

**A New Environmental Chamber for Evaluation of  
Gas-Phase Chemical Mechanisms and  
Secondary Aerosol Formation**

By

William P. L. Carter<sup>\*,†</sup>, David R. Cocker III<sup>†,‡</sup>, Dennis R. Fitz<sup>†</sup>, Irina L. Malkina<sup>†</sup>,  
Kurt Bumiller<sup>†</sup>, Claudia G. Sauer<sup>†,¶</sup>, John T. Pisano<sup>†</sup>, Charles Bufalino<sup>†</sup>, and Chen Song<sup>†,‡</sup>

<sup>†</sup>College of Engineering Center for Environmental Research and Technology,  
University of California, Riverside, California 92521

<sup>‡</sup>Department of Chemical and Environmental Engineering,  
University of California, Riverside, California 92521

<sup>¶</sup>Present Address: USP Indicators, Suppanstrasse 69, A-9020 Klagenfurt, Austria

\*Corresponding author

Accepted for Publication in  
*Atmospheric Environment*

August 15, 2005

## **Abstract**

A new state-of-the-art indoor environmental chamber facility for the study of atmospheric processes leading to the formation of ozone and secondary organic aerosol (SOA) has been constructed and characterized. The chamber is designed for atmospheric chemical mechanism evaluation at low reactant concentrations under well-controlled environmental conditions. It consists of two collapsible 90 m<sup>3</sup> FEP Teflon film reactors on pressure-controlled moveable frameworks inside a temperature-controlled enclosure flushed with purified air. Solar radiation is simulated with either a 200 kW Argon arc lamp or multiple blacklamps. Results of initial characterization experiments, all carried out at ~300-305 K under dry conditions, concerning NO<sub>x</sub> and formaldehyde offgasing, radical sources, particle loss rates, and background PM formation are described. Results of initial single organic - NO<sub>x</sub> and simplified ambient surrogate - NO<sub>x</sub> experiments to demonstrate the utility of the facility for mechanism evaluation under low NO<sub>x</sub> conditions are summarized and compared with the predictions of the SAPRC-99 chemical mechanism. Overall, the results of the initial characterization and evaluation indicate that this new environmental chamber can provide high quality mechanism evaluation data for experiments with NO<sub>x</sub> levels as low as ~2 ppb, though the results indicate some problems with the gas-phase mechanism that need further study. Initial evaluation experiments for SOA formation, also carried out under dry conditions, indicate that the chamber can provide high quality secondary aerosol formation data at relatively low hydrocarbon concentrations.

## **List of Keywords**

Environmental chambers, chamber characterization, atmospheric chemical mechanism evaluation, ozone, PM formation, secondary organic aerosol, oxides of nitrogen, SAPRC-99 mechanism

## Introduction

Environmental chambers have been used for the past few decades to investigate processes leading to secondary pollutant formation such as ozone (Jeffries et al, 1982; 1985a-c; 1990; Gery et al, 1988; Hess et al, 1992; Simonaitis and Bailey, 1995; Simonaitis et al, 1997; Carter et al, 1995a; Carter, 2000; Dodge, 2000 and references therein) and secondary organic aerosol (SOA). (e.g., Odum et al., 1996, 1997; ; Griffin et al., 1999; Kleindienst et al., 1999; Barnes and Sidebottom, 2000; Cocker et al. 2001a-c; Jang and Kamens, 2001; Seinfeld and Pankow, 2003 and references therein, Johnson et al, 2004, Montserrat et al, 2005). These chambers are essential for developing and evaluating chemical mechanisms or models for predicting the formation of secondary pollutants in the absence of uncertainties associated with emissions, meteorology, and mixing effects. Existing chambers have been used to develop the models now used to predict ozone formation (Gery et al, 1988; Stockwell et al, 1990; Carter, 2000; Dodge, 2000 and references therein), and are beginning to provide data concerning formation of SOA (e.g., Pandis et al., 1992; Griffin et al., 2001; Pun et al., 2003; Griffin et al., 2003, Johnson et al, 2004, Montserrat et al, 2005). However, environmental chambers are not without uncertainties in characterization and variability and background effects (Carter et al, 1982; Carter and Lurmann, 1991; Jeffries et al, 1992; Carter et al, 1995a; Dodge, 2000). This limits the utility of the data and the range of conditions under which the models or mechanisms can be reliably evaluated.

For example, because of background effects and analytical limitations, most chamber experiments to date have been conducted using levels of  $\text{NO}_x$  and other pollutants that are significantly higher than those that currently occur in most urban and rural areas (Dodge, 2000). Even lower ambient  $\text{NO}_x$  conditions are expected as we approach eventual attainment of the air quality standards. The nature of the radical and  $\text{NO}_x$  cycles and the distribution of VOC oxidation products change as absolute levels of  $\text{NO}_x$  are reduced. Because of this, one cannot necessarily be assured that the current mechanisms developed to simulate results of relatively high concentration experiments will satisfactorily simulate downwind or cleaner environments.

Background effects can be minimized by using large volume reactors and assuring that the matrix air is adequately purified, that appropriate wall material is utilized, and that steps are

taken to minimize introduction of ambient pollutants due to leaks or permeation. Large volume is also required for minimizing wall losses of aerosols or semi-volatile aerosol precursors, which is important in studies of SOA formation. For this reason, until recently, most studies of SOA formation have been carried out in large outdoor chambers (e.g., Jaoui et al., 2004; Griffin et al., 1999, Montserrat et al, 2005). However, outdoor chambers have diurnal, daily and seasonal changes in temperature and actinic flux, which can increase uncertainties in characterization of run conditions for model evaluation and make systematic studies of temperature and humidity effects difficult. Recently a new indoor chamber was developed to address these concerns (Cocker et al, 2001a), but that chamber was not designed to conduct experiments characterized for low pollutant conditions, and the blacklight light source employed does not represent that of natural sunlight in the longer wavelength region that affects some of the photooxidation processes (Carter et al, 1995b).

This paper describes a new state-of-the-art environmental chamber facility developed to minimize reactor effects in studies of VOC reactivity and provide a platform for low NO<sub>x</sub> and VOC ozone reactivity and secondary aerosol formation experiments. It also provides the technical background of the facility and assesses its ability and limitations for low NO<sub>x</sub> experiments. We discuss current reactor limitations and their implications for studies on ozone reactivity and SOA formation within Teflon reactors.

## **Facility Description**

The indoor facility comprises a 6m x 6m x 12m thermally insulated enclosure that is continually flushed with purified air at a rate of 1000 L min<sup>-1</sup> and is located on the second floor of a laboratory building specifically designed to house it. Located directly under the enclosure on the first floor is an array of gas-phase continuous and semi-continuous gas-phase monitors. Within the enclosure are two ~90 m<sup>3</sup> (5.5 m x 3 m x 5.5 m) maximum volume 2 mil FEP Teflon® film reactors, a 200 kW Argon arc lamp, a bank of 115 W 4-ft blacklights, along with the light monitoring and aerosol instrumentation. A schematic of the enclosure is provided in Figure 1.

## **Enclosure**

The interior of the thermally insulated 450 m<sup>3</sup> enclosure is lined with hard clear anodized aluminum sheeting to maximize the interior light intensity and homogenize the interior light intensity. A positive pressure is maintained between the enclosure and the surrounding room to reduce contamination of the reactor enclosure by the surrounding building air. The enclosure air is well mixed by the large air handlers that draw in air from inlets around the light and force the air through a false ceiling with perforated reflective aluminum sheets. The enclosure is temperature controlled with a ~30 ton (~105 KW cooling power) air conditioner capable of producing a temperature range of 5 to 45 C, controlled to better than  $\pm 1$  C.

