

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

Draft Research Plan and First Progress Report to the
United States Environmental Protection Agency
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ABSTRACT

The objective this project is to develop and employ the next-generation environmental chamber facility needed for evaluating gas-phase and gas-to-particle atmospheric reaction mechanism under more realistic conditions and with lower pollutant concentrations than previously has been possible. Progress was made towards this objective in several areas during the first two years of this project. A successful international workshop was held in Riverside California concerning the atmospheric chemistry of ozone and particle formation and environmental chamber research, and useful input concerning this project was obtained from environmental chamber and other researchers from the United States and Europe. Although the construction of the new facility is behind schedule because of a number of unanticipated delays, the new facility, which is housed in a new laboratory building designed primarily for this purpose, is now mostly completed and is expected to become operational in early 2002. Near-term needs for analytical instrumentation were assessed, and equipment was purchased and evaluated. A quality assurance project plan for experiments to be carried out in the new facility is being developed and a draft should be submitted to the EPA before the new facility becomes operational.

A series of experiments were carried out using smaller reactors to evaluate NO_x offgasing effects in Teflon bag reactors, since this is expected to be the main factor limiting how low pollutant concentrations can be usefully employed in the new facility. These experiments were also used to evaluate analytical methods to be employed to monitor NO_x species and formaldehyde at low concentrations. The results of the NO_x offgasing tests indicated that minimum NO_x offgasing rates of ~0.5 ppb per 24-hour day can be obtained in these small reactors if steps are taken to avoid contamination. This suggests that that useful mechanism evaluation data can be obtained at NO_x levels as low as 2-5 ppb in these small reactors, and probably at lower levels in the larger reactors. No reaction wall material was found to be significantly better than the type of FEP Teflon® that is generally employed. The magnitude of the chamber radical source was measured in these Teflon reactors and was found to be dependent on the average NO₂ concentration, with the results being consistent with the radical source measured in previous Teflon bag reactors at higher NO_x levels. Several evaluation experiments were carried out at low NO_x levels using the small reactors, and some inconsistencies with model predictions were found that will need to be investigated.

A proposed research plan for work to be carried out in the facility was developed and is presented in this report. This includes experiments that might be carried out through mid 2005 using funds not only from this project but also from current and anticipated projects for the California ARB to assess atmospheric impacts of coatings VOCs. The number of experiments that appears to be needed is sufficiently large that it may be difficult to conduct all of them during the period remaining in this project, and external input and review is needed to prioritize the research as well as to critically review the proposed research plan. A proposal for utilizing the Reactivity Research Working Group and paid peer reviewers for providing external input to this project is presented.

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The statements and conclusions in this report are entirely those of the author. No official endorsement by the EPA or any other agency mentioned in this report should be inferred. Mention of commercial products, trade names, or individual corporations or vendors do not constitute endorsement or recommendation for use.

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INTRODUCTION

To meet National Ambient Air Quality Standards, the U.S. EPA and other regulatory agencies must implement regulations to control pollutant emissions. These regulations that achieve the greatest possible benefits at the lowest costs and disruption requires use of airshed models that can accurately predict the effects of changes of emissions on air quality. A critical component of these models is the portion of the model that represents the chemical reactions involved, i.e., the chemical mechanism. 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 reliable way to test the accuracy of the chemical mechanisms is to compare their predictions against results of well-characterized environmental chamber experiments that simulate the range of conditions in the atmosphere. If a model cannot accurately predict results of such experiments, it cannot be expected to reliably predict effects of proposed control strategies on ambient air quality.

As discussed by Dodge (2000), the current chamber data base has a number of limitations and data gaps that could affect the accuracy of the mechanisms currently in use. Uncertainties exist concerning characterization of chamber conditions that could cause compensating errors in the gas-phase mechanism (Carter and Lurmann, 1990, 1991; Jeffries et al, 1992). Most chamber experiments lack measurement data for important species, limiting the level of detail to which the mechanisms can be evaluated, and the types of air quality impact predictions that can be assessed. Furthermore, because of chamber effects and because of inadequate analytical equipment employed, 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 O₃ and PM formation, the College of Engineering, Center for Environmental Research and Technology (CE-CERT) has undertaken a program to develop a "Next Generation" environmental chamber facility for chemical mechanism evaluation and VOC reactivity assessment. California Institute of Technology (Caltech), who has established expertise in using environmental chambers to assess PM formation, is collaborating on this project. The objectives 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 at least 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.

The work carried out during the first two years of this project is discussed in this report. It consisted primarily of designing and constructing the new facility, conducting experiments to evaluate chamber effects, analytical instrumentation and other factors, and developing a research plan. A draft research plan for the remainder of this project is also presented, along with recommendations for a process for external oversight and review involving the Reactivity Research Working Group.

ENVIRONMENTAL CHAMBER WORKSHOP

The research plan described in the proposal called for holding an international 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. This workshop was held in Riverside, California on October 4-6, 1999. The invited attendees included 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 was seen as 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. For this reason, the workshop was combined with the US/German workshops on Ozone and Fine Particle Science, which are held alternately on an approximately biannual basis in the United States and Germany. Because of this Dr. Karl Becker of the Bergische Universität-GH Wuppertal in Germany and Dr. Basil Dimitriadis of the EPA, who have been the organizers of the US-German workshops, worked with the Principal Investigator for this project in organizing this workshop. Because of the relevance of the objectives to this project to the objectives of the Reactivity Research Working Group, a quarterly RRWG meeting was scheduled for Riverside immediately following the workshop. This resulted in good participation of representatives of industry groups who are interested in scientific issues related to VOC reactivity.

Workshop Presentations

The workshop had sessions on Gas Phase Chemistry and Modeling, Heterogeneous Chemistry and Modeling, Measurement Methods, Environmental Chamber Studies, VOC Reactivity Studies, New Chamber Projects, a panel discussion on research needs for environmental chamber studies, and summaries of poster presentations. An excellent response was obtained when papers were solicited, and it was found necessary to have a poster session so all the submitted papers of interest could be presented. The authors prepared full papers or extended abstracts for most of these presentations, and these are published in the workshop proceedings report (EPA, 2000) that was distributed to all attendees. A number of copies of the report have been sent to us at UCR for distribution, and are available upon request¹. Most of the abstracts and papers that were submitted are available at the conference proceedings web site at <http://cert.ucr.edu/~carter/epacham/meeting1.htm>

Panel Discussion and Comments on Project

The meeting ended with a panel discussion on research needs for environmental chamber studies. The discussion focused on the proposed research plan for this project, and the desirability of collaboration among the chamber researchers that were represented. The input provided during the discussion is summarized below, along with our responses.

Dr. Andreas Wahner of KFA Juelich in Germany noted that we need better sensitivity in analytical methods to characterize wall effects. We agree that this is a problem (see discussion of research on wall effects, below).

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Dr. Rafael Villasenor of IMP in Mexico noted the need to characterize light intensity and spectral distribution. Dr. Harvey Jeffries of the University of North Carolina also stated we need to measure light source spectrum. We agree that this is important, though this is not as difficult in indoor chambers than in outdoor chambers using ambient sunlight. Later, Dr. Karl Becker of the Bergische Universität in Wuppertal, Germany stated that a realistic light spectrum is a priority. Use of artificial lights may pose problems if the action spectra of species are unknown. Dr. David Golden of SRI International stated that quantum chemistry in theory can provide action spectra, but only if the species and reactions can be identified. We agree that this is important, and for that reason we have decided to proceed with the purchase of the argon arc lighting system for this project, despite the cost being much higher than initially budgeted (see discussion of chamber and laboratory design, below).

A number of people commented on the problem of wall effects and the need to study and model them better. Dr Hartmuth Hermann of the Institut für Troposphärenforschung in Germany said that we may need to develop separate wall mechanisms that are specific to various VOC systems. Dr. Jeffries stated that we need to recalibrate our mental models of walls, and wondered if there is a new conceptual framework that can stimulate our thinking. For example, do the walls change on a daily basis depending on the mix in the chamber? Dr. Paul Makar of Atmospheric Environment Service in Canada said we should get a surface chemist to work with us on this project. Dr David Golden of SRI agreed that there is a need to study heterogeneous and surface chemistry related to chambers, and said it could be decoupled from chamber studies, since we can design laboratory studies of wall effects. Dr. Jeffries noted that we can work on various tasks in parallel – we don't need to perfect the wall model before starting experiments.

We agree that work on chamber effects and relevant heterogeneous chemistry to be part of this project, and we hope to collaborate with Dr. Jeffries and others who have relevant experience or expertise. For example, Dr. Hermann has been working on developing mechanisms that may be useful in wall models, and we discussed the possibility of collaborating on this problem as part of this project. We subsequently had correspondence with Dr. Hermann in this regard, and further discussions are expected. Someone made the comment that it may be useful to enhance surface effects in order to study them better. This approach is being used in this project in that our initial studies are being carried out using relatively low volume reactors where surface effects should be more evident than in the large reactor planned for use in low concentration or aerosol formation experiments. Additional funding for relevant laboratory studies would also be extremely valuable.

Several people had comments about the objective of this project to study low NO_x or highly “clean” conditions. Dr. Jeffries stated that low NO_x is a rural problem but the secondary organic aerosols and the Caltech particle experiments may be focused on urban conditions. For aerosols, we should start with biogenic experiments that are of more concern for low NO_x conditions. Dr. Makar wondered whether we are eliminating heterogeneous effects that exist in the real world when if we do ultra-clean experiments. Dr. Basil Dimitriadis of the EPA stated that the congressional mandate for “low NO_x” experiments refers to the relatively clean urban atmosphere (i.e., not rural/remote conditions with extremely low NO_x). Perhaps 1 ppb is too low. Perhaps 5-10 ppb is more useful and more feasible. Dr. Rafael Villasenor stated that 1 ppb is reasonable – EUPHORE can do 2-3 ppb NO_x. Dr. Andreas Wahner believes he obtain useful data with below 1 ppb NO_x in the new outdoor chamber being constructed at KFA Juelich. Our position is that we will determine the low end of the NO_x range to study in this project after we have completed our evaluation of chamber effects and determined what is experimentally feasible. Even if the NO_x levels are lower than of interest in clean urban atmospheres, it is useful to obtain data over the full range of NO_x conditions for comprehensive mechanism evaluation.

Several people had comments on the need for radical measurements. Dr. Ulrich Platt of the University of Heidelberg in Germany stated that we need measurements of OH and HO₂. The chemical amplifier method has problems, so use of LIF would be better. DPAS provides absolute reference for OH and can provide many other species as well. Dr. Deborah Luecken of the EPA agreed that we need measurements for HO₂ and OH and also for RO₂, though we would need to find additional sources of funding for this. Dr. Jeffries also said we need radical measurements, and suggested we bring in someone to do chemical amplifier work. We agree that measurements of HO₂ and RO₂ would be extremely valuable, but believe that OH itself is probably less important because it can be measured using tracer methods. Since the budget for this project does not provide for acquiring the necessary instrumentation, we are exploring possibilities of additional funding in this regard. Another alternative is carrying out collaborations where instrumentation from other laboratories are used for special studies.

Several comments were made concerning analyses of organic product species. Dr. Jeffries and Dr. Luecken stated that we need an organic chemist to synthesize standards, particularly for multifunctional products. Dr. Jeffries also said that it is important to measure and speciate organic nitrates. Our response is that the current plan for this project is to reserve the major effort for organic product identification for a later phase of the project.

Dr. Dick Derwent of the Meteorological Office in Britain said that we need to do experiments with complex VOC mixtures that may include exotic compounds. Such experiments will probably be incorporated during the later phases of this project.

Dr. Makar stated that archiving of the chamber data is a concern. Ron Patterson of the EPA said that NARSTO could help with the data archiving. We agree that the data archiving is important and that the data should be made available to other researchers in an appropriate format in a timely manner. The procedures and format to be used have not been determined.

Dr Platt brought up the advantages of collaboration, stating that chamber work should be shared among the various chambers according to their expertise. The UCR chamber does not have to be designed to address all possible research questions. It may be possible to share some sophisticated instrumentation between different laboratories. We agree that collaboration is important. We don't want to duplicate efforts in other laboratories. The capabilities of the chamber will be designed to complement those of existing facilities. For example, using an indoor chamber will complement data obtained from outdoor chambers with advanced instrumentation such as EUPHORE, and doing aerosol studies in a large indoor chamber with xenon or argon arc light source will complement the Caltech outdoor or indoor blacklight chamber data.

Dr. Jana Milford of the University of Colorado said that the initial chamber design should be peer reviewed. Dr. Don Fox of the University of North Carolina and the chairman of the Reactivity Research Working Group suggested we establish an advisory board. Our research plan is to establish an advisory group, though we are behind schedule in this regard. An advisory group will be formed during the coming quarter to provide input on progress for this project and the current research plan.

CHAMBER AND LABORATORY DESIGN

Laboratory and Environmental Chamber Enclosure

It was determined that there is insufficient space in the existing CE-CERT laboratories to accommodate the large-volume environmental chamber facility for this program without adversely impacting existing and anticipated CE-CERT programs. Therefore, University and private funds were used to construct a new laboratory building for the Atmospheric Processes group to accommodate the facility and the associated analytical laboratory and offices for the experimental staff. Funds for this program will be used to pay for the off-campus space charges, which are already on the budget for the project. Construction of this building began in December of 2000, and it was completed and occupied in mid July of 2001.

All facets of the building were designed specifically to meet the needs of this program. The two-story building has the chamber on the second floor and the sampling equipment, and space for the analytical laboratory, support equipment, and offices on the first floor. This arrangement allows sampling directly below the chamber along the centerline between the two sides. The second floor has a clear span height of 22 feet. The chamber enclosure occupies a space 20 feet wide 40 feet long and 20 feet high. Electrical power and chilled water are supplied for the light source. A pad to the side houses the air purification system, water chiller, compressed air cylinders, and cryogenics. Photographs of the building taken shortly after it was completed are shown in Figure 1.

A diagram showing the layout of the environmental chamber enclosure is shown on Figure 2. The reactors will be located in a temperature-controlled housing specifically designed by a contractor specializing in refrigerated rooms and environmental enclosures. The light source and the location of the reactor relative to the light source are discussed in the following section. The enclosure will be flushed with purified air to minimize contamination by pollutants permeating through the reactor walls, as discussed later in this report. The specifications used when construction of the enclosure are as follows:

- Interior dimensions are 20' wide x 20' high x 40' length. No interior structures should obstruct or cast shadows on an 18' high x 18' x 18' reactor within the half of the enclosure opposite the light source, as shown on Figure 1. It was necessary to have large air handlers in the chamber, and a modified design with the handlers located in the corners on the wall with the light and outside the light path had to be adopted. This required an increase in cost above the original proposal by the vendor.
- The temperature control system should maintain the temperature within $\pm 1^{\circ}\text{C}$ at set points ranging from 4°C to 50°C . It must be able to recover temperature control to within desired range within 5 minutes after the heat load changes by ± 100 KW. The performance in this regard is currently being evaluated, but preliminary results indicate this is satisfactory.
- Reflective aluminum panels are installed on all interior surfaces. Polished aluminum was found to have the best reflective capabilities in the UV than all reasonably-priced alternatives examined, so polished aluminum panels were acquired for this purpose. At the present time, the panels are installed on all surfaces except for the floor, where they will be installed after the framework to hold the reaction bag is completed.



Figure 1. Photographs of the laboratory building constructed to house the new environmental chamber facility. (a) Outside view. (b) Equipment area showing the air purification system and the light and chamber enclosure cooling equipment. (c,d) Laboratory area downstairs. (e,f) Upstairs area during early stages of construction of chamber enclosure.

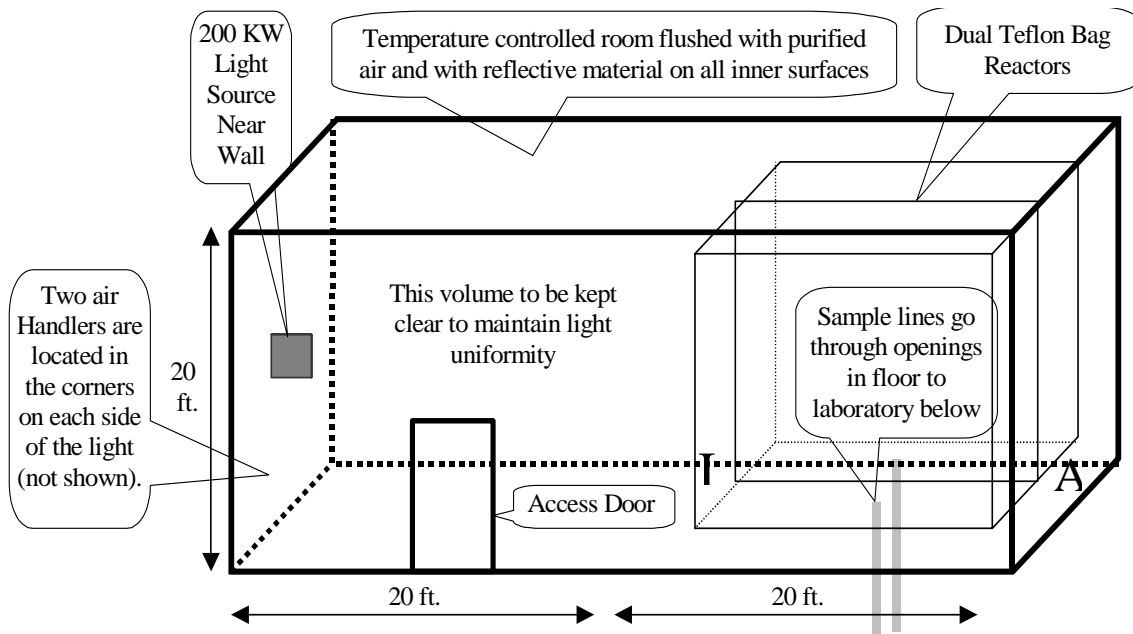


Figure 2. Schematic of the temperature-controlled enclosure to be used for the environmental chamber and light source. The “A” shows the location of the housing to be built for the aerosol instrumentation, and access for sampling of low volatility materials.

- The materials and sealants used in the construction of the interior enclosure walls should not emit reactive contaminants that may affect the experiments. The contractor proposed using materials containing polymeric diphenylmethane diisocyanate [MDI], whose MSDS gave a vapor pressure approximately 5 ppb at 20°C, and a silicone sealant. These materials appeared to be acceptable so they were employed.
- The enclosure has a 48” x 84” access door located as shown on Figure 1.
- The contract specification required that the enclosure must be able to maintain a positive pressure of 1 inch of water and have a leak rate no greater than 5% per hour with a positive pressure of 0.1 inches of water with access openings closed. This is necessary to use the enclosure as a “clean room” to minimize exposure of contaminants to the reactor. Because of the relatively air tight construction of the enclosure, it will be necessary to construct a pressure release system to avoid the enclosure imploding or exploding due to pressure changes caused by sudden changes in temperature.

A single bid to supply such an enclosure for a cost of approximately \$175K was received and accepted. The enclosure was completed in August of 2001 and is currently undergoing acceptance testing for temperature control when operated with the light source. Photographs of the enclosure in its current configuration are shown in Figure 3.



Figure 3. Photographs of environmental chamber enclosure and light source. (a) Outside the enclosure showing the access door. (b) Behind the enclosure showing the controls for the light. (c,d) Inside the enclosure showing the light and the air handler prior to the installation of the light and reflective material on the floor (light above the person's head in picture "d"). (e) Inside the enclosure showing the framework and netting that will hold the Teflon bag reactors in place. (f) Picture of lamp as taken at factory during testing.

Results of initial temperature control tests carried out shortly after the light source was installed are shown on Figure 4. (The light source is discussed later in this report. The light was operated for about two hours with ~86 KW total input power, which the Vortek engineers indicate is about 70% of the maximum power input. Of this, an estimated ~43 KW is entering the enclosure as radiation that is converted to heat that needs to be removed by the temperature control system in the enclosure. Figure 4 shows that the system is quite capable of maintaining a constant temperature to within $\pm 0.5^{\circ}\text{C}$ or better with the lamp operating at this power level, and other measurements indicate that the system has the capability of additional cooling capacity if needed. Note that Figure 4 shows only an initial test, with no attempt being made to minimize temperature swings when the light is turned on or off. We will be investigating optimum procedures to obtain better temperature control during times when the heat loads are changing.

Environmental Chamber Reactor Design

Dual reactors, as shown in Figure 2, above, will be utilized in the initial experiments in this program, each having dimensions of ~8' x 16' x 16', or 58,000 liters (59 m³). This is approximately 10 times the size of the largest indoor chambers we have employed in reactivity research (e.g., Carter et al, 1995a-c, 1997), and approximately half the size as a reactor used in the large UNC outdoor chamber (e.g., Jeffries et al, 1982, 1985, 1990). The dual reactor design is preferred because it is more suitable for reactivity-related research, and the large volume is necessary to minimize chamber effects and wall losses of aerosols, to provide sufficient volume for sampling using equipment with high sampling rates, and to maximize path lengths for in-situ spectroscopic analysis methods. This is probably the largest volume that could be practically employed for an indoor chamber given the budget for this project, and should be sufficient to address the objectives of this project.

Research on wall effects was carried out to determine if there are any better alternatives to our current use of FEP Teflon® film for constructing the walls of the environmental chamber reactor. The results are discussed later in this report, but they indicated that although other types of materials can give

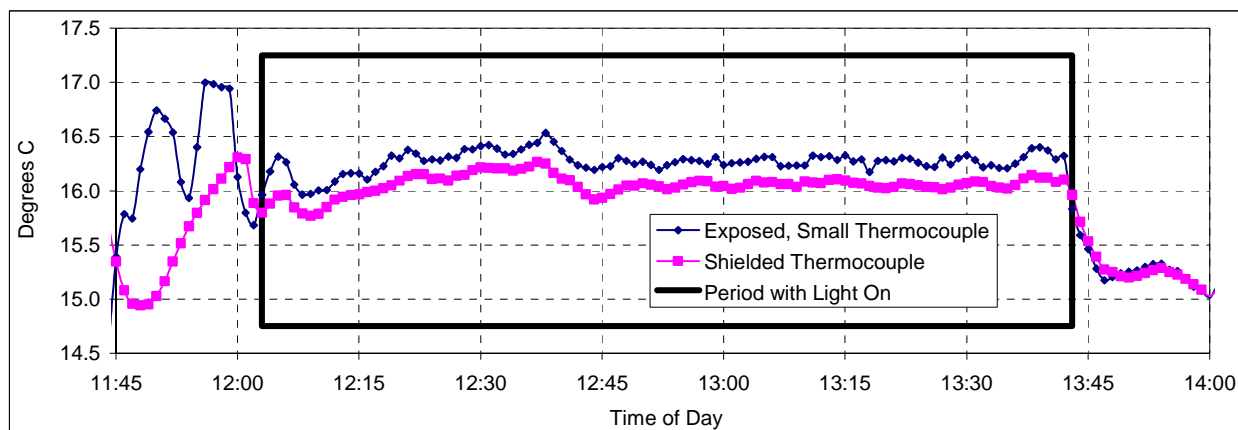


Figure 4. Performance of the temperature control system in the chamber enclosure in maintaining a constant temperature at ~16°C with the light at 70% of maximum recommended power.

similar results, there no alternative were clearly superior. Because we are familiar with constructing and characterizing reactors made with this material, we decided to continue using for the initial experiments in this program. We also decided (at least initially) to continue using a flexible and collapsible reaction bags because dilution due to leakage can be minimized and they can be more rapidly cleaned by collapsing and flushing. Therefore, in many respects the reactors are simply scaled-up versions of the ~6000-liter DTC or ~3000-liter CTC reactors we have previously been using in our mechanism evaluation and reactivity experiments (e.g., see Carter et al, 1997). There will be some differences, however, as discussed below.

As discussed later in this report, permeation through the 2 mil Teflon® film can be non-negligible, and characterization tests indicate that background effects can be significantly reduced if the reactor is inside an enclosure that is flushed with purified air. For that reason, the chamber enclosure discussed in the previous section has a relatively airtight design so it can be continuously flushed with clear air during the experiment. The air purification system, discussed in the following section, was designed to have the capacity to provide purified air at the flow rate needed for this purpose. This should minimize contamination due to contaminants in the laboratory entering the reactor through permeation or leaks.

It is important that the reactors are adequately flushed and cleaned between experiments to minimize contamination from previous experiments. Completely emptying and filling provides a much more rapid way to exchange the air in the reactors than continuously flushing a full reactor, and flushing a nearly empty reactor also provides more exchanges per unit time than flushing a full one. This is one of the reasons we have not adopted a rigid chamber design such as employed at UNC and CSIRO.

To allow for more complete collapse and also to minimize dilution caused by leaks, the initial plan was for the reactor to be attached to a rigid framework only on the bottom, with all sampling, inlet and exit ports only be attached to the bottom. This design minimizes dilution because the weight of the reactor will always exert a slight positive pressure on the contents, and any leaks would cause the reactor contents to exit rather than be diluted. The reactors would be held in place using netting attached to a metal framework. The framework and netting was constructed based on this plan.

One problem with this design is that the flexing caused by the frequent emptying and filling of the reactors may stress the Teflon film and eventually cause leaks. The use of 2 mil Teflon® film is preferred over the thicker films because the thinner film is expected to be less brittle (as well as being less expensive). A more serious concern is the fact that the flexible design requires us to rely on the heat seals to hold the reaction bag together. Although we have extensive experience in building FEP Teflon® reaction bags using heat sealing, we have found that the seals have variable quality and often fail unless reinforced with sealing tape (specifically 3M Polyester tape 8403 with a silicone adhesive), which tests (discussed below) indicate may introduce contamination, at least at elevated temperatures. To improve our heat sealing capability we purchased an 18-inch industrial impulse sealer with variable temperature and pressure control to use instead of the hand sealer we have used previously. Its initial performance has been variable but this may be due to problems that were recently corrected after they became apparent. We are not testing the performance of the sealer using scaled-down models of the reaction bags prior to constructing the full size reactors. The effects of the reinforcement tape on background reactivity are also being further evaluated.

We will not yet know for certain how well the reaction bags perform in practice in terms of leakage until they are constructed and used for a while. Note that because of the chamber design excessive leakage would be manifested by primarily premature collapsing of the bag and not dilution of the contents by pure matrix air being flushed through the chamber enclosure. Thus excessive leakage

would limit the length of time for experiments rather than necessarily compromising the validity of the data obtained. However, multi-day experiments are expected to be useful for evaluating mechanisms under long-range transport conditions and mechanisms for oxidation products, so excessive leakage will have to be corrected. If reactors without the reinforcing tape are found not to be satisfactory we may have to use the reinforcing tape if it is found not to introduce unacceptable contamination.

Generally, the heat sealer works well on straight seals, but less well on corners, so corners are most likely to be sources of leaks and require use of the sealing tape. In view of this, we adopted an alternative design that still allows the reactor to be almost completely collapsed yet eliminates the necessity of heat sealing the corners and has other advantages. In this design, both the top and bottom of the reactor is attached to rigid frameworks, with all the sampling and flanges still on the bottom, but the top framework is allowed to move up and down as the reactors empty and fill, allowing them to collapse nearly as completely as the flexible design discussed above. Counter-weights would be used to control the pressure provided by the weight of the top framework, with the objective being to provide a slight positive pressure to avoid dilution caused by leaks, without unduly stressing the reactor. A diagram of this configuration is shown on Figure 5. Tests using a scale model have shown that the Teflon film folds relatively neatly when collapsed in this way. This design also has the advantage of making access to the inside of the reactors without having to cut and patch the reactors. This access will be useful for measuring light intensity and spectra inside the reactor and other purposes.

Light Source

After the discussions at the workshop it was decided to proceed with our original plans to utilize a large indoor chamber with an artificial light source with a spectrum similar to sunlight. An example of such a lighting system is the set of the xenon arc lights used in our existing CE-CERT xenon-arc Teflon

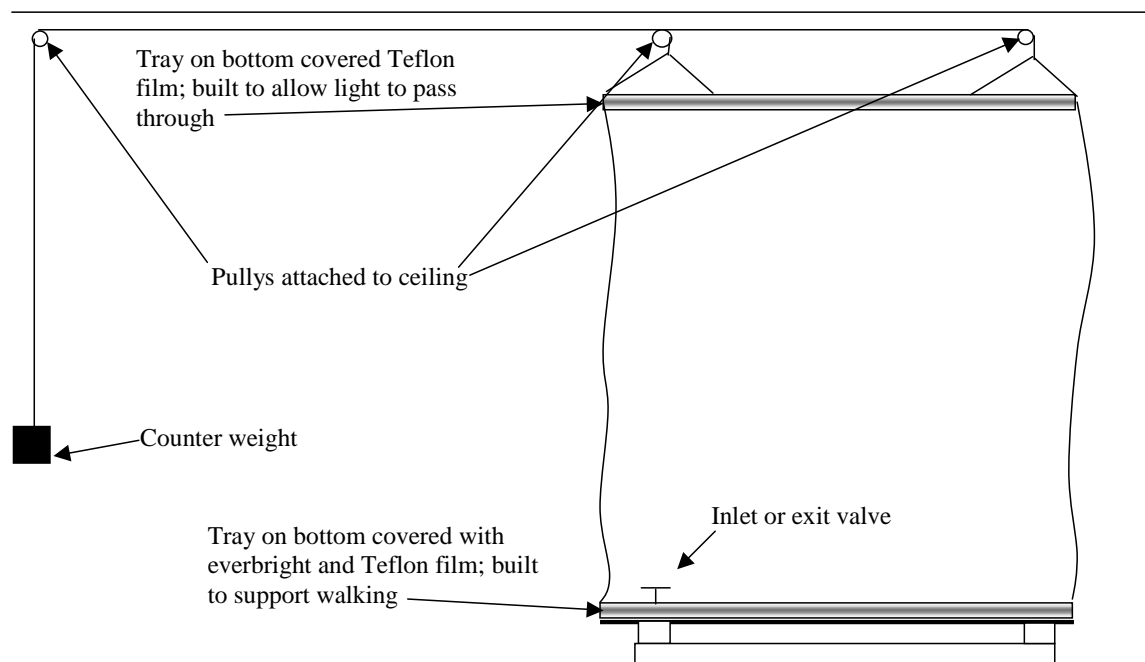


Figure 5. Diagram of configuration currently planned for reactor construction.

chambers (XTC and CTC) (Carter et al, 1995a,b). As discussed by Carter et al (1995a) this type of light source provides a sufficiently good simulation of sunlight in the spectral region of interest to serve the objectives of this project. However, the vendor used to provide the lights used in the XTC and CTC could not supply a source greater than 6.5 kw; this would require too many lamps to be practical or cost-effective. An alternative vendor, Vortek Industries, Inc. of Vancouver BC, Canada, was found who could provide the type of light source needed. They specialize in high intensity argon arc light sources for research and other specialized applications (Vortek, 2001) and appeared to have the capability to support our needs in terms of spectral characteristics, control and stability. They were also able to provide us assistance with light uniformity calculations, as discussed below, and claimed they could develop custom spectral filters to meet our particular specifications. Although we made an extensive search for alternatives to obtain competitive bids, suitable alternatives could not be found.

After discussions with Vortek, it was determined that a single 200 KW light lamp configured relative to the chamber as shown in Figure 2 would provide the necessary intensity at the best spectral uniformity. When the chamber was originally designed, we thought the best uniformity could be obtained if the chamber reactor(s) were located in the middle of the chamber enclosure with one light on each side. Vortek carried out light intensity distribution calculations that showed that the configuration shown on Figure 2, with a single light on one side of the enclosure and the reactor(s) on the other side, gave somewhat better uniformity. This is shown on Figure 6, which shows the results of the uniformity calculations with these two configurations. The points show the average, minimum, and maximum relative light intensities in cross sectional areas in a 20' x 20' x 40' room with reflective Aluminum panels and one or two light sources located in the middle of one or both of the end walls. The proposed position of the reaction chamber is shown for each of the configurations. As seen on the figure, although the configuration with the two lights on the opposite walls gives a slightly more uniform distribution of the average intensity in each cross section, there is a much greater difference in the extremes within each plane. The single light on the opposite wall gives much more uniformity within each cross section plane, with no more than a 6% difference between the sides of the reactor closest or farthest from the light. This is well within our desired uniformity specification

Another reason for using a single light configuration is cost. The cost for a single 200 KW light, with associated power, control, and cooling equipment, from Vortek was almost \$300,000, and 200 KW is the smallest light that they are willing to provide. Even with a single light this cost is more than the ~\$240,000 that was in the original budget for this proposal. A two light configuration with 200 KW lights would provide more intensity than needed and require significant reductions in the analytical equipment that could be obtained for this project.

Considerable discussions were had with Vortek concerning the specifications and acceptance requirements for the spectrum of the light source, particularly in the ≤ 400 nm range that is determined by the spectral filter employed. The desired spectrum used as the standard in our specification is the average of the ground-level actinic fluxes calculated by Peterson (1976) for direct overhead sun and zenith angle of 40°. This is shown in Figure 7, along with a “theoretical” spectrum provided by Vortek at the time their proposal to supply the lamp was evaluated. The latter was calculated using the actual spectrum of their argon arc lamp, and a calculated transmission spectrum for a filter they propose to develop for this order. They could not guarantee that this will be the exact spectrum that will be obtained using their lamps because the spectral filter needs to be developed as part of this contract.

