RESEARCH PLAN FOR “NEXT GENERATION ENVIRONMENTAL CHAMBER FACILITY FOR CHEMICAL MECHANISM AND VOC REACTIVITY EVALUATION

William P. L. Carter

College of Engineering Center for Environmental Research and Technology,
University of California, Riverside, CA 92521

A. Introduction

A critical component for predictions of formation of ozone and other secondary pollutant formation in the atmosphere is the chemical mechanism, i.e., the portion of the airshed models 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. 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.

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 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. 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.

To address the need for improved an improved environmental chamber facility to evaluate mechanism for O_3 and PM formation, the College of Engineering, Center for Environmental Research and Technology (CE-CERT) recently received funding to develop a “Next Generation” environmental chamber facility for chemical mechanism evaluation and VOC reactivity assessment. The objectives of this project are to develop the 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. The project involves 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 NOx 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 $P(O_x)$ sensitivity to precursors for conditions typical of ambient atmospheres.
- Evaluating impacts of various types of VOC sources, such as architectural coatings, on formation of ozone, secondary PM, and other pollutants in various environments.
- Utilizing the facility to test equipment to be used for monitoring trace pollutants in ambient air under controlled conditions where the actual pollutant concentrations, and the history and source of the air mass being monitored, are known.

This project involves a collaboration with Dr. John Seinfeld at the California Institute of Technology (Caltech), whose group is established as representing the state-of-the-art in using environmental chambers to assess PM formation. As such, they complement and enhance the group at CE-CERT, which we believe represents the state-of-the-art for using environmental chambers for evaluating gas-phase mechanisms and assessing effects of VOCs on ozone formation.

The specific approach that will be employed in this project will be determined as part of the development of the research plan, which is still underway. The overall approach that was presented in the proposal for this project is discussed below. The discussion is somewhat general because the specifics of the research plan are still being developed. This plan will evolve as the project is conducted and as the capabilities of the facility are determined.

B. Facility Development and Evaluation

1. 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, N_2O_5 hydrolysis, excess NO to NO_2 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 SAPRC 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 F_2. 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.

2. 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 CO_2 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 O_2 and N_2, recombined to form synthetic air. This has the advantage of removing methane and CO_2 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^o C or lower and ~50^o C or higher, to within ± 0.5^o 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.

3. 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 NO_2 and HNO_3. 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 CO_2 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 NO_2, H_2O_2, HNO_3, formaldehyde, and other difficult to monitor trace species. Monitoring “true” NO_2 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 NO_2, 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, NO_3 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 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.

4. 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 NO_2 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 NO_2 photolysis rate within the reaction bag can also be measured using the steady state method, based on the photostationary state between NO, NO_2, and O_3 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 Cl_2 photolysis rate by measuring the rate of consumption of n-butane in the presence of Cl_2. Relative light intensities on various surfaces within the enclosure can be measured using our LiCor Li-1800 spectraradiometer, 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.

C. 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 data[1]. 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 or 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” NO_2 and H_2O_2 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.) NO_3 radicals and HONO, which are expected to be important species, will be monitored using DOAS.

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.

---

[1] 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.

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.

D. Experimental Determination of Secondary Organic Aerosol Yields

The researchers at the California Institute of Technology, who have conducted much of the previous research in determining the secondary organic aerosol (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.

E. 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.

F. 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.

G. 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 $NO_z = HNO_3 + RNO_3 +$ PAN. At the regional scale PAN can become a net source of NO_x so that NO_x is terminated as $NO_z = HNO_3 + RNO_3$. The O_3 production efficiency per NO_z ($P(O_x)/P(NO_z)$) 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 O_3 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 O_3 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 O_3 levels. Thus, it is important to account for the fate of NO_x and O_3 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 HO_2/OH and RO_2/HO_2 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, 1998a,b), 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/cm^3 for a 5-minute integration. Mather et al (1997) have measured OH and HO_2 using low pressure laser induced fluorescence (LIF), with an OH sensitivity = 10^{-6}, and 1- or 5-minute integration time. Total RO_2+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).