## **Teflon Reactors**

The 2 mil (54  $\mu\text{m}$ ) FEP Teflon® reactors are mounted within the enclosure with a rigid bottom frame and a moveable top frame. The floor of the reactor is lined with Teflon® film with openings for reactant mixing within and between reactors and 8 ports ranging in size from 0.64 to 1.3 cm for sample injection and withdrawal. The moveable top frame is raised and lowered with a motorized pulley system, which enables the user to expand (during filling) and contract (during an experiment or for flushing) the reactors as necessary. The rate of contraction or expansion is set to maintain a differential pressure of 5 pascal between the inside of the reactor and the enclosure. During experiments, the top frames are slowly lowered to maintain positive pressure as the volume decreases due to sampling, leaks, and permeation. The experiment is terminated when the final reactor volume reaches 1/3 of its maximum value (typically about 10 hours, though less if there are leaks in a reactor). The elevator system coupled with differential pressure measurements allows for repeatable initial chamber volumes and allows for reactants to be injected with greater than 5% precision. The Teflon reactors are built in-house using a PI-G36 Pac Impulse Sealer (San Rafael, CA) heat sealing device for all major seams and are mounted to the reactor floor and ceiling.

The Teflon reactors tend to eventually crack and leak after repeated use, with the failures usually occurring at the seams. Because of the positive pressure control this results in shorter times for experiments rather than dilution or contamination of the reactor. Leaks are repaired

using a polyester film tape with a silicone adhesive (3M Polyester Tape 8403) when needed, and the reactors are repaired periodically before leaks and repairs become excessive.

### **Pure Air System**

An Aadco 737 series (Cleves, Ohio) air purification system produces compressed air at rates up to 1500 L min<sup>-1</sup>. The air is further purified by passing through canisters of Purafil® and heated Carulite 300® followed by a filter pack to remove all particulate. The purified air within the reactor has no detectable non-methane hydrocarbons (<1 ppb), NO<sub>x</sub> (<10 ppt), no detectable particles (<0.2 particles cm<sup>-3</sup>), and a dew-point below -40 C.

All the experiments discussed in this paper were carried out with unhumidified air, i.e., with a dew point below -40 C. A humidification system has now been constructed, and experiments employing this are underway or planned. This system and results of humidified experiments will be discussed in a subsequent paper.

The reactors are cleaned between runs by reducing the reactor volume to less than 5% of its original volume and re-filling it to its maximum volume with purified air at least six times. No residual hydrocarbons, NO<sub>x</sub>, or particles are detected after the cleaning process.

### **Light sources**

A 200 kW Argon arc lamp with a spectral filter (Vortek co, British Columbia, Canada) is used as the primary means to irradiate the enclosure and closely simulate the entire UV-Visible ground-level solar spectra. The arc lamp is mounted on the far wall from the reactors at a minimum distance of 6m to provide uniform lighting within both reactors. Backup lighting is provided by banks of total 80 1.22 m, 115-W Sylvania 350BL blacklamps (peak intensity at 350 nm) mounted on the same wall of the enclosure. These provide a low-cost and efficient UV irradiation source within the reactor for experiments where the closer spectral match provided by the Argon arc system is not required. The light spectra and intensity characterization for these sources are discussed below.

## **Interreactor and Intrareactor mixing**

The two reactors are connected to each other through a series of custom solenoid valves and blowers. The system provides for rapid air exchange prior to the start of an experiment ensuring, that both reactors have identical concentrations of starting material. Each reactor can be premixed prior to the start of an experiment by Teflon coated fans located within the reactor.

## **Instrumentation**

The suite of traditional and non-traditional instruments used to monitor gaseous species within the reactors complete with species detected and detection limits is listed and briefly described Table 1. All gas-phase instruments are located directly below the enclosure on the first floor of the building.

The aerosol phase instrumentation present is also included in Table 1, and is similar to that described by Cocker et al. (2001a). Particle size distributions are obtained using a scanning electrical mobility spectrometer (SEMS) (Wang and Flagan, 1990) equipped with a 3077 <sup>85</sup>Kr charger, a 3081L cylindrical long column, and a 3760A condensation particle counter (CPC). Flow rates of 2.5 LPM and 0.25 LPM for sheath and aerosol flow, respectively, are maintained using Labview 6.0-assisted PID control of MKS proportional solenoid control valves and relating flow rate to pressure drop monitored by Honeywell pressure transmitters. Both the sheath and aerosol flow are obtained from the reactor enclosure. The data inversion algorithm described by Collins et al (2001) converts CPC counts versus time to number distribution. In addition, a tandem differential mobility analyzer (TDMA) is available to measure physical changes to aerosol withdrawn from the chamber due to chemical or physical (temperature) changes in its environment (Cocker et al, 2001a).

## **Characterization Results**

### **Light Characterization**

Photolysis rates used when modeling chamber experiments are calculated using the measured NO<sub>2</sub> photolysis rates, the relative measured spectral distributions for the light sources,

and the absorption cross sections and quantum yields for NO<sub>2</sub> and the other photolysis reactions in the chemical mechanism being evaluated. Therefore the measured NO<sub>2</sub> photolysis rates serve as the measure of the absolute light intensity, and the *relative* spectral distributions of the light sources serve as the means to calculate the other photolysis rates relative to that for NO<sub>2</sub>. The precisions of the photolysis rates so derived are determined primarily by the precision of the NO<sub>2</sub> actinometry measurement. These are described below.

### **Argon arc lamp**

Although the intensity of the argon arc light can be varied by varying the lamp power, normally it is operated at 57% power, including all the experiments discussed here. Information about trends in light intensity with time is available from data from the spectral radiometer and PAR radiation instruments (Table 1), and from results of NO<sub>2</sub> actinometry experiments carried out periodically using the quartz tube method of Zafonte et al (1977) modified as discussed by Carter et al (1995a). The results indicated no significant change of light intensity with time during the period the chamber has been operated. Experiments with the quartz tube located inside the reactors yielded an NO<sub>2</sub> photolysis rate of  $0.26 \pm 0.01 \text{ min}^{-1}$ .

The relative spectrum of the arc light source was measured using a LI-COR LI-1800 spectroradiometer, and is shown on Figure 2. (The data are normalized to the same NO<sub>2</sub> photolysis rate because that is how they are used to derive photolysis rates in the experiments. The instrument does not measure the spherically integrated absolute intensities needed to directly calculate photolysis rates, but its data are useful for relative measurements.) No appreciable change in the light source spectrum was observed in the first 18 months of operation.

### **Blacklamps**

A series of NO<sub>2</sub> actinometry measurements inside the reactors with blacklight irradiation were carried out in April-May of 2003 and again in October of that year, and the averages of the results were  $0.19$  and  $0.18 \text{ min}^{-1}$ , respectively. Relative light intensity data taken during blacklight experiments indicated a gradual decreasing trend in light intensity during the experiments that was consistent with the differences between these two measurements. This gradual decrease in intensity with time is consistent with our experience with other blacklight



chambers (e.g., see Carter et al, 1995a). The uncertainty in the NO<sub>2</sub> photolysis rate assignments are estimated to be ~5%. The spectrum of this light source was essentially the same as that recommended by Carter et al (1995a) for modeling blacklight chamber runs, as shown in Figure 1, and did not change with time.