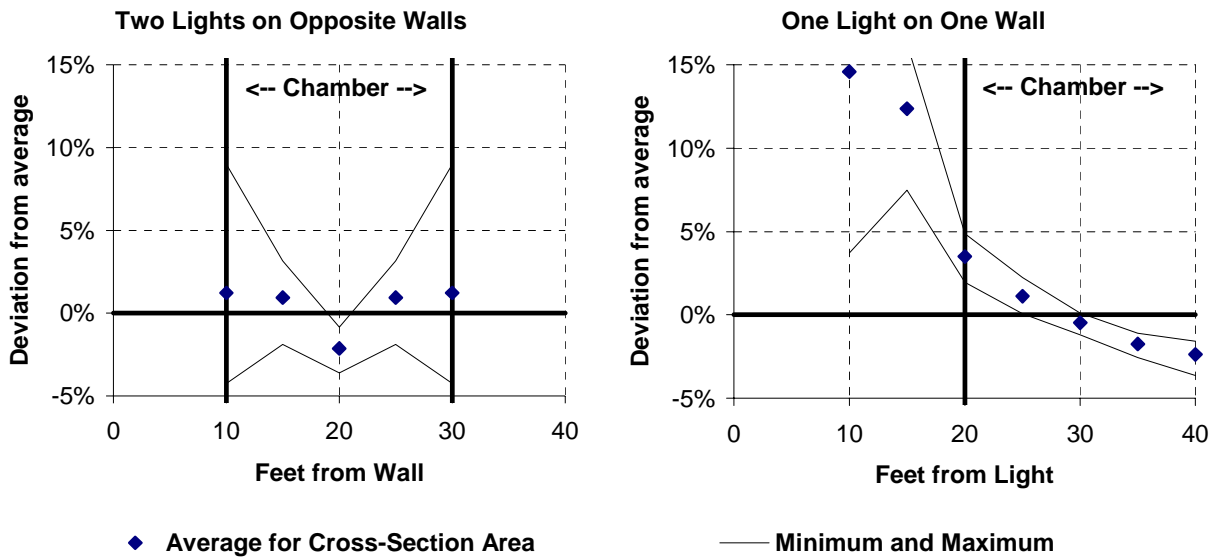


Figure 6. Results of light source distribution calculations provided by Vortek, Inc., for two configurations of the chamber reactor and the light source(s) in a 20' x 20' x 40' room with reflective polished aluminum walls. Points show the average intensities in the planes at the various distances from the wall or light, and lines show the ranges of intensities within the planes, in the regions where the reactor will be located.

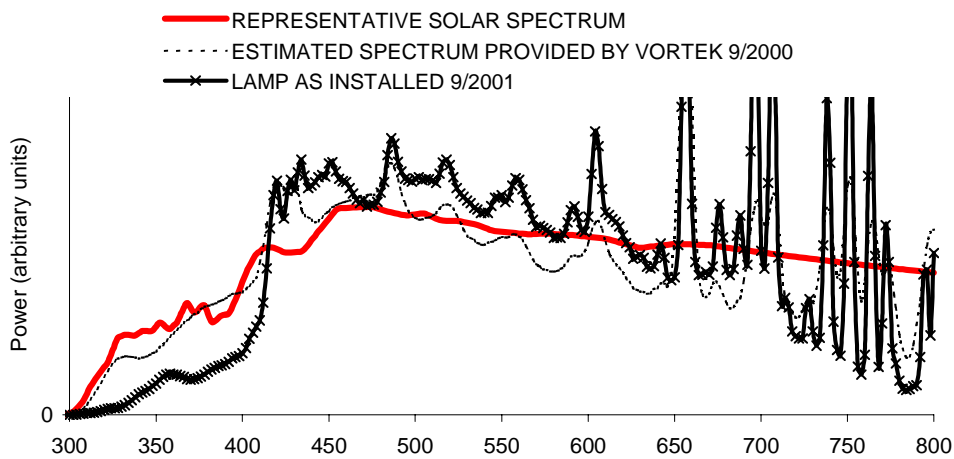


Figure 7. Relative power outputs of the standard solar spectrum, the calculated spectrum for the proposed lights for the new facility as provided by Vortek at the time the order was placed, and the obtained for the light as initially installed. Spectra normalized to give the same total intensity in the ≤ 600 nm region.

Table 1 gives the acceptance criteria we developed in terms of percentage of power output in the ≤ 600 nm range. These were derived based on acceptable ranges of calculated photolysis rates relative to the photolysis rate of NO_2 , with “acceptable” being agreement within a factor of ~ 2 or better of those calculated for ambient sunlight. As indicated on the table, the theoretical spectrum they provided us meets this criterion, and Vortek agreed to include this acceptance criterion in the contract. On the other hand, Table 1 shows that the spectrum of the current light source we use in the CE-CERT xenon arc Teflon chamber does not quite meet this specification in the 300-350 nm range. Therefore, if the new light source meets the specification we agreed to, then the light source for the new chamber should have a somewhat better representation of sunlight in this short wavelength region than the xenon arc light source that we are currently using.

After considerable delays, the major components of the light source were delivered in August of 2001 and were installed in mid September. However, the spectral filter designed to meet our specifications was delayed, and the system was installed using another filter so that the other components of the system could be evaluated. As shown on Figure 7 and Table 1, this filter did not have adequate intensity in the 300-400 nm region to meet our specifications, so the delivery of the system cannot be considered to be complete. However, the present system is sufficient for evaluating the performance of the other components such as the cooling system for the arc, to conduct an initial evaluation of the temperature control system for the enclosure with the lights on as discussed above, and to estimate its capabilities in terms of overall light intensity, as discussed below.

Although actinometry experiments using the current light source have not yet been conducted (and the results would not be representative because of the deficiencies of the spectrum in the 300-400 nm region), a qualitative indication of the light intensity capabilities of the current system can be obtained using our LiCor 1800 spectroradiometer. This instrument measures absolute intensity in terms of power output on a surface, as a function of wavelength, in the 300-800 nm region. Figure 8 shows a comparison of radiative power spectra made around solar noon on September 26 in Riverside with a measurement of the power spectrum made inside the chamber enclosure with the new light source. The solar spectrum was measured with the sensor pointed towards the sun (approximate zenith angle of 0), and the chamber spectrum was made with the instrument on the floor of the chamber enclosure about 10' from the light (in location “I” on Figure 2), with the sensor head pointed to the wall with the light. This measurement was made using a current of 500 amps, which is approximately $2/3$ the maximum current presently recommended by Vortek. Note that when the chamber measurement was made the reflective panels have not yet been installed on the floor, and when they are installed the intensity in the chamber at the floor would be expected to increase.

Figure 8 shows that the light intensity on a surface with the light at $2/3$ maximum currently recommended power is very close to that of the ambient noontime sunlight, at least in the 400-600 nm range. The intensity is low in the ≤ 400 nm range because of the filter used, the unfiltered spectrum, also shown on Figure 8, shows that the system is capable of supplying more than enough intensity in this region.

Photolysis rates are determined by the spherically integrated intensities and not by intensities on a flat surface, as measured by the LiCor 1800 spectroradiometer. Because of the high reflectivity of the walls of the chamber enclosure, the ratio of the spherically integrated intensity to the intensity on a surface facing the light source is expected to be far greater inside the chamber than would be the case for outdoor sunlight. Therefore, the intensity at $2/3$ maximum power may actually be significantly higher than ambient, which means that it may be appropriate to operate the system at lower power for most experiments. This may result somewhat lower operating costs and less frequent maintenance than

Table 1. Specifications and acceptance criteria used for the relative spectrum of the light source in the $\lambda \leq 600$ nm range.

Range (nm)	Percentage of Power Relative to Total Power ≤ 600 nm					
	Desired	Minimum	Maximum	Current CTC 6.5 KW	Proposed Vortek	System as Delivered (9/2001)
<300	0.035%	0.000%	0.080%	0.006%	0.000%	0.000%
300 - 350	6.2%	3.0%	9.0%	2.7%	4.4%	1.2%
350 - 400	11%	8%	14%	12%	11%	5%
400 - 450	19%	15%	25%	17%	21%	21%
450 - 500	23%	18%	28%	25%	24%	26%
500 - 550	21%	16%	26%	22%	21%	25%
550 - 600	20%	13%	27%	22%	18%	22%

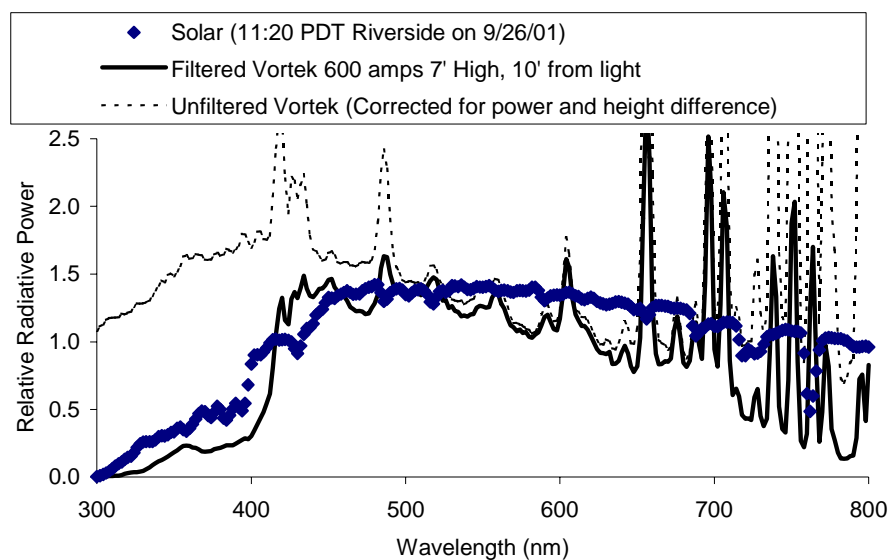


Figure 8. Comparison of power spectra for outside sunlight and the new Vortek light source.

originally estimated. However, this cannot be determined until the appropriate filter is in place and actinometry experiments are carried out.

The uniformity of the light intensity in the enclosure will be determined once the reflective material is installed on the floor and the framework and netting for holding the reactors are installed, but before the reactors themselves are put in place. This can be done by conducting NO_2 actinometry experiments using the quartz tube method of Zafonte et al (1977) as described by Carter et al (1993).

However, we are in the process of acquiring a spherical irradiance sensor to obtain more precise data to supplement NO₂ actinometry measurements. This is discussed further later in this report.

Air Purification System

Highly purified air is needed in large volumes not only to fill and flush the reactor but also to purge the chamber enclosure to minimize contamination by permeation or through leaks. It was determined that a capacity of 1000 liters/minute should be sufficient. Several methods of generating purified air were investigated. Cost, purity, and availability were the primary criteria. The purity specification is NO_x levels less than our current detection limit of ~0.2 ppb and less 1 ppb for other contaminants (except for CO₂). Blending oxygen and nitrogen from cryogenic sources was the thought to be the best approach, since it will also eliminate CO₂, which has the advantage of making analysis of total organic species much more straightforward. However, this requires purified oxygen, which was found not to be available locally at a reasonable price. We settled on a pressure-swing adsorption system similar to what we currently use, but on a much larger scale (1000 L/min). Adsorption towers are used to remove nitrogen oxides, heavier hydrocarbons, and carbon monoxide. In addition, a methane reactor catalytic oxidizer is included to remove methane and light hydrocarbons. (Note that a methane reactor is not the CE-CERT pure air system used in the preliminary experiments discussed in this report, and as discussed below this had implications in interpreting the results of the pure air experiments.). A final cleanup is made by passing the purified air through packed towers containing purafil and heated calulite. If needed at a later date, carbon dioxide can be removed with a soda lime scrubber, though this is not considered necessary during the initial phases of the program.

A system meeting these requirements was obtained from Aadco instruments. This was delivered in July of 2001, though with some shipping damage. Installation was completed in September, and it is currently undergoing evaluation. Although some shipping damage still needs to be repaired, the performance appears to be satisfactory.

Air Mixing and Reactant Injection System

It is necessary to have an appropriate means to mix the contents of the chambers to assure uniform concentrations after the reactants are injected, and, for dual chamber reactivity experiments, to assure that the common reactants in the two reactors are present at the same concentration. In our existing DTC and CTC chambers, the former requirement was addressed by having mixing fans in the chamber, and the latter by using two muffin fans to blow the contents of one reactor into another, with integrated PVC slide valves to isolate the reactors from the fans and connections when the mixing was completed (Carter et al, 1993). The valves employed for the latter were the type normally used for wastewater dump tanks for recreational vehicles, since they were designed to be airtight and had sufficient diameters for our application. Attempts to acquire or make Teflon® versions that did not leak were unsuccessful, but in our previous experiments in the DTC or CTC we had no indication that exposing the mixing air to small amounts of the material on the commercially-available versions provided significant contamination. However, the suitability of exposure of the reactor air to such materials in a chamber designed for low concentration studies is uncertain, and it is desirable to avoid this to the extent possible in the new chamber.

A related issue is the problem of injecting low volatility reactants into the chamber. Contracts we have with the California Air Resources Board (CARB) call for conducting experiments in this facility using 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (see the Research Plan section, below), a slowly evaporating solvent widely used in coatings, and it is expected that experiments with other low volatility

materials may be desired in the future. The procedure employed in our previous experiments involved heating the materials while flushing them into the chamber, which requires either large volumes of a air or nitrogen, long injection times, or high temperature. In practice, this does not work in a reasonable amount of time for very low volatility materials or materials that decompose when heated, as is expected to be the case for the compound to be studied for the CARB.

One approach for injecting low volatility materials into the chamber in a reasonable amount of time without excessive heat is to force large volumes of air at relatively high flow rates through filters or other media containing the material to be injected. This could be done when initially filling the reactor with purified air, but this approach makes it more difficult to conduct dual-reactor incremental reactivity experiments with equal amounts of “base case” reactants in each reactor, and also limits the amount of air available for reactant injection to one chamber volume. An alternative that does not have these limitations is to use an internal air recirculation for this purpose. This will permit injection of the low-volatility material after the base case reactants have been injected and equalized in the dual reactors, without causing additional dilution of the reactor with the air used to inject the test compound.

Based on these considerations, we decided to develop high-volume air recirculation and mixing systems that can be used for all the functions discussed above. The system involves four 10” pipes with Teflon-coated interiors and integrated Teflon-coated blowers to exchange air either between or within the reactors (or both). The latter can be used for injecting low volatility material when needed or for mixing within the reactor after any injections are made. Valves will close off and isolate this system during experiments. Note that these are connected to the reactors through flanges on the bottom, for reasons indicated in the previous section. We are currently in the final stages of designing this system in preparation of ordering or fabricating the necessary parts. This system should be completed in December

Sampling System

As indicated above, most instruments for monitoring gas-phase species will be located in the laboratory room beneath the chamber enclosure, and will be connected sample lines through the chamber floor. A sampling and calibration manifold has been designed where solenoids will be used select the reactor, calibration source, or pure air source for sampling, calibration, or zeroing. The solenoids that determine the reactor or calibration or zero air source being sampled will be controlled by data acquisition and control software currently being programmed using LabView. The state of the valves will be stored with the data from the instruments so that the programs being used to process the data can determine the source of the samples, and process the data accordingly. The data acquisition procedures and software are still being developed, but the goal is to automate the procedures as much as possible to minimize the time and labor required to process the data from the experiments into a format that can be used for analysis, mechanism evaluation, and planning additional experiments. This will include, to the maximum extent possible, automated calibration and zeroing procedures, as well as flagging and rejecting spurious or transitional data.

The sampling system discussed above will not be suitable for sampling for aerosol measurements because of possible loss of aerosols on the relatively long sample lines, and the fact that the aerosol characteristics may change if the temperatures in the sample lines or aerosol monitoring instruments are different from the temperature in the reactors. Therefore, a housing will be created for the aerosol instruments immediately adjacent to the temperature-controlled enclosure for the reactors, which will be kept at the same temperature as the reactors by air exchange with the chamber enclosure. For equal access to each of the dual reactors, the housing will be located in the lower center area of the wall opposite the light, as shown in Figure 2, above.

The sampling system discussed above will probably also not be suitable for analysis of low volatility materials that may stick or be lost on surfaces and valves. Samples for analysis of such materials will be taken by manually extracting them and trapping them on an appropriate material such as Tenax cartridges using, using short sample lines. Access to the reactor for this type of analysis will be either through the floor of the chamber enclosure or (more likely) through the opening created to access the aerosol instruments, as shown on Figure 2.

Analytical Equipment

Table 2 gives a listing of the analytical and characterization instrumentation currently available, being acquired or constructed, or being considered for this project. As indicated on the table, a significant amount of equipment was available from previous programs or became available from other sources of funding. The table includes a brief description of the equipment, species monitored, approximate sensitivity (where applicable), brief comments concerning its status and performance, and approximate cost to project, not counting staff time where applicable. Additional discussion of the various types of equipment, where appropriate, is given below.

Gas-Phase Instrumentation

Ozone, CO, NO, and NO_y can be monitored using commercially available instruments as indicated in Table 2. The commercial CO analyzer acquired for this project was determined to have adequate sensitivity for our needs. The Teco NO_y analyzer uses an external converter in an attempt to avoid losses of HNO₃ in the NO_y channel, though data from our laboratory and elsewhere indicate that responses to HNO₃ are variable, and NO_y data are not considered to be useful when HNO₃ or complex or uncharacterized mixtures are present. Separate analyzers are used for analysis of NO₂, as discussed below. It was desired to have an NO analysis sufficiently sensitive to see steady-state NO levels in the presence of NO_x and O₃ in light. Since the commercial analyzer was not capable of this, we acquired a high sensitivity analyzer from Eco-Physics, on the recommendation of researchers at KFA in Juelich, Germany. Unfortunately it took a long time for the instrument to work because of problems with the pump, but once it finally was working it appears to have sufficient sensitivity for our needs.

Sensitive and specific analysis of NO₂ is a clear priority for this project. Commercial NO_x analyzers lack both the sensitivity and specificity for our needs. The primary NO₂ analysis method for this project will be TDLAS, which is discussed below. However, an alternative method potentially useful for specific and sensitive NO₂ analysis is the GC-luminol system developed in our laboratories by Fitz and co-workers under funding from the CARB (Fitz et al, 2001). This system, based on previous work by Gaffney et al (1998) uses luminol detection combined with GC column to separate NO₂ from PAN and other species that are detected by luminol to provide a specific analysis for NO₂. It will also provide data for PAN, though its reliability and accuracy for this purpose has not yet been established. This system is being evaluated for this project, and results to date are discussed later in this report. The system appears to be more sensitive than the TDLAS, but the possibility of interferences at low NO₂ levels has not entirely been ruled out. If the GC-luminol system can be shown to give a specific and reliable analysis of NO₂ at low levels, it may permit the TDLAS NO₂ channel to be freed up for analysis of another species. However, this has not yet been shown to be the case.

The two GC-FID already available in our laboratories, described by Carter et al (1993), should be sufficient for most of the reactant organic analysis needs for the purpose of ozone and PM reactivity assessment. The main reactant organic not analyzed by this method is formaldehyde, which is monitored using other methods as described below. These systems can also be used to monitor at least some of the

Table 2. List of current and potential analytical and characterization instrumentation for this project.

Type	Model or Description	Species	Approx. Sens. (ppb)	Comments	Cost to Project
Current Instrumentation					
Ozone Analyzer	Dasibi Model 1003-AH. UV absorption analysis	O3	2	Standard monitoring instrument sufficient for this project.	Previously Available
High Sensitivity NO Analyzer	Eco-Physics Model CLD 780 TR. Chemiluminescent analyzer	NO	0.04	Only recently operational. Not fully evaluated.	\$23,000
Conventional NO - NOy Analyzer	Teco model Model 42 C with external converter. . Chemiluminescent analysis for NO, NOy by catalytic conversion.	NO	1	Useful for NO and initial NO2 monitoring. NOy data may be useful if denuders are used to remove HNO3, which can't be reliably quantified by this method.	Instrument on loan from the CARB
		NOy	1		
Luminol GC	Developed and fabricated at CE-CERT for another project. Uses GC to separate NO2 from PAN and other compounds and Luminol detection for NO2 or PAN.	NO2	Currently 0.2	Reliability needs to be improved. Sensitivity variable. Possibility of interferences at low concentrations needs to be investigated. May be possible to improve sensitivity.	\$5,000 - \$8,000 for various supplies. Mostly funded by another project.
		PAN	< 0.5	PAN analysis not yet verified or calibrated. Reliability needs to be improved.	
CO Analyzer	Dasibi Model 48C. Gas correlation IR analysis.	CO	50	Standard monitoring instrument sufficient for this project.	\$10,000
TDLAS #1	Purchased from Unisearch Inc. in 1995, but upgraded for this project. See text.	NO2	0.5	May be necessary to expend funds to improve reliability.	\$17,500 - \$32,000 to upgrade
		HNO3	~ 1 ?	Not completely evaluated. Needs to be repaired.	
TDLAS #2	Purchased from Unisearch Inc. for this project. See text	HCHO	~ 0.5	May be possible to increase sensitivity to 0.1 ppb. Channel may be used for another compound if the continuous analyzer is found to be sufficient.	\$146,000
		H2O2	≤ 1	Not completely evaluated.	
Continuous Formaldehyde Analyzer	Alpha Omega Power Technologies, Model MA-100. Continuous wet chemical analysis method.	HCHO	~ 1 ?	Instrument delivered about a year ago had design problems and was returned. Operational version expected before the end of the year or the order may be cancelled.	\$20,000

Table 2 (continued)

Type	Model or Description	Species	Approx. Sens. (ppb)	Comments	Cost to Project
GC-FID #1	HP 5890 GC with dual columns, loop injectors and FID detectors. Various megabore GC columns available.	VOCs	Currently 10 ppbC	Different columns can be used for different sets of VOCs. Loop injection suitable for low to medium volatility VOCs that are not too "sticky". Trap analysis will be used to increase sensitivity.	Previously Available
GC-FID #2	HP 5890 GC with dual columns and FID detectors, one with loop sampling and one set up for Tenax cartridge sampling. Various megabore GC columns available.	VOCs	Currently 10 ppbC	Different columns can be used for different sets of VOCs. Loop injection suitable for low to medium volatility VOCs that are not too "sticky". Trap analysis will be used to increase sensitivity.	Previously Available
		VOCs	1 ppbC	Tenax cartridge sampling can be used for low volatility or moderately "sticky" VOCs that cannot go through GC valves but can go through GC columns.	
GC-ECD #1	HP 5890 GC with dual columns, loop injectors and ECD detectors. Various megabore GC columns available.	Nitrogen or Halogen-containing VOCs	Depends on VOC	This instrument has not performed satisfactorily and may need to be replaced or modified if needed.	Previously Available
HPLC	Aldehydes collected in DNPH cartridges and derivatized compounds analyzed by HPLC	Aldehydes	0.04 µg per cartridge	The instrument currently available at CE-CERT will be sufficient for the anticipated needs of this project.	Obtained from other funding
Total Carbon Analyzer	Byron Model 301. FID detection. GC backflush used to separate methane from NMHCs.	Methane, NMHC	0.1 ppmC	A used instrument was acquired for evaluation, but it will probably not be suitable for this project except for methane analysis	\$1,500
Gas Calibrator	Model 146C Thermo Environmental Dynamic Gas Calibrator	N/A	N/A	Used for calibration of NO _x and other analyzers. Instrument acquired early in project and under continuous use.	\$10,300
Data Acquisition System	Windows PC with custom LabView software, 16 analog input, 40 I/O, 16 thermocouple, and 8 RS-232 channels.	N/A	N/A	Used to collect data from most monitoring instruments, control sampling solenoids, and carry out initial data processing. Most hardware acquired. Software nearing completion.	~\$3,200

Table 2 (continued)

Type	Model or Description	Species	Approx. Sens. (ppb)	Comments	Cost to Project
Temperature sensors	Various thermocouples, radiation shielded thermocouple housing	Temperature	~0.1 °C	See Text	Not significant
Humidity Monitor	General Eastern HYGRO-M1 Dew Point Monitor	Humidity	Dew point range: -40 - 50°C	Instrument performing as expected	\$4,400
Spectroradiometer	LiCor LI-1800 Spectroradiometer	300-850 nm Light Spectrum	Adequate	Resolution relatively low but adequate for this project. Used in previous projects to obtain relative spectrum. Also gives an absolute intensity measurement on surface useful for assessing relative trends.	Previously available
Broadband Radiometer	Eppley Precision Spectral Pyranometer Model PSP	Broadband Light intensity on surface	Adequate	Used in previous outdoor chamber experiments. May be useful to monitor light output, but does not give spherically integrated information.	Previously available
UV Radiometer	Eppley Total Ultraviolet Radiometer Model TUVR Radiometers	UV intensity on surface	Adequate	Used in previous outdoor chamber experiments and to monitor intensity in SAPRC EC. Not useful for quantitative evaluation because of uncharacterized spectral response	Previously available

Instrumentation Under Fabrication or Being Investigated

Two Scanning Electrical Mobility Spectrometers	See text	Aerosol size and number distribution	See text	These are being fabricated for this project. Two instruments are needed for dual-chamber experiments.	\$70,000
Tandem Differential Mobility Analyzer	See text	Aerosol response to changes in RH or Temp.	See text	This will be fabricated for this project. The funds are committed and construction is expected in early 2001.	\$35,000
Thermal Converter NO ₂ Analysis	Thermal converter interfaced to a specific NO ₂ analysis system as described by Day et al (2001). See text.	Total PANs and Total organic nitrates	Not determined	The applicability of this method using the available TDLAS or GC-luminol NO ₂ analyzers is being investigated. See text.	Being developed under other funding

Table 2 (continued)

Type	Model or Description	Species	Approx. Sens. (ppb)	Comments	Cost to Project
Spherical Irradiance Sensors	Biospherical QSL-2100 PAR Irradiance Sensor or related product. Responds to 400-700 nm light. Vendor will supply spectral response curve.	Spherical Broad-band Light Intensity	Adequate	This should provide a measure of absolute intensity and light uniformity that is much more directly related to photolysis rates than light intensity on surface. May give more precise measurement of light intensity trends than NO ₂ actinometry.	~\$4,000 for three being considered.
Instrument Mentioned in Proposal but Acquisition Uncertain					
Sensitive Total Carbon Analyzer	Not determined	Total VOC	≤ 1 ppbC desired	Commercially available instruments may not be satisfactory for this project.	\$17,600 in original budget
Sample Concentrator	Used to cryogenically trap and concentrate organics for GC analysis.	VOCs	< 1 ppbC	Used in conjunction with GC for automated analysis with improves sensitivity. May not be needed if manual trapping is found to be satisfactory for sample concentration.	\$46,000 in original budget
DOAS	Differential absorption spectroscopy used to monitor compounds with narrow absorption lines in the UV or visible.	NO ₃ , other species	Depends on species	Decision to acquire will depend on priority for experiments. Not needed for O ₃ or PM reactivity studies, but may be useful for mechanism evaluation. Remaining equipment budget may not be sufficient.	\$85,000 in original budget
GC-MS	Gas chromatograph interfaced with mass spectroscopy so compounds can be identified by their mass spectrum.	Identification of organics	Depends on compound	The UCR college of Engineering is attempting to acquire a GC-MS from other funding that may be available when needed for this project. Compound identification is not expected to be a high priority in the current work plan.	\$82,000 in original budget. May be obtained from other funding
GC-FID or ECD	Gas chromatograph with FID ECD detectors. Various GC columns available.	Organics	Depends on detector and VOC	This would supplement our existing GC instruments if needed for simultaneous monitoring of additional species.	Two for \$29,000 in original budget.

oxidation products, such as simple aldehydes, ketones, and organic nitrates, provided that their identities can be established by other means. The loop sampling method is currently used for the more volatile and less sticky compounds is sufficient for monitoring reactant VOCs, but it may not be sensitive enough for monitoring trace VOCs for pure air experiments or to verify the performance of the air purification experiments. A trap sampling method, which has been employed previously in our laboratories (Carter et al, 1993) can be employed when more sensitive analysis is required. The Tenax cartridge sampling method used for the lower volatility or more “sticky” VOCs (Carter et al, 1993) can be readily adapted for more sensitive analysis by sampling larger volumes of air through the trap. The GCs as currently configured allow use of three different columns for loop or trap sampling, and a fourth column for Tenax cartridge sampling. This permits a variety of types of compounds to be separated.

The GC-ECD instrument in our laboratory can be used for analysis of PAN and other species for which ECD is sensitive, and is available for use in this program. Unfortunately, in recent years the system has not given consistent calibration results, with data obtained using it considered to be uncertain by approximately a factor of two. Numerous attempts to improve its performance over the years have not been successful, and if the GC-luminol system is found not to give satisfactory PAN analysis it may be necessary to acquire a different type of ECD system for analysis of PAN and PAN analogues. The older packed column technology has given satisfactory data in the past (e.g., Carter et al, 1995b), and this can be adapted for this program as needed.

A continuous formaldehyde analyzer based on the wet chemical method of Dasgupta and co-workers being developed by Alpha Omega Power Technologies was ordered for use for this project. This would serve to replace the continuous wet chemical formaldehyde analyzer we have used previously (Carter et al, 1995b), which no longer operates reliably and has relatively low sensitivity. However, the instruments delivered (the one for this project and a number of others ordered for a CARB monitoring project) did not operate properly and had to be returned to the manufacturer for further development. A functioning model should be delivered sometime before the end of the year, or the order may be cancelled. Although the TDLAS system provides an excellent and highly sensitive formaldehyde analysis, if this less expensive system proves satisfactory for this project it would free the TDLAS channel for other purposes.

A total carbon analyzer would be useful to assess the purity of the matrix air used for the experiments and to verify analyses of compounds that are difficult to reliably monitor by GC. A system based on using a heated catalyst to convert organics to CO₂ and then monitoring CO₂ using a sensitive CO₂ analyzer is being developed under other funding, but probably will not be suitable for this program because the pure air system currently has no provisions for CO₂ removal. A commercial analyzer was obtained for evaluation, and it may be useful for methane analysis, freeing up a GC that may otherwise have to be dedicated for this purpose. However, its reliability and sensitivity for NMHC analysis may not be satisfactory for this program. This has not yet been fully evaluated.

The largest equipment expense for gas-phase analytical equipment for this project to date has been the acquisition or upgrading of two Tunable Diode Laser Absorption Spectroscopy (TDLAS) systems for monitoring up to four different species. TDLAS analysis is described in detail elsewhere (Hastie et al., 1983; Schiff et al., 1994) and is based on measuring single rotational - vibrational lines of the target molecules in the near to mid infrared using laser diodes with very narrow line widths and tunability. The sample for analysis is flushed through closed absorption cells with multi-pass optics held at low pressure (~25 Torr) to minimize spectral broadening. Because of the narrow bandwidth of the diode lasers required to get the highly species-specific measurement, usually separate diode lasers are required for each compound being monitored. However, both TDLAS systems acquired for this project

have two lasers and detection systems, permitting analysis of up to four different species using this method.

The priority species chosen for analysis by TDLAS are NO_2 , HNO_3 , H_2O_2 , and formaldehyde. As indicated above sensitive and specific measurement for NO_2 is a priority for this project, and although other methods such as GC-luminol may eventually be shown to be suitable, a proven method is needed to serve as the standard for this important species. Although expensive, TDLAS appears to be the most cost-effective of the options with sufficient sensitivity for our needs. Measurements of HNO_3 are also critical to mechanism evaluation because it is one of the major NO_x and radical sink compounds, and because it is suspected of playing a role in chamber wall effects. It is very difficult to measure reliability with adequate sensitivity; methods such as denuders or modified NO_y analyzers are either unproven or known to be unreliable, and in-situ FT-IR has insufficient sensitivity for our application. Although TDLAS analysis for HNO_3 suffers from the need to use sampling lines, sampling can be carried out using heated lines at low pressure to minimize line losses. H_2O_2 is also a priority for mechanism evaluation, because model predictions of this species in low NO_x systems are highly sensitive to mechanism differences. Wet chemical methods are not considered to be reliable because of possible interferences, and FT-IR lacks the sensitivity needed for this application. Formaldehyde is an important reactive product species from almost all VOCs, and it is also suspected of playing a role in chamber wall effects. Although other options exist for measuring this compound, they are either less sensitive than TDLAS, subject to possible interferences or the other problems associated with wet chemical methods, or are not readily adapted to continuous real-time analysis, as is the case for cartridge-based methods.

The first TDLAS instrument has been outfitted for monitoring NO_2 and HNO_3 . Although this instrument was acquired by CE-CERT prior to this project, to enhance the TDLAS sensitivity for smog chamber measurements, the electronics, software and other components were upgraded for this project. Funds from this project are also being used to pay down the loan that was used to acquire this instrument. The temperature control software of the diode laser environment, typically 20-90 K, was enhanced to allow control to within a millikelvin. Temperature line-locking is one of the most critical elements to ensure that the emission frequency of the laser is continuously kept at the absorption frequency of the target gas.