H. 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 [O_3] and P(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 P(O_x) or [O_3] would be identified as the NO_x emissions level which maximized P(O_x) or [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 P(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.

I. Evaluation of Ambient Monitoring Equipment

As discussed above, the proposed large chamber facility will provide a unique test bed for evaluating mew 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.

J. 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.

K. Schedule

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.

L. Budget

The amount budgeted 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

M. References

Cantrell, C.A.; Shetter, R.E.; Gilpin, T.M.; Calvert, J.G.; and Eisele, F.L. (1996) Peroxy radical concentrations measured and calculated from trace gas measurements in the Mauna Loa Observatory Photochemistry Experiment 2. *J. Geophys. Res.* **101:**14,653-14,664.

Cantrell, C.A.; Shetter, R.E.; Calvert, J.G.; Eisele, F.L.; Williams, E.; Baumann, K.; Brune, W.H.; Stevens, P.S.; and Mather, J.H. (1997) Peroxy radicals from photostationary state deviations and steady state calculations during the Tropospheric OH Photochemistry Experiment at Idaho Hill, Colorado. *J. Geophys. Res*. **102:**6369-6378.

Carpenter, L.J.; Clemitshaw, K.C.; Burgess, R.A.; Penkett, S.A.; Cape, J.N.; McFadyen, G.G. (1998) Investigation and evaluation of the NOx/O_3 photochemical steady state, *Atmos. Environ.* **32:**3353-3365.

Carter, W.P.L. (1994) Development of ozone reactivity scales for volatile organic compounds*. J. Air & Waste Manage. Assoc.* **44**:881-899.

Carter, W.P.L.; Atkinson, R.; Winer, A.M.; and Pitts, J.N., Jr. (1982) Experimental investigation of chamber-dependent radical sources. *Int. J. Chem. Kinet.* **14:**1071.

Carter, W.P.L., and Lurmann, F.W. (1990) Evaluation of the RADM gas-phase chemical mechanism. Final Report, EPA-600/3-90-001.

Carter, W.P.L., and Lurmann, F.W. (1991) Evaluation of a detailed gas-phase atmospheric reaction mechanism using environmental chamber data. *Atmos. Environ.* **25A:**2771-2806.

Carter, W.P.L.; Luo, D.; Malkina, I.L.; and Fitz, D. (1995a) The University of California, Riverside, environmental chamber data base for evaluating oxidant mechanism. Indoor chamber experiments through 1993. Report submitted to the U.S. Environmental Protection Agency, EPA/AREAL, Research Triangle Park, NC, March 20.

Carter, W.P.L.; Luo, D.; Malkina, I.L.; and Pierce, J.A. (1995b) Environmental chamber studies of atmospheric reactivities of volatile organic compounds. Effects of varying chamber and light source. Final report to National Renewable Energy Laboratory, Contract XZ-2-12075, Coordinating Research Council, Inc., Project M-9, California Air Resources Board, Contract A032-0692, and South Coast Air Quality Management District, Contract C91323, March 26.

Crosley, D.R. (1997) Tropospheric OH photochemistry experiment: A summary and perspective, *J. Geophys. Res*. **102:**6495-6510, 1997.

Dodge, M.C. (1998) Chemical oxidant mechanisms for air quality modeling, Critical review paper for 1998 Ozone Assessment. *Atmos. Environ.,* submitted for publication.

Fitz, D.R.; Carter, W.P.L.; and Cocker, D. (1998) Evaluation of the PM and ozone producing potential of natural gas-powered vehicles. Draft final report to the California Institute for Energy Efficiency, Lawrence Berkeley Laboratory, Agreement 4910210, October.

Gery, M.W.; Whitten, G.Z.; and Killus, J.P. (1988) Development and testing of the CBM-IV for urban and regional modeling. EPA-600/ 3-88-012, January.