### **Comparison of Chamber and Solar Photolysis Rates**

A comparison of measured or calculated rate constants or rate constant ratios for selected representative photolysis rates for chamber experiments and solar irradiation is shown on Table 2. Solar photolysis rates and photolysis rate ratios are highly variable, and the variation with zenith angle shown on the table is only one of the many factors that need to be considered when modeling ambient photolysis processes. The photolysis rates measured or calculated for the arc light in the chamber are approximately within the range of ambient photolysis rates, and represent what can be achieved using current indoor light sources. Photolysis rates relative to NO<sub>2</sub> tend to be somewhat lower in the chamber than in solar light for photolysis processes that are sensitive to  $\lambda < 350$  nm radiation, such as O<sub>3</sub> photolysis to O(<sup>1</sup>D), because of the somewhat lower relative intensity of the light in the chamber in this wavelength region (see Figure 2). The blacklight light source is significantly less intense than solar or the arc light in the  $\lambda > 380$  nm range, resulting in significantly lower rates for photolysis reactions that are affected by longer wavelength light, such as O<sub>3</sub> photolysis to O(<sup>3</sup>P) or the photolysis of NO<sub>3</sub>.

Note that for mechanism evaluation purposes the differences between solar and in-chamber light intensity and spectra are taken into account by using the measured light intensities and spectra when calculating the photolysis rates used for modeling. Therefore, although a realistic spectrum is desirable in order to more closely approximate ambient conditions, exact matches are not absolutely necessary if the light is sufficiently well characterized.

### **Characterization of Contamination by Outside Air**

Minimizing contamination of the reactor by leaks and permeation of laboratory air contaminants was an important design goal of the new reactors. This is accomplished by providing clean air within the enclosure that houses the reactors. Continuous monitoring of the enclosure contents demonstrates that NO<sub>x</sub> and formaldehyde levels in the enclosure before or

during irradiations are less than 5 ppb and PM concentrations are below the detection limits of our instrumentation (see Table 1). Introduction of contaminants into the reactor is also minimized by use of pressure control to assure that the reactors are always held at slight positive pressures with respect to the enclosure. Thus leaks are manifested by reduction of the reactor volume rather than dilution of the reactor by enclosure air. The leak rate into the chamber was tested by injecting ~100 ppm of CO into the enclosure and monitoring CO within the reactor for more than 6 hours. In addition, since CO is a small molecule, it should provide an upper limit of leak plus permeation into the reactor. No appreciable CO (above the 50 ppb detection limit) was obtained for this experiment. Therefore it was concluded that leaks/permeation into the chamber is negligible for the current reactor configuration.

### **Chamber Effects Characterization**

It is critical to understand the impact of reactor walls on gas-phase reactivity and secondary aerosol formation. Larger volume reactors may minimize these effects, but they cannot be eliminated entirely or made negligible. For mechanism evaluation and SOA studies the most important of these effects include background offgasing of NO<sub>x</sub> and other reactive species, offgasing or heterogeneous reactions that cause “chamber radical sources” upon irradiation (e.g., see Carter et al, 1982), ozone and particle losses to the reactor walls, and background offgasing of PM or PM precursors. Most of these can be assessed by conducting various types of characterization experiments that either directly measure the parameter of interest, or are highly sensitive to the chamber effect being assessed (e.g., see Carter et al, 1995a). The chamber effects relevant to gas-phase mechanism evaluation that have been assessed and the types of experiments utilized for assessing them are summarized in Table 3. These are discussed further below.

Note that as indicated in Table 3 some of the chamber characterization parameters are derived by conducting model simulations of the appropriate characterization experiments to determine which parameter values best fit the data. All the characterization simulations discussed here were carried out using the SAPRC-99 chemical mechanism (Carter, 2000) with the photolysis rates calculated using the light characterization data discussed above, using the measured temperatures of the experiments, and assuming no dilution for reasons discussed in the

previous section. The rates of heterogeneous reactions not discussed below, such as  $\text{N}_2\text{O}_5$  hydrolysis to  $\text{HNO}_3$  or  $\text{NO}_2$  hydrolysis to  $\text{HONO}$ , were derived or estimated based on laboratory studies or other considerations as discussed by Carter et al (1995a). Although the assumed values of these parameters can affect model simulations under some conditions, they are not considered to be of primary importance in affecting simulations of the characterization or other experiments discussed here.

### **$\text{NO}_x$ offgasing**

$\text{NO}_x$  offgasing is the main factor limiting the utility of the chamber for conducting experiments under low  $\text{NO}_x$  conditions. Although this can be derived by directly measuring increases in  $\text{NO}_x$  species during experiments when  $\text{NO}_x$  is not injected, the most sensitive measure is the formation of  $\text{O}_3$  in irradiations when VOCs but not  $\text{NO}_x$  are initially present. Therefore, the  $\text{NO}_x$  offgasing rate is not determined directly, but derived by determining the magnitude of the  $\text{NO}_x$  offgasing rates that it is necessary to assume in the chamber effects model for the model simulations of the experiments to correctly predict the experimentally observed  $\text{O}_3$  yields. The  $\text{NO}_x$  offgasing can be represented in the model as inputs of any species that rapidly forms  $\text{NO}_x$  in atmospheric irradiation systems, such as  $\text{NO}$ ,  $\text{NO}_2$ , or  $\text{HONO}$  (which rapidly photolyzes to form  $\text{NO}$ , along with  $\text{OH}$  radicals), but for reasons discussed below it is represented in our chamber effects model as offgasing of  $\text{HONO}$ , e.g.,



Where  $k_1$  is the light intensity as measured by the  $\text{NO}_2$  photolysis rate, and  $\text{RN}$  is the  $\text{NO}_x$  (and radical) offgasing parameter, which is derived by model simulations of the appropriate characterization experiments to determine which value best fits the data.

The  $\text{NO}_x$  offgasing rates necessary to use in the model simulations to predict the observed  $\text{O}_3$  formation rates in the  $\text{CO}$  - air, formaldehyde - air and  $\text{CO}$  - formaldehyde - air experiments carried out in the first eight months of operation of this chamber are shown as the triangle symbols in Figure 3. The plots are against the EPA chamber experimental run number, which indicates the order that the experiment was carried out. It can be seen that the rates of around 1.5 ppt/min generally fit the data up to around run 85, then these increased to 2-7 ppt/min after that,

being somewhat higher in the “A” reactor compared to the “B” reactor. The reason for this increase is unclear, but it may be related to the fact that maintenance was done to the reactors around the time of the change. The magnitudes of these apparent NO<sub>x</sub> offgasing rates are discussed further below in conjunction with the discussion of the continuous radical source, which is also attributed to HONO offgasing.

### **Chamber radical source**

It has been known for some time that environmental chamber experiments could not be modeled consistently unless some sources of radicals attributed to chamber effects is assumed (e.g., Carter et al, 1982; Carter and Lurmann, 1991; Carter, 2000). The most sensitive experiments to this effect are NO<sub>x</sub> -air irradiations of compounds, such as CO or alkanes, which are not radical initiators or do not form radical initiating products to a sufficient extent to significantly affect their photooxidations. If no chamber dependent radical source is assumed, model simulations of those experiments predict only very slow NO oxidation and essentially no O<sub>3</sub> formation, while in fact the observed NO oxidation and O<sub>3</sub> formation rates are much higher (Carter et al, 1982). It is necessary to assume unknown or chamber-dependent radical sources for the model to appropriately simulate the results of these experiments.