This TDLAS system performed well in monitoring NO_2 for a period, achieving a sensitivity in the ~150 ppt range in some experiments, though for various reasons only nine experiments have useable data. This relatively high sensitivity is attributed to an unusually good laser diode, which unfortunately was eventually destroyed due to a persistent leak in the detector. We are now in the process of ordering a replacement diode and having the laser shroud re-built. Because of problems with the other shroud's heating elements, the system monitored HNO_3 in only three experiments, achieving a sensitivity of about 1 ppb. This defective shrouds heater has been repaired by using the good parts from the NO_2 laser shroud, and preliminary results indicate that the system should have better sensitivity and reliability. Better reliability in the NO_2 analysis is also expected once the shroud is rebuilt, but we cannot be assured that the replacement laser will necessarily attain the sensitivity achieved using the previous one. We also upgraded the two infrared detectors required for the reference and signal beam. New preamps with variable gain and bias were purchased to better match the detector outputs to the signal amplifying electronics.

The second TDLAS instrument was acquired for this project and was outfitted for monitoring formaldehyde and H_2O_2 . It incorporates significant improvements in technology and reliability, though the sample cell has a somewhat shorter path length than the other, yielding somewhat less maximum sensitivity than theoretically attainable for the first instrument. This is also a dual channel instrument, but can be configured to run in single channel mode if greater sensitivity is required. It is rack-mounted in a

configuration taking much less space than the first, with an optical bench with a 100 meter Herriott Cell on top. Unlike the first instrument, the laser shroud does not make use of Sterling type cryogenic coolers but have the cold fingers mounted directly to a LN₂ dewar. This does have an advantage in reduced laser noise to vibration but limits laser choice to those that lase between 77° to 90°K. However for HCHO and H₂O₂, there are adequate lasers available at these temperatures. A photograph of the system and schematic of the optical bench are shown on Figure 9.

The system is currently being operated in single channel mode for formaldehyde, to achieve maximum sensitivity to this species during the chamber effects evaluation experiment. Although we are currently experiencing problems with zero drift due to problems with the temperature compensation software that we are attempting to correct, it can achieve sensitivities of 0.2 ppb when frequently zeroed. This is sufficient to monitor detectable formaldehyde formation in background air experiments. Because the instrument has only recently been acquired and because our current focus is on evaluation of background effects, this instrument has not yet been operated extensively or evaluated for H₂O₂ monitoring. Initial tests indicated a sensitivity of 1 ppb for H₂O₂ monitoring, but it is hoped that better sensitivity can be attained once the system is optimized.

The original budget for this program includes provision for a differential optical absorption spectrometer (DOAS) for monitoring species with sharp features in their UV or visible spectrum, such as NO₃ radicals, NO₂, HONO, formaldehyde, glyoxal, SO₂, and other compounds. However, this has been given lower priority for immediate acquisition for this project because its sensitivity for NO₂, and HONO is insufficient for chamber effects and low NO_x evaluation, and the other species of current interest in this phase of the project can be monitored at lower cost or with greater sensitivity with other methods. However, depending on the specific research plan and priorities for mechanism evaluation once the chamber is operational, the priorities for monitoring species for which this method is well suited, such as NO₃ radicals, may change, and acquisition of a DOAS at a later date of this project is still a possibility.

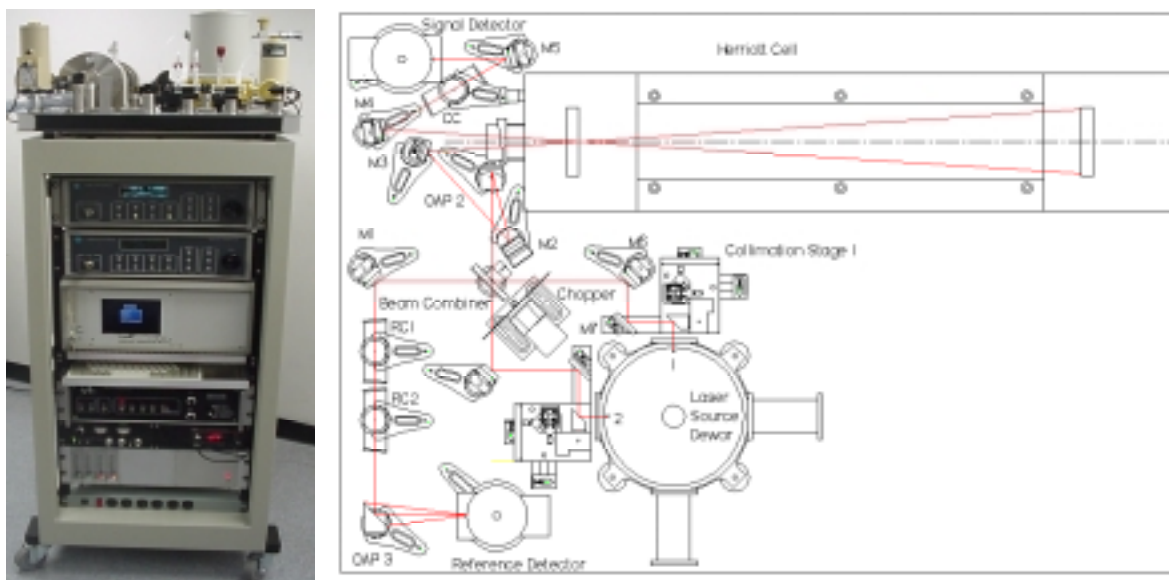


Figure 9. Photograph of the TDLAS system obtained for this project and schematic of its optical bench.

Because of continual improvements of the performance/price ratio of such equipment with time, we believe it is best to defer acquisition until just before they are needed in the research program.

The original budget for this program also includes provision for a GC-MS system for identification of organic products and a HPLC system for analysis of aldehydes and potentially other products using derivatization methods such as DNPH. However, researchers at CE-CERT and the UCR College of Engineering are attempting to acquire a GC-MS under other funding, and if they are successful it can be used for this project as well as their research. In addition, a HPLC system is already available at CE-CERT for use by this project, and occasional DNPH analyses could be carried out by other laboratories if needed. As discussed in the Research Plan section, below, organic product analysis studies are not currently planned to be a major focus of this project, and therefore acquiring dedicated instruments for this purpose is not currently considered to be a priority.

Aerosol Instrumentation

As indicated on Table 2, instrumentation is being acquired so that the environmental chamber can be used to measure yields and major physical properties of aerosols formed in the chamber experiments. Dr. David Cocker, a collaborating faculty member at the UCR College of Engineering and CE-CERT whose graduate work at Caltech was funded by this contract (see Caltech Subcontract section, below) is responsible for fabricating and operating these instruments. This instrumentation is described in more detail by Cocker et al (2001a). Their major features and their current status for this program are summarized briefly below.

Two Scanning Electrical Mobility Analyzers (SEMS) instruments are being constructed to simultaneously measure size and number distributions of aerosols formed in each of the dual reactors. Such data can be obtained approximately every minute during an experiment. Separate instruments are needed for each reactor because aerosol materials can't be expected to pass through solenoid valves without undergoing modification that is difficult to characterize. Aerosol size and number distribution is the primary physical measurement needed to determine amounts of aerosol formed and how they grow or are removed during an experiment. These instruments are being fabricated using TSI 3071 long column differential mobility analyzers, TSI model 3077 ⁸⁵Kr neutralizers, and TSI model 3760A condensation particle counters. The principle of operation and further information is given by Cocker et al (2001). Fabrication of these instruments is nearly complete. However, since these instruments will not be needed for this project for several months, they will be used for another project prior to being interfaced to this chamber. It is expected they will be available for this project by early 2002.

A Tandem Differential Mobility Analyzer (TDMA) will also be constructed for this project. This is used to determine the effects of humidity, temperature, or other changes to the environment to aerosol size and number distributions. This information is useful to investigate important aerosol properties such as hygroscopicity and volatility, and thus gives an indication of their major chemical characteristics. This consists of a SEMS measuring the size and number distribution of particles first selected into a single size range and then passed through a chamber exposing the particles to humidity, heat, or other conditions of interest. The principle of operation and further information about this instrument, which is based on the design of Rader and McMurry (1986), is given by Cocker et al (2001).

The instrumentation discussed above is considered sufficient to characterize the major physical properties of the particulate matter formed in our experiments, which is essential for evaluating models for predicting the effects of VOCs and other pollutants on PM formation. For a fundamental understanding of the chemistry of the aerosols and the molecular processes forming them, it is also

necessary to identify the chemical constituents of the aerosol matter, which requires additional instrumentation. This type of information is ultimately necessary to improve the basic science for models for PM formation. However, it is of somewhat less immediate utility than physical characterization information for evaluating the predictive capabilities of the current generation of models used in regulatory applications (or models likely to be developed for this purpose in the next few years) because the current models lack the capability of predicting this level of chemical detail. As discussed further in the Research Plan section, because of recourse limitations and other considerations, for this project we plan to focus primarily on near-term model development and evaluation needs for regulatory applications, so acquiring instrumentation for detailed chemical characterization currently is given lower priority.

Characterization Instrumentation

Use of chamber data for mechanism evaluation requires that the conditions of the experiment that may affect the results be adequately characterized. This includes measurements of temperature and humidity and light and wall effects characterization. Wall effects characterization is discussed in the following section and in the Research Plan section. The instrumentation to be used for the other characterization measurements is discussed below.

Temperature is monitored during chamber experiments using calibrated thermocouples attached to thermocouple boards on our computer data acquisition system. New thermocouple boards and data acquisition hardware and software was acquired for this project. This measurement is not straightforward because light on thermocouples can cause incorrectly high readings. This is dealt with by having the thermocouples shielded from the light and flushed with air from the experiment being monitored. In our past experiments, the thermocouples were in the sample line as close to the inlet as possible while still being shielded from the light. This is not entirely satisfactory because sampling alternates from reactor to reactor in the dual chamber experiments, and the measurement is useful only when the sample is being taken. Also, the sample line may not be the exact temperature as the center of the reactor. We are experimenting with very small thermocouples that should have less radiation interference, and have acquired a meteorological grade insulated temperature sensor to serve as a standard when comparing other alternatives. The latter will probably be located inside the chamber enclosure during the experiments, while shielded thermocouples will be used to monitor temperature in the reactors themselves.

Light Spectrum and Intensity. In order to calculate photolysis rates for the experiments, the spectrum of the light source and the spherically integrated light intensity need to be specified. The spectrum in the 300-850 nm region can be measured using our LiCor 1800 spectroradiometer, which is periodically calibrated at the factory. As discussed previously (Carter et al, 1995a,b, 1997), the light intensity is monitored by conducting periodic NO₂ actinometry experiments using either the quartz tube method of Zafonte et al (1977) modified as discussed by Carter et al (1995a,b), or by the steady-state method based on simultaneous measurements of NO, NO₂, and O₃ during irradiations. Because of light uniformity uncertainties the quartz tube method is not particularly well adapted to chambers such as this with light only on one wall, and steady-state actinometry in principle gives the best indication of the intensity inside the reactor for the purpose of calculating photolysis rates. However, our experience thus far has indicated that steady-state actinometry results are highly variable, with the sources of variability not being completely characterized (Carter et al, 1997). This has led to some uncertainty in assigning photolysis rates for the CTC chamber, which is similar in design (though much smaller in size) to the chamber being constructed for this project (Carter et al, 1997).

For this project, we will continue to rely primarily on the LiCor 1800 spectroradiometer for spectral measurements, with spectra being taken both inside and outside the reactors with the sensor head

pointing both at and away from the direct beam of the light. We will use a number of methods to characterize the spherically integrated intensity in the chamber and assess light uniformity. Quartz tube NO_2 actinometry will continue to be used, with measurements at various locations in the chamber enclosure being made to assess uniformity, and measurements being made both inside and outside the reactor. Steady state actinometry measurements will be made using data from experiments with appropriate NO_x and O_3 levels, with corrections being made for dark reactions in the sample lines. In addition, we are acquiring scalar PAR irradiance sensors with spherical optical collectors to provide an easier means to measure uniformity and a more precise measure of how spherically integrated intensity varies with time and location within the reactors. If the instrument is accurately calibrated and the response function of the detectors is well characterized, then the measurement would provide essentially the same information as an actinometry experiment, except on a continuous basis and probably with greater precision. The instruments are sufficiently small that they can be located within the reactor, and thus respond to changes in transmission through the chamber walls, if any.

Humidity is another parameter that will need to be accurately monitored because water participates in some gas-phase reactions and because humidity is known to affect aerosol properties and at least some chamber wall effects. This will be measured using an EG&G model Hygro M1 chilled mirror dewpoint sensor. Its lower limit of -40°C is above the expected dewpoint of the purified air but adequate for chamber experiments for determining humidity effects. The relative humidity is calculated from the dewpoint using an algorithm supplied by EG&G.

EXPERIMENTAL STUDIES TO DATE

Objectives and Overall Approach

A number of experiments were carried out during this reporting period to investigate factors involved in designing and conducting environmental chamber experiments under lower pollutant conditions than previously employed in chamber studies. The specific objectives were as follows:

- Quantify NO_x offgasing and other chamber effects that will affect low NO_x experiments, assess their variability and factors affecting them.
- Determine whether alternative materials for constructing chamber reactors have lower NO_x offgasing or other wall effects than the type of FEP Teflon film that is currently used.
- Determine whether permeation through walls of Teflon film reactors is significant and if so which procedures should be used to minimize it.
- Determine if cleaning or other treatments will be useful in reducing NO_x offgasing and other wall effects.
- Determine extent to which exposure to pollutants injected or formed in previous experiments affect results of subsequent runs.
- Obtain data useful for evaluating models for relevant wall effects.
- Obtain preliminary information relevant to mechanism evaluation under lower pollutant concentration conditions.
- Evaluate available instrumentation for monitoring NO_x and other pollutants of interest in the concentration range of interest in this program.

The approach was to use reactors with sufficiently high surface/volume ratios so any wall effects that may be of significance in experiments using larger chambers would be readily apparent, but with sufficiently high volume so that samples could be taken in experiments carried out for extended periods of time. All experiments employed flexible reactors constructed of Teflon or similar transparent material located inside an ~8' high x ~8' high x ~12' long chamber housing enclosure with blacklights backed by reflective material as described previously (Fitz et al, 1998). For the first series of experiments the reactors were constructed by heat-sealing two ~5' x ~12' sheets of 2 mil FEP Teflon film together to form a "pillowbag" of approximately 3500 liters. Similar reactors constructed of PFA Teflon film or Kynar film were also employed. For later experiments the FEP Teflon reactors were constructed by heat-sealing single ~5' x 10' sheets of the same 2 mil FEP Teflon material, yielding a lower volume reactor with fewer seals that was less prone to leaks. For most experiments these reactors were placed inside a larger "outer bag" constructed by heat sealing four ~5' x 12' sheets of 2 mil FEP Teflon film that was continuously flushed with purified air during the experiments. As discussed below, this approach was employed to minimize permeation of pollutants from laboratory air into the inner reactors during the experiments.

Except as noted otherwise, for most experiments the purified air was produced first using the AADCO air purification system employed in our previous chamber experiments (e.g., Carter et al, 1995a-c, 1997), and then by passing through purafil to assure complete removal of NO_x. It should be noted that this is a different AADCO system than new high capacity purchased for this program for the new chamber as discussed above, and in particular this system lacks the methane converter needed to remove

methane from the ambient air. In particular, analyses indicated average concentrations of methane, ethane, and propane concentrations of 2.9 ppm, 8 ppb and 5 ppb, respectively, in the air purified using this system. However, this system was found to remove NO_x, CO, and C_{>3} organics to below our detection limits. The air purification system also dries the air, and no humidification was added for any of the experiments carried out during this period.

The light intensity during the experiments during this period is estimated to correspond to an NO₂ photolysis rate of 0.43 min⁻¹, based on the results of actinometry experiments as discussed in the run summary table, given in the following section. This is somewhat uncertain because the effects of the reactor walls on the light intensity was not completely characterized and had to be estimated. Spectral measurements indicated that the blacklight spectrum given by Carter et al (1995) was also appropriate for the blacklights in these experiments. The temperature during the irradiations was typically ~305°K, but could vary by ~±2-3°K during experiments because of variations in the laboratory air temperature.

Summary of Experiments

A summary of the experiments that were carried out, indicating the conditions and giving a brief summary and discussion of the results, is given on Table 3. As indicated on the table, most experiments were pure air or CO – air runs that are considered to be the most sensitive to NO_x offgasing and other background effects of interest in this study, but various other types of tests and experiments were also carried out. The specific types of experiments and data, and the preliminary conclusions and analyses that can be obtained from them, are discussed further in the following sections.

Comparison of NO₂ Analysis Methods

As discussed in the Analytical Equipment section, above, accurate and sensitive measurements of NO₂ is considered to be essential for low NO_x mechanism evaluation, and three different measurement methods were employed during the course of the experiments listed in Table 3. Because these data have implications in interpreting the results of the experiments, it is useful to present a comparison of the measurements of these different methods in those experiments where all three methods were simultaneously employed. This is discussed in this section.

As indicated in Table 2, above, the three instruments employed that could provide measurements of NO₂ were the TDLAS, the GC-Luminol and the commercial NO-NO_x analyzer utilizing the external heated molybdenum converter. The TDLAS method is considered to be the most specific and the least likely to have interferences because of its principle of operation, and thus can serve as the standard in this regard. Although the luminol detection method is not specific to NO₂, the use of a GC column to separate the NO₂ from PAN and other species that are detected by luminol (and to remove O₃) increases the likelihood that this can provide a specific method, though the possibility of other interferences has not been completely eliminated. The commercial NO-NO_x analyzers are known not to be specific to NO₂ because the molybdenum converters also convert other species to NO for detection in the “NO_x” channel, but it is commonly used and its data are useful for comparison purposes. In particular, it can provide a good provides more stable measurement for NO₂ in the absence of other reactants than the other methods, and gives a lower limit to the NO₂ concentration when other “NO_x” species are present.

The NO₂ and NO_x-NO measurements for most of the experiments where all three measurement methods were employed are given as a function of irradiation time in Figure 10. These consist of four

Table 3. Summary of Pillowbag experiments carried out for this project during this reporting period.

Run	Type	Conditions, Results and Discussion	React'r ID [a]	d[O ₃]/dt (ppb/hr) [b]
1	Pure Air	Preliminary experiment with a reaction bag found to have leaks. Dry, purified air produced by the AADCO system used in our previous chamber experiments (e.g., Carter et al, 1995) was used except as noted. No outer bag used in these preliminary experiments. The NO and NO _x increased when lights turned on. Data not used.	F1	
2	Pure Air	New 3500-liter reaction bag used. Washed with distilled water. No outer bag used. Relatively high ozone formation rate observed.	F2x	4.4
3	Pure Air	Reaction bag placed in outer bag. Ozone formation rate only slightly lower.	F2	4.0
4	Pure Air	Duplicated previous run. Outer bag continuously purged with zero air for this and all subsequent experiments unless noted otherwise. Ozone formation rate reduced.	F2	2.7
5	CO - Air	Same conditions as previous run except ~30 ppm purified CO injected to get O ₃ formation rate in presence of known amount of reactive VOC. Presence of CO increased O ₃ formation rate, as expected.	F2	4.6
6	Permeation Test	Test to determine permeation rates. 0.3 ppm each of NO and NO ₂ , and ~30 ppm CO placed in outer bag, and buildup of these compounds monitored in inner bag. Non-negligible permeation measured. Based on an assumed reactor volume of 3500 liters and surface area of ~18 m ² , the calculated permeation rates (in units of m-2 day-1) were: 0.007 for NO, 0.003 for NO _x -NO, and 0.011 for CO.	F2	
7	Aborted run	Run aborted due to leaks in reactor. Reactor leaks repaired and sealed with polyester/silicone sealing tape.	F2	
8	CO - Air	~40 ppm CO injected. Somewhat less O ₃ formation rate than run 5, as expected due to somewhat lower amount of CO present.	F2	4.1
9	Pure Air	Repeated pure air run after repair of reactor. Comparable results obtained.	F2	2.6
10	Pure Cylinder Air	Pure air run using zero air rather than AADCO air in inner reactor. Main known difference is lack of methane in zero air, which is not removed by the AADCO as used in these experiments. Slightly lower O ₃ formation rate, but uncertain whether the reduction is significant.	F2	2.2
11	Cylinder Air + CO	Comparable amount of CO (~40 ppb) used as run 8, except zero air used rather than AADCO air. Slightly less O ₃ formation rate than run 8.	F2	3.6

Table 3 (continued)

Run	Type	Conditions, Results and Discussion	React'r ID [a]	d[O ₃]/dt (ppb/hr) [b]
12	Pure Air (Washed Bag)	New 3500-liter reaction bag constructed. Teflon film washed with 10% methanol, 90% distilled water before sealing, then purged with pure (AADCO) air over weekend. AADCO air used for this and subsequent runs unless noted. Significantly lower O ₃ formation rate in this reactor compared to the previous one. However, NO _x offgasing rate much higher than expected from the relationship between O ₃ and NO _x formation rates in the other pure air runs.	F3	1.2
13	CO - Air	Comparable amount of CO (~40 ppb) used as runs 8 and 11, but less O ₃ formation observed than in those runs, consistent with the lower O ₃ in the pure air run.	F3	2.6
14	CO - Air	Similar to previous run, but ~50 ppm CO used, and somewhat higher O ₃ formation observed.	F3	3.7
15	Multi-day pure air dark reaction	Inner bag filled with purified air and monitored for 25 days. No significant changes in NO or NO _x observed during this period.	F3	
16	Kynar Dark Reaction and irradiation	New reaction bag constructed using Kynar film. Bag filled with purified air and monitored for three days, and then irradiated. NO _x increased in the dark from about 0.1 to 0.5 ppb, but NO did not change. NO _x increased by about 0.3 ppb in the first 10 minutes of irradiation. No useful data obtained for longer irradiation times because of loss of volume in reactor.	K1	
17	Pure Air	Five day pure air irradiation using Kynar reactor. Relatively low ozone formation rate observed. In contrast with previous runs with the Kynar reactor, the NO _x offgasing rate was also relatively low, and in the range observed with later FTP Teflon reactors with similar ozone formation rates.	K1	1.0
18	O ₃ Dark Decay	Approximately 100 ppb of O ₃ injected in reactor to determine ozone formation rate. 10 ppm CO also present to correct for leaks, though leakage was minor. The average O ₃ decay rate was 2.4 x 10 ⁻⁴ min ⁻¹ (1.5%/hour). GC samples were taken, but no peaks observed.	K1	
19	Pure Air	Replicate pure air irradiation using Kynar reactor. Results similar to run 17.	K1	0.9
20	Pure Air	New reaction bag constructed using PFA Teflon film and installed in outer bag. Pure air irradiation for four days. Ozone formation rate in middle of range for FEP Teflon reactors, and NO _x offgasing rate also comparable.	P1	1.5
21	Test run	Dark test experiments to evaluate leaks in PFA reactor using CO. Data not processed.	P1	
22	Pure Air	Leaks in PFA reactor repaired, filled with pure air, and irradiated for 4 days. Results similar to run 20.	P1	1.4

Table 3 (continued)

Run	Type	Conditions, Results and Discussion	React'r ID [a]	d[O ₃]/dt (ppb/hr) [b]
23	Pure Air	New reactor constructed of FEP Teflon. Narrower than previous reactor because only one pane used, requiring only one seal along its length. Therefore, this reactor has higher surface/volume ratio than previous reactors. Pure air irradiation for 4 days. Somewhat higher O ₃ formation rate than previous reactors, but less than reactor F2. 20 ppm CO observed on 3rd and 4th day, but may be problem with monitor.	F4	1.9
24	Pure Cylinder Air	One-day irradiation of zero air from tank. Ozone formation rate somewhat less than previous run. CO offgasing during 24 hours was about 1 ppm.	F4	1.6
25	Pure Air	One-day irradiation of zero air from AADCO. Ozone formation rate somewhat less than previous run, but CO offgasing was comparable.	F4	1.3
26	Pure Air	Replicate of previous pure air run but no useful data because of leak in reactor.	F4	
27	Pure Air	Reactor repaired. Pure air irradiation repeated. O ₃ formation rate less than previous runs, continuing trend. No significant increase in CO during the one-day irradiation.	F4	0.9
28	Pure Air (O ₃ Treated Bag)	In an attempt to determine if treatment with high concentrations of O ₃ would remove reactants causing background reactivity, reactor was treated with ~1% ozone created by discharge in pure O ₂ . Flushed several times to remove ozone, and multi-day pure air irradiation conducted. Ozone formation and NO _x offgasing rates much higher than in any previous experiment.	F4a	5.2
29	Pure Air	Second pure air irradiation with ozone-treated reactor. Less O ₃ formation formed than previous run, but still much higher than usual. GC samples taken, but no peaks found.	F4a	3.5
30	Pure Air	New FTP Teflon reactor made. New impulse heat sealer used. Pure air irradiation for ~24 hours. Ozone formation rate higher than previous reactors (before O ₃ treatment) and comparable to reactor F2. About 10 ppm CO offgased during run.	F5	2.3
31	Argon+N ₂	Reactor filled with argon/oxygen mixture in ratio simulating N ₂ /oxygen in air. Irradiated for ~4 days. Ozone formation rate comparable to but somewhat less than previous run. Approximately 2 ppm CO offgased, much less than previous run but more than usual.	F5	2.0
32	n-Butane - NO _x	N-butane - NO _x experiment to measure chamber radical source. 1.3 ppm n-butane and ~30 ppb NO _x . NO oxidation and O ₃ formation rates fit using models assuming radical input rate of 26 ppt/min.	F5	

Table 3 (continued)

Run	Type	Conditions, Results and Discussion	React'r ID [a]	d[O ₃]/dt (ppb/hr) [b]
33	Pure Air	Pure air irradiation to determine effect of exposure to injected NO _x in previous experiment. Ozone formation rate comparable to previous runs in this reactor. Almost no CO offgasing in 24 hour irradiation.	F5	2.3
34	n-Butane - NO _x	Repeat n-butane - NO _x radical source experiment using ~1 ppm n-butane and 100 ppb NO _x . Data fit by model assuming 13 ppt/min radical input rate, lower than previous run but consistent with lower NO _x level.	F5	
35	Propene - NO _x	Propene - NO _x experiment for mechanism and characterization model evaluation, and to determine effect of exposure to a reactive VOC - NO _x mixture on chamber effects in subsequent experiments. Injected 0.5 ppm propene and 100 ppb NO _x . Relatively rapid NO oxidation and ~500 ppb O ₃ formed. Results consistent with model predictions. See Figure 22.	F5	
36	Pure Air	Pure air irradiation to determine effect of exposure to high reactivity propene - NO _x experiment. Ozone formation rate comparable to results of previous experiments in this reactor.	F5	2.6
37	Method of addition test	Method of addition experiment conducted to evaluate response of NO and NO _x analyzer to addition to reactor air. Results not conclusive.	F5	
38	Pure Air	Replicate pure air irradiation, in part to evaluate new Eco-Physics NO analyzer. Ozone formation comparable to previous runs in this reactor. Eco-Physics indicated NO not present initially, but jumped up rapidly when lights turned on. Instrument subsequently had a failure and was not operational again for quite a while.	F5	2.2
39	Pure Air	New FEP Teflon reactor made using no sealing tape. Pure air irradiation for 4 days. Ozone formation rate less than in previous reactor but comparable to reactor F4. Approximately 0.6 ppb of CO offgased during first day of experiment, then CO offgasing rate decreased significantly.	F6	1.3
40	Pure Air	One-day pure air irradiation with same reactor. First experiment with useable GC-Luminol NO ₂ data. Ozone formation rate in the normal range. No significant CO offgasing.	F6	1.5
41	Pure Air	Repeat of previous pure air run except that the irradiation began immediately after the reactor was filled with pure air. (In previous runs, the irradiation began some time after filling the reactor and monitoring its contents.) Ozone formation rate slightly lower than previous runs, but difference probably not significant.	F6	1.0
42	Pure Air	Replicate of previous run. Ozone formation rate somewhat less than in previous experiments.	F6	0.6

Table 3 (continued)

Run	Type	Conditions, Results and Discussion	React'r ID [a]	d[O ₃]/dt (ppb/hr) [b]
43	Long Term Dark Reaction	The reactor was filled with purified air and sat for 22 days without significant leakage. About 3 ppb NO ₂ and NO _x observed at the end of this period, with no measurable NO or CO.	F6	
44	Pure Air	Replicate pure air experiment after long dark reaction. Essentially the same results as observed in previous pure air run.	F6	0.7
45	CO-Air	10 ppm CO irradiation to determine ozone formation rate in the presence of CO in this reactor. Ozone formation rate only slightly higher than in previous pure air experiments.	F6	1.1
46	CO-NO _x	10 ppm CO and 40 ppb NO _x irradiation to determine chamber radical source. NO oxidation and O ₃ formation rate consistent with model prediction with ~3 ppt/minute radical input rate.	F6	
47	CO-NO _x	Approximately 25 ppm CO and 120 ppb NO _x irradiation to determine chamber radical source at different NO _x level. Not all NO consumed so no ozone was formed. NO oxidation ate consistent with model prediction with ~3 ppt/minute radical input rate.	F6	
48	N-Butane-NO _x	Attempt to conduct an n-butane run to measure the radical input rate with this method. However, no useful data obtained because of leaks in the reaction bag.	F6	
49	Pure Air	Reaction bag patched using sealing tape. Pure air irradiation conducted to determine background effects in current reactor. Ozone formation rate higher than in previous runs, but comparable to the first few runs in this reactor.	F6	1.3
50	n-Butane-NO _x	N-butane - NO _x experiment to measure chamber radical source. 100 ppb n-butane and ~50 ppb NO _x . NO oxidation and O ₃ formation rates fit using models assuming radical input rate of ~3 ppt/min.	F6	
51	Pure Air	Pure air irradiation to determine background effects in reactor after it was unused for several months. Relatively low ozone formation rate	F6	0.7
52	HNO ₃ Dark Decay	~16 ppb nitric acid injected and nitric acid dark decay was monitored for 6 days using TDLAS. The HNO ₃ data were well fit by a unimolecular decay rate of 45%/day.	F6	
53	HNO ₃ Irradiation	~25 ppb nitric acid injected and irradiated, and HNO ₃ monitored by TDLAS. Nitric acid decay rate was 37%/day, which is not significantly different than observed in the dark. Somewhat higher ozone formation rate observed than with standard pure air runs, but results were reasonably consistent with the somewhat higher NO ₂ levels that were observed.	F6	2.7

Table 3 (continued)

Run	Type	Conditions, Results and Discussion	React'r ID [a]	d[O ₃]/dt (ppb/hr) [b]
54	Pure Air	Pure air run to determine if HNO ₃ exposure affects subsequent background effects. Ozone formation rate was somewhat higher than observed previously for this reactor, but probably not significantly so.	F6	1.8
55	n-Butane - NO _x	Radical source measurement after exposure to HNO ₃ . ~50 ppb NO _x , 100 ppb n-butane irradiated. Data fit by radical input rate of ~5 ppt/min, consistent with previous runs.	F6	
56	NO _x - Air Irradiation	NO _x -air irradiation with ~40 ppb NO _x to determine light intensity by the steady state method. Total light intensity varied.	F6	
57	NO ₂ Actinometry	Light intensity in enclosure measured using quartz tube method. Tube outside reactors in approximate center of enclosure. NO ₂ photolysis rate of 0.54 min ⁻¹ measured. This is much lower than the value of 0.82 min ⁻¹ measured when the lights were new. This reduction due to ageing of the lamps has been observed with other blacklight chambers (Carter et al, 1993).	F6	
58	n-Butane - NO _x	N-butane - NO _x experiment to measure chamber radical source. 115 ppb n-butane and ~40 ppb NO _x . NO oxidation and O ₃ formation rates fit using models assuming radical input rate of ~4 ppt/min.	F6	
59	Propene-NO _x	Low NO _x propene irradiation to evaluate model and measurements, using 120 ppb propene and ~40 ppb NO _x . Most data consistent with model predictions. See Figure 22.	F6	
60	NO ₂ Actinometry	Light intensity measured using the quartz tube method with the tube inside and outside the outer bag. The tube was located in a lower position more representative of the center of the reaction bag than was the case for the previous experiments. Measured NO ₂ photolysis rate was 0.49 min ⁻¹ outside the outer bag and 0.47 min ⁻¹ inside the bag. However, folded up reaction bag may have affected results of outside the bag measurements.	F6	
61	NO ₂ Actinometry	Repeat of outside-the-bag measurements of previous run with reaction bag moved farther away. NO ₂ photolysis rate increased to 0.53 min ⁻¹ . Overall, the data suggest a transmission factor of about 90% for light going through the outer bag. Overall, the actinometry data to date suggest an NO ₂ photolysis rate of ~0.47 min ⁻¹ inside the outer bag, which suggests an NO ₂ photolysis rate of ~0.43 min ⁻¹ inside the inner bag, assuming the same transmission rate. This value was used when modeling the experiments carried out during this period.	F6	

Table 3 (continued)

Run	Type	Conditions, Results and Discussion	React'r ID [a]	d[O ₃]/dt (ppb/hr) [b]
62	Propene-NO _x	Propene irradiation at even lower NO _x to further evaluate model and measurements. Initial propene 50 ppb, NO _x ~10 ppb. Initial NO ₂ /NO ratio higher than expected due to possible injection problems. Attempted to monitor formaldehyde by TDLAS but no valid data taken due to sampling problems. Data not consistent with model predictions unless light intensity is assumed to be about half that indicated by the actinometry experiments. See Figure 23.	F6	
63	Propene-NO _x	Repeated low NO _x propene irradiation at somewhat higher NO _x to evaluate formaldehyde measurements. Initial propene ~50 ppb, NO _x , ~20 ppb. Results not entirely consistent with model predictions, with ozone data better fit by lower light intensity, but with formaldehyde consumption rate faster than predicted by model. See Figure 22.	F6	
64	Formaldehyde - Air	Formaldehyde - air irradiation to test formaldehyde measurements, wall model, and to measure formaldehyde decay rate in absence of NO _x . Ozone formation rate fit by model predictions using wall model derived from pure air and radical source experiments, but again formaldehyde decay rate was faster than model predicted. See Figure 24.	F6	1.4
65	Pure Air	Pure air irradiation to determine current background state of reactor after propene and formaldehyde runs. Ozone formation rate was in low range for this reactor. Formaldehyde data taken using TDLAS. Formaldehyde about 1.5 to 2 times higher than expected formation from reaction of methane in AADCO air.	F6	0.8
66	Formaldehyde-NO _x	Formaldehyde - NO _x irradiation to evaluate model for formaldehyde in presence of NO _x . Initial formaldehyde and NO _x about 10 ppb each. Problems with data consistency during run. Formaldehyde data not yet processed. Run will need to be repeated.	F6	
67	Formaldehyde - Air	Repeated previous formaldehyde - air experiment after improvements made to formaldehyde analysis. Similar results obtained. See Figure 24.	F6	
68	Full Surrogate-NO _x	Full surrogate - NO _x experiments with approximately half the VOC and NO _x levels of standard full surrogate levels used in previous projects. Initial surrogate ~2 ppmC, NO _x 100 ppb. Results reasonably consistent with model predictions. See Figure 25.	F6	
69	Pure Air	Pure air irradiation to determine background effects in reactor after full surrogate experiment. Ozone formation rate higher than previous run, but within variability of data for this reactor.	F6	1.6

Table 3 (continued)

Run	Type	Conditions, Results and Discussion	React'r ID [a]	d[O ₃]/dt (ppb/hr) [b]
70	Dual Pure Air - Taped and Untaped Bags	Two new, smaller (~1000 liter) reactors made at the same time using similar procedures except that one was taped with sealing tape and the other wasn't. Reactors both in chamber enclosure but outside the outer bag. Relatively high ozone formation rates observed in both reactors, but with the highest in the taped reactor. This may be due to permeation and leakage.	F7x F8x	2.9 2.1
71	Pure Air - Taped Bag	The taped reactor was placed in the outer bag flushed with pure air as with most previous experiments. Ozone formation rate much lower than in experiment without outer bag, and within range observed for previous reactors.	F7	1.7
72	Pure Air - Untaped Bag	The un-taped reactor was placed in the outer bag flushed with pure air as with most previous experiments. Ozone formation rate much lower than in experiment without outer bag, and within range observed for previous reactors. Difference between taped and un-taped reactor not significant.	F8	1.6
73	Pure Air - Un-taped Bag	Repeated previous experiment with un-taped reactor. Similar results obtained.	F8	1.3
74	Pure Air - Untaped Bag - Zero Air	Repeated previous experiment with same reactor, except methane-free zero air used instead of methane-containing AADCO air. Similar ozone formation rates and formaldehyde levels obtained. Unable to verify methane levels in experiment.	F8	1.3
75	Pure Air - Taped Bag	Repeated previous experiment with taped reactor. Similar results obtained.	F7	1.4

[a] ID codes used to designate reactors as indicted on Table 4

[b] Ozone formation rate in ppb/hour in pure air or CO-air experiments calculated based on interpolated ozone concentration at 12 hours, divided by 12.

