

**DEVELOPMENT OF A NEXT-
GENERATION ENVIRONMENTAL
CHAMBER FACILITY FOR CHEMICAL
MECHANISM AND VOC REACTIVITY
EVALUATION**

Research Proposal to

The United States Environmental Protection Agency

by

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ABSTRACT

The high cost of ozone and particulate pollution and the regulations needed to abate them means that an ability to reliably predict the effects of emissions on air quality has significant economic value. Because of the complexity of the chemical processes involved, data from environmental chambers are essential to assuring that these models give correct predictions. However, current environmental chamber technology is more than 20 years old and is not adequate for testing models under conditions representative of rural atmospheres or the cleaner urban atmospheres we expect to attain as we approach attainment of air quality standards. This proposal calls for funding design, construction and operation of a next-generation environmental chamber facility capable of obtaining the data needed for evaluating models under conditions relevant to today's control strategy problems. The amount requested is approximately \$3 million, with approximately half that being for design, construction and characterization of the facility, and the remainder to support its operations for four years. This is a relatively low cost relative to the economic cost of ineffective control strategies that might result from use of models that give incorrect predictions.

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STATEMENT OF THE PROBLEM

Despite improvements in urban air quality in recent years, unacceptable levels of ground-level ozone and atmospheric particulate matter (PM) continue to be a persistent problem in urban and rural areas (NRC, 1991). To meet National Ambient Air Quality Standards, the U.S. Environmental Protection Agency (EPA) and state and local agencies must implement regulations to control pollutant emissions. These regulations should be designed to achieve the greatest possible benefits at the lowest costs and with the least disruption to economic activity and lifestyles. Because all the “easy” emissions control regulations already have been implemented, the additional regulations required to meet the air quality goals necessarily must 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 on health considerations, the EPA recently 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.

Factors Affecting Ozone Formation and Data Base for Mechanism Evaluation

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 has quite different effects on the amount of ozone produced. Different types of VOCs also have very different effects on ozone. For example, reducing NO_x emissions actually may cause ozone concentrations to become higher in some urban areas, but NO_x reductions are necessary to reduce secondary particulate matter. Furthermore, NO_x reductions are probably the only means by which significant ozone improvement can be obtained in rural or downwind areas. VOC controls often are 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 factor, but not the only one (Carter and Atkinson, 1989; Carter, 1994).

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 ozone and other secondary pollutant formation is the chemical mechanism, i.e., the portion of the model used to represent the chemical reactions involved. This is because the chemistry is the source of much of the complexity and non-linearity involved. 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 in the atmosphere 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. These experiments involve adding known amounts of representative pollutants to large enclosures, and measuring the changes in reactant concentrations and secondary pollutants formed when they are irradiated with either real or artificial sunlight under controlled conditions for periods of a day or longer. If a model cannot accurately predict observed changes in pollutant levels in such experiments, it cannot be expected to reliably predict effects of proposed control strategies on ambient air quality.

The available environmental chamber data base for evaluating ozone mechanisms has been reviewed by Dodge (1998) as part of the 1998 NARSTO ozone assessment. A fairly extensive set of quality-assured data exist for experiments carried out at our facility (Carter et al, 1995a, 1997, others¹) and at the University of North Carolina (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, 1998; 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) the experiments were designed more for empirical reactivity assessment than for mechanism evaluation (Dodge, 1998). Several new facilities are being developed in Europe (Becker, 1996; Mentel et al, 1996; Wahner, 1998; Wahner et al, 1998; Dodge, 1998, and references therein), though the available data primarily involve specialized studies of specific chemical systems rather than general mechanism evaluation.

As discussed by Dodge (1998), the 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 which can be assessed. Furthermore, because of chamber background and wall effects, and because of inadequate analytical equipment currently available at environmental chamber facilities, the

¹ See downloadable documents at <http://cert.ucr.edu/~carter/bycarter.htm>.

current environmental chamber data base is not suitable for evaluating chemical mechanisms under the lower NO_x conditions found in rural and urban areas with lower pollutant burdens. Relatively low NO_x conditions are also expected to become more typical in urban areas as we approach eventual attainment of the air quality standards. The nature of the radical and NO_x cycles and the distribution of VOC oxidation products change as absolute levels of NO_x are reduced. Because of this, one cannot necessarily be assured that models developed to simulate urban source areas with high NO_x conditions will satisfactorily simulate downwind or cleaner environments where NO_x is low.

While there is a clear need for chamber studies at low NO_x with low VOC levels, it might be argued that there is no need for studies of VOCs at low NO_x with high VOC because VOCs tend to have low impacts on ozone at high VOC/NO_x ratios. However, VOCs have other effects on the environment besides ozone formation, such as promoting secondary PM or forming toxic or persistent products, as discussed below. Furthermore, models predict that some VOCs caused reduced O₃ under low NO_x conditions, though the amount of reduction is highly dependent on environmental conditions (e.g., see Carter and Atkinson, 1989; Carter, 1994). In view of the fact that some are proposing to de-emphasize VOC regulations in low-NO_x areas because they are believed to have low or possible negative effects on ozone, it is even more important that their other air quality impacts be accurately assessed.

There has been work in the United States to address the need for chamber data for mechanism evaluation. In our laboratories there are ongoing studies relevant to evaluating ozone forming potentials of specific individual VOCs or mixtures of interest¹, and studies of other systems are being carried out at the University of North Carolina and the EPA chamber (Dodge, 1998). Although these data are reducing uncertainties in model predictions of ozone impacts of individual VOCs and mixtures under high-NO_x conditions, they are not addressing the need for data suitable for evaluating models under low-NO_x conditions or predictions of impacts other than on ozone. With regard to obtaining data for low-NO_x conditions, the effort in the United States has been limited to work with the TVA chamber in 1993-1996, where the chamber was continuously flushed with the lights on between experiments to minimize chamber background effects (Simonaitis and Bailey, 1995; Bailey et al, 1996). A limited number of experiments with a few single compounds and a few complex mixtures at NO_x levels in the 20-200 ppb range were carried out, along with associated characterization runs, though the data have not yet been fully utilized for mechanism evaluation. Data for mechanism evaluation at NO_x levels lower than 20 ppb have not been obtained, and the existing characterization data from this chamber are not sufficient for determining the lower NO_x limit for which useful data can be obtained. Unfortunately, it appears unlikely that additional data will be available from this facility.

Another major deficiency in the current mechanism evaluation data base is the lack of adequate information on the effects of temperature on VOC reactivity. Outdoor chambers yield data at varying temperatures, but because of lack of temperature control it is difficult to study temperature effects systematically and, probably more importantly, to obtain adequate characterization information concerning how temperature-dependent chamber artifacts may affect the results. The only indoor chamber used for mechanism evaluation where temperature can be varied in a controlled manner is the SAPRC evacuable chamber (EC) (Pitts et al, 1979;

Carter et al, 1995a), and only a limited number of variable temperature experiments have been carried out (Carter et al, 1979, 1984). That facility is not currently being used for mechanism evaluation experiments, and because of its relatively large wall effects is probably not suitable for low-NO_x experiments in any case (Carter et al, 1995a). Other than that, there is currently no environmental chamber facility capable of generating well-characterized mechanism evaluation data under controlled conditions at differing temperatures. Nevertheless, the limited available data indicate that temperature effects can be important (e.g., Carter et al, 1979, 1984, see also Carter et al, 1993), and thus there is a need for a facility which can generate adequate mechanism evaluation data in this regard.

Evaluation of PM Impacts and Secondary Organic Aerosol Formation

Urban fine particulate matter is constituted of a complex mixture of both primary and secondary organic and inorganic compounds and comes from a wide variety of sources. While contributions of primary PM can be estimated directly from the knowledge of emission rates, contributions of secondary PM are more difficult to assess because they are formed by complex homogenous and heterogeneous processes. Secondary PM consists primarily of nitrate, sulfate, and secondary organic aerosol (SOA), and most of it forms as fine particulate matter of less than one micron aerodynamic diameter. Since smaller diameter particles have been shown to be more irritating to the human pulmonary system, these are a particular concern. The nitrate and sulfate are derived largely from gaseous emissions of NO_x and sulfur dioxide, while secondary organic aerosol are formed from the oxidations of VOCs which form products with sufficiently low vapor pressures to partition into the aerosol phase.

The atmospheric chemical reaction pathways of VOC molecules sufficiently large to lead to SOA are complex, and resulting oxidation products are both numerous and difficult to quantify analytically. As a result, it is currently not possible to determine the aerosol formation potential of individual VOCs and their contribution to the secondary organic urban particulate burden strictly on the basis of atmospheric chemical reaction mechanisms. However, secondary organic aerosol yields have been measured in environmental chamber experiments over the past decade or so, primarily using the Caltech outdoor chamber (e.g., see Hoffmann et al., 1997; Forstner et al., 1997, and references therein). Initially it was believed that each VOC should possess a unique value of its aerosol yield, but Odum et al. (1996) found the chamber data are much better described by a two-parameter gas/aerosol absorptive partitioning model. Within that framework, semi-volatile products from the atmospheric oxidation of an ROG can partition into an absorbing organic aerosol phase at a concentration below their saturation concentration, analogous to the partitioning that occurs between the gas and aqueous phases of a water-soluble atmospheric constituent.

Although the outdoor chamber data base provides important information on the effects of individual VOCs on SOA formation, the use of outdoor chambers has a number of limitations. Perhaps the most serious problem is the lack of temperature control and the variability of temperature during the experiment. Inability to control temperature also means that humidity cannot be controlled unless the experiment is carried out under dry conditions. Temperature is

important because of its effect on vapor pressure, which affects the tendency of particles to partition into the aerosol phase. Humidity is important because it will affect the nature of the aerosol material, which in turn will affect the partitioning of the organic products onto that material. Because of the importance of controlling humidity, most outdoor chamber aerosol yield experiments are carried out dry. In addition, the chambers currently used for such studies have a non-rigid design, and aerosol lifetimes may be reduced by the constant stirring due to winds causing turbulent deposition. This makes interpretation of the aerosol dynamics more difficult. In addition, variable lighting conditions make the experiments more difficult to use for model evaluation. Finally, the current outdoor chamber systems are not well suited for carrying out experiments using the low concentrations of NO_x or other pollutants that are more characteristic of regional or near-attainment conditions.