In some chambers at least part of the chamber-dependent radical source can be attributed to formaldehyde offgasing (Simonaitis et al, 1997, Carter, 2004), but as discussed below the magnitude of the formaldehyde offgasing in this chamber is relatively small, and not sufficient by itself for the model to simulate radical-source dependent experiments. For this chamber, assuming HONO offgasing at a similar magnitude as the apparent NO<sub>x</sub> offgasing rate derived as discussed above is usually sufficient to account for most of the chamber-dependent radical source, though results of some of the experiments are somewhat better simulated if a small amount (100 ppt or less) of HONO is also assumed to be initially present.

The round symbols in Figure 3 shows plots of the HONO offgasing rates that are necessary to assume in the model simulations for the model to simulate the NO oxidation and O<sub>3</sub> formation rates in the radical-source sensitive CO - NO<sub>x</sub> and n-butane - NO<sub>x</sub> experiments that were carried out in January-October of 2003. Note that since these experiments had initial NO<sub>x</sub>

levels ranging from 10 - 200 ppb, so they were not sensitive to NO<sub>x</sub> offgasing as such. However, from Figure 3 it can be seen that the magnitudes of the NO<sub>x</sub> offgasing and continuous radical input rates that fit the data for the respective characterization experiments were in the same range, and even changed at the same time when the characteristics of the chamber apparently changed. Whatever effect or contamination caused the apparent NO<sub>x</sub> offgasing to increase around the time of run 85 caused the same increase in the apparent radical source.

### **Comparison of Radical Source and NO<sub>x</sub> Offgasing with Other Chambers**

Although HONO is not measured directly in our experiments, the fact that both the radical-sensitive and NO<sub>x</sub>-sensitive characterization experiments can be simulated assuming HONO offgasing at approximately the same rates is highly suggestive that this is the process responsible for both effects. Direct evidence for this comes from the data of Rohrer et al (2004), who used sensitive long path absorption photometer (LOPAP) instrument to detect ppt levels of HONO emitted from the walls during irradiations in the large outdoor SAPHIR chamber (Brauers et al, 2003) at rates comparable to those observed in the earlier experiments in our chamber. The SAPHIR chamber is similar in design to our chamber, except it is larger in volume and is located outdoors. In particular, like our chamber it has Teflon walls and uses an enclosure configuration to minimize contamination by outside air. Therefore, it would be expected to have similar chamber NO<sub>x</sub> and radical sources, and this appears to be the case.

Figure 4 shows plots of the NO<sub>x</sub> offgasing or radical source parameter (e.g. RN in Equation 1) obtained in modeling appropriate characterization runs in various chambers, where they are compared with direct measurements made in the SAPHIR chamber (Rohrer et al, 2004). In addition to those for this UCR EPA, the radical source parameters shown are those derived by Carter (2000) for previous indoor and outdoor chambers at UCR (Carter et al, 1995a), those derived by Carter and Lurmann (1991) for the University of North Carolina (UNC) outdoor chamber (Jeffries et al, 1982, 1995a-c, 1990), and those derived by Carter (2004) for the Tennessee Valley Authority (TVA) indoor chamber (Simonaitis and Bailey, 1995; Bailey et al, 1996). (Note that the data shown for the UCR EPA chamber includes experiments carried out subsequently to those shown in Figure 3, including a few runs at reduced temperature.) The figure shows that the radical source and NO<sub>x</sub> offgasing rates derived for this chamber are

comparable in magnitude to the HONO offgasing directly measured in the SAPHIR chamber and also comparable to the NO<sub>x</sub> offgasing derived for TVA chamber but are significantly lower than those derived from modeling characterization data from the earlier UCR and UNC chambers. It is interesting to note that parameters derived for the various chambers indicate that the radical source and HONO or NO<sub>x</sub> offgasing rates all increase with temperature.

Therefore, the radical source and NO<sub>x</sub> offgasing rates indicated by the characterization data for the first series of experiments for this chamber is probably as low as one can obtain for reactors constructed of FEP Teflon film, which is generally believed to be the most inert material that is practical for use as chamber walls. Although the radical source and NO<sub>x</sub> offgasing rates for the second series of experiments is higher (see also Figure 3), they are still about an order of magnitude lower than observed for the UCR and UNC chambers previously used for mechanism evaluation.

### **Formaldehyde offgasing**

Low but measurable amounts of formaldehyde were formed in irradiations in this chamber, even in pure air, CO - NO<sub>x</sub>, or other experiments where no formaldehyde or formaldehyde precursors were injected, and where formaldehyde formation from the reactions of methane in the background air is predicted to be negligible. The data in essentially all such experiments could be modeled assuming a continuous light-dependent formaldehyde offgasing rate corresponding to 0.3 ppb/hour at the light intensity of these experiments. Formaldehyde levels resulting from this relatively low offgasing rate could not be detected with formaldehyde analyzers used in most previous UCR and other chamber experiments, and are insufficient to account for the apparent chamber radical source observed in most chamber experiments. This apparent formaldehyde offgasing has a non-negligible effect on very low VOC and radical source characterization experiments, so it must be included in the chamber characterization model. However, it has a relatively minor impact on modeling most experiments used for VOC mechanism evaluation or reactivity assessment.

The source of the apparent formaldehyde offgasing in the Teflon reactors is unknown, but it is unlikely to be due to buildup of contaminants from previous exposures or contamination

from the enclosure. The apparent formaldehyde offgasing rate is quite consistent in most cases and there are no measurable differences between the two reactors. This is despite the fact that the East or “Side B” reactor was constructed several months after the West or “Side A” reactor, which was used in at least 17 experiments before the second reactor was built. In addition the background formaldehyde level in the enclosure was quite variable during this period, and no apparent correlation between this and the apparent formaldehyde offgasing rates in the reactor was observed. The data are best modeled by assuming only direct formaldehyde offgasing, as opposed to some formaldehyde being formed from light-induced reactions of some undetected contaminant.

### **Other Reactive VOC Background or Offgasing**

Because of limitations in the detection and sensitivity of the organic monitoring methods currently available with our chamber, characterization experiments that are sensitive to background reactive VOCs provide the most useful means to assess whether background levels or offgasing of other reactive VOCs are significant. Ozone formation in pure air runs is very sensitive to background reactive VOCs, though it is also sensitive to the NO<sub>x</sub> offgasing effects discussed above. The average 6-hour ozone levels in the pure air runs carried out with the arc lights during this period with the chamber in the standard configuration was only 4±2 ppb. This can be compared with the model simulations of the same experiments, using the NO<sub>x</sub> and formaldehyde offgasing parameters derived from the other characterization experiments as discussed above, and assuming no other reactive VOCs are present, which gave an average 6-hour O<sub>3</sub> of 6±2 ppb. This indicates that background or offgasing of other reactive VOCs is not significantly affecting results of these experiments, and should have even smaller effects on mechanism evaluation experiments with added reactive VOCs.

### **Particle wall losses**

Particle wall losses are expected in finite volume reactors and are somewhat enhanced by the charged surfaces of the Teflon media. Particle wall losses within chambers have been described in detail in Cocker et al. (2001a). Briefly, wall losses are expected to be described by a first order wall loss mechanism with a weak size dependence for the aerosol sizes typical of SOA experiments. Particle wall loss rates can be determined in any experiment where particles are

present for a sufficiently long time that new particle formation is no longer determining. If it is assumed that no new particle formation is occurring, then the decay rate in the particle number can be assumed to be the particle loss rate.

