update of the current funding situation and research plan. These reports and additional information are available at <http://www.cert.ucr.edu/~carter/epacham>.

Some of the results obtained from this chamber are discussed above in the discussion of “New UCR EPA Chamber Data” in the Background section of this proposal. The data obtained have already provided useful information to the evaluation of current mechanism and demonstrated the utility of this chamber for PM studies. Several of the optional tasks in this proposal involve use of this chamber. This includes the EPA OBM project, discussed below, which involves a collaboration with researchers at Penn State to utilize their instrumentation to measure OH and HO₂ radical levels during the experiments, providing a valuable test for this type of instrumentation as well as providing data to test OBMs and chemical mechanisms.

Evaluation of Atmospheric Impacts of Selected Coatings VOC Emissions

California Air Resources Board Contract 00-333. William P. L. Carter, Principal Investigator.

Objectives

The objectives of this three-year project is to carry out, at least in part, research most needed to reduce uncertainties in ozone reactivity estimates for selected major types of Coatings VOCs. The specific types of compounds to be studied were determined in consultation with the CARB staff and the CARB's Reactivity Research Advisory Committee, which includes representatives of interested industry groups. The compounds chosen for study include Texanol®, an important constituent of water-based coatings, and six representative types of petroleum distillates. The program also includes developing improved procedures for estimating reactivities and reactivity uncertainties for petroleum distillates and further development and application of the direct reactivity measurement method developed for a previous CARB project.

Current Status

Environmental chamber experiments have been carried out at two different ROG and NO_x levels for each of the six types of petroleum distillates, and additional chamber experiments with these materials are planned. These experiments are now suspended in order to carry out experiments for the EPA OBM

study discussed below. Methods for injecting and analyzing Texanol® have been assessed, and experiments with that compound will be carried out when the chamber is available.

The petroleum distillate analysis data provided by Censullo et al (2001) were analyzed for their implications for reactivity assessment, and ozone reactivities derived from their data were compared with reactivity estimates using the CARB binning method. The results indicate that the binning method performs reasonably well for these solvents, but additional analysis is needed to assess uncertainty.

Considerable efforts have been made to adapt the direct reactivity assessment method to use with petroleum distillates and other compounds that can't be reliably analyzed by GC. A total carbon analyzer was integrated with the system and found to give reliable total carbon methods needed to replace GC analysis, but the model was not able to quantitatively simulate the direct reactivity measurements obtained using this system. There may not be sufficient resources available in this project to fully investigate this, since it was decided to focus most of the remaining resources in this project to the environmental chamber studies.

Environmental Chamber Studies of VOC Species in Architectural Coatings And Mobile Source Emissions

California South Coast Air Quality Management District. William P. L. Carter, Principal Investigator.

Objectives

The overall objectives of this project is to conduct environmental chamber studies of selected architectural coatings VOCs and mixtures representing current mobile-source-dominated emissions to assess their impacts on ground level ozone and PM formation. This project will build upon and supplement an existing EPA to evaluate and utilize the new “next generation” environmental chamber system for chemical mechanism evaluation and an existing CARB project to conduct experiments in that chamber on selected architectural coatings VOCs. All experiments will be carried out for the purpose of evaluating and/or developing chemical mechanisms for use in airshed models, and will therefore incorporate the characterization and control efforts required for this purpose. The specific objectives are as follows:

- Conduct environmental chamber experiments with reactive organic gas (ROG) surrogates representing current ambient emissions and concentrations in order to determine the most appropriate set of “base case” experiments to use in incremental reactivity assessment experiments for this and the CARB architectural coatings reactivity project. These experiments will also be useful to evaluate models for current emissions that are dominated by mobile sources.
- Conduct environmental chamber for reactivity assessment and chemical mechanism evaluation for at least 3 types of coatings VOCs selected by the SCAQMD in conjunction with discussions with the CE-CERT investigators and RRAC. It is expected that the VOCs will include at least some experiments with ethylene and propylene glycol and other VOCs used in water-based coatings.
- Conduct measurements of PM formation in reactivity assessment and mechanism evaluation experiments not only for this project but also for the CARB reactivity project. The results of these experiments can then be used to evaluate the PM formation potentials of the types of VOCs studied, and be available for developing and evaluating models for their impacts on PM formation in the atmosphere.

- Evaluate the potential utility of the CE-CERT environmental chamber system for testing models for availability of emitted VOCs to react in the atmosphere to form O₃ and secondary PM. This work will be carried out in consultation with the atmospheric availability subgroup of the Reactivity Research Working Group.

Current Status

This project has just been initiated. However, we have already begun conducting PM measurements in conjunction with essentially all of the more recent reactivity experiments carried out for the CARB architectural coatings project. Some control and characterization experiments for PM measurements have also already been carried out for this project. PM measurements are also being made in conjunction with the OBM study and the results will be used to benefit this project.