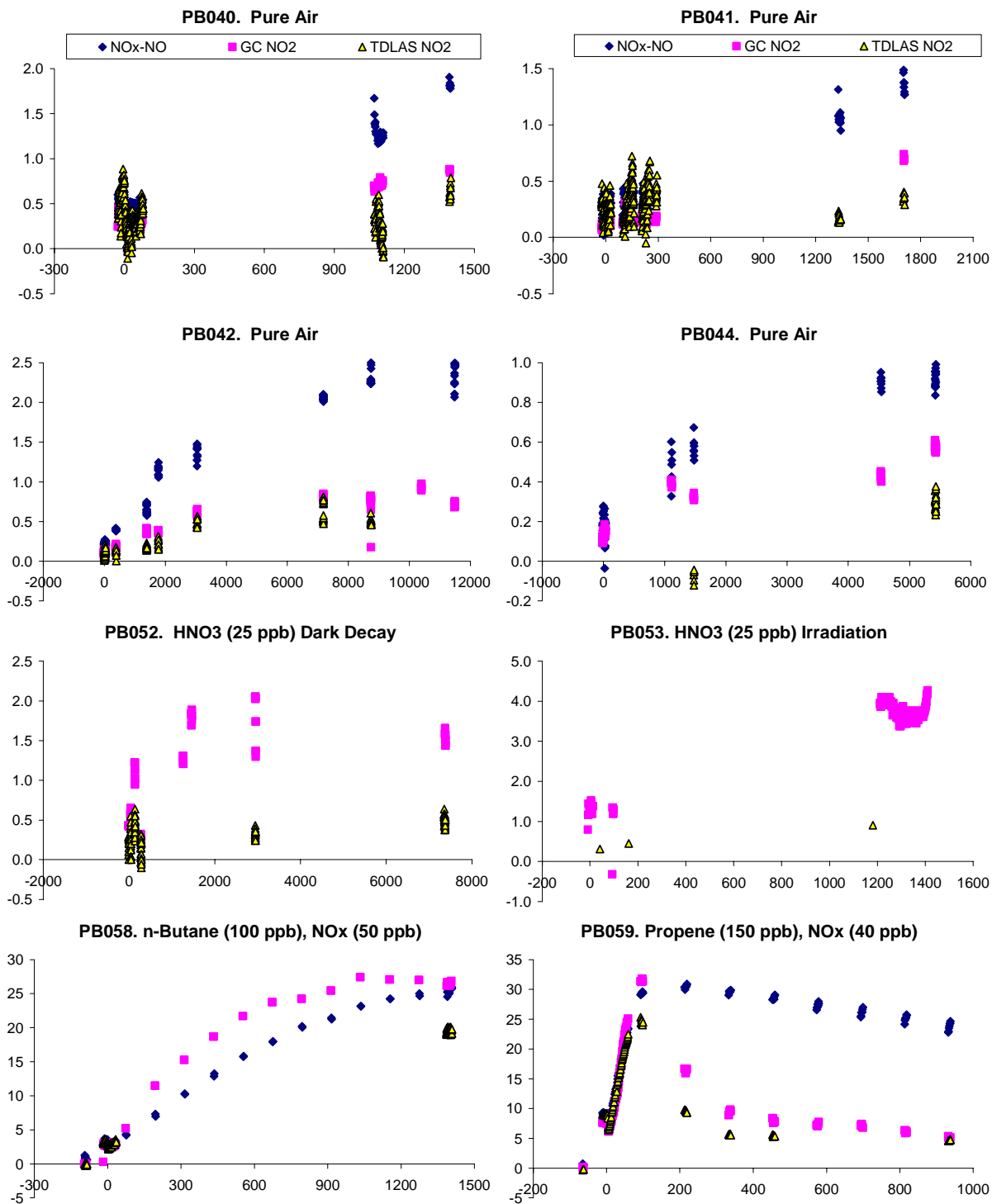


Figure 10. Concentration-time plots of NO₂ measurements taken by various instruments for experiments where intercomparison data are available. Concentration units are ppb; time units are minutes after lights turned on.

pure air irradiations where no NO_x injections were made and only low levels of NO_2 were measured, two experiments with HNO_3 but without NO or NO_2 injections (where the “ NO_x - NO ” data are not shown because they are of a much higher magnitude than the more specific NO_2 measurements because of its response to HNO_3), and two VOC- NO_x experiments where ~ 50 ppb of NO_x was injected.

The results of the pure air experiments give a good indication of the performance of the methods at very low, but still detectable, levels of NO_2 . Both the TDLAS and the GC-luminol method indicate that approximately 0.5 – 1 ppb of NO_2 is formed in a 24 hour period, though the GC-luminol method tends to give slightly higher readings than the TDLAS. Note that these measurements are essentially at the detection capability of the TDLAS, and probably reflect the best sensitivity ever attained for NO_2 by this method. The GC-luminol data appear to be somewhat less scattered than is the case for the TDLAS in most (though not all) the experiments, but clearly these measurements are near the detection limit for this method as well. Because of this, it is uncertain whether the differences between the NO_2 measurements with these two methods during the pure air runs are significant. Because the GC-luminol method tends to give higher readings and its specificity is more uncertain than is the case for the TDLAS, the possibility for non-negligible interferences cannot be ruled out.

The higher NO_x - NO readings obtained during the pure air experiments suggest that some non- NO_x species other than NO_2 is also being produced during these experiments. As discussed in the following section, the most likely species is HNO_3 . The converter for the NO_x analyzer was located adjacent to the reactor to minimize losses of HNO_3 in the sample line, so the NO_x analyzer should detect the presence of HNO_3 . Attempts to detect HNO_3 by TDLAS in the pure air runs carried out during the brief period when the HNO_3 channel was working in the TDLAS were unsuccessful, but at that time the instrument may not have been capable of detecting HNO_3 at this level. This is discussed further in the following section.

Figure 10 shows that the differences between the GC-luminol and TDLAS were significantly greater in the experiments where HNO_3 was present, with the GC-luminol giving significantly higher values for NO_2 . This strongly indicates a significant HNO_3 interference in the GC-luminol measurement. This may also explain the differences in the pure air experiments, since the model predictions (discussed below) and the NO_x - NO data indicate that HNO_3 is formed in these experiments. Since it is unlikely that the HNO_3 is making it through the GC column to reach the luminol detector, the most reasonable explanation is that the HNO_3 is heterogeneously decomposing to NO_2 in the instrument before it reaches the column. This interference probably can be removed by using denuders to remove HNO_3 before entering the instrument, though evaluations will need to be conducted to determine if this affects the NO_2 data when these very low concentrations are being monitored.

The bottom two plots on Figure 10 show the NO_2 data taken during an n-butane or propene irradiation carried out in the presence of ~ 40 - 50 ppb added NO_x . There is clearly a problem with the GC-luminol data in run PB058, since its NO_2 readings are even higher than those obtained by the NO_x analyzer, even though other NO_x species detected on this analyzer are known to be formed in this system. This is probably due to span drift on the instrument, which was observed to occur from time to time. The agreement is somewhat better for the propene - NO_x experiment PB059, though the GC-luminol data were higher than the TDLAS during the middle stages of the run. However, model calculations, discussed later in this report, give somewhat better agreement to the GC-luminol data for NO_2 than to the TDLAS data.

Although additional experiments will be needed before any definitive conclusions can be drawn, the results to date indicate that there are problems with the GC-luminol method that will need to be addressed before it can be relied upon for obtaining NO_2 data for mechanism evaluation purposes. The apparent HNO_3 interference will need to be eliminated and additional data will be needed to determine if

agreement can be obtained between these two methods once the HNO₃ interference is removed. Although the TDLAS is considered to be more reliable in terms of specificity, it is a much more expensive and labor intensive method, appears to be less sensitive than appears to be the capability of the GC-luminol method if it is optimized. Also problems with the TDLAS instrument has limited the number of experiments where useful data was obtained, though repairs are underway that should be helpful in improving its productivity. For that reason, once the TDLAS NO₂ channel is repaired, we will conduct additional tests in an attempt to improve and further evaluate the GC-luminol method for specific monitoring of NO₂ at ppb or sub-ppb levels.

Nitric Acid Measurements and Decay Rate Determinations

The nitric acid channel of the TDLAS was working only for a limited amount of time during this reporting period, and it was not operating with sufficient sensitivity to determine HNO₃ offgassing rates in pure air experiments. However, it was operating sufficiently long to permit nitric acid dark and light decay experiments to be carried out, with ~20 ppb HNO₃ injected into the chamber in the absence of other reactants. The data obtained are shown on Figure 11, and the results of the experiments are also summarized briefly below.

In the first experiment, run BP052, the nitric acid was kept in the chamber in the dark for a period of 5 days. As shown on Figure 11, the HNO₃ data as monitored by the TDLAS were well fit by a first order decay at a rate of 47% per day. The amount of HNO₃ as measured by the NO_x analyzer agreed well with the TDLAS measurements for the first few days of the experiment, and indicated a similar rate of decay. However, the NO_x analyzer indicated significantly higher NO_x on the 5th day than the HNO₃ as measured by the TDLAS. This discrepancy cannot be accounted for by decomposition to NO₂, since as shown on Figure 10, above, the NO₂ as measured by TDLAS was less than 1 ppb at the end of that experiment. Even the higher apparent NO₂ levels as measured by the GC luminol system is not sufficient to account for this discrepancy.

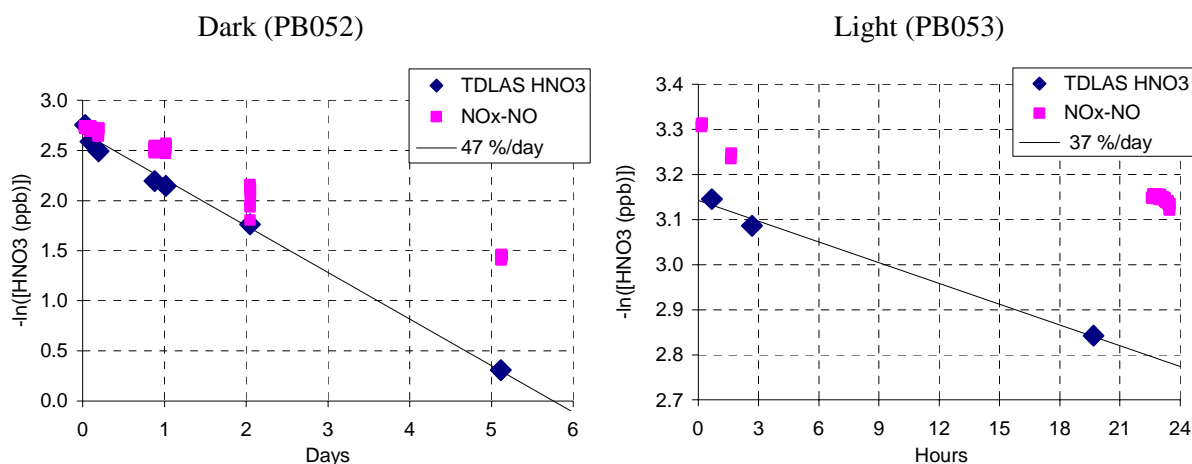


Figure 11. Nitric acid and NO_x data taken during the nitric acid dark and light decay experiments.

In the second experiment, PB053, the nitric acid-air mixture was irradiated for about 24 hours. The results, also shown on Figure 11, indicate that the HNO_3 decayed at a rate of $\sim 37\%$ per day, which probably can be considered to be equal to within experimental uncertainty to the decay rate in the dark. Therefore irradiation does not measurably increase the decay rate of HNO_3 . This is consistent with the fact that its photolysis and known gas-phase reactions are slow under atmospheric conditions, but is of interest because it indicates that light also does not significantly affect its loss on surfaces. The NO_x analyzer gave initial concentrations that were $\sim 20\%$ higher than the HNO_3 as measured by the TDLAS, which may be within the calibration uncertainty of the latter. However, as with the previous experiment the NO_x analyzer also indicated a lower decay rate than the HNO_3 as measured by TDLAS, and again the measured NO_2 levels were too low to account for the difference.

Permeation Tests

As indicated on Table 3, an experiment was carried out early in this project to determine the rate at which NO_x and other species permeate through 2 mil FEP Teflon film. This material is used to construct most of the reactors in our previous experiments and, and is the primary material being considered for the large chamber for this project. The experiment was carried out using a ~ 3500 -liter 2-mil FEP Teflon pillowbag reactor with an approximate total surface area of $\sim 18 \text{ m}^2$, located inside a larger FEP Teflon reactor into which ~ 400 ppb each of NO , NO_2 , and ~ 30 ppm of CO were injected. These three species were monitored in both reactors over a three day period, and the data obtained are shown on Figure 12.

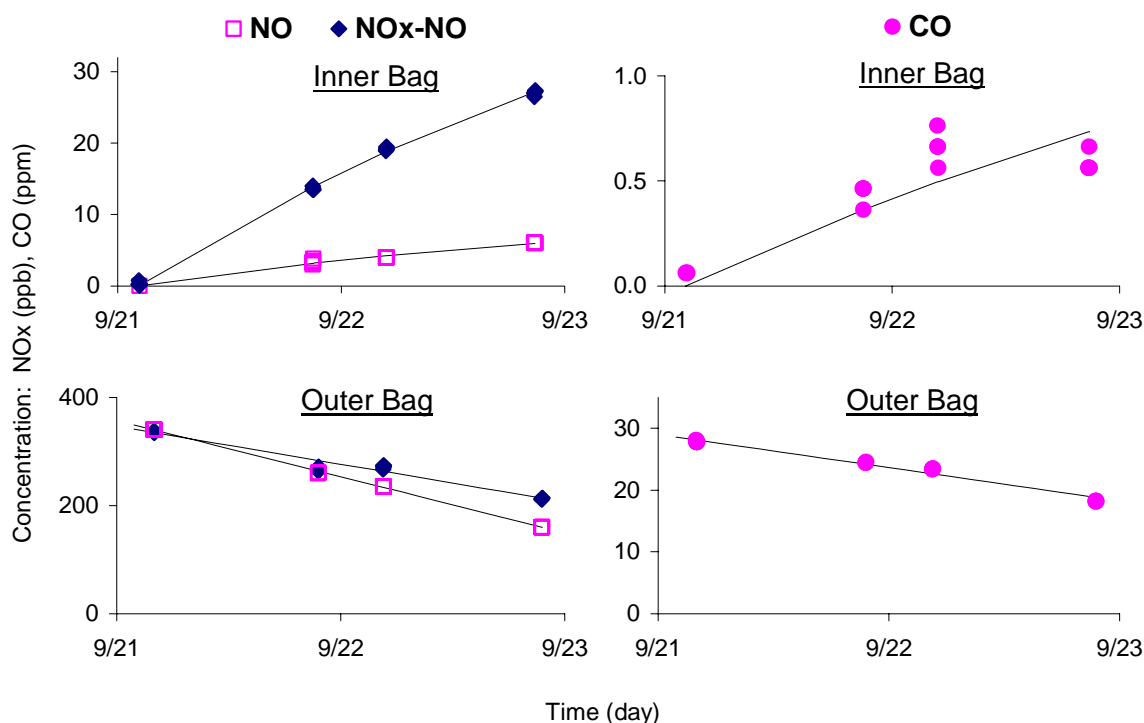


Figure 12. Results of FEP Teflon permeation tests with NO , NO_2 , and CO .

It can be seen that permeation was found to be non-negligible in this experiment, with the inner reactor concentrations increasing to ~13% the outer bag concentrations in the case of NO₂, and ~4% in the case of NO and CO, over the three day period. The higher apparent permeation rate of NO₂ (or NO_x-NO) is somewhat surprising considering the fact that the NO₂ molecule is larger than NO or CO, and suggests that there may be interactions between the NO₂ and the Teflon material beyond simple physical permeation. Note that the fact that the apparent permeation rates are different for different compounds indicates that it is not simply due to leakage.

The solid lines on Figure 12 show the results of calculations using a simple permeation model, as follows:

$$\Delta[C]_{\text{inner}} = \{(\text{Perm. Rate}) \times (\text{Area}) / (\text{Volume})\} \times ([C]_{\text{outer}} - [C]_{\text{inner}}) \times \Delta\text{time} \quad (\text{I})$$

where the permeation rate is a parameter adjusted to fit the data. The data are fit by the following permeation rates:

<u>Compound</u>	<u>Perm. Rate (m day⁻¹)</u>
NO	0.003
NO _x – NO	0.011
CO	0.003

For the surface/volume ration of the pillowbags used in this phase of the study, which is ~5 m⁻¹, this permeation corresponds to input of up to ~6% of the ambient NO_x per day, or ~3 ppb/day if the ambient NO₂ is ~50 ppb. This is clearly non-negligible for the low NO_x evaluations using these reactors. For the expected surface/volume of the large reactors for the new chamber being developed for this project, which is ~1.3 m⁻¹, this corresponds to ~1.5% of the ambient NO_x per day, which can still be non-negligible. This is assuming that there are no significant leaks, which would obviously increase the apparent permeation rates.

Since it appears that permeation can be non-negligible, it is apparent that if this type of Teflon material is used for the reactor then it is necessary that the air surrounding the reactor be purified. As discussed in previous sections, this will be done by using a “clean room” chamber enclosure room that is continuously flushed with purified air. For the exploratory pillowbag experiments carried out during the current phase of the program this is accomplished by placing the reactor where the experiment is conducted inside an outer bag that is flushed with purified air. The contents of the outer reactor were also monitored periodically during the course of the experiments to assure that it does not become contaminated.

Another approach would be to construct the reactor with thicker material to minimize permeation. However, this is not preferred for this project because we believe that collapsible reactors are desirable to minimize cleaning time between experiments, and thicker materials may be less suitable for this purpose. Thicker material is also more expensive and may be more difficult to seal. Even if thicker material is used, it may still be necessary to enclose it in a clean room or outer enclosure to minimize contamination due to leaks, further reducing the advantages of using the thicker material.

Chamber Effects Evaluation Experiments

Uncharacterized chamber effects, particularly those related to NO_x offgasing and background reactivity, are probably the most important factor limiting the potential utility of environmental chamber experiments for simulating low NO_x conditions. Background reactivity and NO_x offgasing is known to be non-negligible in existing environmental chambers, as evidenced by the formation of O₃ in pure air

experiments and in aldehyde – air or VOC – air irradiations with no added NO_x. For that reason, most of the experiments carried out were aimed at investigating this problem and assessing procedures to quantify and minimize it.

As indicated on Table 3, above, a number of different reactors were employed in experiments carried out during this reporting period to assess background reactivity effects. A summary of these reactors is given in Table 4, which also indicates the codes used to identify the reactors in the run summary listing in Table 3. The “Taped” column indicates whether the green polyester reinforcing tape with silicone adhesive was used to reinforce the reactors, since high temperature offgasing experiments, discussed later, suggest that this tape may be a source of background NO_x. As discussed above, all reactors were of “pillowbag” construction, though with some differences in size and construction method as indicated on the table. Although most of the reactors were constructed of the 2 mil FEP Teflon film that is currently the preferred material for constructing environmental chambers, reactors made of PFA Teflon and Kynar were also evaluated.

NO_x offgasing effects were evaluated both in dark and upon irradiation. The results of the individual dark offgasing measurements made during the various experiments are indicated where applicable in the run listing on Table 3. Generally offgasing of species in the dark was found to be very low or below detection limits except for a few cases where leaks or other problems were expected. For example, in run PB015 there was no measurable increase in NO, NO_x or CO levels in the FEP Teflon reactor after 25 days, and in run PB043 there was no measurable NO or CO after in the reactor after 22 days, and the final measured NO_x was only ~3 ppb. (It is uncertain what the initial concentrations were in the latter experiment, so this ~3 ppb NO_x may not necessarily be due to offgasing. Also, the outer bag was not continuously flushed with pure during the long term experiments, so some permeation of NO_x may have been occurring.

As indicated on Table 3, most of the chamber experiments carried out during this reporting period consisted of pure air experiments in order to measure background reactivity effects upon irradiation. Although measurements of NO_x and NO₂ were made during these experiments, the most sensitive measure of NO_x offgasing in these experiments is ozone formation. This is because NO_x is required for ozone formation, and at low reactant levels the productivity for NO_x to form ozone is quite high, calculated to be on the order of ~30 moles of O₃ per mole of NO_x under the conditions of most of the pure air experiments carried out in this project. Therefore, offgasing of NO_x at or below the detection limits of our instruments yields easily measured levels of ozone, particularly in multi-day irradiations.

The results of representative pure air experiments are shown on Figure 13. In these experiments approximately 30 ppb of O₃ was formed in about 30 hours of irradiation, though as discussed below this varied somewhat from run to run, depending on the reactor and other factors. The figure shows that measurable amounts of NO, NO₂, formaldehyde, and PAN are also formed, though it should be noted that the PAN yields were not quantified and are probably very low. CO is also formed in some experiments but as discussed below its yields varied more from run to run than was the case for the other pollutants.

The results of a model simulation adjusted to approximately fit these data are also shown on Figure 13. The model assumes that the only reactive compounds present initially are ~3 ppm of methane, ~8 ppb of ethane and ~5 ppb of propane. This is based on results of GC analyses carried out in comparable experiments, and is consistent with the fact that the pure air system employed does not remove methane or completely remove the lightest hydrocarbons. In order to fit the observed O₃ formation, it is necessary to assume some source of both radicals and NO_x in the system. (The NO_x source is necessary for O₃ formation to occur in the first place, and the radical source is necessary to drive the

Table 4. Summary of reaction bags and reaction bag designations used in the wall effects and other experiments carried out during this reporting period.

ID	Material	Taped?	Comments
F1	FEP Teflon	yes	This reactor was originally built for the BTC (Carter et al, 1995b) in 1998. Only in first experiment. Not used subsequently because it was found to leak excessively. No outer bag used.
F2x	FEP Teflon	yes	New reactor constructed for this project. Washed with deionized water prior to construction. No outer bag used in first experiment.
F2	(Same reactor as above)		Same reactor as above except that outer bag flushed with pure air was used. This was used for all subsequent reactors unless noted otherwise.
F3	FEP Teflon	yes	Slightly shorter than F2 to fit into outer reactor better. Washed with 10% methanol 90% water solution before sealing, then purged
K1	Kynar	yes	Similar construction and size as F3, except that Kynar was used instead of FEP Teflon.
P1	PFA Teflon	yes	Similar construction and size as F3, except that 2 mil, heat-sealable PFA Teflon (Type TPT) employed.
F4	FEP Teflon	yes	Constructed with only one pane, so only one side sealed. Subsequent bags made this way. Made using heat sealer that better controls sealing temperature.
F4a	(Same reactor as above)		Reactor F4 after exposure high concentration O ₃ produced by an ozonizer
F5	FEP Teflon	yes	Similar construction as F4.
F6	FEP Teflon	no	Constructed with only one pane, so only one side sealed. Subsequent bags also made this way. Made using new heat sealer.
F6na	(Same reactor as above)		Same as F6, but experiment had ~25 ppb HNO ₃ present.
F7x	FEP Teflon	yes	Smaller reactor. Made simultaneously and using same procedures as F8, except sealing tape was used. No outer bag used in first experiment with this reactor.
F7	(Same reactor as above)		Same reactor as above except that outer bag was used.
F8x	FEP Teflon	no	Made with same material at same time and using same dimensions as F7 except no sealing tape was employed. No outer bag used in first experiment with this reactor.
F8	(Same reactor as above)		Same reactor as above except that outer bag was used.

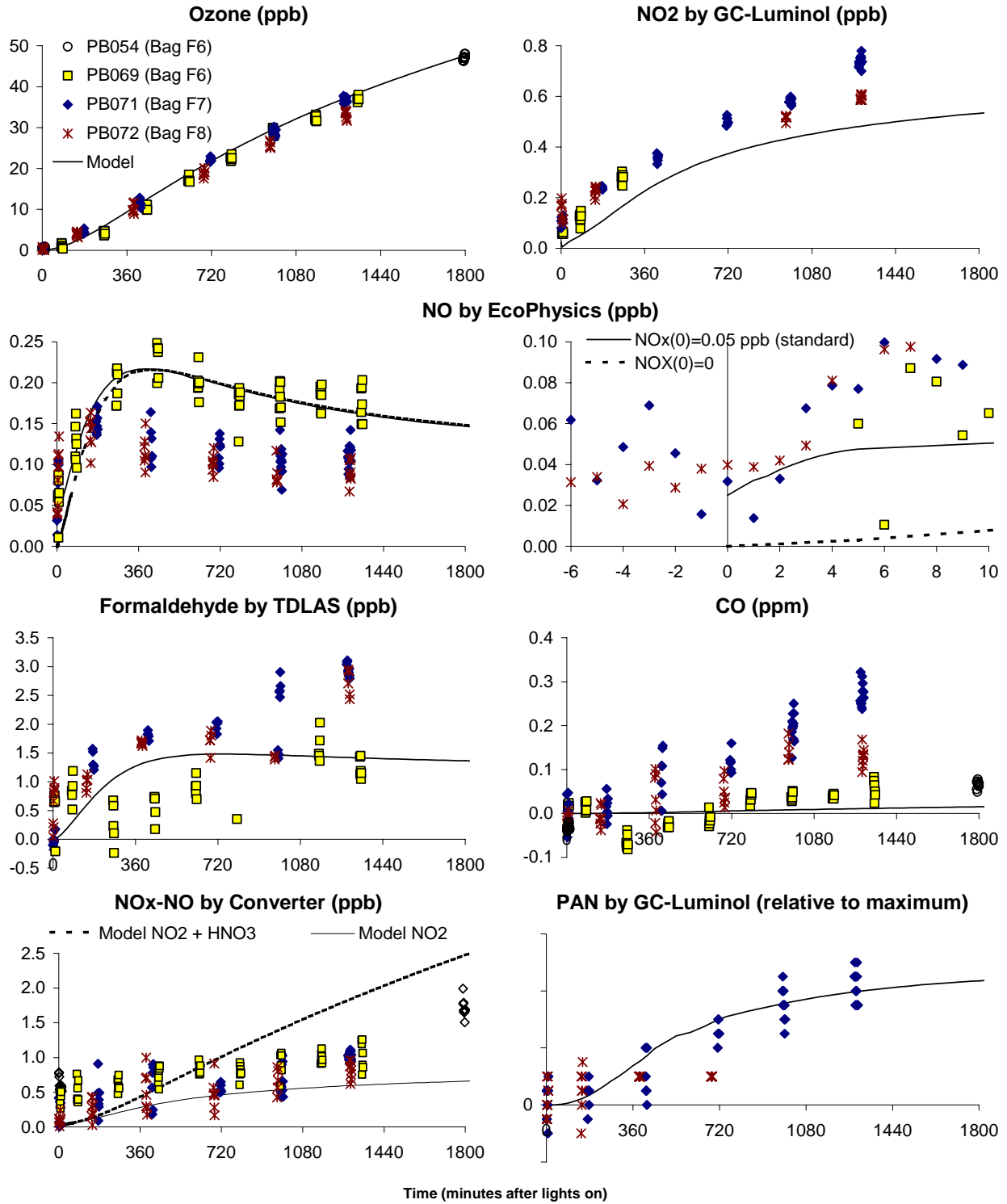


Figure 13. Experimental and calculated concentration-time plots for selected species in three representative and comparable pure air irradiations.

photochemical reactions involving O₃ formation from the NO_x and methane and trace amounts of VOCs – i.e., the methane, ethane and propane – that are present). As with model simulations of previous chamber experiments (e.g., Carter et al, 1997, 2000), both these can be accounted for by assuming offgasing of HONO, whose rapid photolysis supplies both NO_x and radicals. The simulation on the figure uses a HONO offgasing rate of 0.13 ppb HONO per hour and an NO₂ photolysis rate of 0.43 min⁻¹. It also assumes that a small amount (~0.1 ppb) of NO₂ is present initially in order simulate the relatively rapid rise of NO at the beginning of the simulation, as discussed below.

It can be seen that the model adjusted to fit the approximate ozone formation rate also gives a reasonable good simulation of the NO₂ levels as measured by the GC-luminol instrument, though it appears that if the model were adjusted to exactly fit O₃ it would tend to somewhat underpredict NO₂. However, the comparisons with the TDLAS NO₂ data, discussed above, suggest that the GC-luminol measurement may be somewhat high. It also gives a reasonably good simulation of NO in run PB069, though the NO concentrations in the other two experiments with high sensitivity NO data are somewhat lower. This is despite the fact that these three experiments had essentially the same measured O₃ and NO₂ concentrations. The reason for this discrepancy in the NO data is not presently known.

The dotted lines on the plots with the NO data show the results of calculations assuming that no NO_x is present initially, and shows that it is necessary to assume that a small amount of NO_x is present when the lights are turned on. The differences of the simulations of the other species (not shown) are minor. This amount is less than can be reliably detected by the current NO₂ or NO_x instrumentation, but clearly greater than the amount of initial NO. Therefore, it is not currently possible to determine whether the apparent NO₂ is present initially or rapidly released when the lights are turned on. This may be investigated later in this program using a more sensitive NO₂ analyzer as part of a collaborative project with Dr. Ronald Cohen of U.C. Berkley.

The model gives a fairly good simulation of the formaldehyde observed in the experiments, though it tends to somewhat underpredict the formaldehyde more often than otherwise. The predicted formaldehyde formation comes from the oxidation of the ~3 ppm methane, which is the greatest source of VOC reactivity in these experiments. The possibility of direct formaldehyde offgasing cannot be ruled out, and will be investigated in subsequent experiments using methane-free air.