Evaluation of Impacts of VOC Oxidation Products

Emitted organic pollutants may have other adverse impacts on air quality besides contributing to ozone and secondary PM formation. If the emitted VOC itself is toxic or has other adverse direct impacts, this can be assessed given a knowledge of the VOC's atmospheric reaction rates and deposition velocities. A more difficult problem is assessing the impacts of the oxidation products of the VOCs. For example, VOCs may react to form toxic products, products that persist in the environment, or products (such as PANs or organic nitrates) which can serve as NO_x reservoirs whose subsequent reactions may significantly enhance ozone formation in downwind, NO_x -limited environments. An assessment of this requires a knowledge of the identities and yields of the VOC's major reaction products. This is difficult because the products are not known or not quantified for many VOCs. In addition, the products formed when a VOC reacts in the atmosphere will change when NO_x levels become sufficiently low that radical-radical reactions begin to dominate in the photooxidation mechanisms.

Conducting laboratory studies of products formed from the photooxidations of VOCs of interest is one approach for obtaining the data needed for assessing VOC impacts in this regard. However, conditions in laboratory experiments designed for product studies are usually not very similar to atmospheric conditions, particularly those with lower pollution levels. In principle, identifying and quantifying products in simulated atmospheric conditions in environmental chambers should provide information on the actual products formed under more realistic conditions, the subsequent lifetimes and fates of these products, and how they vary with conditions. Furthermore, obtaining product concentration-time profiles in conjunction with chamber experiments for mechanism evaluation permits a much more comprehensive evaluation of the details of the overall mechanism than otherwise would be possible. However, with the possible exception of the Europhore chamber in Europe (Becker, 1996), environmental chamber facilities currently in use for mechanism evaluation do not have the advanced analytical capabilities necessary for carrying out comprehensive product measurements in conjunction with environmental chamber experiments.

Evaluation of Model Representations of NO_y and Radical Budgets

It has been recognized for a number of years that the tropospheric production of O₃ and other oxidation processes are governed by the budgets of free radicals and the fate of nitrogen oxides (NRC, 1991; Seinfeld, 1989; Kleinman et al., 1997). There is a growing awareness that models cannot be adequately evaluated by simply comparing observed versus simulated O₃ (Tesche et al., 1992; Reynolds et al., 1994). Furthermore, because models can have compensating errors in representations of radical budgets and NO_x removal processes, even comparing observed and simulated yields of oxidation products may not necessarily provide a good evaluation of how well the model represents these processes. For these reasons, a state-of-the-science model evaluation requires process level diagnostics that characterize the budgets of HO_x and NO_x (Arnold et al., 1998). Furthermore, because the budget of HO_x also affects the production and removal of VOC, hazardous organic pollutants, and certain greenhouse gasses, the use of process diagnostics to test the radical budget will increase our confidence in chemical tracer models used to simulate certain hazardous air pollutants and green house gasses.

A number of process-level diagnostics have been used or proposed for use in model evaluations using ambient data (Kleinman, 1994; Jeffries and Tonnesen, 1994; Milford et al., 1994; Sillman, 1995, 1998; Arnold et al., 1998; Kleinman et al., 1997; Tonnesen and Dennis, 1998a,b). Process diagnostics have also been compared with ambient observations to evaluate grid models (Sillman et al., 1995, 1997; Imre et al., 1997). The ability to confirm the model representation of chemical processes in those studies is uncertain, however, for the following reasons:

- The complete set of measurements necessary to characterize HO_x and NO_x budgets has not been available in field studies because measurements are difficult to collect or are of uneven quality due to the difficulties of operating instruments in field conditions,
- In ambient conditions, the concentrations of important species are affected by transport, dispersion, and deposition, and by variability in temperature, humidity and actinic flux, thereby complicating the interpretation of the chemical processes.
- There is the possibility that important ambient processes may be unrepresented in the model simulations, but that compensating errors still enable the model to match observations.

Chamber experiments present an opportunity to obtain a more complete and rigorous evaluation of chemical processes. For any given chemical process, two types of process diagnostics can be defined: (1) local measures of instantaneous production and loss rates; and (2) air-parcel diagnostics that represent the cumulative production and loss in an air parcel over a period of time. Table 1 lists examples of process diagnostics that can be used to characterize elements of the radical cycle for each of these types. In principle, we can obtain a more rigorous test of certain portions of the radical cycle because, for example, local radical initiation must be balanced by local radical termination, and the integral of both the local initiation and local termination rates should be approximately balanced by the cumulative production of termination products. For ambient conditions, however, transport and dilution prevent a direct comparison of

Table 1. Process diagnostics and species ratios useful for characterizing radical budgets.

<i>Local Diagnostics</i>	<i>Air-parcel Diagnostics</i>
I(NO,RO ₂), I(HC,NO ₂) – characterize local radical propagation efficiency and chainlength.	O ₃ /(2*ROOH+2*H ₂ O ₂ +NO _z) – approximation of the OH chain length in an air parcel
(k*HO ₂ ² + k*HO ₂ ² H ₂ O)/(k*OH*NO ₂) – characterize local termination ratio.	2*ROOH + 2*H ₂ O ₂ versus NO _z –competing radical termination pathways in air parcel
J-values and HCHO, H ₃ CHCO, HONO, H ₂ O ₂ , PAN, etc. – local initiation	2*ROOH + 2*H ₂ O ₂ + NO _z – radical termination in an air parcel
Rate constants and concentrations of OH, HO ₂ , RO ₂ , NO ₂ , O ₃ – local termination.	2*ROOH + 2*H ₂ O ₂ + NO _z – radical termination in an air parcel.
<p><i>Other Diagnostic ratios:</i></p> <p>HO₂/OH, RO₂/HO₂, NO₂/NO</p> <p>O₃-NO₂-NO Photostationary State</p>	

local and air-parcel diagnostics. Chamber experiments could be especially useful for evaluating radical budgets because the confined volume makes it possible to balance local and air-parcel diagnostics.

Chamber experiments do present additional problems due to the wall effects and deposition to or off-gassing from walls. However, as discussed below, the proposed chamber will be designed to minimize these effects. In any case, in an appropriately designed and characterized chamber it should be easier to quantify these effects than in the ambient atmosphere. Thus, characterization of radical budgets in carefully controlled chamber presents an important opportunity to investigate the adequacy of current photochemical mechanisms for a wide range of precursor levels and environmental conditions.

For these reasons, it is desirable to investigate the usefulness of process diagnostics in an environmental chamber where the system inputs and chamber conditions can be carefully controlled. The use of a chamber would also facilitate the operation and calibration of analytical instruments and could provide a complete set of necessary measurements thereby reducing the possibility of compensating errors in unmeasured processes.

Evaluation of Ambient Monitoring Methods

Although environmental chamber data are essential for evaluating chemical mechanisms used in airshed models, they do not eliminate the need for measurement data on real background and pollution episodes in the ambient atmosphere. Such data are required not only for evaluating airshed model performance as a whole, but also to determine air quality trends, evaluate emissions inventories, and support various observational analysis methods which are proving to be valuable for assessing control strategies in situations where modeling is too uncertain to be useful. Such data are only as good as the measurement methods used to obtain them. While routine monitoring of species such as ozone, CO, NO, and SO₂ is relatively straightforward, measuring many other critical species under field conditions, such as NO_x species other than NO, speciated organic precursors and products, is extremely difficult and uncertain. Considerable research is being carried out on developing advanced methods and instrumentation for monitoring species in ambient air, which are then used in major field programs such as the Southern Oxidant Study. An important component of such research is evaluating the reliability of such methods under real world conditions, where the presence of complex mixtures may cause interferences or otherwise affect model performance.

One way to evaluate instrument performance under real world conditions is to carry out intercomparison studies, where the same species are measured using differing methods in the same air mass. Such studies are useful, but have limitations. Because one does not know *a priori* what is actually in the air mass, it is necessary that at least one of the methods being intercompared be considered reliable, or it must be assumed that the instruments being compared are not subject to the same types of interferences or biases. Therefore, agreement of different methods only indicates that it is possible that they are accurate, but does not provide definitive evidence that this is the case. Furthermore, it may not always be obvious which method is incorrect when they disagree, or it may be that the more “reliable” method may actually have an unsuspected problem.

Use of an environmental chamber system provides an obvious method to get around the limitations of field intercomparison studies for evaluating analytical methods. At a minimum the history of the air mass and the initial pollutants injected will be known, and in many cases the correct concentrations of the subject compounds will also be known or can be computed, or at least varied in a systematic way. However, most existing environmental chamber systems also have limitations. Some ambient air analysis methods require long path lengths or require large sample volumes, which requires use of very large chambers. Most large outdoor chambers, such as that at UNC, are not useful for simulating environments with the relatively low pollutant levels characteristic of much of the ambient atmosphere. No existing large chamber system allows for controlling conditions such as temperature and light intensity, which may be useful for some types of instrument evaluation. The availability of a large chamber capable of simulating low pollutant conditions under controlled and variable environmental conditions would be a valuable asset in this regard.

Evaluation of Indicators of Ozone Sensitivity to Precursor Emissions

One type of ambient monitoring method that requires evaluation under controlled conditions is the proposed use of observational methods or indicator species to determine sensitivity of ozone production to precursor emissions in ambient air parcels. Given the large uncertainties in model inputs of emissions, meteorology, and photochemistry, an air quality model can be made to reproduce observed O_3 concentrations, yet produce a variety of sensitivities of O_3 to changes in VOC and NO_x emissions (NRC, 1991). This uncertainty has led to a search for observational methods to evaluate control strategy effectiveness independently of the model. As noted by Sillman (1995), the goal is to find indicator species or species ratios “which consistently assume different values under conditions of NO_x -sensitive and VOC-sensitive ozone.” If such indicators are found to be consistent and robust for a wide range of atmospheric conditions, ambient measurements of the indicators could in theory provide a means, independent of models, to determine O_3 sensitivity to small changes in VOC and NO_x emissions (Sillman et al., 1997a,b). Use of environmental chambers provide a means for evaluating the predictive capability of use of such indicators.