Figure 5 shows plots of particle wall loss obtained from data from various experiments in this chamber from the time particle measurements were made through the summer of 2004. It can be seen that although there is run-to-run variability, the decay rates are reasonably consistent at approximately  $7 \text{ day}^{-1}$ , with no significant differences among reactors. This is within the range reported for other large chamber facilities (Barnes and Sidebottom, 2000, Griffin, 1999). While the maximum particle volume in the experiments ranged from less than  $0.1$  to almost  $80 \mu\text{g}/\text{m}^3$ , there was no correlation between maximum particle volume and measured decay rate.

### **Background Particle Formation**

The reactor walls could be a source of particles as well as gas-phase species. This could be due to either direct release of particles from the walls during the irradiations, or offgasing of compounds that react to form secondary PM. Background PM formation could also occur if there were impurities in the air that reacted to form secondary PM. This would be manifested by the formation of particles in pure air irradiations or irradiations of reactants that are not expected to form condensable products.

Maximum PM number and PM volume levels measured after 5 hours of irradiation in pure air, CO - air, CO - NO<sub>x</sub> - air, and propene - NO<sub>x</sub> experiments carried out in the second set of reactors, installed immediately before run 169, are shown on Figure 6. (Characterization data for the first set of reactors are sparse but generally consistent with the results shown here.) Measurable PM formation is seen in pure air and propene - NO<sub>x</sub> experiments, but essentially no PM formation is seen in the CO - air or CO - NO<sub>x</sub> irradiations. The lack of measurable PM in the CO - air or CO - NO<sub>x</sub> experiments suggests that PM is not directly emitted from the irradiated walls, though this is considered to be unlikely in the first place. The fact that background PM is formed in the pure air and propene - NO<sub>x</sub> experiments but not the CO - air or CO - NO<sub>x</sub> experiments could be attributed to PM formation from the reaction of OH radicals with some background contaminant(s). Model calculations predict that OH levels are suppressed in the CO



experiments because of its reaction with CO combined with the lack of homogeneous radical sources in CO - air or CO - NO<sub>x</sub> systems.

The background PM in the pure air and propene - NO<sub>x</sub> experiments is the highest when the reactors were new, and eventually decline as the reactor is used. This suggests that, at least for these reactors, contaminants due to the experiments are less important than contaminants on the new Teflon film or that are introduced during its construction. The apparent background PM in eventually declined in both reactors, becoming very low in Reactor B, but continued to be non-negligible in Reactor A. Reactor A also had higher levels of background PM at the start.

Although the reaction of O<sub>3</sub> with background contaminants could be another source of background PM, this does not appear to be as significant in this chamber. Higher levels of O<sub>3</sub> are formed in CO - air than in pure air runs, yet the PM levels are much lower in the presence of CO. PM levels in O<sub>3</sub> dark decay experiments are relatively low. In particular, the PM volume in the 0.2 ppm O<sub>3</sub> dark decay experiment 179 was only ~0.1 μg/m<sup>3</sup> in both reactors after ~5 hours, despite the fact that this was during period with new reactors when the background was relatively high. The PM levels increased only slightly when O<sub>3</sub> was irradiated.

## **Initial Experiments**

### **Gas-Phase Characterization and Mechanism Evaluation Experiments**

Table 4 gives a summary of the initial experiments carried out in this chamber for gas-phase characterization and mechanism evaluation. All these experiments were carried with unhumidified air (dew point < -40 C), at atmospheric pressure (~740 torr local pressure) and at 303±1 K for arc light runs and at 301±1 K for blacklight experiments. The various characterization experiments were used to derive the chamber characterization parameters and evaluate the chamber characterization model as discussed above. The single organic - NO<sub>x</sub> experiments were carried out to demonstrate the utility of the chamber to test the mechanisms for these compounds, for which data are available in other chambers, and to obtain well-characterized mechanism evaluation data at lower NO<sub>x</sub> levels than previously available. The formaldehyde + CO - NO<sub>x</sub> experiments were carried out because they provided the most

chemically simple system that model calculations indicated was insensitive to chamber effects, to provide a test for both the basic mechanism and the light characterization assignments. The aromatic + CO - NO<sub>x</sub> experiments were carried out because aromatic - NO<sub>x</sub> experiments were predicted to be very sensitive to the addition of CO, because it enhances the effects of radicals formed in the aromatic system on ozone formation. The ambient surrogate - NO<sub>x</sub> experiments were carried out to test the ability of the mechanism to simulate ozone formation under simulated ambient conditions at various reactive organic gas (ROG) and NO<sub>x</sub> levels.

The ROG surrogate used in the ambient surrogate - NO<sub>x</sub> experiments consisted of a simplified mixture designed to represent the major classes of hydrocarbons and aldehydes measured in ambient urban atmospheres, with one compound used to represent each model species used in condensed lumped-molecule mechanism. The eight representative compounds used were n-butane, n-octane, ethene, propene, trans-2-butene, toluene, m-xylene, and formaldehyde. (See Carter et al, 1995c, for a discussion of the derivation of this surrogate).

It is important to note that these experiments represent only dry conditions and a single temperature and therefore do not represent the full range of conditions in the atmosphere. The very dry conditions of these experiments are not representative of most ambient atmospheres, though they have the significant advantages for mechanism evaluation because chamber effects tend to be lower and more straightforward to characterized. For this reason, experiments under dry conditions are important in the evaluations of the current SAPRC (Carter, 2000) and RADM-2 (Stockwell et al, 1990; Carter and Lurmann, 1990) mechanisms, and represent an necessary starting point in any comprehensive evaluation study. Previous data from our laboratories with other chambers indicate that increasing humidity does not significantly affect mechanism evaluation results until it approaches ~100% (Carter et al, 1997). This will be evaluated further in future experiments with this chamber.

The ability of the SAPRC-99 mechanism (Carter, 2000) to simulate the total amount of NO oxidized and O<sub>3</sub> formed in the experiments, measured by  $([O_3]_{final} - [NO]_{final}) - ([O_3]_{initial} - [NO]_{initial})$ , or  $\Delta([O_3] - [NO])$ , is summarized for the various types of experiments on Table 4 and shown for the individual runs on Figure 7. This gives an indication of the biases and run-to-run variability of the mechanism in simulating ozone formation. In experiments with excess NO the

processes responsible for O<sub>3</sub> formation are manifested by consumption of NO, so simulations of  $\Delta([\text{O}_3]-[\text{NO}])$  provides a test of model simulations of these processes even for experiments where O<sub>3</sub> is not formed.

Note that the characterization runs were modeled using the same set of characterization parameters as used when modeling the mechanism evaluation runs, which are based on averages of best fit values for the individual experiments, and not with the values that were adjusted to fit the individual runs. Therefore, the relatively large variability and average model error for the model simulations of  $\Delta([\text{O}_3]-[\text{NO}])$  in those experiments provides a measure of the variability of the chamber effects parameters (e.g., HONO offgasing) to which these experiments are sensitive. The relatively low average bias is expected because the chamber effects parameter values were derived based on these data.