The observed formation of very low levels of PAN suggest that some other reactive organic pollutants must be present besides methane, and it is most likely due to the reactions of the very small amount of ethane and propane that are also detected in the reactor air. The model predicts that ~35 ppt of PAN is formed in the simulation shown on Figure 13. Although the calibration of the present GC-luminol system for PAN is uncertain, preliminary PAN calibration data for this instrument suggest that this amount should be detectable when the instrument is operating well, and the data obtained are not inconsistent with this prediction.

The CO concentrations in the pure air irradiations were found to depend primarily on the age of the reactor. As indicated in the comments on Table 3, relatively high rates of CO formation was observed in the first pure air irradiation carried out in a new reactor, but the CO formation decreased significantly in subsequent experiments, and eventually was minor. The relatively high CO formation rates shown for Runs 71 and 72 on Figure 13 reflect the fact that in both cases these were the second experiments for the reactors used. Much lower CO formation was observed in runs 54 and 69, which were both carried out in a well-used reactor. Although the CO formed in the aged reactor experiments is somewhat larger than predicted by the model to be formed from the oxidations of the small amounts of reacting methane and other VOCs, the difference is insignificant in terms of effects on photochemical reactivity.

The rate of ozone formation in the pure air irradiations gradually decreased with time during an experiment, suggesting that eventually ozone maxima would be reached given a sufficiently long irradiation time. The results of essentially all the pure air irradiations, including those carried out for multiple days, could be fit by the following parameterization that takes this behavior into account:

$$O_3(t) = O_3^0 + O_3^F (1 - e^{-tR/O_3^F}) \quad (II)$$

where $O_3(t)$ is the ozone concentration at time= t , O_3^0 , O_3^F , and R are parameters adjusted to fit the data, where O_3^0 reflects the initial ozone concentration and is close to zero, R reflects the ozone formation rate at the beginning periods of the experiment, and O_3^F is the limiting final ozone concentration eventually achieved at sufficiently long irradiation times. It is the “ R ” parameter, which measures the instantaneous initial O_3 formation rate that is of most relevance to NO_x offgasing assessment. However, for experiments with relatively short irradiation times the O_3^F and R parameter are not both well determined, so we use the interpolated 12-hour O_3 formation rate, given as

$$12 \text{ hour } d[O_3]/dt = O_3^0 + O_3^F (1 - e^{-(12 \text{ hr}) \cdot R/O_3^F}) / (12 \text{ hr}), \quad (III)$$

for run-to-run comparisons. From Figure 13 it can be seen that the O_3 formation rate at 12 hours is not greatly different from the O_3 formation rate at the beginning of the experiment, and thus gives a useful measure that is sensitive to NO_x offgasing rates for comparison purposes.

Figure 14 shows a plot of the 12-hour interpolated O_3 formation rates in the pure air experiments against run number, where different symbols are used for the different reactors or reactor conditions, using the designations given on Table 4. It can be seen that the O_3 formation rates, and thus the NO_x offgasing rates they reflect, tend to be variable, ranging from no more than 0.5 ppb/hour to higher than 5 ppb/hour. The highest O_3 formation rates occurred in the reactor after it was treated with high concentration O_3 . The next highest O_3 formation rates were observed in the first reactor that was used in this study, which may have had some contamination initially since the O_3 formation rate was declining with time after a series of repeated pure air irradiations. On the other hand, the O_3 formation rates in the experiments with Reactor F5 were relatively high initially and did not decline. Higher O_3 formation rates were observed in the few experiments carried out without using the outer bag flushed with pure air, as expected due to permeation. Most of the pure air experiments reactors tended to have O_3 formation rates in the 0.5 – 2 ppb/hour range, with relatively little difference between them. In particular, the results of the pure air irradiations in the PFA Teflon or Kynar reactors were within the range observed for the “cleaner” FEP Teflon reactors.

The largest number of experiments employed Reactor F6, and Figure 14 shows that the results were somewhat variable. Figure 15 shows the O_3 formation rates in the pure air runs in that reactor in relationship with the other experiments carried out using that reactor. It can be seen that the O_3 formation rate declined monotonically in the new reactor and then leveled off at the minimum of ~0.5-0.7 ppb/hour, but higher O_3 formation rates were observed in experiments following runs where added NO_x was employed. Pure air runs following pure air runs or a formaldehyde – air run without added NO_x tended to have O_3 formation rates within the low range. However, the experiments following runs where 50-100 ppb of NO_x or ~20 ppb of HNO_3 was present tended to have somewhat higher O_3 formation rates.

Figure 16 shows plots of the experimentally measured interpolated 12-hour O_3 formation rates against the interpolated 12-hour NO_x formation rates for the same experiments, obtained from the NO_x channel of the $NO-NO_x$ analyzer. The latter was obtained in an analogous manner as the 12-hour interpolated O_3 formation rates, except that the initial NO_x , which in many experiments was a non-negligible fraction of the final levels, was not included. Therefore, it reflects only the increase in the NO_x

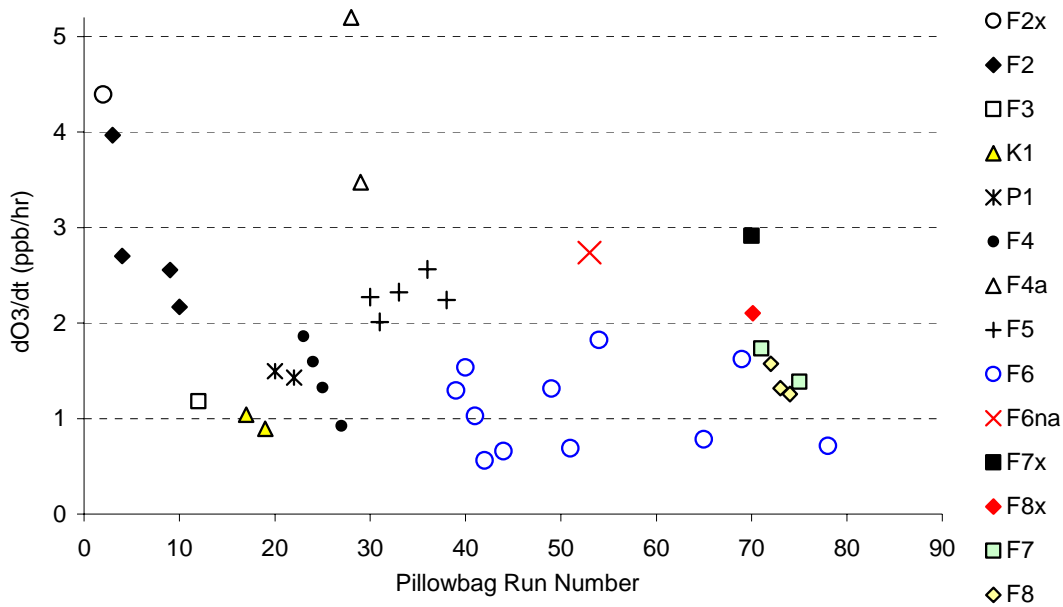


Figure 14. Plots of 12-hour ozone formation rates in the pure air runs against run number in the pure air and HNO₃ irradiation experiments. Reaction bag designations are given on Table 4.

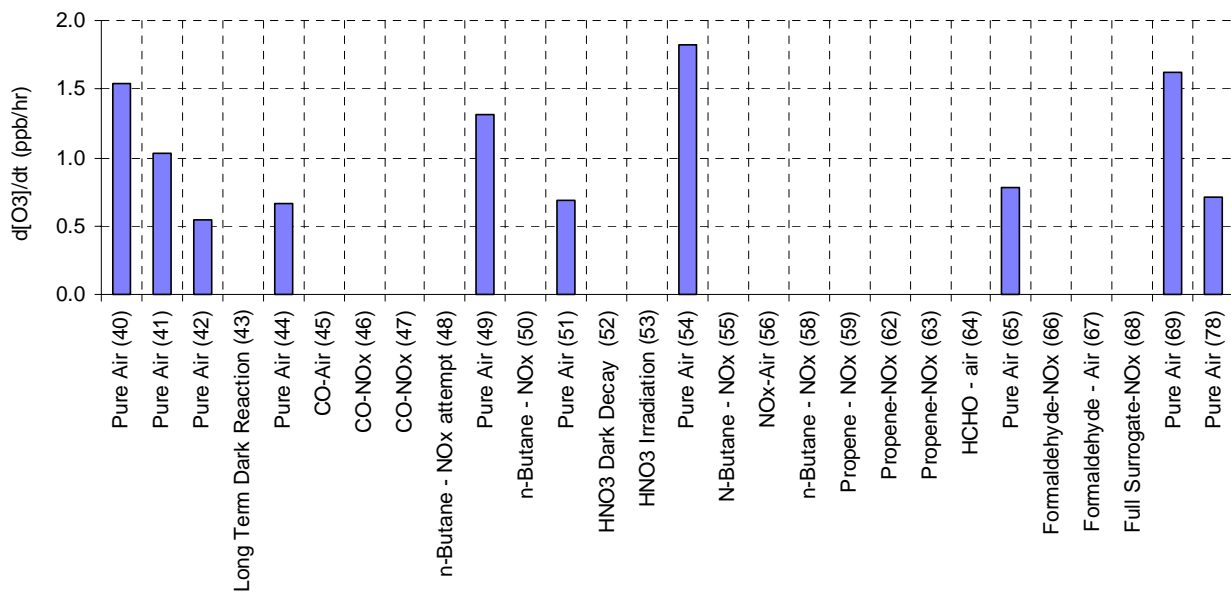


Figure 15. Ozone formation rates in pure air experiments in Reactor F6, showing types of experiments carried out previously in that reactor.

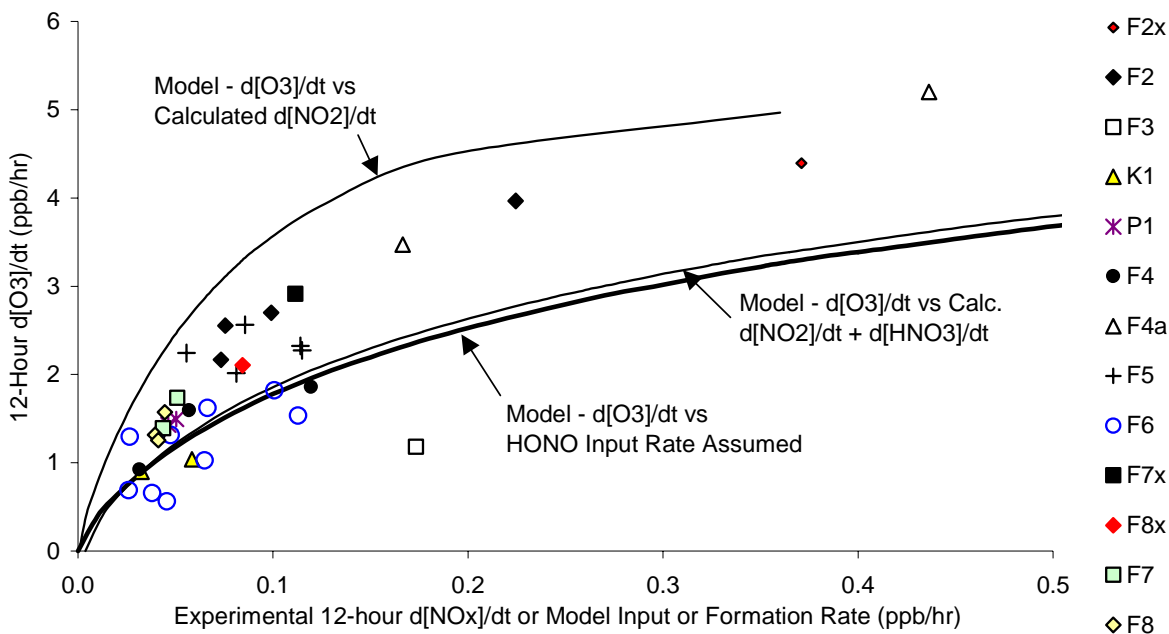


Figure 16. Plots of interpolated 12-hour ozone formation rates against interpolated 12-hour NO_x formation rates in the pure air experiments. Reaction bag designations are given on Table 4.

levels as measured during the experiment. A similar plot the ozone formation rates against the NO₂ formation rates for those experiments with useable NO₂ data is shown on Figure 17.

It can be seen from Figure 16 that there is a definite correlation between O₃ formation rates and the measured increases in NO_x during the experiments, except for run PB012, where the NO_x input rate appears to be anomalously high. Other than that apparently anomalous experiment, the relationship between d[O₃]/dt and d[NO_x]/dt does not appear to depend on the reactor or the treatment of the reactor. However, there is some scatter in the data, particularly in the experiments in Reactor F6 where the lower level of O₃ formation rates were observed. The relationship is clear, however, in the experiments with the highest O₃ formation rates, indicating a clear relationship between O₃ formation and measured NO_x offgassing in those runs.

Results of model calculations of the relationship between NO_x and O₃ formation in the pure air runs are also shown on Figure 16. All those calculations used the initial methane, ethane and propane based on the GC measurements discussed above, and modeled NO_x offgassing at a continuous HONO flux, which was varied to determine the dependence of NO_x input on O₃. The figure shows the calculated dependence on the O₃ formation rate as a function of the HONO input rate used in the model, and also the calculated O₃ formation rates against the calculated rates of input of NO₂ or NO₂ + HNO₃, all interpolated for 12 hours of irradiation. Note that the curves for the d[O₃]/dt vs HONO input is very close for that for d[O₃]/dt vs (d[NO_x]/dt + d[HNO₃]/dt) because essentially all the NO_x input ends up as NO₂ or HNO₃, and the amount of HNO₃ lost on the walls in a 12-hour irradiation is calculated to be minor, based on the results of the HNO₃ dark decay rate experiment. On the other hand, the curve for d[O₃]/dt vs d[NO₂]/dt is significantly higher because only a fraction of the NO_x input ends up as NO₂, which means that the O₃ formation rate corresponding to a given NO₂ level is higher than the rate corresponding to the same NO_x level.

Most of the experimental data, particularly for the higher O_3 and NO_x experiments where the relationship is more clear, fall between the calculated curves for NO_2 and $NO_2 + HNO_3$. This suggests that either the “ NO_x ” measurements made by the commercial $NO-NO_x$ analyzer is not responding to all the HNO_3 that is present, or that the HNO_3 wall losses are much higher in these experiments than in the experiment where ~ 20 ppb of HNO_3 was injected and irradiated. Measurements of HNO_3 by TDLAS or other direct means, when available, may be helpful in elucidating this issue.

Figure 17 shows that the relationship between O_3 and NO_2 is even clearer than is the case for O_3 and NO_x , because there is less scatter in the data. The relationship is also in reasonable agreement with model predictions, though the model consistently predicts a higher O_3 / NO_2 ratio than is observed experimentally. The presence of ~ 20 ppb of HNO_3 does not appear to have a large effect on the relationship between O_3 and NO_2 ; although the O_3 / NO_2 ratio is somewhat lower in the run with HNO_3 there are too few experiments to determine whether the difference is significant.

Figure 18 shows a plot of the extrapolated maximum O_3 against the 12-hour O_3 formation rate. The results of model calculations with the variable NO_x input rates are also shown. These are $O_3(F)$ parameters derived to fit the data for those experiments with sufficiently long irradiation time to give a reasonably unambiguous determination of the extrapolated maximum ozone. It can be seen that the maximum O_3 levels tend to be ~ 100 - 200 ppb, with no clear differences between reactors or relationship with the O_3 formation rates observed in the reactors. Given that the O_3 maxima are all extrapolations, the experimental results can probably be considered to be the same to within the uncertainty of the derivations. The model is consistent with the data in predicting only a relatively weak relationship between O_3 formation rate and maximum O_3 level, but it tends to underpredict the by a factor of 2-3. This could be attributed to small amounts of reactive VOC impurities besides the methane, ethane, and

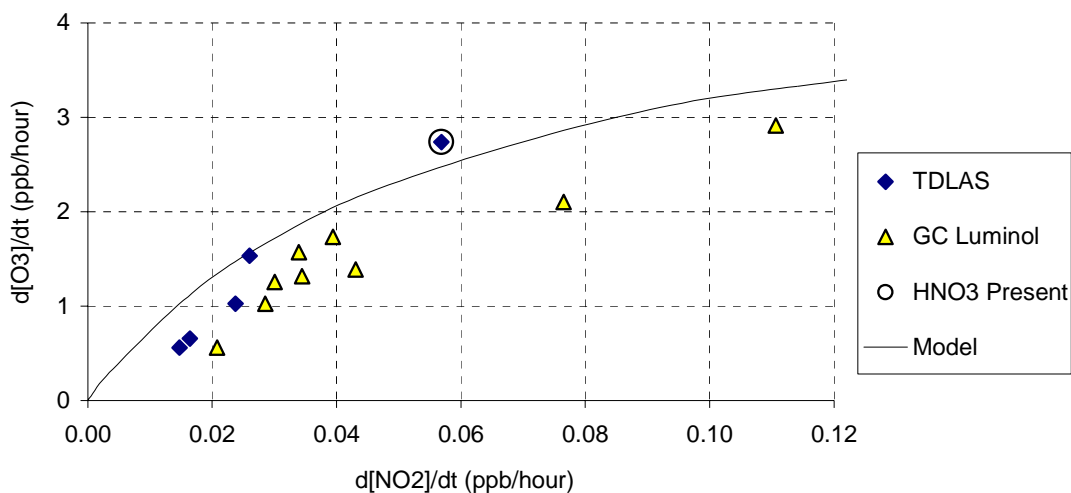


Figure 17. Plots of 12-hour ozone formation rates against NO_2 formation in the pure air and HNO_3 irradiation experiments where NO_2 data are available. Results of model predictions of the relationships between these rates are also shown.

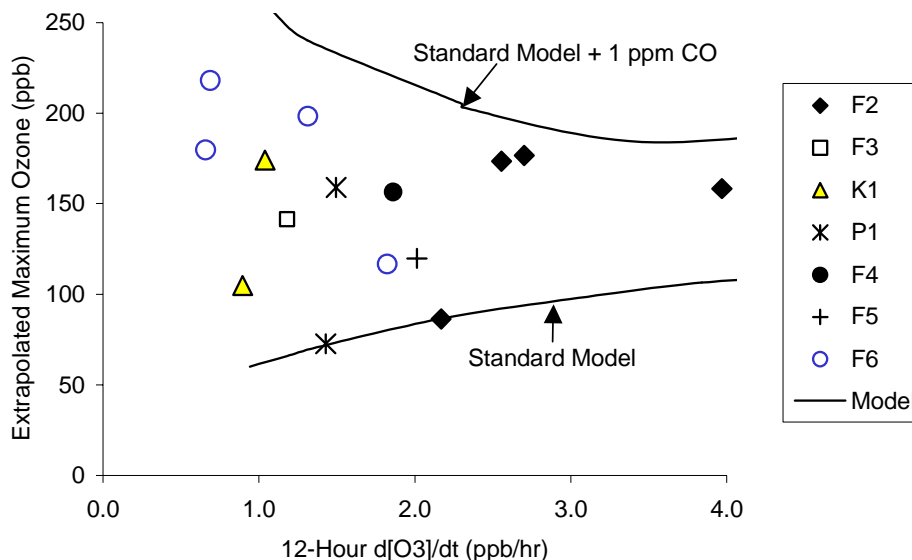


Figure 18. Plots of extrapolated maximum ozone (the O_3^F Parameter of equation III) from fits of concentration-time data for ozone formation in pure air irradiations lasting at least 36 hours against 12-hour ozone formation rate. Reaction bag designations are given in Table 4.

propane measured in the matrix air, since calculations indicate that small amounts of additional VOC can significantly increase this maximum ozone. The effect of additional reactive VOC can be simulated by adding additional CO in the simulation, and the figure shows that the equivalent of less than 1 ppm of CO is sufficient to account for this discrepancy. Note that the small amount of added VOC does not significantly affect the predicted O_3 formation rates, as discussed below.

The effects of added VOCs on results of irradiations without added NO_x were investigated by carrying out several CO – air irradiations and a formaldehyde – air irradiations in these reactors. The 12-hour ozone formation rates observed in these experiments are shown in Figure 19, along with results of pure air irradiations carried out in the same reactor under the most similar conditions. The data are plotted against the amount of reactive VOC initially present expressed as “CO equivalents”, which the concentration of the VOC multiplied by its OH rate constant and the number of NO to NO_2 conversions in its mechanism, divided by the OH rate constant for CO and its number of NO to NO_2 conversions. The NO to NO_2 conversion numbers used in this computation was 1.0 for CO and formaldehyde and 2.0 for methane, ethane, and propane. Results of model calculations of the effects of the O_3 formation rates on the CO equivalents (represented by added CO), with NO_x inputs adjusted to fit the O_3 formation rates in the representative pure air runs, are also shown on the figure.

The results of the experiments and model calculations indicate that although the added VOCs can affect the final O_3 yield given sufficiently long irradiation time, the effects on O_3 formation rates in a 12-hour experiment are relatively small, especially in reactors with low NO_x input rates. The largest effect of added VOCs is predicted for the conditions Reactor F2, which had the highest apparent NO_x input rate, and the data obtained are reasonably consistent with model predictions. The effect of the added CO was larger than model prediction in Reactor F3, perhaps due to variable NO_x input in the reactor. The model predicted that the added VOC would have almost no effect on O_3 formation rates under the conditions of

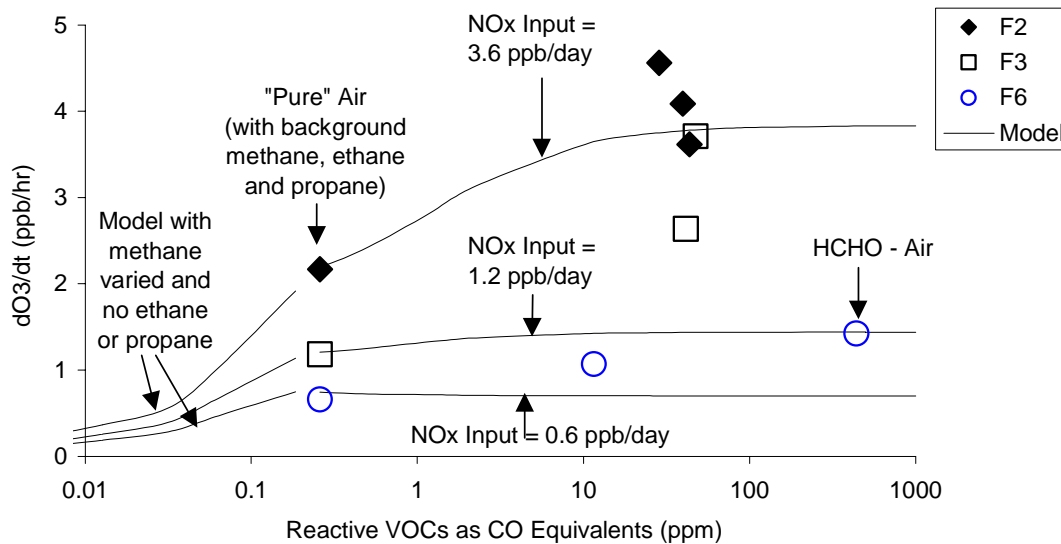


Figure 19. Plots of experimental and calculated 12-hour interpolated ozone formation rates in CO – air, formaldehyde – air, and selected comparable pure air irradiations against initial VOC concentrations as CO equivalents. The model simulations with lower CO equivalents than the “pure air” experiments are with the background ethane and propane removed and the background methane reduced by variable amounts, while those at higher CO equivalents are with the background pure air with variable amounts of CO added.

the relatively low NO_x input rate indicated by the results of the in pure air runs following other pure air runs in Reactor F6. Although the experimental O_3 formation rates in the added CO or formaldehyde runs carried out in that reactor were somewhat higher than predicted by this model, they were within the variability of the results of the pure air runs in that reactor. Note that the formaldehyde – air run was carried out following an added NO_x experiment, which may result in higher apparent NO_x input rates (see Figure 15).

Although additional work is required once the full analytical capability is available, the results to date have provided useful information concerning NO_x offgasing effects that will have relevance to this project. The following observations and tentative conclusions can be made based on the results of the experiments discussed in this section.

- Offgasing of NO , NO_2 , or other NO_x species in the dark is not significant, and if it occurs at all the rate is not sufficient to account for the apparent NO_x offgasing indicated by the results of the irradiation experiments.
- Regardless of which reactor or cleaning treatment was used, pure air irradiations were always found to result in measurable formation of O_3 and measurable increases in NO_2 and NO_x . The rates of O_3 formation appear to be highly correlated to the rates of increase in NO_2 and NO_x . The relationship between formation rates for NO_2 and O_3 is reasonably consistent with model predictions, though the model may be underpredicting the NO_2 when adjusted to fit the O_3 .
- Regardless of which reactor or cleaning treatment was used, the ozone formation rates were never less than 0.5 ppb/hour, indicating a lower limit for NO_x offgasing for the types of reactors examined. Based on the light intensity and the measured background VOC levels, this

corresponds to a lower limit NO_x offgasing rate of ~0.02 ppb per hour, or ~0.4 ppb per 24-hour day.

- The ozone formation had some variability from run to run for the same reactor, with the variability range for the reactor with the lowest O₃ formation rates being ~0.5 ppb/hour to ~2 ppb/hour. The higher rate corresponds to an estimated NO_x offgasing rate of ~3 ppb per 24-hour day. The variability may be due to the experiment carried out previously in the reactor, since pure air runs in Reactor F6 tended to have lower O₃ formation rates if they followed other pure air runs than if they followed runs where NO_x or HNO₃ were injected. This suggests that pure air irradiations (or flushing the reactors with the lights on) may serve as a means to clean the reactor following runs where NO_x is injected.
- Newly constructed FEP Teflon reactors tend to have significantly higher CO offgasing rates and (in most cases) somewhat higher apparent NO_x offgasing rates than reactors that have been conditioned using pure air irradiations. The source of the CO and NO_x offgasing is unknown. Although the CO offgasing becomes negligible after conditioning, as indicated above the apparent NO_x offgasing eventually levels off and does not decrease further.
- The ozone formation rates were higher in the first reactor employed in this study (F2), and for reactor F5, compared to most of the other reactors, at least for the standard experiments. The reason for this is not entirely clear. The O₃ formation rates in Reactor F2 appeared to be declining with subsequent pure air experiments, but this did not appear to be the case for Reactor F5.
- Washing the reactors with distilled water or with water/methanol solution did not eliminate the NO_x offgasing that caused the ozone formation in the pure air runs. It may, however, result in reactors that do not have high ozone formation rates initially.
- The ozone formation rates in the PFA Teflon and Kynar reactors were not significantly different than observed in the FEP Teflon reactors that had the lowest ozone formation rates. Therefore, there does not appear to be any advantage of using these materials for the reactors in place of the type of FEP Teflon that is commonly employed.
- Treatment of the reactor walls with high concentration O₃ does not remove the NO_x (or NO_x precursors) that is responsible for this O₃ formation. Instead, it caused NO_x offgasing and therefore O₃ formation to increase significantly, perhaps due to the NO_x introduced with the O₃ due to the action of the discharge in the ozonizer on the N₂ impurity in the O₂. The apparent NO_x contamination decreased in subsequent experiments, but not to the level observed prior to the O₃ treatment.
- The use of the outer reactor flushed with pure air reduced the O₃ formation rate in the pure air runs, though the effect was not large except for Reactor F7. This indicates that permeation may be playing a role, in the case of Reactor F7 a physical leak may also be a factor.
- The experiment with added HNO₃ had a somewhat higher O₃ formation rate than the pure air runs in the same reactor, but not dramatically so. The photolysis of the ~20 ppb of HNO₃ in that experiment is calculated to provide a NO_x input at a rate of ~0.02 ppb/hour, which is comparable to the NO_x input rate indicated by the results of the pure air with the lowest O₃ formation rates. Although this is a non-negligible NO_x input, it is not sufficient to account for the increased O₃ formation rate observed when HNO₃ is added. This suggests that the presence of HNO₃ tends to increase NO_x offgasing due to heterogeneous processes.

Note that these conclusions are applicable for the relatively small “pillowbag” reactors that were used in this investigation, which have a significantly larger surface/volume ratio than the larger reactors that will be constructed for the new chamber facility. Therefore, the offgasing and background effects in

the new chamber should be less than observed in these experiments. For this reason, the lower limit NO_x offgasing rate of ~ 0.4 ppb/day indicated by the data from these experiments may be considered to be an upper limit for the minimum NO_x offgasing rate in the new chamber. This suggests that mechanism evaluation experiments with NO_x levels of at least ~ 5 ppb should be feasible without the data being dominated by these NO_x offgasing effects. Useful data from lower NO_x experiments may be feasible in the larger reactor, especially if the NO_x offgasing effects are found to be predictable and well characterized after the reactors are appropriately conditioned.

Radical Source Experiments

Another important chamber effect that needs to be characterized when using chamber data for mechanism evaluation is the chamber radical source (Carter et al, 1982). As discussed previously (Carter et al, 1995), this is best measured by conducting n-butane - NO_x or CO - NO_x experiments and determining the radical input rate needed to assume for models to simulate the observed NO oxidation and O_3 formation rates. Previous experiments that the radical source depended on NO_2 levels in the SAPRC evacuable chamber, but no consistent dependence of the magnitude of the radical source on NO_x levels could be determined in experiments using FEP Teflon film reactors such as employed in this study.

As indicated on Table 3, a total of 8 n-butane - NO_x or CO - NO_x irradiations were carried out in the pillowbag reactors in conjunction with the NO_x offgasing experiments discussed in the previous section. The initial NO_x in most experiments ranged from 50 to 150 ppb. The data were modeled by assuming that the radical source consisted entirely of light-induced HONO offgasing, which is the same processes assumed when modeling the NO_x offgasing effects discussed in the previous section. As discussed below it is more likely that in the higher NO_x experiments the process more likely involves heterogeneous conversion of NO_2 to HONO rather than simply HONO offgasing, but since the loss of NO_2 caused by this conversion is insignificant compared to the amount of NO_x injected, the net effect is the same as simple HONO offgasing.

The conditions and results of the radical source experiments are summarized on Table 5, and Figure 20 shows the HONO input rates that best fit the results of these experiments against the initial NO, NO_2 , and NO_x concentrations. The “zero NO_x ” point is the HONO input rate that best fit the CO - NO_x experiment PB045, which at 0.03 ppb/hour is near the middle of the range that best fits the data for the pure air irradiations in Reactor F6, which was used in most of these experiments (see Figure 16). It can be seen that the radical source rate needed to fit the data for these experiments is significantly higher than the NO_x offgasing rates needed to fit the pure air and other no-added- NO_x experiments, and that there is a relationship between the NO_x levels and the apparent radical source in these experiments.

Figure 20 shows that the correlation between the apparent radical input rate and initial NO, NO_2 , and total NO_x levels is not perfect, with scatter on each of the corresponding plots. The best correlation of the three is with initial NO_x , where a smooth apparently quadratic relationship is observed for all experiments except for run PB047, where the radical source is much less than predicted by the relationship that fits the results of the other runs. This can be explained if it is assumed that the radical source depends on the instantaneous NO_2 concentrations, which in most experiments are better represented by the initial NO_x levels than the initial NO_2 . This is because in most experiments most of the initial NO is converted to NO_2 , and the amount of NO_2 formed from the initially present NO is generally higher than the amount of NO_2 initially present. Run PB047 does not fall into this relationship because less than half of the initial NO is converted to NO_2 , as indicated by the relatively high final NO concentration in the experiments.

Table 5. Summary of conditions and results of the radical source experiments carried out during this reporting period.