Two types of indicators have been proposed: (1) local indicators of the instantaneous rate of odd oxygen production ($P(O_x)$); and (2) long-lived indicators of O_3 concentration ($[O_3]$). Because $[O_3]$ is determined by the cumulative production and losses of O_x in an air parcel over time, long-lived indicators provide information about the history of an air parcel, while local indicators provide information about current conditions at a particular site. The two approaches are complementary and their combined use provides a more rigorous form of model evaluation. Table 2 lists indicators that have been proposed based on modeling studies for both $P(O_x)$ sensitivity and $[O_3]$ sensitivity.

Indicators have been evaluated for two types of closely related conditions: conditions where $P(O_x)$ or $[O_3]$ are equally sensitive to VOC and NO_x :

$$\frac{\partial P(O_x)}{\partial E_{NO_x}} = \frac{\partial P(O_x)}{\partial E_{VOC}} \quad \text{or} \quad \frac{\partial [O_3]}{\partial E_{NO_x}} = \frac{\partial [O_3]}{\partial E_{VOC}} \quad (1)$$

and for conditions on the ridgeline where $P(O_x)$ or $[O_3]$ are maximized as a function of NO_x at fixed VOC:

$$\frac{\partial P(O_x)}{\partial E_{NO_x}} = 0 \quad \text{or} \quad \frac{\partial [O_3]}{\partial E_{NO_x}} = 0 \quad (2)$$

The conditions described by (1) and (2) are closely related, where equal sensitivity occurs for NO_x emissions slightly lower than for the ridgeline. Local sensitivity is evaluated in terms of $P(O_x)$ rather than $P(O_3)$ because $P(O_x)$ includes total oxidation of NO to NO_2 . Thus, $P(O_x)$ provides a more complete description of photochemical reactivity because it includes oxidation of NO for conditions with high NO emissions and low $[O_3]$.

Table 2a. Modeling studies of indicators of [O₃] sensitivity.

<i>Reference:</i>	<i>Indicator ratios evaluated</i>
<i>Blanchard et al., 1993; Chang et al, 1997</i>	extent parameter
<i>Milford et al., 1994</i>	NO _y
<i>Sillman, 1995, 1998; Kleinman et al., 1997</i>	NO _y , O ₃ /NO _y , HCHO/NO _y , O ₃ /HNO ₃ , H ₂ O ₂ /HNO ₃
<i>Lu and Chang, 1998</i>	O ₃ /NO _z , HCHO/NO _y , H ₂ O ₂ /HNO ₃
<i>Tonnesen and Dennis, 1998b</i>	O ₃ /HNO ₃ , HCHO/NO ₂ , H ₂ O ₂ /(O ₃ +NO ₂), O ₃ /NO _x , H ₂ O ₂ /HNO ₃

Table 2b. Modeling studies of indicators of P(O_x) sensitivity.

<i>Reference:</i>	<i>Indicator ratios evaluated</i>
<i>Tonnesen and Dennis, 1998a</i>	O ₃ /NO _x P(H ₂ O ₂)/P(HNO ₃) HO ₂ $\sum k_{OH,i} VOC_i / (k_{OH} NO_2 + \sum k_{OH,i} VOC_i)$ $k_{HO_2} NO / (k_{HO_2} (HO_2 + RO_2) + k_{HO_2} O_3 + k_{HO_2} NO)$

To date, the usefulness of indicators has been asserted based on theoretical considerations. Their usefulness has not been experimentally confirmed in controlled conditions. Indicators cannot be confirmed in ambient experiments because it is not possible to control the transport and dilution of emitted species. Instead, indicators must be evaluated in chamber experiments where precursor emissions and concentrations can be carefully controlled.

OBJECTIVES

The objectives of this 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 will then be employed to provide data that are most relevant to today's pollution problems and control strategy issues. We propose a four-year program, with the first one to two years being for research on chamber design, facility development, and chamber characterization and evaluation. The remainder of the program will involve conducting experiments needed for model evaluation and to address issues of relevance to regulatory assessment and control strategy development. These would include, but not necessarily be limited to, 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 O_3 and $\text{P}(\text{O}_x)$ 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.

BENEFITS

The high cost of regulations needed to meet current air quality standards means that an ability to reliably predict effects of regulations on air quality has significant economic value. This program will result in an chamber facility capable of providing data needed to evaluate predictions of effects of regulations on environments where such evaluations were not previously possible, but which are most relevant to current regulatory issues. If the results indicate that current models developed to represent higher pollutant conditions are giving inappropriate control strategies for approaching attainment, the cost savings resulting from correcting the strategies will be many orders of magnitude greater than the cost of this program. Once the facility is in place and its utility demonstrated, we anticipate no difficulty for the foreseeable future in obtaining ongoing funding. Therefore, the benefits of developing this facility should continue far after the lifetime of this four-year project.

APPROACH

Location and Qualification of the Investigators

This proposal is to build upon the existing environmental chamber facility at the University of California, Riverside (UCR), which is already the most active in the United States in this area of research. Researchers at UCR have been active in atmospheric chemistry, atmospheric chemical mechanism development, and conducting environmental chamber experiments for chemical mechanism development since the early 1970s. Environmental chamber data from UCR have played a major role in the development and evaluation of the chemical mechanisms currently used in regulatory and research models in the United States, and the UCR environmental chamber data base is the largest existing documented data base currently available for this purpose. Furthermore, the chamber facility at UCR is the only one being used on an ongoing basis for generating data for developing and evaluating mechanisms for VOC reactivity assessment, under funding from the California Air Resources Board and various chemical industry sources.

The Principal Investigator for this program will be Dr. William P.L. Carter. Dr Carter has been involved in environmental chamber research since 1979 and chemical mechanism development research since 1974. More recently, he has been conducting experimental and modeling studies of VOC reactivity. Chemical mechanisms he developed are widely used in research and regulatory applications, and environmental chamber data from his compilations or programs have been used in the evaluations of the other mechanisms in use in the United States.

He is responsible for the compilation of the UCR environmental chamber data base (Carter et al, 1995a) and participated in developing the proposed protocol for evaluating mechanisms using environmental chamber data (Jeffries et al, 1992). His biographical sketch is attached.

Dr. Carter has a joint appointment with both the Air Pollution Research Center (APRC) and the College of Engineering-Center for Environmental Research and Technology (CE-CERT). APRC is the site of the original UCR environmental chamber facility, and remains a leading facility for basic kinetic and mechanistic studies. The projects involving use of environmental chambers for atmospheric simulation and mechanism evaluation were moved to CE-CERT in 1992 to take advantage of opportunities to interface with the state-of-the-art vehicle and stationary source emissions programs being developed there, though collaboration with researchers at APRC continues when appropriate. Because of this, this proposed chamber facility will be located at CE-CERT, which is where the project will be administered.

Dr. John H. Seinfeld and Dr. Richard C. Flagan of the California Institute of Technology (Caltech) will be collaborating in this project. Their collaboration is important because although UCR is a leader in use of environmental chambers for gas-phase mechanism evaluation, Dr. Seinfeld's group at Caltech is the recognized leader in the use of environmental chamber studies for studies of secondary aerosol formation. Dr. Seinfeld, who will be a co-investigator for this project, is a world-recognized authority in many areas of air pollution, in particular experimental and theoretical studies of aerosol formation. Dr. Flagan's research focuses on studies of the chemical and physical processes involved in formation and growth of atmospheric aerosols, and he is an expert in the development of aerosol monitoring instrumentation. As such, he has been a major contributor to developing the capabilities of the state-of-the-art aerosol chamber studies at Caltech. These researchers will play a major role in planning and providing assistance in carrying out the PM-related portions of this project, and Caltech students under Dr. Seinfeld and/or Flagan's direction will participate in carrying out the experiments and analyzing the results. Participation of Dr. Seinfeld in this project will assure that this project best complements the ongoing or planned studies at Caltech, and participation of Dr. Flagan will assure that the most appropriate and advanced instrumentation is employed. Their biographical sketches are attached.

Additional co-investigators of this project will be Mr. Dennis R. Fitz and Dr. Gail S. Tonnesen. Mr. Fitz was formerly a member of the APRC research team, where he managed the Outdoor Chamber Facility, and is currently the manager of the Atmospheric Processes and Stationary Source Emission Control Group at CE-CERT. He specializes in the measurement of trace atmospheric pollutants, especially the minimization of gas-particle sampling artifacts. Dr. Tonnesen developed a process analysis method for analyzing model simulations with Professor Jeffries at the University of North Carolina, and she has continued to apply this method to the evaluation of photochemical models in research with Dr. Robin Dennis at the U.S. EPA. Biographical sketches of Mr. Fitz and Dr. Tonnesen are attached.

UCR in general and CE-CERT in particular are an ideal venue for developing a next generation environmental chamber facility. The campus has a number of active atmospheric researchers at APRC, CE-CERT and the Department of Chemistry. We are also close to the researchers at Caltech with whom we are collaborating and to other researchers in Southern

California, including those at UC Irvine and UC Los Angeles. CE-CERT has 15,000-square-foot laboratory with sufficient space for additional facilities. This laboratory contains both chassis and engine dynamometers in addition to stationary source testing equipment, so that we are able to readily introduce actual emissions into chambers. The analytical laboratory is also housed in this facility, thus simplifying sample transport. We currently have five smog chambers and perform simulations almost daily. More information about the current CE-CERT facilities are attached to this proposal.

Development of a Research Plan

Proper research planning is a critical component for a project of this scope. This proposal describes the research needs and gives an outline of a program to address these needs, but additional work is needed to develop a full research plan for a project such as this. At the beginning of this project a proposed work plan will be developed to address the design and research priorities for the facility. This will include, but not be limited to, the following:

- Compilation and review of existing information concerning chamber effects, particularly those which may affect the reliability and characterization of data obtained at low pollutant (especially NO_x) concentrations. The characterization data reported for the TVA chamber (Simonaitis and Bailey, 1995; Bailey et al, 1996) may be particularly useful in this regard. The aerosol characterization data from the Caltech chambers will also be important.
- Specification of additional experiments which can be carried out in the near term to obtain information relevant to determining how best to design a chamber to minimize chamber effects and/or make them reproducible and predictable.
- Developing the specifications and plans for constructing the major components of the facility, including the air purification system, and temperature control and lighting system for the chamber housing. The experience with the Caltech chamber will be useful in developing an appropriate design for PM experiments.
- Developing a protocol for chamber characterization and control experiments that will be utilized once the chamber is constructed. These would include, but not necessarily be limited to, characterization runs already being carried out at the CE-CERT, Caltech, and other chamber facilities, and experiments with well characterized chemical systems such as propene - NO_x , etc.
- Developing a proposed priority of experiments to be carried out once the chamber is constructed and adequately characterized. Specific types of research being proposed are summarized in the following sections. Input will be obtained from the other atmospheric scientists, the EPA and other regulatory agencies, and interested members of the regulated community, as discussed in the following section.
- Setting priorities for the list of analytical equipment to be obtained for this project. The first priority will be equipment useful for characterization of chamber effects, such as those for monitoring background species at low concentrations. The ranking for the

additional equipment will depend on the research plan that is established. In some cases, it may be advantageous to defer acquisition of equipment until later in the program, to take advantage of results of ongoing developments.