For the single VOC - NO<sub>x</sub> or VOC - CO - NO<sub>x</sub> experiments, the model is able to simulate the  $\Delta([\text{O}_3]-[\text{NO}])$  to within  $\pm 25\%$  or better in most cases, which is better than the  $\pm \sim 30\%$  seen in previous mechanism evaluations with the older chamber data (Carter and Lurmann, 1990, 1991; Gery et al, 1989, Carter, 2000). However, there are indications of non-negligible biases in model simulations of certain classes of experiments. The cleaner conditions and the relatively lower magnitude of the chamber effects may make the run-to-run scatter in the model performance less than in the simulations of the previous data, and this tends to make smaller biases in the model performance more evident. For example, Figure 7 shows that the mechanism tends to underpredict O<sub>3</sub> formation in aromatic - NO<sub>x</sub> experiments with added CO, even though it has a slight tendency to overpredict O<sub>3</sub> in the aromatic - NO<sub>x</sub> experiments without added CO. This suggests problems with the aromatics mechanisms that need further investigation (Carter, 2004).

The mechanism tended to have a bias towards underpredicting  $\Delta([\text{O}_3]-[\text{NO}])$  in the ambient surrogate - NO<sub>x</sub> experiments, though as indicated in Figure 7 this underprediction did not occur for all experiments. The underprediction bias had very little correlation with the initial ROG and NO<sub>x</sub> levels in the experiments but was highly correlated with the initial ROG/NO<sub>x</sub> ratio. This is shown in Figure 8, which gives plots of the  $\Delta([\text{O}_3]-[\text{NO}])$  model underprediction bias against the initial ROG/NO<sub>x</sub> ratio the experiments. The “error bars” show the effects of

varying the HONO offgasing parameter over the extreme values shown in Figure 4 for this chamber for the  $303 \pm 1$  K temperature range, which applicable to these experiments. It can be seen that the model has a definite tendency to underpredict  $\Delta([O_3]-[NO])$  at the low ROG/NO<sub>x</sub> ratios. Although the HONO offgasing parameter has a non-negligible effect on the simulations of the experiments at the lowest and highest ROG/NO<sub>x</sub> ratio (because of sensitivities to the radical source in the first case and to the NO<sub>x</sub> source in the second), the sensitivity is not sufficient to account to the trend in the bias with ROG/NO<sub>x</sub>. This trend was not evident in the previous mechanism evaluations, perhaps in part because of the greater variabilities of the model simulations due to greater chamber effects or characterization uncertainties, and perhaps in part because this is not as evident at higher reactant concentrations. This suggests problems with the mechanism that also needs further investigation (Carter, 2004).

As indicated in Table 4, the initial evaluation experiments included runs with NO<sub>x</sub> levels as low as 2-5 ppb, which is considerably lower than in experiments used previously for mechanism evaluation. Most of the experiments used in the previous SAPRC-99 mechanism evaluation had NO<sub>x</sub> levels greater than 50 ppb, and even the “low NO<sub>x</sub>” TVA and CSIRO experiments had NO<sub>x</sub> levels of ~20 ppb or greater, except for a few characterization runs (Carter, 2004, and references therein). However, other than the ROG/NO<sub>x</sub> effect for the ambient surrogate experiments discussed above, there is no indication in any difference in model performance in simulating the results of these very low NO<sub>x</sub> experiments, compared to those with the higher NO<sub>x</sub> levels more representative of those used in the previous evaluation. This is an important finding because there has been a concern about using mechanisms evaluated at higher than ambient NO<sub>x</sub> levels for ambient simulations of remote areas or future case attainment scenarios (Dodge, 2000).

For example, Figure 9 shows concentration-time plots for selected measured species in ambient surrogate - NO<sub>x</sub> experiment carried out at the lowest NO<sub>x</sub> levels in the initial evaluation runs. To indicate the sensitivity of the experiments to NO<sub>x</sub> offgasing effects, the effects of varying the HONO offgasing parameter from zero to the maximum level consistent with the characterization experiments is also shown. It can be seen that the model using the default HONO offgasing parameter value gives very good fits to the data. Although the O<sub>3</sub> simulations

are somewhat affected when the HONO offgassing rate is varied within this somewhat extreme range, the sensitivity is not so great that the uncertainty in this parameter significantly affects conclusions one can draw about the ability of the model to simulate this low NO<sub>x</sub> experiment. However, the sensitivity would increase as the NO<sub>x</sub> levels are reduced, and ~2 ppb NO<sub>x</sub> probably represents a reasonable lower limit for NO<sub>x</sub> levels useful for mechanism evaluation.

Overall, the results of the initial characterization and evaluation indicate that this chamber can provide high quality mechanism evaluation data for experiments with NO<sub>x</sub> levels as low as ~2 ppb, considerably lower than employed in previous experiments. Chamber effects are not absent, but they are as low or lower than in observed in any previous chambers used for mechanism evaluation, in some cases by an order of magnitude or more. Although a larger number of experiments would be required to fully assess this, the results also suggest a higher degree of precision in mechanism evaluation than observed previously, making smaller biases in mechanism performance more evident. The initial dataset from this chamber indicate no significant problems with mechanism performance that are characteristic of low NO<sub>x</sub> conditions as such, but do reveal problems with the mechanisms for aromatics and the ambient ROG surrogate (Carter, 2004).

### ***m*-Xylene-NO<sub>x</sub> SOA Yield**

A series of *m*-xylene/NO<sub>x</sub> experiments photooxidations were performed using the blacklights as an irradiation source. These blacklight experiments were carried with unhumidified air (dew point < -40 C), at atmospheric pressure (~740 torr local pressure) and at 301±1 K. These experiments were used to determine our ability to perform SOA experiments. The data is analyzed following the original schemes outlined by Pankow et al. (1994a,b) and Odum et al. (1996). Briefly, SOA yield, *Y*, is defined as the ratio of aerosol (μg m<sup>-3</sup>) to hydrocarbon reacted (μg m<sup>-3</sup>).

$$Y = \sum_i Y_i = \Delta M_{org} \sum_i \frac{\alpha_i K_{om,i}}{1 + K_{om,i} \Delta M_{org}} \quad (2)$$

where  $\alpha_i$  is the mass-based stoichiometric fraction of species *i* formed from the parent hydrocarbon,  $K_{om,i}$  is the gas-particle partitioning coefficient (m<sup>3</sup> μg<sup>-1</sup>), which is inversely

proportional to the compound's vapor pressure, and  $\Delta M_{org}$  ( $\mu\text{g m}^{-3}$ ) is the total mass concentration of organic material and associated water present in the aerosol phase. The fraction of secondary organic material condensing into the aerosol phase is seen to depend on the amount of organic aerosol mass present. The two-product semi-empirical model then assumes that two surrogate species can be used to estimate the SOA yield: one surrogate product representing low vapor pressure compounds and one surrogate product representing high vapor pressure compounds. ( $i=1,2$  in equation 2)

A set of characterization runs was carried out to demonstrate the ability of the chamber to perform SOA formation experiments. *m*-xylene was chosen as the initial test compound. Four experiments with initial *m*-xylene and NO initial concentrations of 75 ppb and 50 ppb respectively,  $T=300\text{K}$ , no initial aerosol present, and blacklight irradiation source were conducted until measurable aerosol volume growth (corrected for wall loss) had ceased (approximately 8 hours irradiation time,  $\sim 90\%$  *m*-xylene consumption). The experiments were conducted on both reactors with a couple of months time separating the first and last experiment. Average total aerosol production for the four reactions was  $21.4 \pm 0.3 \mu\text{g m}^{-3}$ .