Jacob, D.J (1999): “NARSTO Critical Review Paper, Heterogeneous Chemistry and Tropospheric Ozone,” Atmospheric Environment, (in press). This manuscript can be downloaded from http://www.cgenv.com/Narsto/critrev.papers.html.

Jeffries, H.E.; Gery, M.W.; and Carter, W.P.L. (1992) Protocol for evaluating oxidant mechanisms for urban and regional models. Report for U.S. Environmental Protection Agency Cooperative Agreement No. 815779, Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC.

Lu, C-H, and Chang, J.S. (1998) On the indicator-based approach to asses ozone sensitivities and emissions features. *J. Geophys. Res.* **103:**3453-3462.

Luecken, D.J.; Tonnesen, G.S.; and Sickles, J.E., II (1999) Differences in NO_y speciation predicted by three photochemical mechanisms. *Atmos. Environment*, in press.

Odum, J.R.; Jungkamp, T.P.W.; Griffin, R.J.; Forstner, H.J.L.; Flagan, R.C.; and Seinfeld, J.H. (1997a) Aromatics, reformulated gasoline, and atmospheric organic aerosol formation. *Environ. Sci. Technol*., **31:**1890-1897.

Odum, J.R.; Jungkamp, T.P.W.; Griffin, R.J.; Flagan, R.C.; and Seinfeld, J.H. (1997b) The atmospheric aerosol-forming potential of whole gasoline vapor, *Science,* **276:** 96-99.

Mather, J.H, Stevens, P.S., and Brune, W.H (1997): “OH and HO2 mesaurements using laser-induced fluorescence,” J. Geophys. Res., 102, 6427-6436.

Plummer, D.A.; McConnell, J.C.; Shepson, P.B.; Hastie, D.R.; and Niki, H. (1996) Modeling of ozone formation at a rural site in southern Ontario, *Atmos. Environ.* **30**:2195-2217.

Sillman, S. (1995) The use of NO_y, H_2O_2, and HNO_3 as indicators for ozone-NOx-hydrocarbon sensitivity in urban locations, *J. Geophys. Res.* **100:**14175-14188.

Simonaitis, R., and Bailey, E.M. (1995) Smog chamber studies at low VOC and NO_x concentrations: Phase I. Report on Interagency Agreement DW64936024 to EPA/NREL, Research Triangle Park, NC.

Stevens, P.S.; Mather, J.H.; Brune, W.H.; Eisele, F.; Tanner, D.; Jefferson, A.; Cantrell, C.; Shetter, R.; Sewall, S.; Fried, A.; Henry, B.; Williams, E.; Bagman, K.; Goldan, P.; and Kuster, W. (1997) HO2/OH and RO2/HO2 ratios during the Tropospheric OH Photochemistry Experiment: Measurement and theory. *J. Geophys. Res.* **102:**6379-6391.

Tanner, D. J.; Eisele, F. L.; and Jefferson, A. (1997) Ion-assisted OH instrument, *J. Geophys Res.*, **102:**9295-9308.

Tonnesen, G.S., and Dennis, R.L. (1998a) Analysis of radical propagation efficiency to assess ozone sensitivity to hydrocarbons and NO_x. Part 1: Local indicators of odd oxygen production sensitivity. Submitted to *J. Geophys. Res.*

Tonnesen, G.S., and Dennis, R.L. (1998b) Analysis of radical propagation efficiency to assess ozone sensitivity to hydrocarbons and NO_x. Part 2: Long-lived species as indicators of ozone concentration sensitivity. Submitted to *J. Geophys. Res.*

Wennberg, P.O.; Hanisco, T.F.; Jaegle, L.; Jacob, D.J.; Hintsa, E.J.; et al (1998) Hydrogen radicals, nitrogen radicals, and the production of O_3 in the upper troposphere. *Science* **279**:49-53.

Zafonte, L., P. L. Rieger, and J. R. Holmes (1977): "Nitrogen Dioxide Photol-ysis in the Los Angeles Atmosphere," Environ. Sci. Technol. 11, 483-487.