The initial research plan will be developed in consultation with the Caltech collaborators and the EPA project officer where appropriate. A preliminary version will be presented at the research workshop, discussed in the following section, and modified as appropriate based on the input received. The work plan will be finalized in consultation with the Research Advisory Committee, as also discussed in the following section.

Research Planning and External Coordination

An important component of the planning and execution of this project will be obtaining appropriate input from the regulatory and regulated community concerning the most important policy-relevant research needs, and from the scientific community concerning how this facility can best address these needs. This will be done through the mechanisms of holding periodic scientific workshops where this and other relevant research is discussed and presented, participation in the NARSTO process, and forming a Research Advisory Committee to oversee and provide input into this project and related research utilizing this facility. These are discussed further below.

Research Workshops

At the start of this program, we will hold a workshop concerning the state of the science related to environmental chamber research, and related areas in atmospheric chemistry, model development and evaluation, and priorities for model applications that require research in these areas. The invited participants will include U.S. and international experts on environmental chambers, modeling, and other relevant aspects of air pollution and representatives of the EPA and other regulatory agencies, and private sector or other organizations who are affected by or are interested in such research. Participation of European researchers will be important to take advantage of the experience gained from the environmental chamber facilities recently developed in both Spain and Germany and to complement rather than duplicate research being carried out there.

In view of the importance of European participation, an appropriate forum for the initial workshop would be to incorporate this as a part of the next in the series of U.S./German workshops on the Photochemical Ozone Problem and its Control, which has been planned in the United States at about the time this program is scheduled to begin. Because the EPA budget may not include funding for U.S. participation in this workshop, we propose that this workshop be held in Riverside, with the U.S. participation funded by this project. This obviously will require the agreement between the EPA and the Europeans. An alternative will be to include sessions related to this project in an appropriate NARSTO workshop. If necessary, we will have a separate workshop, with European participation funded to the extent feasible given the available budget for this purpose.

This workshop will include technical presentations concerning available information and research needs related to this program. Note that the scope of this workshop will be expanded beyond ozone to research related to PM formation and assessment of other VOC impacts such as toxic or persistent product formation. Representatives of other environmental chamber research groups will be invited to give presentations on the studies they are conducting, problems they have encountered, and anticipated future utilization of their facility. This will include use of environmental chambers related to PM formation as well for evaluating gas-phase chemical mechanisms or ozone reactivity. Chemical mechanism developers will be invited to give presentations concerning their use of environmental chamber data for mechanism development and evaluation, and concerning what they see as the greatest environmental chamber data needs. Modelers and model developers will be invited to give presentations on current and anticipated model applications which will require improved chemical mechanisms or models for PM formation, and types of research needed to improve these model components. Researchers working in analytical methods development and field researchers will be invited to give presentations on analytical instrumentation and analysis methods which may be useful in environmental chamber systems. Researchers working on studies of surface effects that may potentially be relevant to chamber artifacts will also be encouraged to participate and give presentations at this workshop.

The workshop will also include presentations on policy issues as they relate to modeling, VOC reactivity assessment, assessment of secondary PM formation, and other areas where environmental chamber studies can potentially provide relevant information. The objective will be to relate these policy needs to research needs, to help set priorities for near-term and long term research.

The research plan for this program will also be presented at this workshop, and participants will be invited to give feedback on all areas of this plan. This will include discussions of the policy relevance and priorities of the proposed research, as well as the discussions of the scientific utility and technical merits or problems. A goal is that other chamber researchers (particularly the Europeans) can provide feedback concerning whether this program duplicates or complements their projects, as well as their experience concerning minimizing or characterizing chamber effects. If any projects are going to be adequately studied elsewhere, they obviously should be given lower priority for this program. On the other hand, there may be cases where complementary or cooperative studies with other chamber researchers may provide valuable information which otherwise could not be obtained.

It is expected that other workshops may be held later in the program as information becomes available, or it may be appropriate to obtain external input concerning the research plan, from a scientific or policy-relevance perspective. These probably would be held in conjunction with NARSTO meetings, as discussed below.

Research Advisory Committee

External input concerning the overall direction and priorities of the program will also be obtained through use of a Research Advisory Committee, an approach which is being used

successfully in a number of the larger policy-relevant projects at CE-CERT. This will include invited representatives of regulatory agencies (including the EPA and the California ARB), representatives of industry groups interested in these issues, and appropriate experts in academia, probably including other chamber researchers. This group will be formed after receiving input from the initial workshop, which will include input on the appropriate composition of this committee. The initial meeting will include a discussion of the research plan in light of input received at the initial workshop, and general issues on how the program will be carried out, including how often the Advisory Committee should meet. In subsequent meetings, which would be carried out at least annually, progress on the program will be reviewed, and the implications of the results of the program, and related scientific or policy developments, on the overall research plan, will be discussed.

Participation in NARSTO and the Reactivity Research Working Group

NARSTO is a public/private partnership whose mission is to coordinate and enhance policy-relevant scientific research related to tropospheric pollution², and which is being used to coordinate much of the EPA-funded research in this area. The investigators in this program will participate in the appropriate NARSTO working groups to enhance the coordination of this project with other NARSTO projects. This participation will also have the advantage of providing an additional means to obtain feedback concerning the priorities and approach in this project. We expect that participation would be through the Modeling and Assessment team (of which the Principal Investigator is a member), though the primary coordination mechanism will probably be through the Reactivity Research Working Group (RRWG).

The RRWG is an independent group formed to provide an improved scientific basis for reactivity-related regulatory policies³, which has recently become part of NARSTO. Its participants include the EPA, the California ARB and other regulatory agencies, the Chemical Manufacturers Association and other industry groups, and a number of academics active in areas related to reactivity. The Principal Investigator is presently the leader of the Reactivity Science Assessment Group, and two of the Co-Investigators (Seinfeld and Tonnesen) contributed to the initial reactivity assessment document that was prepared for this group. The specific approach for how this program will be coordinated within RRWG has not yet been determined, and will be discussed in the upcoming RRWG meeting scheduled for March 24, 1999.

It may be that the workshops and the Advisory Committee activities will also be coordinated with RRWG or NARSTO, to avoid duplication of effort. This is yet to be determined.

² See <http://www.cgenv.com/Narsto> for further information concerning NARSTO's missions and programs.

³ See <http://www.cgenv.com/Narsto/reactinfo.html> for further information related to the Reactivity Research Working Group.

Evaluation of Approaches to Minimize or Control Chamber Effects

Other than analytical limitations, the main factor limiting use of environmental chambers for mechanism evaluation at low pollutant conditions is chamber wall effects. Known chamber effects that are taken into account during mechanism evaluation include the chamber radical source (which is believed to be due at least in part to HONO absorption and offgasing), ozone wall losses, NO_x absorption and offgasing, N₂O₅ hydrolysis, excess NO to NO₂ conversions attributable to background VOC contamination, etc. (Carter and Lurmann, 1990, 1991; Carter et al, 1995a; Gery et al, 1989). Of these, perhaps the most serious factor limiting utility of chamber data under low NO_x conditions is NO_x offgasing effects, while background VOC contamination would limit the utility of data under low VOC conditions.

Before finalizing the design and specifications for the chamber, we will investigate approaches to minimize these effects or at least make them predictable and reproducible. Most chambers currently used for mechanism evaluation consist of heat-sealed FEP Teflon reaction bags, which have good UV transmission characteristics and are relatively inert. Previous evaluations have indicated that metal is unsatisfactory, and work in our laboratories and elsewhere indicated that chambers constructed of glass (unpublished results from this laboratory) or Teflon coated metal (e.g., the APRC evacuable chamber [Carter et al, 1982, 1995a]) have higher radical sources. Although comprehensive research may reveal that there is a superior surface material than Teflon film, we suspect that there will probably not be time (or funds) to carry out such comprehensive research and still have an operational chamber within the desired time frame, which is about 1 – 1 ½ years. Therefore, it is expected that the chamber will be constructed of FEP Teflon film.

Assuming that this will be the case (though use of alternative materials is not ruled out), the problem becomes how to treat or clean FEP Teflon film to minimize chamber effects and make them predictable and reproducible. In our laboratory and at Caltech, the normal procedure has been to flush the reaction bags between runs, carry out periodic characterization experiments (e.g., CO – NO_x and n-butane - NO_x runs to measure the radical source, and pure air or acetaldehyde – air experiments to measure NO_x offgasing effects, and standard propene – NO_x runs) and replace them if anomalous characterization results indicate contamination. Although this yields sufficiently well characterized chamber effects for reactivity experiments with NO_x levels above ~50 ppb and sufficient VOC for ozone formation, this will not be suitable for the purpose of this program.

The approach that was employed at the TVA chamber (Simonaitis and Bailey, 1995) was to flush the chamber for a relatively long period of time. This approach is occasionally used in our facility, and it is often found to be successful in reducing contamination effects when anomalous results are seen after exposure of the chamber to unusual reactants. Results of the limited relevant characterization data given in the TVA reports indicate that this results in significantly lower apparent NO_x offgasing rates than observed in our chamber. However, an important issue in terms of chamber productivity is the amount of flushing time required to achieve satisfactory results. If long flushing times are required, a multi-reactor chamber facility

will be constructed to allow experiments to be carried out in some reactors while others are being flushed.

This and other approaches for cleaning will be evaluated using small (~50-100 liter) Teflon reaction bags, where contamination effects will be much more evident. Examples of other approaches which might be tried might include treatment with water to remove absorbed NO_x and other materials, followed by flushing with light, or perhaps even treatment with F₂. Small reactors will also be used to examine effects of temperature variation, since the chamber is expected to be operated at a range of controlled temperatures. Obviously, any approach that will be employed will have to be scalable to a large volume chamber at a reasonable cost.