Development and Evaluation of a Gas Phase Atmospheric Reaction Mechanism for Low NO_x Conditions

California Air Resources Board Contract No. 01-305. William P. L. Carter, Principal Investigator.

Objectives

The overall objective of this project is to evaluate and improve the performance of current versions of the SAPRC chemical mechanism for simulating atmospheric transformations under low and very low NO_x conditions. The specific objectives will include the following:

- Complete the development of the “Low NO_x” version of the SAPRC-99 mechanism that is designed to more accurately predict organic product formation under very low NO_x conditions.
- Evaluate the performance of both the standard and the low NO_x versions of the SAPRC-99 mechanism in simulating available environmental chamber simulating low NO_x conditions, including TVA and CSIRO chamber experiments not used previously in SAPRC mechanism evaluation.
- Utilize the new UCR environmental chamber facility being developed under EPA funding to carry out selected low NO_x mechanism evaluation experiments deemed to be the most useful for mechanism evaluation in the near term.
- Update or modify the mechanisms as appropriate based on the results of the evaluation against chamber data and other data that may become available.

The results of this study will then be used to develop recommendations concerning mechanisms to use when modeling low NO_x conditions in regional model simulations, and priorities for future research aimed at reducing uncertainties in chemical mechanisms used in regulatory and research applications.

Current Status

The TVA chamber data have been evaluated and modeled and determined to be essentially consistent with the predictions of the SAPRC mechanism. Ambient surrogate and other experiments were carried out in the UCR EPA chamber with NO_x levels as low as ~2 ppb, and the results were found to be generally consistent with model predictions, with no significant differences in performance observed compared to results of simulations at higher NO_x conditions. It was determined in view of the limited number of CSIRO chamber experiments available for modeling, the level of effort and uncertainties required to model outdoor chamber runs with uncertain light characterization, and the fact that the other chamber data do not indicate low NO_x mechanism evaluation problems, we will probably not model the

TVA experiments for this project. In addition, we understand that there is an independent effort to model a larger CSIRO chamber database using SAPRC-99 (Robert Hynes, CSIRO, personal communication), and the results will be made available to us for use for mechanism evaluations and updates for this project. Instead the remaining effort on this project will be on assessing the advantages of using a more detailed mechanism to represent peroxy + peroxy reactions and, if time and resources permit, making a beginning in improving the aromatics mechanisms to improve model performance under *high* NO_x conditions.

Utilization of A Next-Generation Environmental Chamber Facility for Chemical Mechanism And VOC Reactivity Evaluation

Proposal to the U.S. Environmental Protection Agency. William P. L. Carter, Principal Investigator.

Objectives

The overall objectives of this project are to complete the characterization facility improvements to enhance the utility and capabilities of the UCR EPA chamber, and utilize it for selected research that complement and enhance the value of our existing project and further the research agenda discussed in the original proposal for this project. The specific experiments will focus characterization of the chamber for mechanism evaluation experiments at different temperatures and humidities, investigations of the effects of selected VOCs on PM formation and how they are affected by temperature and humidity, and investigating the effect of PM on gas-phase processes such as ozone formation. A focus of this project will be on aromatics, since they are important ozone and PM precursors in the atmosphere whose mechanisms continue to be highly uncertain. In addition, aromatics are the main PM precursors in the base case mixture used in our coatings reactivity experiments for other projects, and systematic studies the PM impacts of these aromatics under the conditions of our experiments would greatly enhance the value of the PM measurements being made in the reactivity experiments.

Current Status

The proposal has been submitted to the EPA as part of a larger proposal covering work to be carried out under a Congressional earmark for CE-CERT. It is currently undergoing technical and administrative review. It is expected to be funded before the end of the year.

Implementation of the SAPRC Chemical Mechanism into the SMOKE Emissions Processing System for the CMAQ/Models-3 Airshed Model

Subcontract to the University of North Carolina for a project funded by the American Chemistry Council. Marc Houyoux, Principal Investigator. William P. L. Carter, Co-Investigator.

Objectives

The objective of this project is integrate the Statewide Air Pollution Research Center (SAPRC) chemical mechanism with the Sparse Matrix Operator Kernel Emissions (SMOKE) modeling system within the Models-3 framework. The integration includes speciation database improvements, updates to SMOKE and preparation of SMOKE inputs, Models-3 framework updates to the SMOKE Tool, and a new capability for creating reactivity packets. This involves a number of tasks to be carried out by researchers at UCR and UNC. The tasks to be carried out at UCR include the following:

- Create the speciation database organization and assignments that appropriately represent relationships between mixtures, actual chemical compounds, and the model species in SAPRC 99 and other mechanisms.
- Develop the software and essential data to update both emissions processing methods and SMOKE for SAPRC and other mechanisms using the reorganized speciation database and existing emissions datasets.
- Assist the UNC researchers in testing SMOKE with the redesigned speciation database and SAPRC and other mechanism lumped species as modified by reactivity packets using data available from one previous modeling application.