Additional *m*-xylene/NO<sub>x</sub> experiments were performed with blacklights for comparison to previously published yield data. The yield data are most easily compared to recent *m*-xylene irradiations at Caltech at comparable experimental conditions (indoors, blacklight source, similar temperatures) (Cocker et al. 2001c), and the results for the various chambers are shown on Figure 10. The "Empirical Fit through UCR Data" is the the best fit two product semi-empirical fit yield curve for the current dataset from this chamber, for which the parameters are 0.075, 0.105, 0.139, 0.010 for  $\alpha_1$ ,  $\alpha_2$ ,  $K_{om,1}$ ,  $K_{om,2}$ , respectively. The overall agreement between this chamber and the Caltech chamber helps to verify the ability of the new chamber to accurately simulate gas-to-particle conversion processes. More details on the current dataset for *m*-xylene/NO<sub>x</sub> aerosol production can be found in Song et al. (2005).

## Discussion and Conclusions

This chamber facility was designed to provide more precise and comprehensive mechanism evaluation data, and at lower simulated pollutant concentrations, than previously possible. Although the dataset from this chamber is still limited, the results to date demonstrate its utility for providing valuable data for mechanism evaluation. The major background effects parameters in the chamber appear to be lower than those observed in other chambers used for mechanism evaluation, including the TVA chamber, which was also designed for experiments at lower pollution levels (Simonaitis and Bailey, 1995; Simonaitis et al, 1997).

The lower background levels in this chamber permitted successful mechanism evaluation experiments to be carried out with NO<sub>x</sub> levels as low as 2 ppb. This is at least an order of magnitude lower than in the mechanism evaluation dataset from other chambers used for gas-phase mechanism evaluation. In addition, we believe that the lower background effects attainable in this chamber provided an improvement in the precision of the mechanism evaluation dataset. The results of modeling the relatively large number of surrogate - NO<sub>x</sub> experiments give some information regarding this. Although the model had systematic biases in simulating many of these experiments, as shown in Figure 8, plots of model biases against ROG/NO<sub>x</sub> ratios had relatively little scatter, suggesting fits to within  $\pm 10\%$  could be obtained if the current problem(s) with the mechanism can be corrected. This is less than the scatter for the fits to comparable experiments in other chambers (Carter and Lurmann, 1991; Carter, 2000, 2004). This is important since if the scatter in these fits were on the order of  $\pm 30\%$ , which was observed in mechanism evaluation studies using other chamber data sets (e.g., Carter and Lurmann, 1991), the ROG/NO<sub>x</sub> dependences may not have been statistically significant, and the mechanism performance would have been concluded to be satisfactory. With this more precise dataset the low ROG/NO<sub>x</sub> problem with the mechanism is evident.

We believe that this chamber is also well suited for studies of secondary aerosol formation. The good reproducibility of multiple experiments and general agreement with past work demonstrates our ability to accurately and precisely measure SOA formation potentials. Further work is clearly needed to characterize and eventually reduce or control background aerosol formation in this chamber, though this appears to be a problem with all environmental

chambers used for aerosol studies. The relatively low chamber background effects and degree of characterization for gas-phase processes is also a significant advantage in studies of secondary PM formation, since it is the gas phase processes that lead to the formation of secondary PM. The ability to control temperature (and therefore humidity) is important, since data are needed to systematically study gas-to-particle conversion processes in well-controlled reactors.

Although the experiments reported here were carried only under dry conditions and at a single temperature, a humidification system has been constructed and the chamber is capable of controlled experiments in a wide temperature range of relevance to tropospheric pollution. Experiments to assess effects of varying humidity and temperature are currently underway or planned and will be discussed in subsequent papers.

### **Acknowledgements**

The construction and initial characterization of this facility was funded by the United States Environmental Protection Agency Cooperative Agreement No. CR 827331-01. Some of the later experiments were also funded through EPA Cooperative Agreement No. CR-830957-01, Gail Tonnesen, Principal Investigator, and the lowest NO<sub>x</sub> surrogate experiments were funded by California Air Resources Board Contract 01-305. Additional funding from NSF grant no. 024111 is also acknowledged. Helpful discussions with Dr. Basil Dimitriades and Deborah Luecken, the EPA project officers, are acknowledged. Assistance in the design and construction of this facility was provided by Mr. Matthew Smith. Dr. Joseph Norbeck provided valuable assistance in developing the necessary infrastructure to house this facility.



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Table 1. List of analytical and characterization instrumentation

Type	Model or Description	Species	Sensitivity	Comments
Ozone Analyzer	Dasibi Model 1003-AH. UV absorption analysis. Monitor Labs Chemiluminescence Ozone Analyzer Model 8410	O <sub>3</sub>	2 ppb	Standard monitoring instruments.
NO - NO <sub>y</sub> Analyzer	Teco Model 42 C with external converter. Chemiluminescent analysis for NO, NO <sub>y</sub> by catalytic conversion.	NO NO <sub>y</sub>	1 ppb 1 ppb	Useful for NO and initial NO <sub>2</sub> monitoring. Converter close-coupled to the reactors so the “NO <sub>y</sub> ” channel should include HNO <sub>3</sub> as well as NO <sub>2</sub> , PANs, organic nitrates, and other species converted to NO by the catalyst.
CO Analyzer	Dasibi Model 48C. Gas correlation IR analysis.	CO	50 ppb	Standard monitoring instrument
Tunable Diode Laser Absorption Spectroscopy (TDLAS) #1	TDLAS analysis is based on measuring single rotational - vibrational lines in the near to mid infrared using tunable laser diodes with very narrow line widths (Hastie et al., 1983; Schiff et al., 1994), Two such instruments purchased from Unisearch Inc. and adapted for this chamber. Data transmitted to DAC system using RS-232.	NO <sub>2</sub>	0.5 ppb	NO <sub>2</sub> data from this instrument are considered to be interference-free.
TDLAS #2		HNO <sub>3</sub>	~ 1 ppb	HNO <sub>3</sub> data were not available for all experiments discussed in this paper.
		HCHO	~ 1 ppb	Formaldehyde data from this instrument are considered to be interference-free.
		H <sub>2</sub> O <sub>2</sub>	~2 ppb	H <sub>2</sub> O <sub>2</sub> measurements were not made during the experiments discussed in this paper.
GC-FID #1	HP 5890 Series II GC with dual columns, loop injectors and FID detectors. Various megabore GC columns available. Controlled by computer interfaced to network.	VOCs	~10 ppbC	Equipped with: 30 m x 0.53 mm GS-Alumina column used for the analysis of light hydrocarbons and 30 m x 0.53 mm DB-5 column used for the analysis of C <sub>5+</sub> alkanes and aromatics. Loop injection suitable for low to medium volatility VOCs that are not too “sticky” to pass through valves.
GC-FID #2	HP 5890 Series II GC with dual columns and FID detectors, one with loop sampling and one set up for Tenax cartridge sampling. Various megabore GC columns available. Controlled by computer interfaced to network.	VOCs VOCs	~10 ppbC 1 ppbC	30 m x 0.53 mm GSQ column. Loop injection suitable for low to medium volatility VOCs that are not too “sticky”. Not used as primary analysis for most of these experiments. 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. Equipped with a 30 m x 0.53 mm DB-1701 column.
Luminol GC	Developed and fabricated at our laboratory based on work of Gaffney et al (1998). Uses GC to separate NO <sub>2</sub> from PAN	NO <sub>2</sub>	~0.5 ppb	NO <sub>2</sub> measurements were found to have interferences by O <sub>3</sub> and perhaps other species and may not be useful for quantitative mechanism evaluation.