Experience in our laboratory with a ~12,000-liter chamber suggests that simply increasing the volume of the chamber can be a major factor in reducing chamber effects such as NO_x offgasing rates (Fitz et al, 1998). However, the extent to which the lower apparent chamber effects in that reactor may be due to other factors such as use of newer reaction bags or higher light intensity. Our existing larger chambers, which range in volume from ~1000 to ~12,000 liters, can be used to investigate the effects of chamber size on chamber effects and efficacy of cleaning and conditioning processes, if appropriate. In any case, any cleaning or conditioning process which gives good results for ~100-liter reaction bags should work at least as well in larger chambers.

Chamber and Facility Design and Fabrication

Based on the results of the evaluation of prototypes and other tests, the design of one or more larger research chambers will be developed. It may well be that more than one chamber may be necessary, especially if it is found that flushing for long periods of time is necessary to control chamber effects. Separate chambers may also be used for different research objectives, such as simulations of nearly clean air, measurements of particle formation under more polluted conditions, or assessments of VOC reactivity under more urban-like conditions using the facilities' advanced analytical instrumentation. It is expected that chambers for low NO_x and particle research will need to be of large volume to minimize surface effects, and also to permit analyses using instrument with high sample flow requirements. The latter will be particularly important when using the chamber to test instrumentation designed for field use.

Another design goal would be to have a chamber that can be operated in multi-day simulations without significant dilution or loss of volume, and without buildup of wall effects. Multi-day experiments will be critical for simulations of rural or long range transport scenarios.

Utilizing highly purified air and avoiding outside contamination is also critical. Exploratory experiments in our laboratory using procedures to improve air purification have shown that this reduces some effects that were attributed to chamber walls. To avoid introduction of contaminants from laboratory air into the chamber (through leaks or diffusion through the Teflon walls), the reactors will be located in a "clean room" which itself is flushed with purified air.

The first construction priority will be a high capacity air purification system that is capable of removing CO as well as NO_x and organics and other pollutants to the lowest practical level. Removal of methane is a lower priority, but if feasible that will also be desirable. Removal of methane, CO, and CO₂ would be desirable if feasible because it would permit use of simplified (and therefore more reliable) methods to measure total reactive carbon present. High capacity is essential because the system will be used for flushing the clean room that will house the reactors, as well as multiple large volume reaction bags. Reliability will also be a priority, as well as reasonable cost. Various air purification approaches have been used at different facilities, and an initial evaluation has been carried out in the process of developing budget estimates for this proposal. One possibility that shows potential is the use of evaporated O₂ and N₂, recombined to form synthetic air. This has the advantage of removing methane and CO₂ as well as other species. Although the operating costs of this approach will be higher than an air purification system, the initial costs may be lower, and the reliability will probably be significantly greater.

Another design issue will involve temperature control. A temperature control system will be constructed with the design goal of holding the chamber enclosure at a constant and controlled temperature between ~5° C or lower and ~50° C or higher, to within ± 0.5° C. An evaluation of available options is needed to indicate what is feasible within the budget for this proposal.

Lighting is also an important consideration. The chamber will be constructed indoors with artificial lights to allow for complete temperature and lighting control and adequate characterization of chamber conditions. Xenon arc lights probably will be employed because among the options which have been used for indoor chambers, they provide the most realistic spectrum (Carter et al, 1995b). Although blacklights are less expensive and give an adequate spectrum in the UV, they would be unsatisfactory for a temperature-controlled chamber because their output is affected by temperature. However, blacklights may be employed for lighting the reaction bags for cleaning and flushing, should that approach be employed for chamber cleaning and conditioning.

It has not been decided exactly where the chamber facility and associated analytical laboratory will be located within CE-CERT, since there is insufficient space in the room currently housing the CE-CERT Atmospheric Processes Laboratory (APL) for this purpose. A space has been identified in the high bay area near the APL which may be sufficient for this purpose. However, it may be less costly to place the facility housing the chamber outdoors, which would allow for more options in terms of space and configuration. An existing modular building could be used to house at least some of the equipment, though additional structures to house the chamber enclosure and its associated lights and temperature control system would have to be constructed. The current budget estimate is based on assuming the latter option, which is believed to be more cost effective, and whose cost is easier to estimate.

Analytical Instrumentation

An essential component of any environmental chamber facility is the instrumentation used to measure trace pollutant levels. Much of the needed instrumentation is the same as that needed to support experiments for ozone model evaluation at higher NO_x conditions, such as

ozone and CO monitors, gas chromatographs for monitoring hydrocarbons, etc. In addition, CE-CERT already has a tunable diode laser system for monitoring trace levels of NO₂ and HNO₃. However, significant additional instrumentation would be needed to support the objectives of this program, most of which are not presently available at current environmental chamber facilities in the United States. Since acquisition of analytical equipment will be limited by the budget for this program, an important subject of the initial planning workshop will be to determine the priorities of advanced equipment needed. However, the priorities for instrumentation acquisition are expected to be as follows.

Instrumentation for Gas-Phase Analyses:

- High sensitivity NO - NO_x analyzers. This will be the first priority for instrumentation acquisition because it will be needed in the experiments to evaluate minimizing chamber effects and for evaluating the air purification system. Our laboratory has analyzers which may be satisfactory for this purpose, though the need for additional or more sensitive analyzers will have to be evaluated.
- High sensitivity total carbon, NMHC, and CO analyzers. These will also be priorities for evaluating the air purification system. Our laboratories have such analyzers, but they are not sufficiently sensitive. Note that if methane and CO₂ can be removed from the background air, a relatively simple total carbon analyzer can be used to measure NMHC with reliability and without need for calibration, by converting everything to methane and detecting the methane by flame ionization detection.
- FID Gas Chromatographs for Monitoring Organic Species. GC/FID provides the most sensitive, accurate, and precise analysis available for hydrocarbons and other low to moderate volatility VOCs that can be analyzed by this method. Our laboratory already has several such instruments, where loop sampling is used for more volatile or less “sticky” compounds, and Tenax cartridge sampling is used for others. The present systems at our facility will probably be sufficient for the initial evaluations, but additional GC/FID systems will be needed once the facility becomes operational. An automated sampling and concentration system will be acquired to maximize sensitivity, productivity and data precision.
- Tunable Diode Laser Systems (TDLAS) can be used for analysis of NO₂, H₂O₂, HNO₃, formaldehyde, and other difficult to monitor trace species. Monitoring “true” NO₂ is particularly important, and because of interferences commercial NO - NO_x analyzers are not suitable for this purpose. Our laboratory presently has a TDLAS system that has been used successfully to monitor NO₂, though it uses somewhat older technology and lacks the reliability for routine use. Although the present system will probably be satisfactory for evaluation of chamber effects, additional systems for monitoring other species (whose priorities will be determined subsequently), or a replacement to the existing system, will probably need to be acquired later in the program.
- A Differential Optical Absorption Spectrometer (DOAS) provides a means to monitor nitrous acid, NO₃ radicals, formaldehyde, glyoxal, certain aromatic compounds, and other species with highly structured UV absorption spectra. It provides the most sensitive available analysis for nitrous acid, which is believed to be a key species affecting

chamber radical sources and may be important in initiating radical formation when lights are turned on in multi-day simulations. It also provides the only known means to monitor NO_3 radicals, a key nighttime species, under atmospheric conditions. Because of its ability to monitor nitrous acid, a DOAS instrument will be useful for chamber characterization, and will probably be a priority for early acquisition in this program.

- A Gas Chromatograph / Mass Spectrometer (GC/MS) will be a priority once we begin experiments with test compounds because it provides a means to identify as well as quantify organic compounds which can be monitored by gas chromatography. Its primary use will be organic product identification. It is expected that a mass selective detector (MSD) will be employed, though the final decision concerning the instrumentation options will be determined later in the program.
- A HPLC System will also be a priority once we begin experiments with test compounds because it provides a means to identify and quantify certain aldehydes and other compounds that are not suitable for GC analysis. It will also be needed for analysis of constituents of organic aerosols in experiments where these are collected.
- ECD Gas Chromatographs for Monitoring PANs, Organic Nitrates, and Other Species. GC/ECD provides a means to routinely monitor PAN analogues and monitors other nitrogenous or halogenated compounds with high sensitivity. Although our laboratory has a GC/ECD system, its performance is not satisfactory for quantitative work. Options for an improved system will be investigated.
- A Fourier Transform Infrared (FT-IR) system provides a means for monitoring trace species that cannot be monitored in other ways. It is a lower priority for acquisition for this program because it lacks sufficient sensitivity to be useful for studies carried out using ambient or lower pollutant levels. For that reason, acquisition of a FT-IR system is not in the budget for this program. However, it may turn out to be desirable for special studies, verifications, or calibrations. Therefore, the possibility that the priority for acquisition of this system for this program cannot be ruled out at this time.

Aerosol Instrumentation:

- An Ion Chromatograph will be used to analyze particulate matter for anions following extraction with an aqueous solvent.
- An Organic Carbon Analyzer will be used to determine the organic content of particulate matter collected from the chamber using high purity quartz filters.
- A TSI model 3320 Aerodynamic Particle Sizer will be used to determine the particle size-number distribution for particles greater than 0.3 μm aerodynamic diameter.
- TSI 3080L Electrostatic Classifier w 3080 Controller, 3077 Neutralizer, 3081 LongDMA, TSI 390087 SMPS Interface and Software, TSI 3010S Condensation Particle Counter with fast scan EPROM. This combination of instruments will provide particle size number distribution from 0.003 to 0.5 μm aerodynamic diameter.

- TSI 3076 Constant Output Atomizer, TSI 3062 Diffusion Dryer, TSI 3077 Aerosol Neutralizer. This combination of equipment will be used to add a synthetic seed aerosol to allow SOA to condense on existing aerosol rather than self-nucleate.

It is important to recognize that organic photooxidation products that are expected to be formed under low-NO_x conditions will be different than those formed under higher-NO_x conditions, and among these low-NO_x products there will be unstable and difficult to monitor species such as hydroperoxides. One high-priority focus of the analytical development for this program will be to develop and evaluate methods suitable for monitoring hydroperoxides and other low-NO_x organic product species. Where necessary, the participation of synthetic organic chemists will be utilized to prepare authentic samples for analytical development and calibration.