If successful, the result of this project should be an ability to assign model species to emissions profiles more readily and in a more consistent manner among mechanisms, and to more readily prepare emissions data for different mechanisms or for VOC reactivity assessment modeling assessments.

Current Status

A new speciation database that assigns individual chemical compounds to all the various chemical categories used in emissions maintained by the CARB, EPA, and Texas and that assigns detailed and condensed SAPRC-99 and CB4 model species to the compound was developed under separate funding from the University of Houston. The current database, and a more detailed description of this work, is available at <http://www.cert.ucr.edu/~carter/emitdb/>. The current database, which is in the form of an Excel spreadsheet, already has macros that output files assigning model species to emissions categories (e.g., SAROAD numbers), and these have already been used for implementing the updated SAPRC-99 mechanisms in several models. Work is underway to incorporate these assignments into the SMOKE system to address the other objectives of this project. Existing emissions profiles from various sources are being compiled so they can be used as inputs for this system, and so that consistent speciation assignments can be used for as many of the major emissions databases as possible. It is expected that the assignments and programs used for assigning model species to profiles can be adapted for use by other emissions systems besides SMOKE, and the outputs will be documented so that they can be adapted for use by other emissions processing systems if desired.

Experimental Evaluation of Observation Based Methods (OBMs) for Assessing the Sensitivity of Ozone to VOC and NO_x

U.S. Environmental Protection Agency Contract. William P. L. Carter and Gail S. Tonnesen co-Principal Investigators.

Objectives and Overall Approach

The primary objective of this project is to provide data needed to experimentally evaluate the performance of various Observation Based Methods (OBMs) for predicting sensitivities of O₃ concentrations and O₃ production rates to changes in precursor concentrations. A related objective will be to provide data to evaluate model predictions of indicator ratios and of radical levels. These data are needed to evaluate the utility of indicator species and radical measurements in field studies for predicting the sensitivities of air quality to VOC and NO_x emissions changes. These data are also needed to evaluate the accuracy and completeness of the models we use to predict the effects of control strategies on air quality.

The overall approach will be to conduct well-characterized environmental chamber irradiations of VOC and NO_x mixtures in the range of concentrations that occur in ambient atmospheres, and make

measurements of most of the indicator species that have been evaluated in previous modeling studies. This will include measurements of HO₂ radical levels to evaluate the predictions of Tonnesen and Dennis (2000a). Experiments with varying VOC and NO_x concentrations will be conducted to directly determine the particular values of the OBMs that are associated with the transition from VOC sensitive to NO_x sensitive conditions for O₃. The experiments will be conducted at several different O₃-VOC-NO_x combinations to determine if the OBMs are robust for a variety of conditions.. Direct measurements OH, HO₂ and of OH reactivity will also be made to evaluate the theoretical basis for several of the OBMs and to evaluate its consistency with model predictions.

The measurements of OH, HO₂ and OH reactivity are being made in collaboration with Dr. William Brune of Penn State University, whose LIF instrumentation will be move to CE-CERT for the period of the project.

Current Status

The Penn State group installed their LIF instrumentation at CE-CERT in late September of this year, and it is expected to remain here, with their personnel to operate it and process the data, until the end of October or early November. The project has completed surrogate - NO_x experiments at a variety of ROG and NO_x levels, and additional experiments are underway, along with control experiments and selected experiments with simpler chemical systems. Measurements of OH, HO₂, OH reactivity, H₂O₂, HNO₃ are being made along with the other species measured during UCR EPA chamber experiments, and the data are being compared with model predictions as they are being processed. Since the experiments for this project require the LIF instrumentation and that is available only for a limited time, the chamber is 100% devoted to this project during the period while the Penn State researchers are still here.

The results of the experiments are being compared to model simulations as soon as possible after the data are compiled in order to assess the program and the measurement data. Since the data are still being finalized and additional control experiments and tests are needed to evaluate the radical data, it is too soon to provide any interpretation of the results except to note that they support the bias of the model to underpredict O₃ at low ROG/NO_x conditions, as discussed previously. In addition to testing OBMs, the data will provide valuable tests for mechanism predictions under varying ROG and NO_x conditions, with the measurements of H₂O₂, HO₂, and HNO₃ providing significant new information in this regard.

Western Regional Air Partnership Regional Modeling Center

Western Governors' Association Contract 30203-33. Gail S. Tonnesen Principal Investigator.