Run	React'r	Initial NO (ppb)	Initial NO ₂ (ppb)	Final NO (ppm)	Initial CO (ppm)	Initial n-Butane (ppm)	Best Fit d[HONO]/dt (ppb/hr)
PB045	F6	0	0	0	11		0.03
PB050	F6	47	3	17		0.10	0.19
PB046	F6	42	15	7	11		0.21
PB047	F6	116	7	62	22		0.21
PB058	F6	40	3	8		0.11	0.26
PB055	F6	9	42	2		0.13	0.31
PB034	F5	65	35	5		1.01	0.8
PB032	F5	95	47	2		1.33	1.6

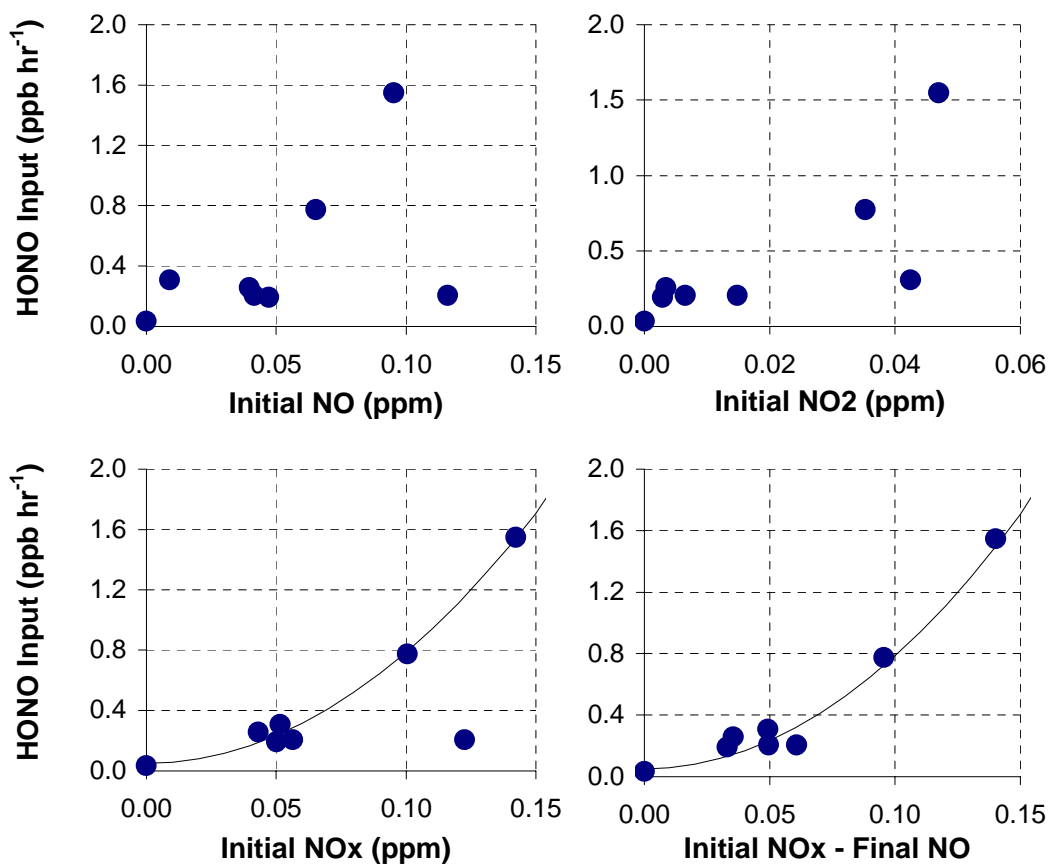


Figure 20. Plots of best-fit HONO input rates against initial NO_x, initial NO₂, and initial NO_x – final NO for the n-butane - NO_x and CO - air irradiations. Quadratic fit of the relationship to initial NO_x is also shown.

This suggests that the apparent radical source should have the best correlation to the *average* NO₂ concentration, whose relationship to the initial concentrations will vary from run to run. Unfortunately, specific NO₂ data for most of these experiments are sparse or unreliable, so the average NO₂ for all the experiments could not be computed. However, the initial NO_x – final NO concentration can give an indication of the average NO₂ concentration which, while not perfect, is better than just the initial NO_x. Figure 20 shows that if this is used, then the data for PB045 becomes consistent with the radical source vs. NO_x relationship derived from the other experiments.

It is interesting to see if the relationship between initial NO_x – final NO and the radical source observed in the experiments in these clean pillowbag reactors under relatively low NO_x conditions also holds for the radical source experiments carried out under higher NO_x conditions in the larger Teflon bag reactors used in our previous chambers. Figure 21 shows a plot of the radical input rate (modeled as HONO offgassing) divided by the NO₂ photolysis rate against the initial NO_x – final NO for these experiments and also for the experiments carried out in the CE-CERT DTC that were used when evaluating the SAPRC-99 mechanism (Carter, 2000). Experiments with anomalously high radical input rates attributable to known contamination effects are not shown. Although the experiments in DTC characterization set 3 were also considered to have anomalously high radical input rates (Carter et al, 1995b), Figure 21 shows that this is probably because these experiments were carried out using higher NO₂ levels than most radical source determinations in this reactor. Although there is some scatter, Figure 21 shows that there is indeed a dependence of the radical source rate on the estimated average NO₂ levels, and when the data are adjusted for differences in light intensity the relationship is entirely consistent with that derived from the data in this study at lower NO_x levels. However, if the DTC Characterization set 3 data are included, the data are better fit by a linear fit rather than the quadratic fit indicated by the lower NO_x data obtained in this study.

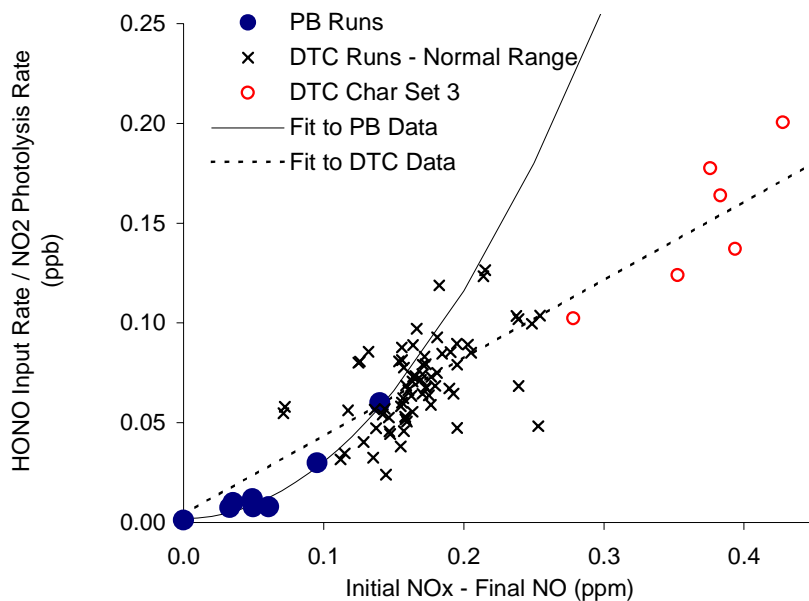


Figure 21. Plots of ratios of best-fit HONO input rates to NO₂ photolysis rates against initial NO_x – final NO for radical source characterization runs carried out in this study and in the CE-CERT DTC.

These data suggest that the radical source is probably light-induced heterogeneous reaction of NO_2 , presumably being converted to HONO on the reactor walls. This is probably a separate process than the NO_x offgasing, contrary to the way it is represented in the current chamber model. The low concentration radical source data suggest second-order kinetics for this process, but this does not appear to be consistent with the data at higher concentrations using another reactor. However, the DTC data were obtained in a reactor with much larger volume and lower surface/volume ratio, so the fact that they appear to fit by the same line as the data obtained in this study may be coincidental. It clearly would be useful to conduct radical source experiments at higher NO_x levels in this reactor, and investigate the appropriate wall model that would fit the full range of conditions.

Other Evaluation Experiments

As indicated on Table 3, above, four propene - NO_x , two formaldehyde – air, and one surrogate - NO_x experiment were carried out in the pillowbag reactors during this reporting period. The objectives included evaluating the analytical instrumentation and the chamber characterization, determining the effects of exposure of the reactor to the conditions of the experiments on the results of subsequent characterization runs, and obtaining preliminary model evaluation information under lower reactant concentration conditions than previously employed. The experiments were modeled using the SAPRC-99 mechanism (Carter, 2000), using photolysis rates calculated using an assumed NO_2 photolysis rate of 0.43 min^{-1} and the blacklight spectral distribution as discussed above, and the quadratic radical source vs. NO_x dependence that fit the data on Figure 21 as discussed in the previous section.

The experimental and calculated results of the propene - NO_x experiments with 15 ppb of NO_x or higher are shown on Figure 22. The model fit the ozone data well for the run with the highest reactant concentrations, but tended to overpredict ozone somewhat in the lower concentration experiments, especially the run where the lowest levels were employed. Only run PB059 had NO_2 data from both the TDLAS and GC-luminol, and although the TDLAS gave lower concentrations than measured by the GC-luminol and predicted by the model in the middle of the experiment, both instruments and the model gave essentially the final NO_2 concentration in the experiment. Formaldehyde data by TDLAS were available for run PB063, and although the model gave a reasonably good prediction of the maximum formaldehyde concentration, it significantly underpredicted the formaldehyde decay rate. This is despite the fact that the O_3 and NO data for run PB063 would have been better simulated had a lower light intensity been assumed.

The results of the propene - NO_x experiment at the lowest NO_x level (~9 ppb) are shown on Figure 23. An attempt was made to measure nitric acid by TDLAS during this run, but although the model predicted the HNO_3 should have been formed at levels just above the detection limit, it was not detected. Although the model gave a good simulation of the propene decay rate, it significantly overpredicted the O_3 and the O_3 and NO data would have been much better fit had a much lower light intensity been assumed. The reason for this poor model performance has not been determined.

The results of the two formaldehyde – air experiments are shown on Figure 24. The two runs give essentially the same ozone formation, and the implications of these results in terms of our NO_x offgasing evaluation were discussed previously. The NO_x input rate in the model was adjusted to fit the O_3 data. It can be seen that the model underpredicted the formaldehyde consumption rate, which is consistent with the discrepancy observed in the simulation of the formaldehyde data in the propene - NO_x experiment discussed above. It has not been determined whether this is a problem with the mechanism or the light characterization. The data obtained in the new chamber should be helpful in elucidating this.

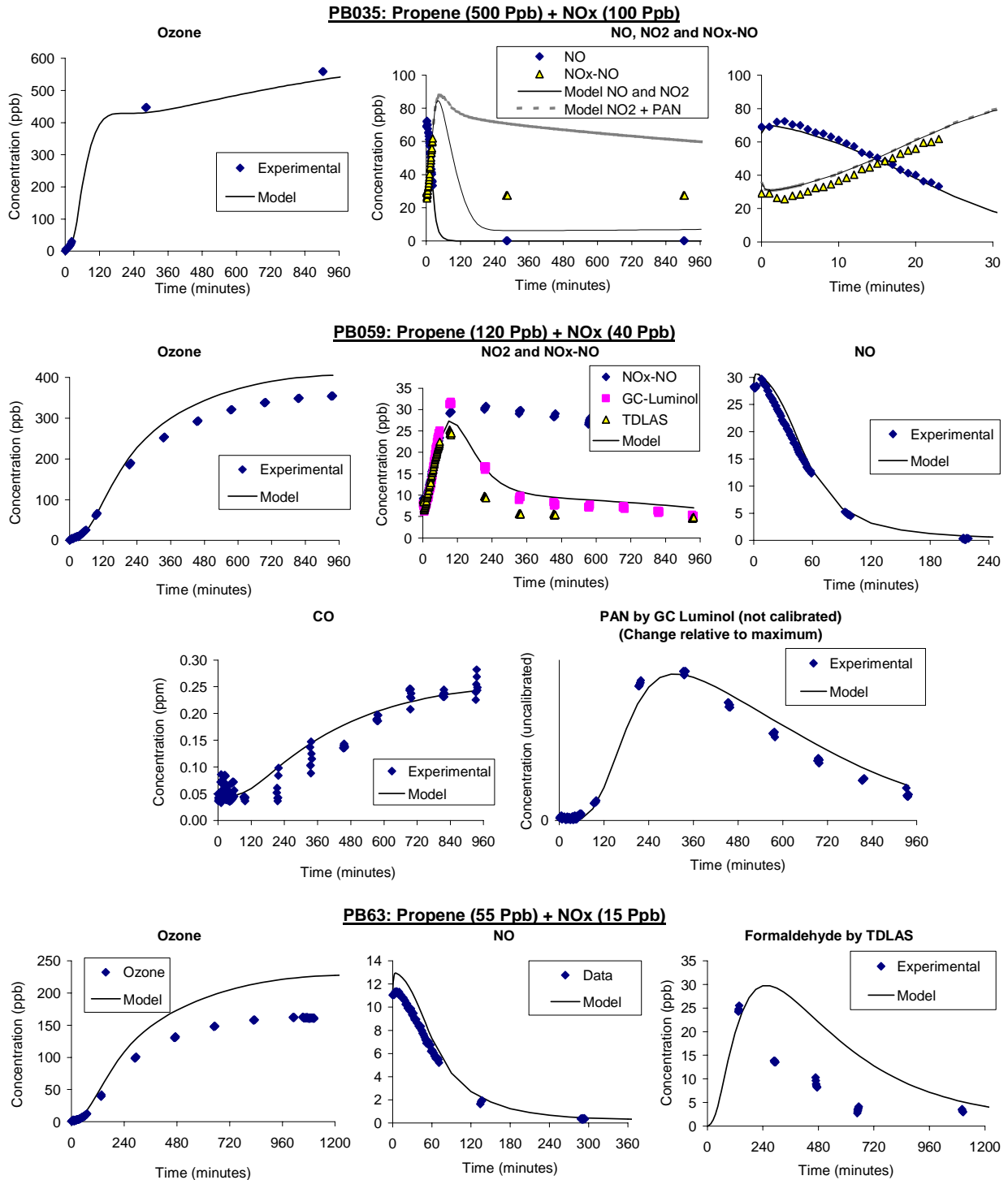


Figure 22. Experimental and calculated concentration-time plots for selected species in the three propene - NO_x experiments with initial NO_x of 15 ppb or higher.

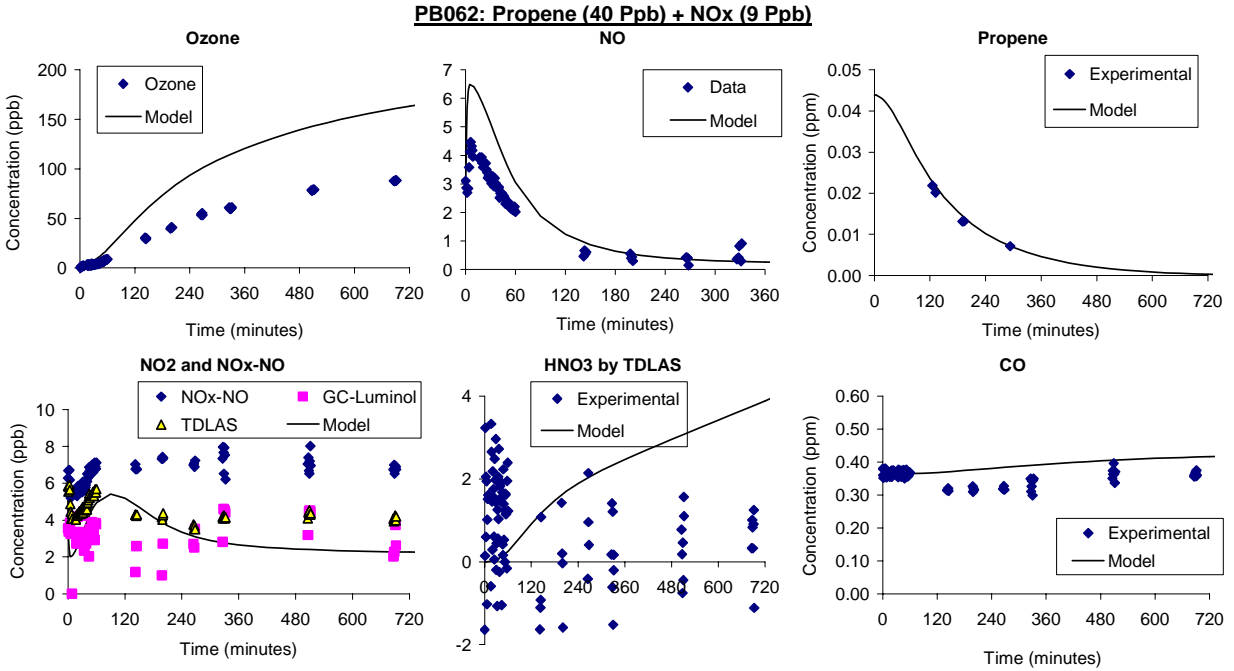


Figure 23. Experimental and calculated concentration-time plots for selected species in the propene - NO_x experiment with ~9 ppb initial NO_x.

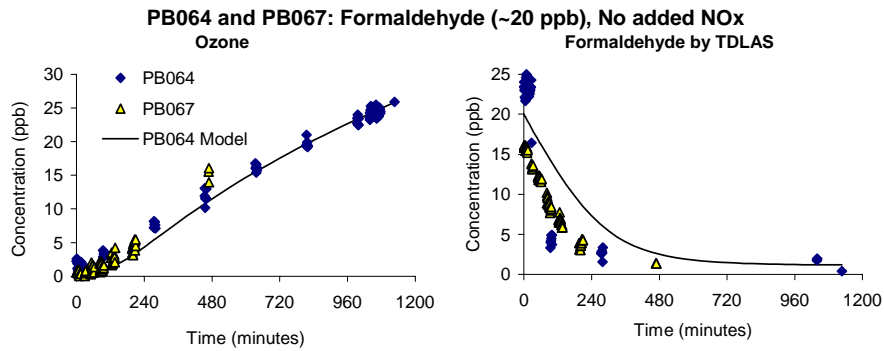


Figure 24. Experimental and calculated concentration-time plots for ozone and formaldehyde in the formaldehyde - air irradiations.

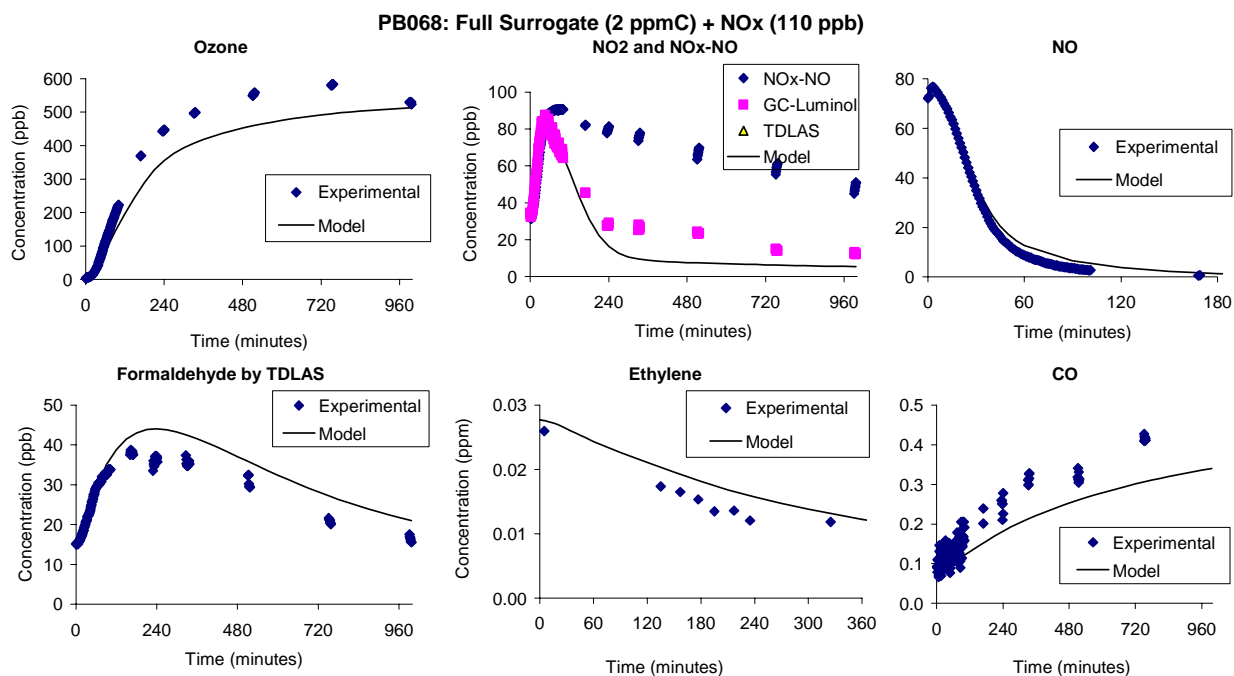


Figure 25. Experimental and calculated concentration-time plots for selected species in the formaldehyde - air and full surrogate - NO_x irradiations.

A surrogate - NO_x experiments was also carried out in the pillowbag reactor during this period, employing the 8-component “full surrogate” used in our previous reactivity programs (e.g., Carter et al, 1995c, 1997; Carter, 2000, and references therein). Although this was actually carried out for another project, the results have relevance to the evaluations for this project. Selected results of this experiment are shown on Figure 25, where results of model simulations are also shown. In contrast to the simulations of the propene - NO_x experiments, the model slightly underpredicted the O₃ yield, but otherwise the simulation of the data was reasonably good. It is interesting to note that the model also simulated the formaldehyde consumption rate reasonably well, unlike the propene or formaldehyde experiments where this rate was underpredicted. The possibility that this is due to compensating errors in the mechanism of the more complex surrogate system cannot be ruled out. Although the model gave good simulations to the NO and NO₂ data during the first ~3 hours of the experiment, the NO₂ concentrations as measured by GC-luminol during the latter period of the experiment was higher than the model predicted. Although this could be due to a mechanism problem, it could also be due to interferences in the GC-luminol analysis by nitric acid, as indicated by the data obtained in the added HNO₃ experiments, discussed above.

Heated Teflon NO_x Offgasing Experiments

Because of evidence of NO_x offgasing from FEP Teflon obtained from the pure air irradiations and other experiments, a series of experiments were carried out to determine if this offgasing increased at elevated temperatures, and if so how different types of Teflon differ in this respect. If offgasing at elevated temperatures were found to be significant, then heating may serve as a possible means to remove NO_x contamination from the material. Comparing offgasing at elevated temperatures may also serve as a convenient means to screen and compare different types of material for potential NO_x contamination effects.

Small pillow bags were made from 2 mil FEP Teflon film, about 20" x 20" in size, and filled with pieces of the same material to enlarge the surface. The bags were placed in an oven and purged with a stream of zero air at 5 L/min, which was sampled by a NO-NO_x analyzer. The oven temperature was varied from ambient to ~200°C.

The general procedure employed was as follows. First the bag was purged with zero air at room temperature (25°C) until the readings of the NO_x analyzer were stable. Then the oven was heated to 50°C. After the readings had stabilized again, the temperature was stepwise raised further. Finally the oven was shut off and allowed to cool to room temperature. Before and after the first experiment with each bag the bags were weighed. No significant loss in mass was observed for each of the experiments.

The various tests that were carried out are summarized on Table 6, and selected data from these tests are shown on Figure 26. The following conclusions can be made based on these results.

- There does not appear to be any significant differences in high-temperature NO_x offgasing characteristics between heat-sealable and non-heat sealable FEP Teflon film.
- FEP Teflon film does not have significant NO_x offgasing at high temperature unless the film has been contaminated somehow.
- Exposure of the FEP Teflon film to ~1 ppm of NO_x for long period of times does not significantly affect NO_x offgasing at high temperatures. This indicates that absorption of NO_x in the dark is not significant.
- Experiments on the effects of heat sealing on NO_x offgasing were not reproducible. One reactor made using the older heat sealer was found to have significantly more NO_x offgasing than observed in other experiments. However, experiments with sealed pieces of Teflon in the bag made with the old or new heat sealer had only slightly more NO_x offgasing when heated than the empty reactors made with the new heat sealer. It is likely that the reactor used in Test #3 was somehow contaminated, and that the process of heat sealing only slightly increases NO_x offgasing if contamination is avoided. However, the NO_x offgasing even from the contaminated reactor appears to decrease with time if heat is continually applied.
- The green polyester/silicone sealing tape that has been extensively used to reinforce or seal the FEP Teflon reactors used for our previous chambers causes significant increases in NO_x offgasing when heated. However, the NO_x offgasing from this tape decreases rapidly with time if heat is continuously applied.

The applicability of these results to low levels of light-induced NO_x offgasing observed in the chamber experiments is somewhat uncertain. The data suggest that the FEP Teflon itself does not contain significant NO_x that is released upon heating, but that the heat sealing process used to construct the reactors, and in particular the polyester/silicone tape used to reinforce and seal them, may introduce some NO_x contamination that is released upon heating. However, this contamination-induced NO_x offgasing appears to rapidly decline with continued heating, so it may not be a significant source of background effects in well-conditioned reactors. Nevertheless, it appears desirable to take care to avoid introduction of contaminants when constructing the reactors, and to avoid use of the sealing tape when constructing the reactors, to the maximum extent possible.

Table 6. Summary of heated Teflon NO_x offgasing experiments.

Bag Description	Heating Test Results
<p><u>Test #1.</u> Bag constructed of non-heat-sealable Teflon film and filled with the same material. Bag sealed using new impulse sealer purchased for this program.</p>	<p>Upon heating to 100°C NO_x outgased from the Teflon bag with a peak concentration of 3.2 ppb. At constant temperature the concentration in the purging air fell down to the level of pure zero air within about 10 hours. Repeating the experiment with the same bag using a lower range of the NO_x analyzer, and thus higher resolution, gave a peak concentration of NO_x of about 1.3 ppb. The measured NO concentrations were in the range of the detection limit of the analyzer (below 1 ppb) for both experiments. Results of the first experiment are shown on Figure 26 (a).</p>
<p><u>Test #2.</u> Same bag but after exposure to 650 ppb NO + NO₂ in zero air for 75 days.</p>	<p>At 100°C about the same NO_x and NO concentrations were observed as before treating the bag with nitrogen oxides. A second heating to 100°C resulted in no outgasing at all; raising the temperature to 150°C, 175°C and finally 199°C resulted in slightly higher NO_x emissions with maximum concentrations of about 5.7 ppb NO_x and 1.4 ppb NO at 199°C.</p>
<p><u>Test #3.</u> Bag constructed with heat-sealable Teflon film and filled with the same material. Bag sealed using new impulse sealer.</p>	<p>Upon heating to 100°C NO_x outgased from the Teflon bag with a peak concentration of 4.6 ppb. At constant temperature the concentration in the purging air fell down to the level of pure zero air within about 17 hours. The measured NO concentration did not exceed 1 ppb. Results are shown on Figure 26 (b).</p>
<p><u>Test #4.</u> Bag constructed with heat-sealable Teflon film and filled with the same material. Bag sealed using old hand-held impulse sealer that has been used for many years at SAPRC and CE-CERT.</p>	<p>The observed NO_x and especially the NO concentrations were significantly higher than with the first bag. Further heating to 150°C and finally 199°C resulted in much higher concentrations, exceeding the chosen NO_x range of the instrument of 50 ppb. This reproduces the results obtained earlier, which is not reported here because of inadequate information on the bag characteristics. Results are shown on Figure 26 (c).</p>
<p><u>Test #5.</u> Bag constructed of the non-sealable Teflon film and heated twice to verify low NO_x offgasing from the bag itself. Several sealing lines (100" total length) were made on the sealable Teflon film using the old heat sealer, the edges of the seals were folded open, and these strips were placed inside the bag.</p>	<p>The purpose of this experiment was to test if the seals were the source of the high NO_x in the previous experiment. Upon heating higher concentrations of NO_x were measured than in the empty bag, but less than observed in the previous run. Results are shown on Figure 26 (d).</p>

Bag Description	Heating Test Results
<p><u>Test #6.</u> Bag constructed of the non-sealable Teflon film and heated to verify low NO_x offgasing from the bag itself. Several strips of polyester with sealing tape, ~1 meter in length total, folded in half lengthwise to cover the adhesive surface, were placed in the bag.</p>	<p>The tape caused the peak NO_x at ~200°C to increase to a maximum of ~160 ppb, but then it rapidly declined. A second heating to ~200°C caused the NO_x to increase to ~20 ppb. Some NO increases also occurred, but they were much less. Results are shown on Figure 26 (e).</p>
<p><u>Test #7.</u> Same bag as above, but tape removed and bag heated to verify low NO_x offgasing. Three cuts were made in the bag of approximately 3 cm length and the cuts were sealed with the green sealing tape.</p>	<p>This is a more realistic simulation of how the sealing tape is used than the previous experiment. Heating to ~200°C caused the NO_x to increase to ~100 ppb. Results are shown on Figure 26 (f).</p>

Research on Aerosol Formation At Caltech

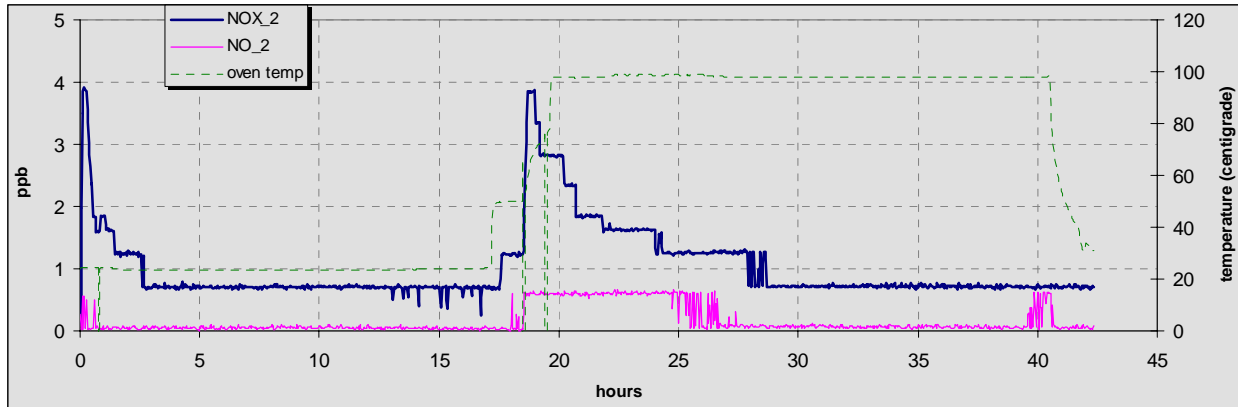
During the period covered by this report, the funds for the subcontract to Caltech were used primarily to support the graduate research by David Cocker, who under Dr. Flagan and Seinfeld's direction was responsible for the upgrades to the Caltech environmental chamber and the humidity effects studies discussed below. After receiving his PhD at Caltech, Dr. Cocker has joined the faculty at the UCR College of Engineering and CE-CERT, and is now a collaborator on this project with regard to aerosol studies. In addition to its training function, the Caltech subcontract provided valuable experience and input concerning chamber design and research that will be used when conducting aerosol-related research at the facility being developed at CE-CERT.

The new aerosol chamber facility at Caltech was designed to improve the quality of data being produced from chamber experiments, and to permit studies of humidity effects to be carried out under characterized and controlled conditions. The major improvement was constructing an enclosure around what was an outdoor chamber to allow for environmental control with regard to temperature, relative humidity and lighting conditions. The new lab walls are heavily insulated which enables temperature settings to remain constant. A humidification system to control RH in the chamber, which would not measurably introduce contaminants to the chamber, was designed. Automating the data acquisition and control of the system enhanced the precision and accuracy of the scanning electrical mobility spectrometers. The improvements of the design of the chamber lab and instrumentation allowed for the investigation of the effect of relative humidity on gas to particle conversion. The design and characteristics of this facility and associated aerosol instrumentation are described in a published journal article (Cocker et al, 2001a), which is included as Appendix A to this report. As indicated above, much of the instrumentation and design features described in this article will be utilized in this project.

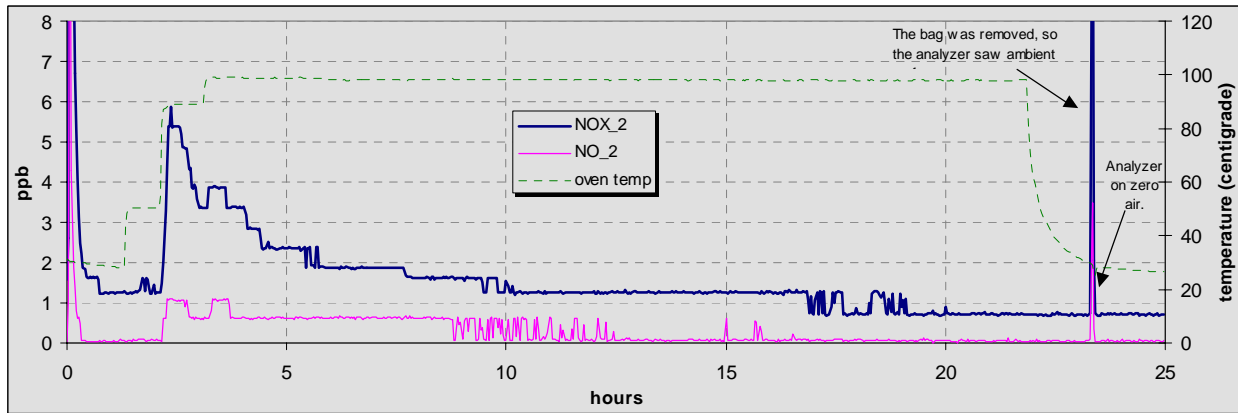
The redesigned Caltech chamber facility was then used to investigate the role of relative humidity in secondary organic aerosol formation. The first system investigated was the α -pinene/ozone reaction in the presence of sec-butanol, a hydroxyl radical scavenger. In the absence of seed aerosol, the aerosol formation increased in the presence of gas-phase water. The increase could be attributed to the

Figure 26. NO, NO_x, and temperature measurements made during selected heated Teflon offgassing experiments.