Once the equipment needs are identified, the necessary equipment will be ordered and the appropriate procedures will be evaluated for utilizing and calibrating them. They can be evaluated utilizing the existing chambers available at CE-CERT, and intercompared with data from other relevant instrumentation where applicable. A quality assurance plan for measurement data will also be developed and evaluated during this period. This analytical development can be done on a time frame parallel to the design, construction, and characterization of the new environmental chambers.

Chamber Characterization and Evaluation

Once the chamber(s) are constructed, appropriate characterization experiments will be carried out to evaluate their performance and characterize them for use for model evaluation. The types of characterization experiments employed for this purpose are discussed elsewhere (e.g., see Carter and Lurmann, 1990, 1991; Carter et al, 1995a), and will include, but not necessarily be limited to, the following:

- Light Intensity is measured using actinometry experiments and by other methods. The NO₂ photolysis rate can be measured at various positions in the chamber enclosure using the quartz tube method developed by Zafonte et al (1977), modified as discussed by Carter et al (1995a). The net NO₂ photolysis rate within the reaction bag can also be measured using the steady state method, based on the photostationary state between NO, NO₂, and O₃ in the absence of other reactive compounds (Carter et al, 1995a,b). An alternative method that has proven to be more reliable for measuring overall photolysis rates in the chamber is to measure the Cl₂ photolysis rate by measuring the rate of consumption of n-butane in the presence of Cl₂. Relative light intensities on various surfaces within the enclosure can be measured using our LiCor Li-1800 spectroradiometer, which is also used to measure the spectrum of the light source, and radiometers sensitive to various spectral regions can also be employed. These or other appropriate methods may be employed for this purpose.
- Temperature Characterization experiments will be conducted to evaluate the performance of the temperature control system at various temperatures within its range of control. This

will include experiments with and without the lights, and measurements taken at various points within the chamber enclosure.

- Pure Air Experiments will be used to measure background effects such as NO_x offgasing and the presence of other reactive species in the matrix air or offgased from the walls. Ozone formation in such experiments is highly sensitive to NO_x offgasing (or NO_x in the matrix air), but is also sensitive to background VOCs (or CO) which can enhance ozone formation by converting NO to NO_2 . Because O_3 formation in pure air runs is sensitive to several factors, pure air runs are best used in conjunction with other types of experiments, which have differing sensitivities to these factors. Monitoring for trace species can also indicate if such species are offgased from the walls during photolysis.
- Aldehyde – air or VOC or CO – air experiments can also be used to measure NO_x offgasing and are useful in conjunction with pure air runs because they are much more sensitive to other background effects. Formation of ozone or (in the case of aldehyde – air runs) PAN provides a sensitive measure of NO_x offgasing.
- NO_x - air experiments are sensitive to the presence of background (or offgased) VOCs, and thus provide another useful complement to pure air runs. The rate of NO consumption provides a measure of the rate of NO to NO_2 conversion caused by reactions of background VOCs. They are also sensitive to chamber radical sources, and have been used, with reactive organic tracers present to monitor OH radical levels from their rates of consumption, to measure the chamber radical source (Carter et al, 1982). However, subsequent analysis indicates that this method tends to give overestimates of the chamber radical source in chambers where the radical source is low (Carter et al, 1995b), which is expected to be the case for the chambers developed for this program. NO_x air experiments are best used in conjunction with other experiments used to measure the radical source, so the rate of NO consumption in the NO_x -air experiment can provide a more unambiguous indication of the levels of background VOCs.
- Alkane (usually n-Butane) - NO_x or CO - NO_x have been found to provide the most sensitive and reliable method to measure the chamber radical source. The rates of NO to NO_2 conversion in these experiments are highly sensitive to the radical source, and the other aspects of the mechanisms that affect these observations are well characterized. Such experiments can also be used to indicate whether the injected NO_x is contaminated by nitrous acid, which can occur if improper NO_x injection procedures are employed. If HONO is present initially, it will be indicated by relatively high NO to NO_2 conversion rates during the initial periods of the experiments.
- Dark Decay Experiments are used to measure wall losses of species, such as ozone and nitric acid, which tend to be destroyed or absorbed on surfaces. It will also be used to evaluate whether compounds which are not expected to be lost on surfaces, such as hydrocarbons and (at least under dry conditions) formaldehyde and other oxygenates indeed remain in the gas phase in this chamber. Dark decay experiments with low levels of NO_x will also be conducted to assess whether these species also go to the surfaces.
- Smog Simulation Control Experiments, such as propene - NO_x or surrogate - NO_x experiments, will be carried out to assess reproducibility, consistency with results in other

chambers, equivalency of results in different reactors, and consistency with model predictions for well characterized chemical systems. Such experiments are also useful for evaluating analytical methods because the amounts of various species formed are known or can be simulated using well evaluated mechanisms. A new set of standard control experiments will be developed to assess reproducibility and consistency of results of experiments at low reactant concentrations. Results of experiments using known or previously studied systems will be compared with previous data and with model simulations. Any discrepancies or unexpected results will be fully investigated prior to proceeding with the remainder of the experimental program.

The above experiments are necessary for characterizing the chamber for evaluating gas-phase mechanisms. However, since this chamber will also be used for assessing aerosol formation and evaluating models in this regard, additional experiments are needed to characterize the chamber for this purpose. The most important factor is the aerosol lifetime. This will be characterized by adding seed aerosol and measuring its number concentration as a function of time. This will be done in both the light and dark.

The characterization experiments will be carried out at varying temperatures and humidities, representing the range of conditions expected to be used for model evaluation or reactivity assessment experiments. The number of such experiments will depend on the sensitivities found for the various chamber effects. In addition, since the facility will be used for multi-day simulation experiments, appropriate multi-day characterization runs will also be carried out. It is expected that there will be some extreme conditions (e.g., extremes of temperature, near 100% humidity, or very long irradiation periods) where the characterization data will indicate unacceptably large or irreproducible chamber effects, or unexpected results which cannot be modeled. Therefore, in addition to characterizing chamber conditions, such experiments will also provide information on the range of conditions for which useful experimental data can be obtained.

Model Evaluation Experiments

Once the performance of the facility and the reactors are adequately characterized, and any discrepancies or unexpected results in control experiments have been accounted for, we will begin using it for model evaluation experiments. Because of the special capabilities of this facility, the focus will be on model evaluation under low-NO_x conditions, and evaluation of model predictions of temperature effects. However, the model evaluation experiments will not be limited to these areas, and will be determined largely by scientific and regulatory needs. The objective will be to complement and extend the existing mechanism evaluation data base to provide the data of greatest scientific utility for evaluating models for regulatory applications, taking advantage of the special capabilities of the facility.

The plan for specific experiments will be finalized after receiving input at the workshops and from the Advisory Committee, and after taking into account the results of the characterization experiments. It is expected that they would include, but not necessarily be limited to, the following types of runs:

- CO - NO_x – air and Methane - NO_x – air runs. Note that some of these will also be carried out for characterization purposes. Concentrations and temperatures will be varied.
- Single organic - NO_x – air runs. The organics studied will include representative alkenes (including isoprene and other biogenics), aromatic hydrocarbons, formaldehyde, acetaldehyde, and other representative compounds with sufficient internal radical sources that single compound - NO_x experiments provide useful data⁴. The compounds chosen will include representatives of the major types of compounds in anthropogenic and biogenic emissions. This will include compounds that are known or expected to be SOA precursors, as discussed in the following section. Concentrations, temperature and (for SOA-forming compounds) humidities will be varied.
- Ambient surrogate - NO_x experiments will be carried out using surrogate mixtures of varying complexity, both with and without representative biogenic compounds. Note that some of these will be used as base cases in incremental reactivity experiments, which are discussed separately below. For the purpose of aerosol assessment studies (see below), surrogates with varying aerosol forming potentials will be evaluated. Concentrations, temperature and (for SOA-forming surrogates) humidities will be varied.

Synergistic effects arising from interactions of radicals from different types of reacting VOCs are expected to be more important under lower NO_x conditions than under more polluted conditions where most of the organic radicals react with NO_x. Therefore, mixture experiments will be important for evaluating mechanisms under realistic conditions. If experiments with complex, atmospherically realistic mixtures give results which are not expected based on results of the single compound runs, experiments with varying simple mixtures may be appropriate to elucidate the synergistic effects which may be occurring.

The full array of available analytical instrumentation will be employed during these experiments. Note that data on “true” NO₂ and H₂O₂ will be priorities in all low-NO_x experiments. In addition to the injected organic(s), data will be obtained on as many organic products as can be detected using the available instrumentation. A priority will be to determine how product formation differs under conditions when NO_x has been consumed compared to products formed in the presence of NO_x.

Multi-day experiments will be conducted using representatives of various types of experiments, to obtain mechanism evaluation data over longer time periods, and also for evaluating mechanisms for nighttime chemistry. Since artificial lights will be employed, nighttime will be simulated by turning off the lights, and mornings will be simulated by turning them on again. (Differences between immediately turning on and off the lights and changing the light intensity gradually will be assessed.) NO₃ radicals and HONO, which are expected to be important species, will be monitored using DOAS.

⁴ NO_x-air irradiations of single alkanes and other species without internal radical sources are not useful for mechanism evaluation because of their sensitivity to the chamber radical source.

The results of the experiments will be compared with model predictions as soon as the data are processed and characterized for modeling. Experience has shown that this provides important feedback for quality control and for planning the most useful follow-up experiments. If results of a particular experimental system are as expected based on the current model, follow-up experiments are obviously of lower priority than if unexpected results are obtained. Therefore, modeling will be an integral part of the experimental program, as it has been with most other environmental chamber programs at CE-CERT.

Because of the number of compounds and types of mixtures which are relevant to ambient simulations, and the wide range of conditions which can be simulated using this chamber, it obviously will not be possible to obtain comprehensive data on all possible systems. Therefore, determining priorities for experimental systems that provide the most useful data for model evaluation will be important. Immediate modeling of the data obtained, combined with external input through the workshops and Advisory Committee as discussed above, will be essential for maximizing the utility of this facility.