Objectives

The Western Governors' Association and the Western Regional Air Partnership (WRAP) have implemented a regional planning process to provide the necessary technical and policy tools needed by states and tribes to comply with Clean Air Act requirements for Regional Haze. As part of this effort, the WRAP has established a Regional Modeling Center (RMC) at the University of California, Riverside (UCR). The WRAP RMC provides assistance to State and Tribal agencies in conducting regional haze analyses over the western United States. This analysis is being performed by operating regional scale, three-dimensional air quality models that simulate the emissions, chemical transformations, and transport of criteria pollutants and fine particulate matter (PM) and consequent effects on visibility in Class I Areas in the western US. The first 3 years of this work focused on modeling to support those states which were part of the Grand Canyon Visibility Transport Commission (CGVTC) which have the option to submit an accelerated SIP under Section 309 of the CAA. Beginning in 2003 the focus of this work shifted toward developing better PM science and models to be used in Section 308 SIPs and TIPS that will be due

beginning in 2007. As part of this effort UCR has worked in development or applications of several regional PM models including REMSAD and CMAQ. Funding from 2001 to 2003 was \$1.7 million, and work is expected to continue until completions of section 308 SIPs in 2008. This project includes collaborations with researchers at ENVIRON Corporation and the University of North Carolina.

Current Status

Beginning in the fourth year this of this project UCR will perform annual model simulations of gas phase chemistry, PM and haze for a continental US domain for calendar year 2002. High resolution nested domains will be modeled for selected regions in the western US. UCR has obtained ambient monitoring data from several networks including AIRS, and PM data from IMPROVE, CASTNet, the National Acid Deposition Program (NADP), the Speciated Trends Network (STN), PAMS, PM Supersites. UCR has developed model performance evaluation software to compare model predictions with ambient data.

Visibility Improvement – State and Tribal Association of the Southeast (VISTAS): Emissions and Air Quality Modeling: Phase I

VISTAS Award No: 06-11312 Gail S. Tonnesen Principal Investigator.

Objectives

VISTAS is the Regional Planning Organization (RPO) responsible for developing technical support for regional haze SIPs and TIPs in the southeastern US. Thus, a major emphasis of this project is to provide a rigorous evaluation of several new, alternative science algorithms and models to identify the configuration that best meets the needs of VISTAS future regulatory haze modeling. The objective is to identify the modeling system that provides the best possible model performance while meeting all computational constraints imposed by the regulatory modeling schedule.

Current Status

Phase I of the project will be completed in December, 2003. Model sensitivity simulations have been completed for several different input uncertainties including NH₃ emissions, vertical mixing algorithms, fugitive dust emissions, and alternative meteorological data sets. Simulations have included 36 km grid resolution continental domains and high resolution, nested 12 km resolution grids. Simulation have been completed for winter episode in 2002 and for summer episodes in 1999 and 2001. A final selection will be made for the “best” model and science configuration in December, 2003. Phase II will include annual modeling and work will begin in January 2004.

Comprehensive Evaluation of Different PM Models (Phase 1): Diagnostic Evaluation of PM-CAMx, CMAQ and CMAQ-MADRID for the July 1-10, 1999 episode

Electric Power Research Institute, Award No: EP-P12363/C6141 Gail S. Tonnesen Principal Investigator.

Objectives

The current PM models, irrespective of their complexity, do not always perform as well as expected. Moreover, the more complex models do not necessarily perform better than their simpler counterparts. The objective of this project is to evaluate three PM models that may be used in a regulatory framework to understand the model performance. As much as possible, the three models will be operated using consistent input data bases (emissions, meteorology, air quality) so that differences among the

models should represent the effects of the different approaches used to implement science algorithms in each model.

The models to be evaluated include PM-CAMx, CMAQ and CMAQ-MADRID. The emphasis will be on diagnosing why the models perform as they do, understanding why models behave differently, and determining reasons for poor performance in certain cases. Although this is primarily a diagnostic evaluation (as opposed to an operational performance evaluation) UCR will include some comparisons of model predictions to ambient data to support the diagnostic evaluation. Several diagnostic or sensitivity simulations and process analysis (where available) will be used to understand the three models' behavior.

Current Status

Model simulations have been completed for a summer, 1999 episode using a continental scale coarse grid and a high resolution 8 km grid for the southeastern US. Ambient data from the several monitoring networks and from the SOS/Nashville 1999 field study is being used to compare model performance, and process analysis is being used to investigate the gas phase chemistry and certain components of the aerosol chemistry and dynamics. Phase I work will be completed in December, 2003.

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APPENDIX A. BUDGET FORMS AND DETAILS

(Please contact the Principal Investigator or the California Air Resources Board
if budget detail information is desired.)