(a) Test #1, First Experiment



(b) Test #3



(c) Test #4

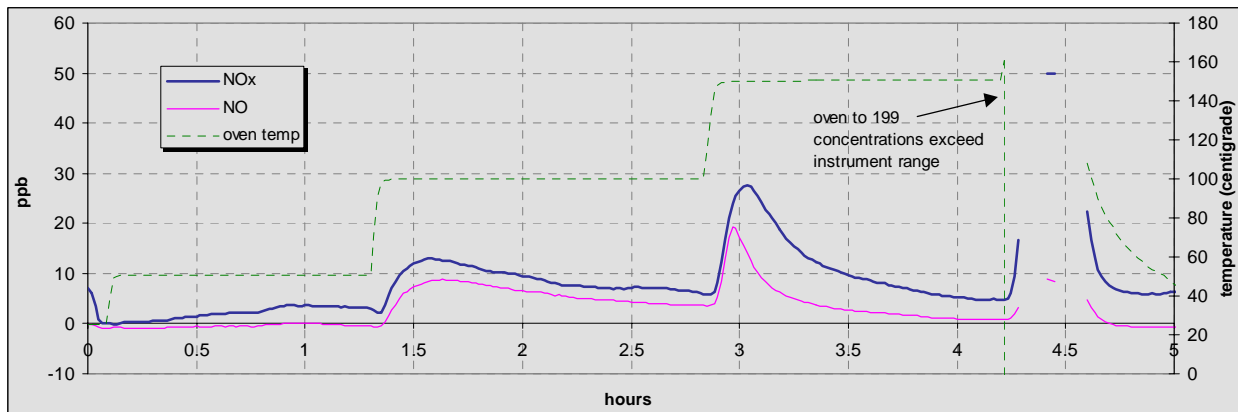
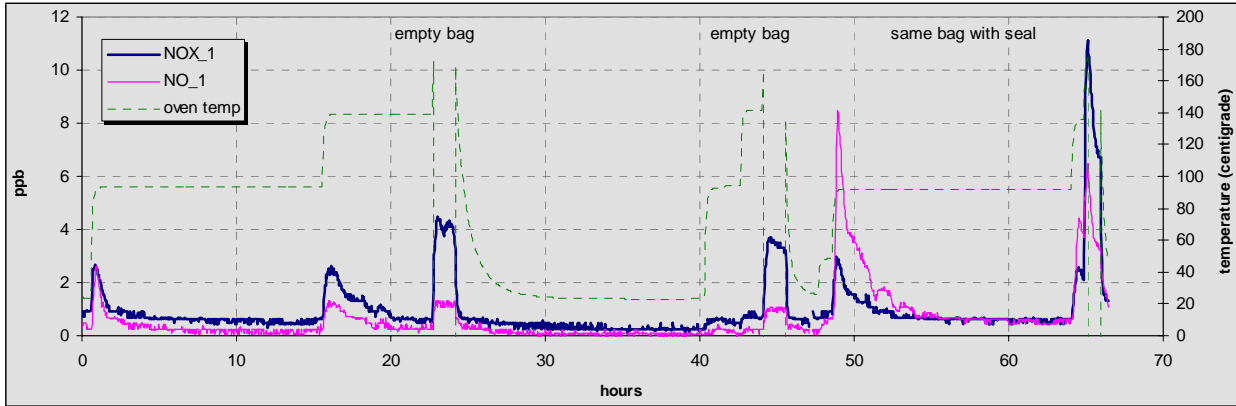
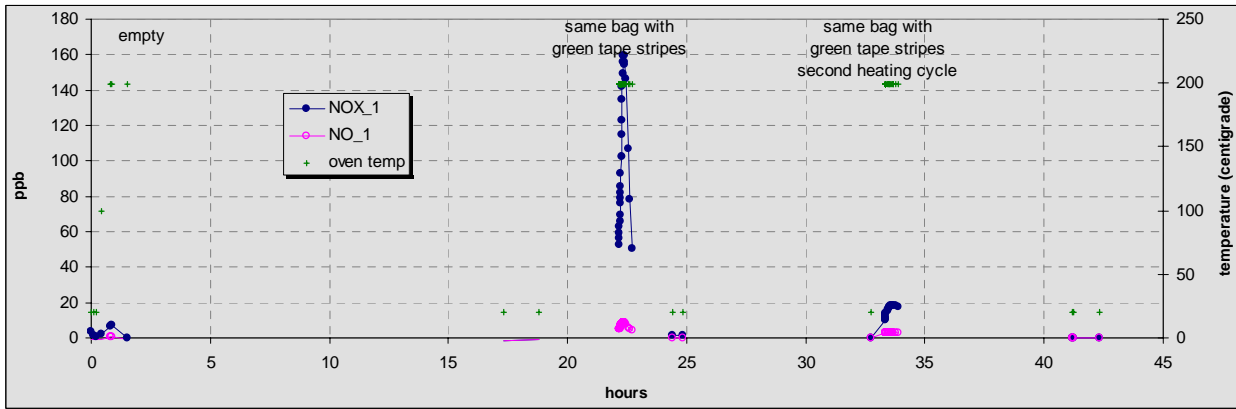


Figure 26 (continued)

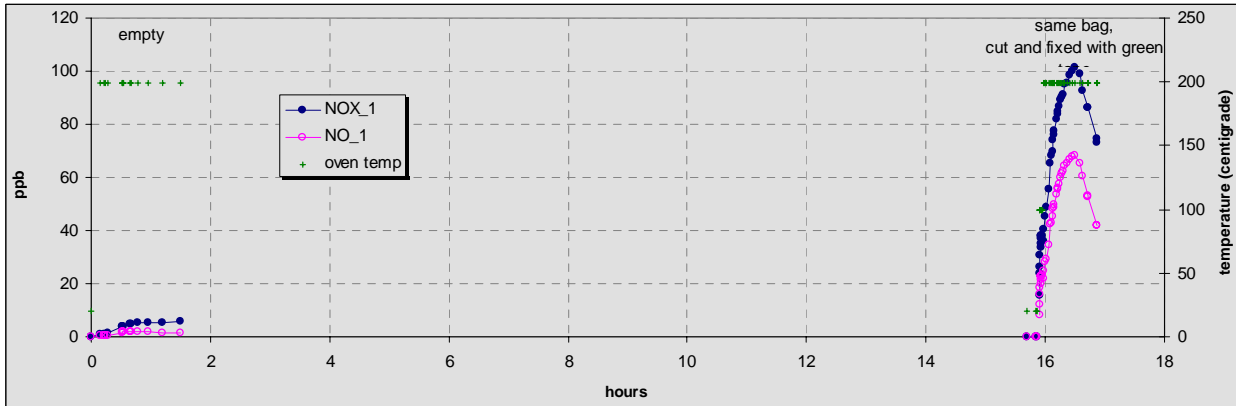
(d) Test #5



(e) Test #6



(f) Test #7



hygroscopic nature of the organic aerosol. Aerosol formation potential was then measured in the presence of dry salt aerosol at low and elevated relative humidity. Again, increased aerosol formation was noted at elevated relative humidity that was attributed to the hygroscopic nature of the organic fraction of the aerosol. Finally, aqueous salt aerosol was used as a seed aerosol, providing a strong electrolytic solution for semi-volatile oxidation products to partition to. In this case, the aerosol formation in the system was lower than the dry systems discussed above indicating a negative effect on aerosol production due to the presence of the strong electrolytic solution. Details of this study are described in a journal article that is in press (Cocker et al, 2001b).

The facility was then used to investigate the role of relative humidity on the aerosol formation potential in the NO_x – air photooxidations of the representative aromatics the *m*-xylene and 1,3,5-trimethylbenzene. The data had larger scatter than the α -pinene/Ozone system and the water uptake for the aromatics products as measured using a tandem differential mobility analyzer for the was minimal at 50% relative humidity. The effect of the aqueous salts and salt composition was not noted for this system. Additional experiments were performed to identify the chemical composition of the aerosol produced. Details of this study are also described in a journal article that is in press (Cocker et al, 2001c).

The work on the Caltech subcontract during the upcoming period will be coordinated in consultations between Drs. Cocker, Flagan, and Seinfeld so that the research at both institutions will continue to be as complementary and mutually beneficial as turned out to be the case during the period covered by this report.

COST SUMMARY AND BUDGET

Figure 27 gives the projected and actual cumulative expenses for this project through August, 2001 and Figure 28 shows the breakdown for the actual cumulative expenses in terms of the major budget categories. As indicated on Figure 27, the expenditures for this project lagged significantly behind the projections because of delays in initiating this project as indicated above in the Summary section. Note that some of the major equipment expenditures significantly lag the time the equipment was specified and ordered because of the time required for delivery and (in some cases) acceptance.

The actual expenditures and liens to date reflect most of the major facilities equipment and fabrication expenses except for some of the budgeted analytical that has not been purchased, as discussed in the Analytical Equipment section, above. Some additional facility fabrication expenses will be required to complete the chamber and associated equipment and hardware, but other than ~\$45-50K for the final invoice for the chamber enclosure and completion of fabrication of the mixing and sampling system, these should be relatively minor compared to the budget for the project.

Figure 27 shows the projected cumulative expenses for the remainder of the project. This includes salary expenses at the rate estimated to be necessary to conduct experiments once the chamber is complete, and known or anticipated analytical equipment or related expenses, as follows:

Remaining aerosol instrumentation required for project	\$33,300
Repairs and needed upgrades to TDLAS#1	\$20,000 (estimate)
NO _x analyzer to replace instrument on loan from CARB	\$20,000
Additional ozone analyzer, if needed	\$8,000
Additional or upgraded GC data acquisition software	\$9,000

With these estimated expenses, it is anticipated that approximately \$100,000 will be unspent at the end of the project if no additional equipment is purchased and if the project period is not extended. The last three items on the list may not be needed, and if so the amount available for additional equipment or salary may be somewhat greater, but not significantly so. This amount will be held in reserve to cover unanticipated expenses, and may be used for either additional equipment purchases, collaborative studies, or to extend the project period to permit additional experiments, depending on the development of the research plan, as discussed in the following section.

This projection indicates that unless some other funding becomes available to cover the salary expenses required to operate the facility it will not be possible to purchase all the analytical equipment that was in the budget of the original proposal. This is because the costs for the chamber enclosure and light source were significantly higher than budgeted. However, as discussed in the following section, some additional funding is becoming available from the CARB that will offset some of the operating costs. However, the current research plan, discussed in the following section, involves using this primarily to extend the period of performance of the project to give sufficient time for the experiments in the research plan to be carried out. Because of uncertainties in the budget projections, we believe it is prudent to defer acquisition of significant additional equipment for this project until the operating budget and additional sources of income for this facility become less uncertain.

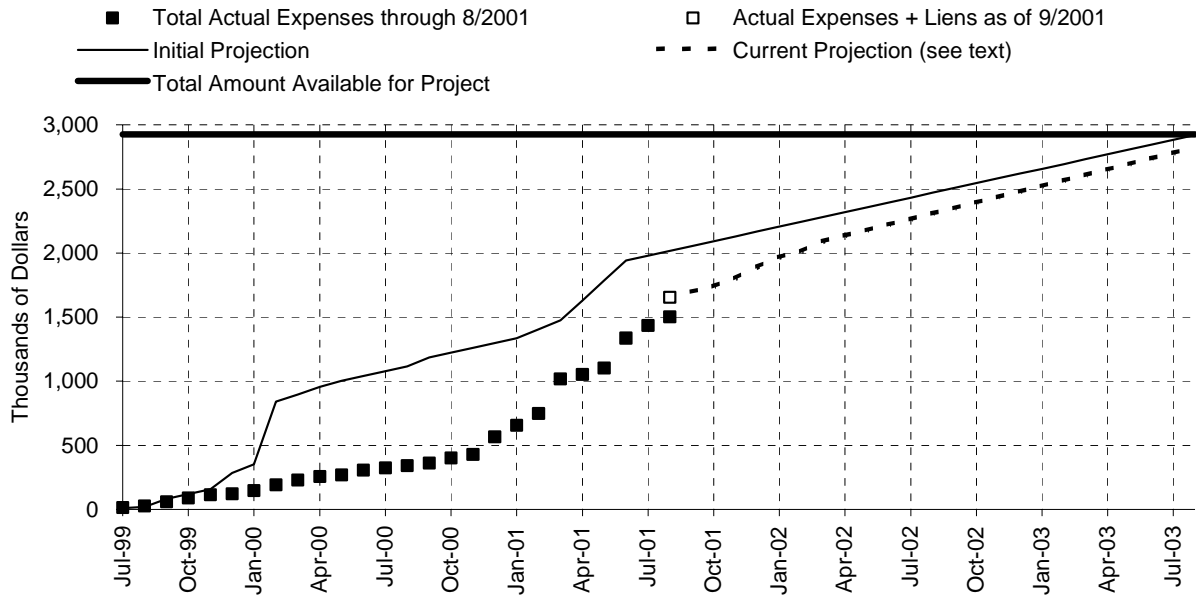


Figure 27. Projected and actual cumulative expenditures for the total period of this project.

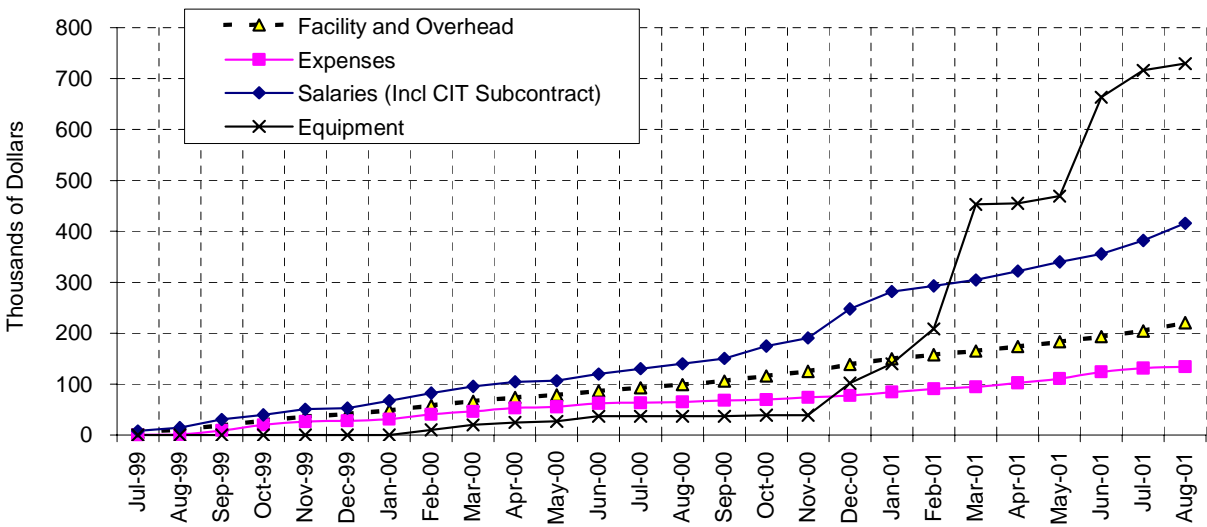


Figure 28. Cumulative actual expenditures for various budget subcategories for this project through August, 2001.

RESEARCH PLAN

Overall Objectives

As discussed in the proposal for this project, the primary reason for developing the new facility is to use it to conduct experiments most needed for model evaluation and to address issues of relevance to regulatory assessment and control strategy development. The broad objectives include, but are not necessarily 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 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 ozone 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.

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.

A proposed research plan for the new facility is described below. Some of this work is dictated by the necessity for adequate chamber characterization for mechanism evaluation, and to conduct work to support the objectives that we are committed to carry out under the current or anticipated CARB contracts discussed in the following section. However, this research plan will evolve as the project proceeds, based

on results of ongoing experiments and input from the EPA, the Reactivity Research Working Group (RRWG), the California ARB's Reactivity Research Advisory Committee, and others. The proposed process for external input is discussed further below.

Additional Funding

Before discussing the specifics of the research plan for the new facility, it is useful to summarize other existing or anticipated projects that will make use of this facility, and that are appropriately incorporated in this research plan. In particular, the California Air Resources Board has funded or has approved for funding three contracts that include approximately \$240,000 for 55 or more experiments over the next three years. All of these experiments serve to further the overall objectives of this project, and therefore they are included in the Research Plan discussed in the next section. These projects and their status and objectives are briefly summarized on Table 7.

Although these CARB projects represent the only currently known or anticipated additional funding for this facility, it is expected that there will be interest in additional projects utilizing it once its performance and capabilities have been demonstrated. Interest in possible future projects using it has been expressed in informal discussions with the South Coast Air Quality Management District and at least some industry groups. A greater level of industry and regulatory support for such research is also likely once the EPA and other regulatory agencies clarify their policies on how they will take differences among VOCs on ozone and PM impacts into account in their VOC control regulations. The significant support by the CARB is a direct result of their interest in reactivity-based regulatory approaches.

Several proposals have been submitted to the NSF and other agencies to obtain additional equipment for this facility or to use it to conduct mechanistic research. The equipment proposals have focused on obtaining instrument to measure peroxy and other radical levels necessary to investigate radical and NO_x cycles under realistic but controlled conditions. This is important to investigate because of the importance of radical cycles in controlling air pollution formation, and because ambient radical measurements have been found not to be consistent with model predictions. We also submitted a proposal to NSF in collaboration with Caltech to utilize this facility as part of a larger program to develop molecularly-based mechanisms for gas-phase and PM-forming reactions in air pollution. Unfortunately, none of these proposals have been successful to date. Additional proposals for radical measurement or other equipment or for utilizing this facility for basic and applied mechanistic research are in preparation or being considered.

Chamber Characterization

The first priority once the facility is completed will be to conduct the experiments necessary to characterize run conditions and chamber effects needed for mechanism evaluation. The following measurements will be made when the reactor is new and at appropriate times subsequently if there is reason to believe they may change.

Temperature. The temperature will be measured as a function of time and location in the reactor at various temperature settings. This will be carried out when the reactor is new and after any modifications are made to the temperature control or air handling system. During experiments the temperature will be measured at a set location in the reactor, and if any spatial variability is observed the variability relative to this set location will be determined.

Table 7. Summary and objectives of current or anticipated California Air Resources Board projects that will support research in the new chamber facility.

Title:	EVALUATION OF ATMOSPHERIC IMPACTS OF SELECTED COATINGS VOC EMISSIONS.
Period:	6/30/01 – 6/29/04
Amount:	\$59,984, of which about \$20 K is available for ~5 chamber runs
Status:	Funded. CARB Agreement No. 00-333
Objectives:	<p>The purpose of this three-year project is to carry out priority research needed to reduce uncertainties in ozone reactivity estimates for selected major types of Coatings VOCs. The project will be carried out in consultation with the CARB staff and the CARB’s Reactivity Research Advisory Committee. The specific tasks include the following:</p> <ul style="list-style-type: none"> • Further develop and evaluate the direct reactivity method developed under the current ARB and ACC projects so they can be applied to low volatility materials. • Utilize the new environmental chamber facility being developed for the EPA to investigate the ozone and other atmospheric impacts of 2,2,4-trimethyl-1,3-pentanediol isobutyrate (trade name Texanol®), which is widely used in water-based coatings. This will require developing procedures for conducting environmental chamber experiments for low volatility materials such as this. • Develop improved procedures for estimating ozone impacts of various types of petroleum distillates and quantifying uncertainties of reactivity estimates for these materials in cases where limited data are available.
Title:	IMPROVED REACTIVITY ESTIMATES FOR VOLATILE ORGANIC COMPOUNDS USED IN ARCHITECTURAL COATINGS
Period:	12/1/01 - 11/30/04
Amount:	\$240,129, of which about \$185 K is available for ~45 chamber runs
Status:	Approved for funding by the CARB Governing Board but contract not yet in place.
Objectives:	<p>The purpose of this three-year project is to supplement our existing CARB contract 00-333 by carrying out the additional research needed to reduce uncertainties in ozone reactivity estimates for Coatings VOCs. The specific tasks include the following</p> <ul style="list-style-type: none"> • Conduct environmental chamber experiments to determine the effects of at least five selected types of coatings constituents on ozone and PM formation under a range of reactant concentrations. At least four of these would be selected types of petroleum distillates representing different reactivity ranges, but an additional water-based coatings constituent may also be studied. The results will then be used to evaluate the

Table 7 (continued)

	<p>predictions of existing and updated atmospheric reaction mechanisms or reactivity estimation methods for this compound or mixture.</p> <ul style="list-style-type: none"> • Apply the direct reactivity screening method to the full range of compounds and petroleum distillates being used or considered for use in architectural coatings in California. <p>The priorities for specific compounds or mixtures to be studied will be determined as part of the overall project, in conjunction with discussions with the CARB staff and the CARB Reactivity Research Advisory Committee. The procedures to be developed under CARB contract 00-333 to assess reactivities and uncertainties in petroleum distillates, along with results of market surveys and input from industry groups, will be used to guide the selection of specific types of petroleum distillates chosen for study.</p>
Title:	DEVELOPMENT AND EVALUATION OF A GAS-PHASE ATMOSPHERIC REACTION MECHANISM FOR LOW NO_x CONDITIONS
Period:	12/1/01 - 11/30/04
Amount:	\$79,884, of which about \$35 K is available for 7-9 chamber runs
Status:	Approved for funding by the CARB Governing Board but contract not yet in place.
Objectives:	<p>The purpose of this project is to evaluate and improve the performance of the SAPRC chemical mechanism for simulating atmospheric transformations under low and very low NO_x conditions. The specific objectives will include the following:</p> <ul style="list-style-type: none"> • Complete the development of the “Low NO_x” version of the SAPRC-99 mechanism that is designed to more accurately predict organic product formation under very low NO_x conditions. • Evaluate the performance of both the standard and the low NO_x versions of the SAPRC-99 mechanism in simulating available environmental chamber simulating low NO_x conditions, including TVA and CSIRO chamber experiments not used previously in SAPRC mechanism evaluation. • Utilize the new environmental chamber facility being developed under EPA funding to carry out selected low NO_x mechanism evaluation experiments deemed to be the most useful for mechanism evaluation in the near term. • Update or modify the mechanisms as appropriate based on the results of the evaluation against chamber data and other data that may become available. <p>The results of this study will then be used to develop recommendations concerning mechanisms to use when modeling low NO_x conditions in regional model simulations, and priorities for future research aimed at reducing uncertainties in chemical mechanisms used in regulatory and research applications.</p>

Light Source Spectrum. The spectrum of the light source will be measured as a function of time and orientation using the LiCor LI 1800 spectroradiometer. The spectra will be measured in the enclosure prior to installing the Teflon reactors with the sensor head oriented in different directions (facing the light, away from the light, or towards the other walls, ceiling or floor) to determine the extent of variability due to orientation. Once the reactor is complete, the spectrometer will be placed inside the reactor and spectra will again be measured as a function of orientation. The latter measurements will be made from time to time as the reactor ages or when new reactors are installed. During most experiments, the spectrometer will be placed on a standard location facing the light, so changes over time can be monitored. From time to time spectral measurements will be made with the spectrometer in a standard location behind the reactors, where light reaching it passes through both reactor walls.

Light Intensity. Although their suitability for this purpose has not yet been established, we expect the primary means of measuring total light intensity will be the spherical PAR irradiance sensors we will be acquiring for this project. These measure near-spherical irradiance in the 300-700 nm region, with the spectral and directional response curves and absolute calibrations being supplied with the instrument by the vendor, Biospherical Instruments, Inc. They will also be calibrated by comparing their measurements to results of co-located NO₂ actinometry runs at various light intensities and using different light sources. With an absolute calibration and a known spectral response of the instrument, and the known relative spectral distribution of the light source, the spherically integrated absolute intensity at a function of wavelength can be readily calculated.

The light intensity will be measured as a function of location within the chamber housing prior to installation of the reactors, and then as a function of location within the reactors. During most experiments or at least periodically the PAR irradiance sensors will be located at a standard position *within* the reactors to determine variation of light intensity with time. This will give information not only on changes in intensity due to changes in the light source, but also effects of ageing of the reactor walls on intensity within the reactors. The sensors will be periodically recalibrated at the factor and compared with results of NO₂ or other actinometry measurements.

Background Offgasing. Background effects such as NO_x offgasing will be measured using pure air, CO – air and aldehyde – air experiments similar to the pillowbag experiments discussed in this report. Since the air purification system to be used with the new chamber should be free of methane and other background VOCs, the ozone formation in the pure air runs may be either very low or sensitive to trace VOC contaminants. Therefore, CO – air or aldehyde – air experiments will probably be more useful for characterizing NO_x offgasing effects, since the VOC contribution will be well characterized. The difference between the pure air and the CO or aldehyde – air runs will thus give a good indication of background VOC effects.

These experiments will be carried out when the reactor is new and periodically as the reactor is used for experimental runs. A comprehensive set of such experiments, carried out at various temperatures and humidity and following various types of experiments in the reactor, will be conducted as part of the initial reactor characterization. Since new reactors appear to have higher background effects than ones exposed to repeated pure air irradiations, the reactor will be conditioned by flushing with the lights on and replicate experiments will be conducted to assure they have attained reproducibility. The effect of HNO₃, H₂O₂ and nitrate aerosol on NO_x offgasing will also be determined, though the aerosol experiments will probably not be part of the initial assessment (see Schedule, below).

Background offgasing experiments will be carried out periodically during the course of conducting mechanism evaluation experiments to assure that they are within the appropriate range, as

established during the initial evaluation process. This will be particularly important when conducting very low NO_x experiments that may be sensitive to such offgasing.

Radical Source Measurements. The magnitude of the chamber radical source will be assessed by conducting n-butane - NO_x and/or CO - NO_x irradiations at various NO_x levels, temperatures and humidities. The effect of added HNO₃ and (eventually) aerosols on the magnitude of the radical source will also be assessed. Radical source measurement experiments for the appropriate conditions will also be carried out in conjunction with mechanism evaluation experiments, to assure that the conditions of the reactor are not changing in this regard. Note that some additional radical source assessments are planned for the current pillowbag system, and the results will be used to guide the types of assessments most useful for the new chamber.

Wall Loss Measurements. Dark decay experiments will be carried out for O₃, HNO₃, H₂O₂ and formaldehyde when the reactors are newly conditioned and periodically once they are in use. Possible interactions of these species in affecting their dark decays will be assessed by measuring their dark decays when mixed together as well as each separately in pure air. The effects of varying temperature, humidity, and (eventually) the added aerosols will also be assessed. During the initial evaluation period they will be preceded and followed by NO_x offgasing or radical source experiments to determine if they have any effect on the results. The effect of light on HNO₃ wall losses will be determined from the data taken during the experiments assessing the effects of HNO₃ on NO_x offgasing and the radical source.

Side Equivalency Tests. As discussed previously, the chamber will have a dual reactor design to increase productivity and make reactivity assessment more straightforward, so side equivalency is clearly important. Most of the characterization runs discussed above will consist of the same experiment in both reactors, allowing side equivalency to be determined. Side equivalency will also be determined by conducting various types of standard or control experiments in both reactors, to assure equivalency under conditions representative of mechanism evaluation.

Control Experiments. Various types of standard VOC - NO_x experiments will be carried out at appropriate intervals to assure that reproducible conditions are obtained within the reactors and for quality assurance for the various measurement methods. These will represent NO_x conditions and O₃ levels characteristic of the mechanism and reactivity evaluation experiments of interest. These will include standard propene - NO_x experiments (though at much lower NO_x levels than employed previously, probably ~10-20 ppb), surrogate - NO_x experiments of the type used for the base case in the reactivity experiments, and perhaps others. Standard aerosol-forming experiments will also be used for control purposes in conjunction with studies of PM formation; the type of experiment most appropriate in this regard has not yet been determined, and more than one type may be appropriate.

Aerosol Effects Characterization Experiments. The effects of the chamber on wall losses of aerosol materials will be determined by adding aerosols of appropriate types and measuring changes in size and number distribution with time. This will be done both in the dark and with the lights on, and in the temperature and humidity ranges that are associated with the experiments where aerosol effects or secondary organic aerosol (SOA) formation is measured. Further aerosol characterization studies are discussed in the “Initial Evaluation of Aerosol Effects” section, below.

Additional Characterization Experiments. The above may not necessarily be the only type of characterization or control experiments that will be conducted. Additional types of experiments or characterization tests may be appropriate based on results of the ongoing study, and external input.

Evaluation of Simplified Gas-Phase Chemical Systems

Although the ultimate objective of this program is to conduct experiments to assess model performance under chemical conditions representative of the atmosphere, it is necessary to conduct experiments with simpler chemical systems. Such experiments are needed not only to assess performance of important components of the mechanism independently of other uncertainties, but also to assess performance of analytical methods. The ideal for mechanism evaluation is to conduct a hierarchical series of experiments of incrementally increasing complexity to build up our confidence of the model performance in simulating the subsets of the mechanism before evaluating the whole. However, a comprehensive study would require a very large number of experiments and is probably not necessary given our current knowledge of atmospheric chemistry and the fact that there already exists a large database of chamber experiments with chemical systems of varying complexity. The approach will therefore be to use appropriate judgments of experiments would be most useful for reducing mechanism and analytical uncertainties in light of the main objectives of this project. This will include considerations of which current data gaps and uncertainties can be most usefully elucidated given the analytical and performance capabilities of the new facility, and how best to investigate problems encountered in modeling or measurements in more complex and realistic systems.

One important goal will be to assess and validate our new measurement capabilities so we can rely upon them when using the data for mechanism evaluation. This requires measurements in simplified chemical systems where the amount of compound present or formed is sufficiently well established that the measurement can be assessed. Some of the experiments already conducted in this project have provided information about our analysis of NO_2 and formaldehyde, though it is clear that additional experiments to assess these measurements, particularly NO_2 , are still required. Our eventual capability to measure H_2O_2 and HNO_3 will be extremely valuable to mechanism evaluation but these are difficult and “sticky” compounds, and the data cannot be trusted for this purpose unless the methods are completely evaluated. The evaluation of the HNO_3 has begun, but much work is needed to evaluate measurements at low concentrations and determine if it is feasible to obtain useful HNO_3 data in the presence of humidity. No evaluation of H_2O_2 has yet been carried out, and because of its critical importance to low NO_x mechanism evaluation it is essential that these measurements be validated.

The measurement evaluation will be carried out by measuring known amounts of the compounds when injected into the chamber under various conditions, but also by measuring their yields and concentration-time profiles in chemically simple systems where their formation and consumption rates should be known. Some of the latter data can be obtained in conjunction with mechanism evaluation and characterization experiments. If the experimental measurement is different than expected in one chemical system, then they will be examined in other chemical systems to assess the extent to which the mechanism may be the source of the problem. Model calculations will be used to determine which simple chemical systems will form the compounds of interest in the concentration ranges of interest in yields that are not highly sensitive to uncertain characterization or mechanism parameters.

The major objective will be to assess mechanism predictions for the simpler chemical systems under the lower NO_x conditions that can be achieved in this chamber. This will include testing the ability of the mechanism to simulate key species, such as NO_2 , H_2O_2 , and HNO_3 , for which previous mechanism evaluation data have been lacking or limited. Obviously we cannot test the mechanism for all systems under all conditions, with representative systems being chosen, and additional systems studied based on the results and on external input. The following chemical systems will be examined in the initial evaluation. Note that this is in addition to experiments such as pure air, formaldehyde - air, n-butane - NO_x and CO - NO_x , etc carried out for characterization purposes as discussed above.

- H_2O_2 - air, H_2O_2 - NO_x and H_2O_2 - CO - NO_x experiments will be conducted to evaluate measurement methods for H_2O_2 , model predictions of its loss and radical input rates by photolysis, and to evaluate whether there are any heterogeneous or other unexpected interactions with NO_x .
- The above experiments will be carried out with HNO_3 also present to assess whether there are any unsuspected interactions involving H_2O_2 and HNO_3 .
- Formaldehyde - NO_x and formaldehyde - CO - NO_x experiments will be conducted to further evaluate the mechanism, measurements, and photolysis rates for formaldehyde. Previous experiments in this program indicate there is a potentially serious problem with the formaldehyde mechanism or photolysis rate mechanism, as indicated by the failure for the model to predict formaldehyde consumption rates in some experiments, as discussed above. Experiments with the presence of CO will be useful in that the CO inhibits the reaction of OH radicals with formaldehyde and also enhances the effects of the radicals formed from formaldehyde photolysis on the formation of O_3 . The CO experiments will also be useful for evaluation of H_2O_2 predictions.
- Methane - NO_x irradiations provide a chemically simple system where formaldehyde formation and consumption can be measured and where measurable levels of H_2O_2 are predicted to be formed. In addition, measurable levels of methanol from the methyl peroxy self reaction are predicted to be formed, and such data would provide a useful evaluation of the extent to which the mechanism can simulate peroxy + peroxy reactions that become important under low NO_x conditions. If the mechanism cannot predict H_2O_2 and peroxy + peroxy products in this chemically simple system, it probably can't be relied to do so in more chemically complex and realistic systems.
- Low NO_x irradiations of the following VOC - NO_x systems will be carried out to evaluate performance for the mechanisms of the following representative VOCs: acetaldehyde, propene, isoprene, toluene, and perhaps others. Experiments with the aromatics will be conducted at various temperatures to assess whether the parameterized mechanisms are temperature-dependent. Temperature effects experiments will also be conducted with other compounds in conjunction with reactivity experiments conducted at different temperatures if problems are encountered in simulating the base case surrogate experiments at the different temperatures.
- Various simple and more complex VOC mixture - NO_x irradiations will be conducted for mechanism evaluation under more realistic conditions and interactions in mixtures. This will include surrogate - NO_x experiments for being considered for use as base case experiments in experimental reactivity studies.