Experimental Determination of Secondary Organic Aerosol Yields

Background

The approach that has been most successful to estimate the SOA forming capability of a ROG involves the direct measurement of secondary organic aerosol yields. The SOA yield Y is a measure of the mass of aerosol that is produced from the atmospheric oxidation of an ROG and is defined as

$$Y = \frac{\Delta M_o}{\Delta \text{ROG}}$$

where ΔM_o is the amount of aerosol produced for a given reacted amount of an ROG, ΔROG . In the study of secondary organic aerosol formation, typically a smog chamber is initially filled with a mixture of NO_x , inorganic seed particles, and an aerosol-producing hydrocarbon. The chamber is then exposed to sunlight, or other UV sources, that initiates photooxidation. As the hydrocarbon reacts it forms semi-volatile products that condense on the seed particles. If mass transport to the available particles cannot keep up with the rate of product formation or when a seed aerosol is not initially present, the semi-volatile products accumulate in the gas phase until supersaturation is reached, and nucleation occurs (Bowman et al., 1997). Studies show that the amount of aerosol produced for a given amount of reacted ROG is independent of whether a seed aerosol is present. Reactions are ordinarily run until the entire initial amount of ROG is consumed. Typically the volume of the initial seed aerosol is small compared to the organic aerosol volume generated.

Ozone-forming potential of organics is determined based on atmospheric reaction mechanisms. In principle, aerosol-forming potential could be calculated based on a similar atmospheric oxidation mechanism that includes all significant semi-volatile product species. The actual amount of aerosol that would be formed under a particular set of circumstances, unlike

ozone, depends on the amount of aerosol available to absorb the semi-volatile products. The relative aerosol-forming potential of a group of organics could, in principle, be determined based on their oxidation products and the thermodynamic properties of these products. This *ab initio* approach represents a goal that has not been attained because of incomplete knowledge of the semi-volatile oxidation products of the important aerosol-forming compounds. Thus, it has been necessary to rely on experimentally measured aerosol yields.

Over the past several years, SOA yields for over 30 aromatic and biogenic organics have been measured in the California Institute of Technology outdoor smog chamber (Odum et al., 1996, 1997a, 1997b; Hoffmann et al., 1997; Griffin et al., 1998). To fit the observed yields to the theory, the mix of semi-volatile oxidation products for each parent compound has been represented by two empirical products. It has been determined that observed yields cannot be fit by assuming only a single product and that three products is superfluous (Odum et al., 1996). Roughly speaking, one of the empirical semi-volatile products tends to represent a relatively lower vapor pressure compound and the other a relatively higher vapor pressure compound.

Odum et al. (1997a,b) showed, moreover, that aerosol yields for the photooxidation of a mixture of parent hydrocarbons could be predicted simply as the sum of the SOA yields for the individual parent compounds. This suggests that, at least for the case of a pure organic absorbing phase, oxidation products of different parent hydrocarbons are as soluble in a mixed organic product phase as in an organic phase consisting exclusively of their own oxidation products.

The experimentally determined SOA yields reported by Odum et al. (1997a,b) and Griffin et al. (1998) have been measured at relative humidity (RH) less than 5%. At this level of RH the seed aerosol, $(\text{NH}_4)_2\text{SO}_4$, is dry and the resulting organic aerosol is water-free. Experiments are presently under way at Caltech to measure SOA yields as a fraction of RH over realistic ambient RH ranges. Because organic products will likely be most soluble in their own liquids, SOA yields measured at essentially 0% RH can be expected to represent an upper limit to the aerosol partitioning that will result. While many SOA products are water soluble (Saxena and Hildemann, 1996), they are not expected to be more soluble in an aqueous mixture than in a pure organic phase.

Experimental Plan

The researchers at the California Institute of Technology, who have conducted much of the previous research in determining the SOA-forming ability of VOCs, will work with CE-CERT in designing a chamber appropriate for state-of-the-art aerosol research, specifying the instrumentation needed, and defining a research plan. It is expected that the low surface-to-volume ratio and lack of wind buffeting will provide longer particle lifetimes than has been possible previously, and temperature, lighting, and humidity control will allow experiments to be carried out under more controlled conditions than possible using outdoor chambers such as that at Caltech. This will be evaluated using appropriate characterization experiments, as discussed above.

The initial experiments will be designed to duplicate experimental systems that have been well studied using the Caltech chamber, to see if comparable results can be obtained in the new chamber. This will include determination of SOA yields for selected aromatics and biogenics, and modeling the results using the approach discussed by Odum et al. (1997a,b) to see whether similar parameters are obtained. If differing results are obtained, the sources of the discrepancies will be investigated in consultation with the Caltech researchers. Note that this may well include carrying out at Caltech as well as using the CE-CERT chamber, though significant experimental work at Caltech may require additional funding or modifying the budget proposed for this program. Assuring that consistent results can be obtained at the different chamber facilities, and that any differences observed can be understood and taken into account, will be an important priority, since it reflects on the general utility of chamber data for this type of research.

Assuming that the aerosol data obtained from this facility are consistent with those from Caltech or that differences are understood, the new experiment will then be used to conduct experiments for which this facility is best suited. This will include extending the range of conditions under which SOA are determined for the representative aromatics, biogenics and mixtures which were previously studied, as well as studying additional compounds which may be of interest in regulatory applications (see below). These would include experiments with varying reactant concentrations and variable temperature and humidities. Product analysis (both gaseous and particulate phases) will also be a component of this research, to provide information useful for developing and evaluating mechanistic models for SOA formation. The overall goal is to provide information needed to evaluate models for aerosol formation under controlled and varied conditions, and to characterize the SOA forming ability of individual VOCs of interest.

It is important to recognize that in most cases the full complement of aerosol measurements will be carried out in conjunction with the full complement of gas-phase measurements, to provide data for evaluating both gas-phase mechanisms and aerosol formation model evaluations and measurements. In many cases, the SOA yield determinations can be made while conducting appropriate types of mechanism evaluation experiments discussed in the previous section, or while conducting reactivity experiments discussed below. Likewise, gas-phase measurements made during experiments carried out as part of aerosol-related studies can also be used for gas-phase model evaluation. This is advantageous not only because it makes maximum use of the facility, but also because gas-phase and aerosol dynamic processes are interdependent, and ultimately will need to be incorporated in a unified model.

VOC Reactivity Assessment

Since organic compounds differ significantly in their effects on ozone formation, VOC regulations based on considerations of relative reactivity are receiving increased attention because of their potential as a more cost-effective alternative to mass-based controls. However, existing reactivity scales have been developed for high-NO_x conditions, and some have questioned whether they are relevant, or even directionally correct, in very low-NO_x environments. An additional issue is the question whether replacing emissions of rapidly reacting VOCs with more slower reacting VOCs in order to reduce ozone in urban areas may degrade air

quality in downwind areas because of the greater persistence of the slowly reacting compounds. These issues can be addressed by model simulations, but as discussed above existing environmental chamber data have not been adequate to evaluate the accuracy of model predictions under such conditions.

It might be argued that since VOCs are believed to have relatively little effect on ozone formation under low NO_x conditions, assessing VOC reactivities under such conditions is not a priority. However, since the proposed facility will provide data concerning a wide range of VOC impacts, the term “reactivity” can be considered in a context which is broader than just ozone impacts. Furthermore, in view of the fact that some are proposing to de-emphasize VOC regulations in low- NO_x areas because they are believed to have low or possible negative effects on ozone, it is even more important that their other air quality impacts be accurately assessed. That is what is meant by “reactivity evaluations under low- NO_x conditions.” Obviously, the model predictions that VOCs indeed have low or negative impacts on O_3 under those conditions still need to be verified. But this is not the only, or even the most important, reason for doing this research.

Reactivity evaluation experiments consist of determining the effects of adding (or removing) the subject VOCs from mixtures representing the ambient environment of interest. In this case, the experiments will be designed to simulate various low- NO_x rural or regional-scale episodes or urban areas of the future, which may be approaching or attaining the air quality standards. This may include multi-day simulations to assess long-term effects of VOCs on downwind air quality. Since it is expected (though not yet actually experimentally demonstrated) that ozone levels in these scenarios will be relatively insensitive to VOCs, an important focus will be determining the effects of the VOCs on other measures of air quality in addition to ozone. This would include determining effects on secondary particle formation, where applicable.

Experiments will also be carried out to assess the effects of temperature on the reactivities of selected VOCs. These would include higher NO_x as well as low NO_x experiments, since temperature dependence data on VOC reactivities is highly limited. The range of temperatures employed will represent the range of ambient conditions relevant to air pollution in the United States, to within the capability of the facility. Note that this may include temperatures that may be too low for significant ozone formation, but where VOCs may have other impacts that need to be assessed.

The compounds studied will include representatives of the major classes of emitted VOCs, which include alkanes, alkenes (both anthropogenic and biogenic), aromatic hydrocarbons, and simple oxygenates. Representatives of major classes of solvent species used in industrial and consumer product applications also will be studied. One important example would be studies of representative compounds present in architectural coatings, to assess the impacts of emissions of such VOCs on low- NO_x or regional environments. The specific compounds to be studied, and the number of scenarios or conditions employed, will depend on how well the results obtained in the initial compounds correspond to model predictions, as well as regulatory needs concerning data on individual types of VOCs, as discussed in the following section.

The second type of study that will be carried out will simulate environments that might result if large substitutions of current emissions with low reactivity compounds are carried out. The specific approach employed, and substitution scenarios examined, will be determined after consultation with the RRWG and others. However, it is expected that these would be multi-day experiments whose results will be compared with simulations using mixtures representing current or potential future mixtures of emitted VOCs. Since different results are expected for differing types of low reactivity compounds that might be used, experiments will be carried out using several representative types of such compounds.

Useful compounds to study, which are expected to yield significantly different results, might include ethane, acetone, and a long chain n-alkane such as n-hexadecane. Ethane and acetone have low reactivity because they react relatively slowly. Although they have similar incremental reactivities under urban conditions, they differ in that acetone is a strong radical source while ethane is nearly neutral in this regard. Long chain alkanes in fact react relatively rapidly, but have low ozone reactivities under urban conditions because of their strong radical sinks. Major increases in levels of such compounds may result in greater persistent of other reactive pollutants.