Note that alkane - NO_x and single VOC - NO_x irradiations with radical inhibiting species of alkanes will not be relied upon for mechanism evaluation because their results are dominated by the chamber radical source. Therefore, the primary means of evaluating their mechanisms will be reactivity experiments, as discussed below. However, if problems or complications are encountered in the reactivity evaluations using the more complex surrogate systems, we may investigate use of simpler systems for this purpose. An example may be VOC - formaldehyde - NO_x irradiations, which would provide a very sensitive system to the mechanism of the added VOC that would be useful for mechanism evaluation. However, such experiments would be useful for assessing the test VOC only if we are able to successfully simulate the results of the formaldehyde - NO_x and formaldehyde - CO - NO_x runs, discussed above.

Although ideally these experiments with simple chemical systems should be thoroughly investigated prior to studying the more complex systems as discussed below, it must be borne in mind that the objective of this project include providing data of immediate utility to policy-relevant model

applications. Therefore, we would expect to proceed with some of the other projects discussed below before completing the evaluation with all the chemically simple systems, and use the results analysis of the simpler systems to refine the analysis of the more complex and realistic systems when the data become available. This is discussed further in the Schedule section, below.

Initial Evaluation of Aerosol Effects and Aerosol Formation

An important objective of this project is conducting chamber experiments to assess effects of VOCs on aerosol formation as well as on ozone and other impacts. Before assessing aerosol effects for specific compounds in atmospherically realistic systems, it is necessary to assure we can adequately characterize aerosol effects in chemically simple systems, and to determine if we can duplicate aerosol formation data obtained in other laboratories in well-studied systems. Although the research plan relative to aerosol studies is still being developed, given below is a brief summary of the types of experiments we expect to include as part of the initial evaluation.

- Aerosol lifetimes in the chamber will be determined under various conditions, as discussed above in the “Chamber Characterization” section.
- Aerosol formation in the α -pinene - O₃ dark reaction and in m-xylene - NO_x irradiations will be conducted for comparison with results at Caltech and other laboratories.
- A selected subset of the humidity effects studies of Cocker et al (2001b,c) on the α -pinene - O₃ reaction will be duplicated to assure that consistent results are obtained in our laboratories.
- The effects of aerosols on chamber effects such as NO_x offgasing rates, the chamber radical source, and wall loss rates for O₃, HNO₃, and H₂O₂ will be investigated. This will be done by conducting the appropriate types of characterization experiments with aerosols injected into the chamber. Different types of aerosol materials will be investigated, including nitrate aerosols. This will be investigated in the humidity range used for aerosol effects studies. If any effects are found at the standard temperature, then the effects of temperature on these effects will also be investigated.
- The effects of added aerosols on results of various types of VOC - NO_x irradiations will be investigated. If aerosols are found to have non-negligible impacts on chamber effects, model calculations will be used to determine if differences observed in VOC - NO_x experiments can be adequately explained by the chamber effects only.
- Secondary aerosol formation will be determined for the various surrogate - NO_x experiments being considered for use as the base case in reactivity assessment studies. Base case surrogates will be developed that have different levels and types of aerosol formation, so the effects of the base case aerosol on the secondary organic aerosol (SOA) reactivities of the test VOCs can be assessed, if appropriate.
- Sufficient replicate experiments will be conducted to assess reproducibility and side equivalency. If the results are not considered to be satisfactory, effects of chamber treatments or history on the results will be investigated in order to find means to improve the situation in this regard.

Note that this list of types of aerosol assessment experiments is preliminary, and does not yet reflect input from our collaborators at Caltech or other researchers experienced in chamber studies for SOA formation. Therefore, this may be subject to revision after further evaluation. Initial feedback from Dr. Cocker indicates that a larger number of experiments will be required for adequate aerosol characterization than envisioned in the current plan.

VOC Reactivity Assessment

A major objective of this project is evaluating models for predicting the effects of VOCs on O₃, secondary aerosol, and other air quality impacts when added to the emissions in ambient air. This will be assessed primarily by conducting “incremental reactivity” experiments, where the effects of adding the test VOCs of interest on results of standard surrogate - NO_x experiments will be assessed. This provides the most realistic simulation of the effect of the VOC on ambient atmospheres that can be carried out under controlled conditions. Note that “reactivity” in this context we include effects of the test VOCs on SOA formation and other manifestations of air quality, and not just effects on ozone. However, the emphasis and priority for specific impact(s) being assessed may vary with VOC, depending on why it is being studied. This is discussed further below.

As discussed by Carter et al (1995c), base case experiments with differing VOC and NO_x levels and sensitivities to radical initiation/inhibition effects are needed for comprehensive mechanism evaluation. An important part of the work plan will be determining the most useful base case experiments for comprehensive mechanism evaluation. Obviously a large number of highly varied base case experiments would give the most comprehensive evaluation, but this would permit only a few compounds to be studied with the available resources. Although comprehensive evaluation is appropriate for representative compounds of various types, for reducing uncertainties of reactivity assessments for the full range of materials of interest in regulatory applications it is of greater important that reactivity data be obtained for as many different types of compounds as possible.

Model calculations and other considerations will be used to determine candidate types of base case experiments that may be most useful for reactivity assessments for various purposes. These will then be used for reactivity experiments on compounds with known mechanisms and different reactivity characteristics, probably CO, acetaldehyde, and n-octane. The results will be used to determine the priorities for use in studies where only a limited number of experiments can be carried out per compound. The criteria will include obtaining a set of 2-3 experiments with different sensitivities to important aspects of the mechanisms, and the ability of the model to simulate the results of the base case experiments and the effects of additions of compound with presumably well-established mechanisms.

Note that some of the base case experiments considered will probably be multi-day irradiations. Such experiments will be useful in assessing effects of slowly reacting compounds in long range situations that are important in regional models, and also in assessing effects of reactions of the VOCs oxidation products on their overall impacts. One problem with the 6-hour, relatively high NO_x base case experiments used in previous studies is that model simulations of these experiments tend to be less sensitive to the representation of the reactions of the VOC oxidation products than is the case of simulations of ambient scenarios. Model calculations indicate that base case experiments with lower NO_x levels and longer irradiation times are much more sensitive to this important aspect of the mechanisms that have not been well evaluated by previous data.

Impacts on aerosol formation will be assessed for VOCs where such impacts are known or suspected to be non-negligible. It is important to recognize that in such 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 such as experiments for reactivity assessment. 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.

The specific compounds to be studied will be determined based on several factors, with the priorities for study being as follows:

1. Utility in assessing the suitability of a particular VOC - NO_x mixture as the base case experiment in reactivity studies and in evaluating the base model performance in predicting effects of added VOCs with known mechanisms. This is essential for evaluating the overall utility of the methodology for reactivity evaluation of VOCs with unknown mechanisms
2. Representativeness of the compound of the major classes of VOCs that are most important in affecting overall air quality, such as representative types of alkanes, alkenes, aromatics, and aldehydes. This is essential for assessing consistency with previous reactivity assessment data and for assessing the validity of the base case mechanism.
3. Inclusion of the compound in the statement of work for a project that is explicitly funding the experiments, such as the coatings VOCs to be studied in the projects for the CARB as discussed in "Additional Funding" section, above.
4. Compounds or materials determined by the EPA project officer as being of particular concern to the EPA, after consultation with the Principal Investigator, the RRWG and the scientific advisory group for this project.
5. Compounds determined by the Principal Investigator as being particularly useful for mechanism for air quality modeling and general VOC reactivity assessment, but not falling into the categories above. This will be determined only after consultation with the EPA project officer, the scientific advisory group for this project, and the RRWG.
6. Other compounds or materials determined by the RRWG to be of utility for policy-relevant reactivity assessment, after consultation with the Principal Investigator and the EPA Project officer, if time and resources permit. Note that the recommendations of groups that are actually funding research in this facility or other RRWG projects will be given priority if a consensus is not reached.

Regardless of which compounds are studied, the Principal Investigator and the scientific advisors and collaborators for this project must agree that the data obtained would be of actual utility to mechanism evaluation and that use of this facility is the most appropriate way to address the issues of concern. In addition, the Principal Investigator must agree that the experiments are feasible that the material will not adversely affect the reactor or instrumentation.

Based on criteria 1-3, above, the specific compounds that we initially plan to study, and the range of conditions for which they will be studied, are indicated below. It is expected that resources and time, and perhaps additional funding, will permit studies of additional compounds.

- Carbon Monoxide will be studied using the full range of base case experiments for control purposes because it has the simplest known mechanism and no significant radical sources or sinks. If the model cannot simulate the effect of this compound on the results of a base case experiment, then it must be due to a problem with the base case model.
- Assuming that results of the chemically simpler experiments with H₂O₂ are as expected, experiments will be carried out using H₂O₂ as the test "VOC" because it essentially acts as a pure radical initiator. This therefore serves as an additional test of the base case model. However, H₂O₂ will not be used as a control test compound if experiments indicate problems with reliably modeling and measuring H₂O₂.
- Formaldehyde and acetaldehyde will be studied both for control purposes and because of the importance of aldehydes in ambient scenarios. Although formaldehyde has nominally the simpler

mechanism, experience has shown that acetaldehyde experiments tend to be more consistent with model predictions and therefore may be more useful for assessing base case mechanisms. Acetaldehyde also differs from CO, H₂O₂, and formaldehyde in having NO_x sinks in its mechanism, and thus provides a different type of test of the mechanism.

- The reactivity of n-octane will be studied under the full range of conditions. This compound is important to study for control purposes because it has been well studied previously and has stronger inhibiting characteristics than the other well-studied VOCs, and thus provides an evaluation of inhibition effects. This is also important because it is a representative of the higher molecular weight alkanes that are important in emissions. Studies will include multi-day irradiations to evaluate the mechanism used for the oxidation products. At least some experiments will be conducted to determine if it has measurable SOA impacts.
- The reactivities of the representative aromatics toluene and m-xylene will be studied under a range of conditions. Aromatics are important reactive compounds that must be appropriately represented in the base mechanism, and have highly uncertain mechanisms. Their mechanisms are particularly uncertain under low NO_x conditions where the parameterized mechanisms currently used have not been adequately evaluated. Aromatics are known to have non-negligible PM impacts, so the full set of aerosol measurements will be made in conjunction with the aerosol experiments.
- Isoprene is an important compound in natural emissions and an appropriate representation of its mechanism is critical in regional models. The emphasis will be on assessing its impacts in low NO_x simulations representing the types of environments where it is emitted, though its impacts on other appropriate conditions will also be examined.
- Reactivity experiments with 2,2,4-trimethyl-1,3-pentanediol isobutyrate (trade name Texanol®) will be carried out because this is an important component of water-based coatings emissions that has not been adequately studied, and studies of this compound are included in the statement of work for our existing CARB project (see “Additional Funding”, above). The appropriate conditions to use will be based on the analysis of the results of the experiments with the other VOCs, discussed above, particularly n-octane, which is expected to have the most similar reactivity characteristics. At least some, if not all, experiments will be conducted in conjunction with measurements of aerosol formation.
- Reactivity experiments with several representative petroleum distillate samples will be conducted because they are important as solvents and components of coatings emissions, and because such experiments are included in the statement of work for an anticipated CARB project. The specific solvents to be studied will be determined in consultation with CARB staff and the CARB’s RRAC. At least some experiments for each type of material will be conducted in conjunction with aerosol formation measurements.
- Reactivity experiments with other selected coatings VOCs will be conducted based on results of consultation with the CARB staff and the CARB’s RRAC, as part of the statement of work of an anticipated CARB project.

The other compounds to be studied will be determined in consultation with the EPA, RRWG, and advisory groups for this project as indicated above. Recommendations for additional compounds to be studied will be made after receiving input from these groups.

Other Research Objectives

Given below is a summary of the other research objectives and types of experiments discussed in the proposal and initial work plans for this project (Carter et al, 1999), and a discussion of how they fit in with the current work plan. The specific experiments and level of effort regarding these objectives may change depending on external input and possible availability of new funding.

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 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 O₃ and precursor levels, while Tonnesen and Dennis (1998a,b) found small variations in the indicator value depending on the O₃ 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 whether experimentally measured ratios of indicator species are consistent with model predictions, and thus assess the extent to which such measurements have the utility for predicting ozone sensitivities as predicted by the modeling studies. The robustness and consistency of the indicator method can be evaluated by determining the indicator values in additional series of experiments with different VOC, light, temperature and humidity levels. If simultaneous aerosol measurements are made, then

Most of the necessary data to address this objective can be obtained in conjunction with experiments carried out to evaluate the various candidate base case surrogate - NO_x experiments, and experiments carried out for general mechanism evaluation purposes using realistic surrogate - NO_x mixtures. However, additional experiments, such as with varying light intensity or temperature, may be carried out if comparisons of the measured and modeled indicator species ratios indicate that such data would be useful to investigate any discrepancies or further evaluate the indicator ratio methodology.

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. The O₃ production efficiency per NO_z [$P(O_3)/P(NO_z)$] 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. (2000) 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, 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/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 RO₂+HO₂ has been measured by the chemical amplifier technique (Cantrell et al, 1997). Unfortunately, the current project does not have sufficient funds to acquire this instrumentation, so additional funding sources will be required before such measurements can be made.

Although additional analytical methods are needed to characterize NO_y and HO_x budgets, 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, 2000). For this reason, it would be most beneficial if the funding for the needed instrumentation could be acquired as soon as possible, to take advantage of the large number of experiments we will be conducting to address the other objectives of this project, as discussed in the previous sections.

Organic Product Studies

Product identification is clearly important when conducting fundamental mechanistic studies that provide the basic data ultimately needed for mechanism development. However, because of limited resources and other considerations, for the current project we decided to place a higher priority on the monitoring the key species most needed for evaluating mechanisms for models to address near-term regulatory needs, with organic product identification, while desirable, taking second priority. This is in part because the unique chamber facility being developed for this project provides greatest added value to measurements of known priority species, while useful product identification studies can in most cases be adequately carried out using facilities already available at many other laboratories. If needed, HPLC system that can be used for occasional DNPH and other analyses is available at CE-CERT, and the UCR College of Engineering is attempting to obtain funding for a GC-MS that would be available for our use. In addition, colleagues at the Air Pollution Research Center, at which the Principal Investigator has a joint appointment, have a variety of state-of-the-science product identification instrumentation that could be for collaborative studies of mutual interest.

This emphasis obviously could change if new funding is obtained to support the necessary equipment, personnel and/or collaborations, or if a revision in the current priorities is determined to be appropriate after consultation with the EPA, RRWG, and other advisory groups for this project. However, without new funding any increase in emphasis on product studies would require a reduction in the number of experiments carried out under the existing cooperative agreement.

Evaluation of Ambient Monitoring Equipment

The large chamber facility will provide a unique test bed for evaluating new monitoring equipment using well-characterized chemical systems that 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.

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.

We already have a collaboration with Dr. Ron Cohen involving adapting the method he and co-workers developed to measure NO₂, total PAN, total organic nitrates, and HNO₃ in ambient air (Cohen, personal communication, 2000; Day et al, 2001) to mechanism evaluation studies. As part of that project, his thermal dissociation laser induced fluorescence system (LIF) for monitoring NO₂ and (by thermal dissociation) PANs, organic nitrates and HNO₃ will be brought to CE-CERT for evaluation in our chamber. In this case, the LIF NO₂ measurements will be used to evaluate our TDLAS and GC-luminol measurements, as well as evaluating the total PAN, organic nitrate, and HNO₃ measurements under controlled and well-characterized conditions.

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.

Summary of Experiments

Based on the work remaining to complete the chamber facility and the time required to complete this work, we do not expect the new chamber facility to become operational until around the middle or end of January 2002. Considering occasional down time, time required to prepare the chamber for experiments, and the need for occasional multi-day experiments, we estimate that on the average we should be able to complete approximately two experiments per week once the facility is operational. The available funding for this project and the current CARB projects is sufficient to operate this facility until Spring of 2004 assuming no new major equipment is obtained, and that no significant unexpected costs are encountered in completing or maintaining the facility. This yields approximately 230 experiments in the period when the chamber is expected to be operational and the time the available funding is exhausted. Since this includes CARB funding, this necessarily includes the experiments required for those

contracts. If new funding is obtained, the time period and therefore number of experiments can be increased. However, new funding will not increase experiments that can be carried out between now and Spring of 2004, which will be used as the time period for the experiments discussed in this section.

Table 8 summarizes the specific experiments discussed in the previous sections needed to address the objectives of chamber characterization, evaluation of simplified gas-phase systems, initial evaluation of aerosol effects, and VOC reactivity assessment, including the runs for the CARB projects. The estimated minimum numbers of experiments of various types considered appropriate to address these objectives are indicated on the table. It can be seen that the total number of experiments listed on the table is 232, essentially the same as the estimated maximum number of experiments that can be conducted during the period covered by the available funding.

The fact that the experiments listed on Table 8 takes up essentially all the capacity of the chamber during the remaining period covered by the available funding presents a problem because it does not allow for flexibility for adding new projects or studying additional VOCs during this period. Some characterization experiments may not be necessary if chamber effects involving H_2O_2 and HNO_3 can be investigated in pillowbag runs carried out prior to the completion of the chamber and the results indicate no evidence of anomalous that would be need to be investigated in the larger chamber. It may also be appropriate to reduce the number of mechanism evaluation experiments with simpler chemical systems if the results indicate similar consistency with model predictions as observed in previous chamber runs. On the other hand, the number of aerosol characterization experiments listed on the table may not be adequate. As discussed in the following section, external input will be obtained concerning which experiments are most appropriate to remove if higher priority experiments need to be added.

The experiments will not necessarily be carried out in the order given on Table 8. Some of the characterization runs (e.g., pure air and n-butane - NO_x irradiations) will need to be carried out periodically to assure consistency of chamber effects, and it is not necessary for all the experiments with on the simplified gas-phase systems be conducted before the reactivity experiments begin, except for those necessary to evaluate analytical methods. However, it is appropriate that a minimum set of characterization runs and the appropriate experiments needed to evaluate the analytical methods be given priority, and that the aerosol characterization experiments be conducted for conditions of a particular temperature and humidity be conducted prior to conducting aerosol experiments for VOC aerosol reactivity assessment. This is discussed further in the following section.

Schedule

A tentative schedule for the experiments to be carried out in the next 12 months of this project is summarized in this section. This assumes that external input does not result in a major change in the work plan for this project. Therefore, this is subject to change.

In the first half of 2002 we expect to be focusing on the minimum set of experiments for characterization and initial mechanism evaluation under dry conditions. We will also evaluating types of experiments to use as base cases in reactivity studies. Dry conditions will be studied first because wall effects are expected to be less, allowing us to focus more on gas-phase mechanism evaluation. This is expected to include the following types of experiments:

Table 8. Summary of proposed experiments in new chamber facility for 2002 through mid-2004.

	Temperature: Standard Temperature			Low	High	Reps	Total	
	Humidity: Unhumidified ~50%			Unhumidified	Unhumidified	or	Runs	
	NO _x Level: Low	Med	High	Med	Med	Med	Other [a]	
<u>Characterization Experiments</u>								
Pure Air	3			2	2	2	4	13
CO-Air & HCHO- Air	2				1	1	1	5
n-Butane - NO _x (vary NO _x)	2	2		2	2	2	4	14
CO - NO _x (vary NO _x)		1			1	1	1	4
n-Butane - HNO ₃ - NO _x [b]		1						1
HNO ₃ - air (dark and Light)	1			1	1	1	1	5
H ₂ O ₂ - air (dark and light)	1			1			1	3
H ₂ O ₂ - HNO ₃ (dark and light) [b]	1			1				2
O ₃ (dark)	1			1	1	1	1	5
<u>Aerosol Characterization Experiments</u>								
Pure Air - Added Aerosol	1			1	1	1	1	5
n-Butane - NO _x - Added Aerosol (Vary NO _x)		2		2				4
O ₃ - H ₂ O ₂ - HNO ₃ - Aerosol (dark)	1			1			1	3
a-Pinene - O ₃ (dark)	3			3				6
Aerosol-forming surrogate (Vary NO _x)		2		2			4	8
a-Pinene - NO _x (Vary a-Pinene)		3					1	4
m-Xylene - NO _x (Vary m-Xylene)		3						3
Surrogate - NO _x : Added aerosol (Vary NO _x)		2		2				4
<u>Mechanism Evaluation - Simple Systems</u>								
H ₂ O ₂ - air	1			1			1	3
n-Butane - H ₂ O ₂ - NO _x		1						1
HCHO - NO _x & HCHO - CO - NO _x	1	1					2	4
H ₂ O ₂ - CO - NO _x (vary NO _x)		1					1	2
HCHO - CO - HNO ₃ - NO _x [b]		1					1	2
H ₂ O ₂ - CO - HNO ₃ - NO _x [b]	1	1					1	3
Methane - NO _x (Vary NO _x)		1					1	2
Propene - NO _x (Vary NO _x)	1		1	1	1	1	2	7
Acetaldehyde - NO _x (Vary NO _x)		1					1	2
Isoprene - NO _x (Vary NO _x)		2					1	3

Table 8 (continued)

	Temperature: Humidity: NO _x Level:			Standard Temperature Unhumidified Low	~50% Unhumidified Med	Low Unhumidified Med	High Unhumidified Med	Reps or Other	Total Runs [a]
Toluene - NO _x (Vary NO _x)	1	1	1	1	1	1	1	1	6
Other simple mixtures	2	2						2	6
<u>Surrogate Evaluation</u>									
Candidate Surrogate #1 (Vary NO _x)	2								2
Candidate Surrogate #2 (Vary NO _x)	2								2
Standard Surrogate - NO _x	1	1	1	1	1	1	1	1	7
Surrogate - NO _x : Vary ROG	1	1	1	1				1	5
<u>Reactivity Experiments (Base Case Evaluation)</u>									
CO	1	1	1					1	4
H ₂ O ₂	1	1	1					1	4
<u>Reactivity Experiments (Representative Major VOCs)</u>									
Formaldehyde	1	1	1					1	4
Acetaldehyde	1							1	2
n-Octane	1	1	1					1	4
Toluene	1	1	1		1	1		1	6
m-Xylene	1	1	1		1	1		1	6
Propene	1							1	2
Isoprene	1	1	1					1	4
a-Pinene		1		1				1	3
<u>Reactivity Experiments (CARB Projects)</u>									
Texanol®	1	1	1					2	5
Petroleum Distillates [c]	5	5	5					11	26
Other Coatings VOCs [c]	3	3	3					7	16
<u>Totals</u>	59	36	18	25	14	14		66	232

[a] Total number of dual reactor runs. Note that two experiments can be carried out simultaneously in the two reactors except for reactivity experiments.

[b] This run may not be needed if a comparable if a comparable pillowbag run is conducted and the results show no HNO₃ effect.

[c] The number of runs shown is less than required on statement of work for this CARB project because some of the CARB runs will be carried out after the conclusion of this EPA project.

- A minimum set of ~20 experiments necessary for chamber characterization at the standard, high, and low temperature levels under dry conditions. The high and low temperature characterization experiments are needed not only to conduct evaluation experiments at those temperatures, but also to adequately characterize these effects for modeling at any temperature.
- A minimum set of ~3 experiments to evaluate the mechanism and measurements for H₂O₂ at the standard temperature, needed to serve as a basis for using H₂O₂ data for mechanism evaluation in more complex experiments
- A set of ~4 propene - NO_x experiments for control purposes and for mechanism evaluation of this chemically at various NO_x levels and temperatures, and an acetaldehyde - NO_x and methane - NO_x experiment at the standard temperature for similar reasons.
- A series of ~5 toluene - NO_x experiments at various NO_x levels and temperatures to assess whether there are problems with the current aromatics mechanisms at low NO_x levels or different temperatures. Depending on the magnitude of the effects and model performance, the results would determine the research priority for additional runs involving aromatics or mixtures containing aromatics.
- ~10-15 experiments evaluating various candidate surrogate - NO_x experiments at various NO_x levels for use in reactivity experiments at the standard temperature and under dry conditions.

During the second half of 2002 we will begin to evaluate aerosol effects, conduct additional mechanism evaluations of chemically simple systems, begin reactivity experiments for representative VOCs, and begin studies of coatings VOCs for the CARB projects. All experiments will be at the standard temperatures and again only dry conditions will be employed. Aerosol measurements will be made for those mechanism evaluation experiments where appropriate. The specific types of experiments are as follows.

- A set of ~5 characterization runs to assure the chamber characteristics are consistent with those observed during the previous period. More such runs may be needed if anomalous results are obtained or if the reactors have to be replaced.
- At least ~13 experiments to characterize aerosol effects and for comparison with results obtained in the Caltech or other chambers. This will include experiments with added aerosol and various experiments to measure aerosol formation from α -pinene.
- A set of ~8 experiments on with single VOCs or simple mixtures to evaluate mechanisms of important representative VOCs, including formaldehyde, acetaldehyde, isoprene, toluene and perhaps others. Aerosol measurements will be made during the aromatic experiments.
- A set of ~6 additional experiments for base case reactivity evaluation, including reactivity experiments for CO and H₂O₂.
- At least one reactivity experiment each for formaldehyde and acetaldehyde and at least 3 reactivity experiments for n-octane. The reactivity of n-octane is important to assess for the conditions of the new base case experiments because it has very similar reactivity characteristics to those expected for the representative coatings VOCs to be studied for the CARB.
- At least six reactivity experiments for the selected coatings VOCs to be studied for the CARB.

During the following year of the project we conduct experiments for additional VOCs and begin assessing effects of humidity on reactivity and aerosol formation. Additional characterization experiments will be necessary so the data can be used for mechanism evaluation. Based on previous experiments

(Carter et al, 1997) it is expected that humidity will not have a large effect on ozone reactivity, but humidity is expected to significantly affect aerosol formation effects.

External Input

External input is critical to assure that this project represents the state of the art in environmental chamber research and that maximum advantage is taken of the unique characteristics of the facility to address mechanism evaluation issues of greatest relevance to regulatory assessment and control strategy development. Although the proposal called for forming an advisory group for this project, thus far external input has primarily been through the workshop held at the beginning of the project, consultation with the CARB staff and various industry groups concerning research needs for coatings VOCs through the CARB's RRAC, and informal discussions with the EPA/ASRL staff and other researchers. However, a more comprehensive process for external input is needed to review the draft research plan given in this report.

It is proposed that the Reactivity Research Working Group (RRWG) serve as the primary vehicle for providing external input and oversight for the overall project, with additional input being provided by the CARB's RRAC and selected experts in atmospheric chemistry and environmental chamber research being added as consultants, as discussed below. The RRWG is considered as the best vehicle to serve for the following reasons:

- The RRWG is was formed to coordinate reactivity-relevant research, and the overall objectives of this project directly address important components of the RRWG's medium and long-term research objectives.
- The EPA/ASRL staff and contractors responsible for oversight of this project, the head of the Atmospheric Processes group in the CARB Research Division, and the Principal Investigator are active in the RRWG, as are the industry groups that have shown the greatest interest in the need for VOC reactivity research, and an improved environmental chamber facility for this purpose.
- The RRWG science team includes technical experts in various areas of reactivity-related research, and previously prepared an assessment of the state of the science concerning VOC reactivity and reactivity models who can provide input on technical aspects of this project.
- The RRWG policy team includes representatives of regulatory agencies and regulated industries and can provide needed input on policy-relevance of proposed research for this project.
- The RRWG is a division of NARSTO, which provides guidance and resources for technical review, quality assurance, and data archiving and distribution.
- Informal discussions with EPA staff and consultants and with Dr. Don Fox, the chairman of the RRWG, indicate that there is a desire and willingness for the RRWG to participate in this manner. Dr. Fox is planning to put discussion of this project on the agenda for the next meeting, scheduled for January 16-17, 2002.

It is recommended that this report, after initial review by the EPA, be made available to the membership of the RRWG so they can be prepared to discuss it at the upcoming meeting in January. At that time, the mechanism for the RRWG oversight and input should be formulated. One approach would be to form a sub-group that would include appropriate technical experts, the EPA project officer, project officers for other projects using the chamber (currently only the CARB), and representatives of industry groups interested in this project, with those actually funding RRWG research projects being given priority. This group would review the research plan for this project and provide input and recommendations to the Principal Investigator through teleconferences and email, and present its overall

recommendations and criticisms at the following RRWG meeting, which probably would be in the Spring of 2002. Updates on the project, and comments on its outputs and modified research plans would then be discussed at the approximately quarterly RRWG meetings. The general RRWG meetings probably provide the best vehicle to provide input on policy-relevance of the research plan, though it is expected that at least some members of the oversight group for this project would also be members of the RRWG policy team.

It is also recommended that the RRWG oversight group select two or three scientists with appropriate expertise and understanding of the research objectives to serve as *paid* peer reviewers for this project. Although the Principal Investigator can suggest names for possible reviewers, the choice should be up to the EPA project officer in consultation with the RRWG oversight group. It is important that the reviewers be paid for their efforts, to assure that they give the project the attention it requires, and that the input is provided in a timely manner. However, an industry group or a regulatory agency could provide in-kind support by assigning this task to an appropriate expert in their employ. Fairly obvious candidates for peer reviewers include the membership of the CARB's Reactivity Science Advisory Committee, and the CARB may wish to consider using this committee for this purpose.

Their first task of the reviewers should be to review and criticize the work carried out thus far on this project and the draft research plan. They would then be retained to periodically conduct reviews of outputs of this project or provide recommendations to the RRWG and the Principal Investigator concerning the progress and current research plans. Although the Principal Investigator would obviously prefer it if the EPA or RRWG could find a source of funds to cover the costs of this review effort, if necessary (and with the approval of the EPA project officer) it could come from the funds for this cooperative agreement. The level of effort and funding needed should be discussed at the upcoming RRWG meeting.

The CARB's Reactivity Research Advisory Committee (RRAC) is already overseeing the Principal Investigator's projects concerning architectural coatings reactivity, which includes experiments in the current work plan. It is expected that this group will continue in this advisory and oversight capacity for the CARB projects. Although many of the industry participants in the RRAC are also active in the RRWG, the RRWG and RRAC meetings would probably have to continue to be separate because the CARB meetings must be in California, and the EPA participation in the RRWG meetings require that most RRWG meetings be on the East Coast.

QUALITY ASSURANCE

CE-CERT is in the process of preparing a comprehensive Quality Assurance Project Plan (QAPP) for use on this project. It is currently expected that this QAPP will be presented to EPA for review in January of 2002. A goal will be to have this QAPP approved and implemented before data collection begins in the new facility, or as soon thereafter as possible. This QAPP will present an overview of the entire project, but its emphasis will be on descriptions of the measurement methods, test protocols, and detailed descriptions of all the quality assurance activities that will be applied to the project. Appended to this QAPP will be the Standard Operating Procedures (SOPs) and Research Protocols (RPS) for the operation of all the measurement equipment to be used within the project, including procedures for operation of the chamber facility itself and for the fabrication and testing of the reactor bags.

Although this QAPP will contain each element presented in the EPA Guidance for Quality Assurance Project Plans, QA/R-5, the format for this QAPP will be based on the NARSTO Quality Integrated Work Plan Template for Monitoring and Measurement Research and Development Projects. This template is in Appendix A of the NARSTO Quality Planning Handbook, which may be found at the Narsto web site (www.cgenv.com/Narsto). In addition, where applicable, sections will be added from Appendix B of this document, Quality Integrated Work Plan Template for Model Development Projects.

This QAPP will contain specific definitions of the following quality assurance indicators as they apply to the chamber measurements: accuracy, bias, detection limits, precision, comparability, and completeness. In addition, the representativeness indicator will also be addressed in the areas of potential losses of aerosols and low volatility materials due to collection on chamber surfaces and/or sampling systems. Each of these will be defined with regard to the intended uses of the data and the limitations of the measurements themselves. Thus the validated data resulting from the chamber experiments will contain the necessary uncertainty limits as prescribed by NARSTO guidelines.

The QAPP will contain a table presenting the gaseous and particulate measurement methods to be utilized, including all ancillary measurements such as temperature and relative humidity. The table will present each method's measurement quality objectives for accuracy, precision, and detection limits. This will be followed by detailed summaries of the quality control systems to be established to evaluate the accuracy and precision of each parameter. These systems will consist of calibration and audit systems that will be utilized with sufficient frequency to demonstrate that each measurement within a given experiment is within prescribed control limits. In addition, the necessary corrective actions will also be prescribed in the event that the measurement device is found to be out of control.

The QAPP will also discuss the data archiving procedures. The standards and procedures used by NARSTO will be adopted where relevant, though it should be noted that there is no official NARSTO format for chamber data. The format for the archive will be determined by the Principal Investigator in consultation with the EPA project officer and relevant personnel responsible for the NARSTO archives.

The format for all the SOPs will be based on Guidance for the Preparation of Standard Operating Procedures (SOPs), EPA QA/G6. These SOPs will contain the approved, step-by-step techniques that will be used for performing the routine tasks associated with the chamber measurements. They will also contain clear and explicit descriptions of the activities to be performed. They will be written in a style and format so that a person knowledgeable in the general concept of the procedure easily understands them. At the same time they will contain a sufficient level of detail to ensure operational consistency, thus providing sufficient data comparability, credibility, and defensibility. Each SOP utilized on this project will be approved by the Principal Investigator and will be subject to approval by EPA.

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