Studies of Impacts of Representative VOC Sources Relevant to Regulatory Issues

It is expected that during the course of this program studies of environmental impacts of particular compounds or source categories may be of particular relevance to current regulatory needs. Examples might include impacts of emissions of architectural coatings or of changes in motor vehicle fuel reformulation. In the case of architectural coatings, it is important to determine whether the environmental benefit strict regulation of these VOCs will be worth the economic costs and potential loss in coatings quality that such regulations might entail. This is a particular concern when they are used in low-NO_x environments where ozone may not be sensitive to their emissions. Results will help to determine whether their regulation needs to be a priority in the future if significant NO_x controls are implemented. Experiments simulating various scenarios involving coatings emissions can be conducted to elucidate this. This could include determining the effects of adding the coatings VOCs to simulated rural mixtures that might be high in biogenic compounds, as well as simulations of mixtures more representative of urban scenarios. CE-CERT is proposing to develop a coatings research center under separate funding, so the appropriate expertise should be available for designing such a study to yield maximum utility and relevance.

With regard to studies of impacts of vehicle emissions, it should be noted that CE-CERT already has an advanced research dynamometer facility and vehicle emission expertise that can be made available to this project. The low NO_x chamber will be particularly useful for studies of impacts of very low emissions (i.e. ULEV) vehicles whose emissions are too low for useful study using currently available chamber technology. Although the emissions from these vehicles are low, they are not completely negligible, and will become increasingly important in the future as other sources are controlled and higher emission older vehicles are removed from service.

Experimental Characterization of NO_y and Radical Budgets

Uncertainty in the budget of NO_y will particularly limit our confidence in model simulations of the effectiveness of NO_x reduction strategies. On the urban scale, NO_x emissions can be terminated in the form of relatively inert nitrogen compounds NO_z = HNO₃ + RNO₃ + PAN. At the regional scale PAN can become a net source of NO_x so that NO_x is terminated as NO_z = HNO₃ + RNO₃. The O₃ production efficiency per NO_z (P(O₃)/P(NO_z)) is thought to vary considerably as a function of both the ratio of VOC/NO_x and the absolute levels of VOC and NO_x. The photochemical mechanisms most commonly used in AQMs, particularly the CB4, were designed for use in urban scenarios with high NO_x levels. For those conditions, predictions of O₃ were relatively insensitive to uncertainty in the NO_y budget. Even in the case of mechanisms such as RADM2 that were designed to handle rural conditions with low NO_x, there are large uncertainties in the production of NO_z for low NO_x conditions. In a recent mechanism inter-comparison, Luecken et al. (1999) found large differences in the speciation of NO_z and in O₃ per NO_z production efficiencies, particularly for low NO_x conditions. Uncertainty in the NO_y budget will become increasingly important with the increased emphasis on fine particulate matter and regional O₃ levels. Thus, it is important to account for the fate of NO_x and O₃ production efficiencies per NO_x at low NO_x conditions, and low NO_x chamber experiments will be needed to evaluate the mechanisms for those conditions.

Uncertainty in the budget of HO_x will limit our confidence in model simulations of the effectiveness of VOC reduction strategies. Recent field studies (Carpenter et al., 1998; Wennberg et al, 1998; Stevens et al, 1997; Crosley, 1997; Cantrell et al, 1997; Cantrell et al, 1996; Plummer et al, 1996) have found large discrepancies between model simulated and observed HO_x levels and ratios. Thus, there remains considerable uncertainty in the budgets of HO_x in current photochemical mechanisms. We note that the magnitude of chamber wall effects are inferred from the presence of apparent artifacts in chamber experiments, *i.e.*, the experimental results differed from expectations based on well accepted aspects of the photochemistry. The discrepancies between measured and modeled ratios of HO₂/OH and RO₂/HO₂ in these field studies raises an important concern that real ambient processes are being subsumed in chamber wall mechanisms. Thus, it is important to characterize radical budgets in chamber experiments as fully as possible.

To characterize the radical budget, it is necessary to experimentally evaluate the initiation, propagation and termination of radical species. Rates of radical initiation can be estimated by measuring actinic flux and the concentrations of radical precursors (*i.e.*, those species that photolyze or decompose to produce radicals). Radical propagation efficiency can be estimated by measuring concentrations of species that control the rates of radical propagation (Tonnesen and Dennis, 1998), and radical termination can be calculated by using kinetics data and measuring the concentrations of species involved in termination reaction. Radical termination can also be estimated by measuring the accumulation of radical termination products.

Several techniques exist to measure the concentrations of HO_x. Tanner et al (1997) have measured OH using ion-assisted (IA) mass spectrometry, with a lower limit of 10⁻⁵ molec/cm³ for a 5-minute integration. Mather et al (1997) have measured OH and HO₂ using low pressure laser

induced fluorescence (LIF), with an OH sensitivity = 10^{-6} , and 1- or 5-minute integration time. Total $\text{RO}_2 + \text{HO}_2$ has been measured by the chemical amplifier technique (Cantrell et al, 1997).

We note that additional analytical methods are needed to characterize NO_y and HO_x budgets, but special chamber experiments are not required. Rather, the budget analyses should be performed on all chamber experiments if measurements are available. Comparison of HO_x budgets in the aerosol experiments (described above) with gas-phase experiments will be useful to investigate theories that aerosols can play an important role in peroxy radical termination (Cantrell et al, 1996; Jacob, 1998).

Experimental Evaluation of Indicators of Ozone Sensitivity to Precursor Emissions

Modeling studies have suggested that nearly unique values of particular indicator ratios are robustly associated with $[\text{O}_3]$ and $\text{P}(\text{O}_x)$ ridgeline conditions (or conditions of equal sensitivity to VOC and NO_x) for a wide range of precursor levels. For example, Sillman (1995) found that values of certain indicators were constant as a function of O_3 and precursor levels, while Tonnesen and Dennis (1998a,b) found small variations in the indicator value depending on the O_3 and precursor concentrations. In a modeling study of the San Joaquin Valley, however, Lu and Chang (1998) found that the values of the indicators differed from previous modeling studies, and they suggested that the indicator values may vary as a function of environmental conditions.

Experiments in an environmental chamber will be useful for assessing the variability of the indicator values as a function of environmental conditions. Furthermore, Tonnesen and Dennis (1998a) found that the utility of the indicators derived from chemical processes associated with radical propagation efficiency. Thus, it is likely that chamber artifacts that affect radical initiation will not interfere with the experimental investigation of indicator ratios, and values measured in chamber can be compared with values determined in modeling studies. On the other hand, if chamber artifacts significantly affect radical propagation and termination, indicator values measured in the chamber might not be directly comparable with ambient values.

The approach to experimentally validate the usefulness of indicators requires a series of simulations with fixed VOC emissions (and all other inputs fixed) while NO_x emissions are incrementally changed. The ridgeline conditions for $\text{P}(\text{O}_x)$ or $[\text{O}_3]$ would be identified as the NO_x emissions level which maximized $\text{P}(\text{O}_x)$ or $[\text{O}_3]$. The full set of indicators could be evaluated in each series of simulations, subject only to the requirement that measurements of each of the indicator species must be collected. Although $\text{P}(\text{O}_x)$ cannot be measured directly, it can be determined by model simulations of the experimental conditions, or it can be calculated directly using measurements of NO , HO_2 and RO_2 if these are available. The robustness and consistency of the indicator method would then be evaluated by determining the indicator values in additional series of experiments with different VOC, light, temperature and humidity levels. Finally, the aerosols experiments described above can also be utilized to determine the effects of aerosols on indicator values.

Evaluation of Ambient Monitoring Equipment

As discussed above, the proposed large chamber facility will provide a unique test bed for evaluating new monitoring equipment using well characterized chemical systems which nevertheless are representative of field conditions. The large volume of the chamber will permit evaluation of equipment with larger sampling requirements than are practical for use with most current indoor chambers. Most of this work would be carried out in collaboration with the developers or intended users of this equipment, who in most cases would be expected to provide funding for this effort. However, some of these tests can be carried out in conjunction with experiments already being carried out for other purposes.

No specific projects of this type are described in this proposal because it is unknown what will be the priorities for evaluation of monitoring equipment at the time this chamber is operational. Once the facility is operational and its performance is evaluated, the availability of this facility for evaluations of this type will be communicated to relevant researchers through various means, including NARSTO meetings and workshops. For example, the facility could be utilized for this purpose as part of upcoming NARSTO field projects, with the research coordinated through NARSTO. This will be determined once the project is under way.

Other Studies

The projects discussed above are obviously not the only ways in which this facility can be utilized, and it is expected that other studies will be carried out depending on regulatory needs, interests and capabilities of collaborating researchers, and input received from the advisory committee and the workshops. It is expected that the priorities of the program will evolve as needs evolve, and in response to results of experiments carried out not only at this facility but at other laboratories.

SCHEDULE AND DELIVERABLES

This project will be carried out over a four-year period. The first six months will be devoted to developing the work plan, holding the initial workshop and forming the advisory committee, evaluating the experience and data obtained at other chamber facilities, and evaluating chamber design options. Acquiring the analytical equipment and developing analytical methods and quality assurance plans will also begin during this period, and continue throughout the first year of the program. Chamber construction should begin during the second six months of the program, and characterization should be completed during the first half of the second year. The scheduling and priorities for the subsequent experiments will be determined in consultation with the advisory committee and the funding agencies, and will depend on availability with collaborators, where applicable.

Annual reports will be submitted to the funding agencies and the advisory committee concerning the work accomplished on the project during the previous year. Relevant scientific

results will be submitted for publication in peer-reviewed journals, and reports on policy-relevant results will be produced as appropriate. A quality assurance plan for measurement data will be included as an appendix to the first annual report, and subsequent reports may include revised plans if major revisions or additions are necessary. The data obtained in the chamber will be made available to interested researchers at an FTP site on the Internet within one year after the experiments are carried out. The facility will not be used for confidential research and funding will not be accepted which involves use of the facility to obtain data whose publication or distribution will be restricted.

BUDGET

The estimated cost for this program is approximately \$3 million, with approximately half of that being for design and construction of the chamber and acquisition of necessary analytical equipment, and the other half for researchers and staff salaries and operating the chamber for four years. The cost for the initial workshop is included in the estimated design cost while the cost of the periodic advisory committee meetings is covered in the operating budget. An itemized budget is attached.

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