Type	Model or Description	Species	Sensitivity	Comments
	and other compounds and Luminol detection for NO <sub>2</sub> or PAN. Data transmitted to the DAC system using RS-232.	PAN	~0.5 ppb	Reliability of measurement for PAN not fully evaluated. Calibration results indicate about a 30% uncertainty in the spans. However, interferences are less likely to be a problem than for NO <sub>2</sub> .
Gas Calibrator	Model 146C Thermo Environmental Dynamic Gas Calibrator	N/A	N/A	Used for calibration of NO <sub>x</sub> and other analyzers. Instrument acquired early in project and under continuous use.
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 and control sampling solenoids. In-house LabView software was developed using software developed by Sonoma Technology for ARB for the Central California Air Quality Study as the starting point.
Temperature sensors	Various thermocouples, radiation shielded thermocouple housing	Temperature	~0.1 °C	Primary measurement is thermocouples inside reactor. Corrections made for radiative heating effect with arc light irradiation.
Humidity Monitor	General Eastern HYGRO-M1 Dew Point Monitor	Humidity	Dew point range: -40 - 50°C	Dew point below the performance range for the unhumidified experiments discussed in this paper.
Spectroradiometer	LiCor LI-1800 Spectroradiometer	300-850 nm Light Spectrum	Adequate	Resolution relatively low but adequate for its purpose. Used to obtain relative spectrum. Also gives an absolute intensity measurement on surface useful for assessing relative trends.
Spherical Irradiance Sensors	Biospherical QSL-2100 PAR Irradiance Sensor or related product. Responds to 400-700 nm light. Spectral response curve included.	Spherical Broad-band Light Intensity	Adequate	Provides a measure of absolute intensity and light uniformity that is more directly related to photolysis rates than light intensity on surface. Gives more precise measurement of light intensity trends than NO <sub>2</sub> actinometry, but is relatively sensitive to small changes in position.
Scanning Electrical Mobility Spectrometer (SEMS)	Similar to that described in Cocker et al. (2001a). See text	Aerosol Number and Volume concentration	Adequate	Provides information on size distribution of aerosols in the 28-730 nm size range, which accounts for most of the aerosol mass formed in our experiments. Data can be used to assess effects of VOCs on secondary PM formation.

Table 2. Representative photolysis rates calculated or measured for chamber or solar irradiation conditions. Photolysis rates calculated using the absorption cross sections and quantum yields used in the SAPRC-99 mechanism (Carter, 2000).

	Solar [a]			Chamber [b]	
	Z=0	Z=40	Z=70	Arc Light	Blacklights
Photolysis rate ( $\text{min}^{-1}$ )					
$\text{NO}_2 \rightarrow \text{NO} + \text{O}(^3\text{P})$	0.53	0.46	0.21	0.26	0.19
Photolysis rate relative to $\text{NO}_2$					
$\text{O}_3 \rightarrow \text{O}_2 + \text{O}(^1\text{D})$	4.9e-3	3.2e-3	8.0e-4	6.8e-4	1.6e-3
$\text{O}_3 \rightarrow \text{O}_2 + \text{O}(^3\text{P})$	0.054	0.056	0.074	0.040	0.004
$\text{HONO} \rightarrow \text{OH} + \text{NO}$	0.19	0.19	0.19	0.20	0.28
$\text{NO}_3 \rightarrow \text{NO} + \text{O}_2$	2.3	2.5	3.5	1.9	1.9e-3
$\text{HCHO} \rightarrow \text{H} + \text{HCO}$	3.7e-3	3.1e-3	1.8e-3	1.1e-3	1.8e-3
Acetone photolysis	6.7e-5	4.6e-5	1.4e-5	1.1e-5	2.4e-5
Methyl Glyoxal photolysis	0.017	0.016	0.015	0.015	0.014

[a] Calculated using actinic fluxes given by Peterson (1976) for his “best estimate” surface albedos. Data given are for three selected zenith angles, where “Z=0” refers to direct overhead sun.

[b]  $\text{NO}_2$  photolysis rates are based on results of  $\text{NO}_2$  actinometry experiments as discussed in the text. Photolysis rate ratios are calculated using the absorption cross sections and quantum yields for the reactions and the measured spectral distributions as discussed in the text.



Table 3. Summary of types of characterization experiments and types of chamber effects parameters relevant to gas-phase mechanism evaluation derived from these experiments.

Run Type	No. Runs	Sensitive Parameters	Comments
Ozone Dark Decay	4	O <sub>3</sub> wall loss rate	The loss of O <sub>3</sub> in the dark is attributed entirely to a unimolecular wall loss process.
CO - Air	8	NO <sub>x</sub> offgasing	Insensitive to radical source parameters but O <sub>3</sub> formation is very sensitive to NO <sub>x</sub> offgasing rates. Formaldehyde data can also be used to derive formaldehyde offgasing rates.
CO - HCHO - air	2	NO <sub>x</sub> offgasing.	Insensitive to radical source parameters but O <sub>3</sub> formation is very sensitive to NO <sub>x</sub> offgasing rates. Also can be used to obtain formaldehyde photolysis rates
CO - NO <sub>x</sub>	6	Initial HONO, Radical source	O <sub>3</sub> formation and NO oxidation rates are very sensitive to radical source but not sensitive to NO <sub>x</sub> offgasing parameters. Formaldehyde data can also be used to derive formaldehyde offgasing rates.
n-Butane - NO <sub>x</sub>	1	Initial HONO, Radical source	O <sub>3</sub> formation and NO oxidation rates are very sensitive to radical source but not sensitive to NO <sub>x</sub> offgasing parameters.
Pure Air	6+	NO <sub>x</sub> offgasing, Background VOCs	Used primarily to screen for background VOC effects with the NO <sub>x</sub> offgasing and chamber radical source parameter set at values that fit the other types of characterization experiments.

Table 4. Summary of initial experiments carried out in the chamber.

Run Type [a]	Runs [b]	NOx (ppb)	CO (ppm)	VOC (ppb except as noted)	Average $\Delta(\text{O}_3\text{-NO})$ Model Fits [c]	
					Bias	Error
Pure Air	6	0	0	0	See note [d]	
Other Characterization	32	0-202	0-168	0-490	-3%	28%
HCHO – NOx	2	8 - 23		35-50	-23%	23%
HCHO - CO - NOx	2	16 - 21	14-76	39-49	-10%	10%
Ethene – NOx	2	10 - 25		617-650	-15%	15%
Propene – NOx	2	5 - 24		42-52	16%	16%
Toluene – NOx	3	5 - 24		61-152	11%	11%
m-Xylene - NOx (arc light)	1	5		18	6%	6%
m-Xylene - NOx (blacklight)	18	17-100		25-215	[e]	
Toluene - CO - NOx	5	4 - 27	24-50	55-165	-16%	17%
m-Xylene – CO - NOx	1	6 - 6	47	18	-21%	21%
Surrogate - NOx	61 [f]	2 - 315		0.2 - 4.2 [g]	-10%	13%

[a] Arc light used unless indicated otherwise

[b] Each reactor irradiation is counted as a separate run, so two runs are done at once.

[c] Error and bias for model predictions of  $\Delta([\text{O}_3]-[\text{NO}])$  using the SAPRC-99 mechanism. Bias is (calculated - experimental) / calculated. Error is the absolute value of the bias.

[d] The average 6-hour  $\text{O}_3$  yields for the pure air runs with blacklights and standard conditions are  $4\pm 2$  ppb experimental and  $6\pm 2$  ppb calculated.

[e] Not used for gas-phase mechanism evaluation. See discussion of SOA yield experiments.

[f] Includes experiments carried out for subsequent projects

[g] ppmC

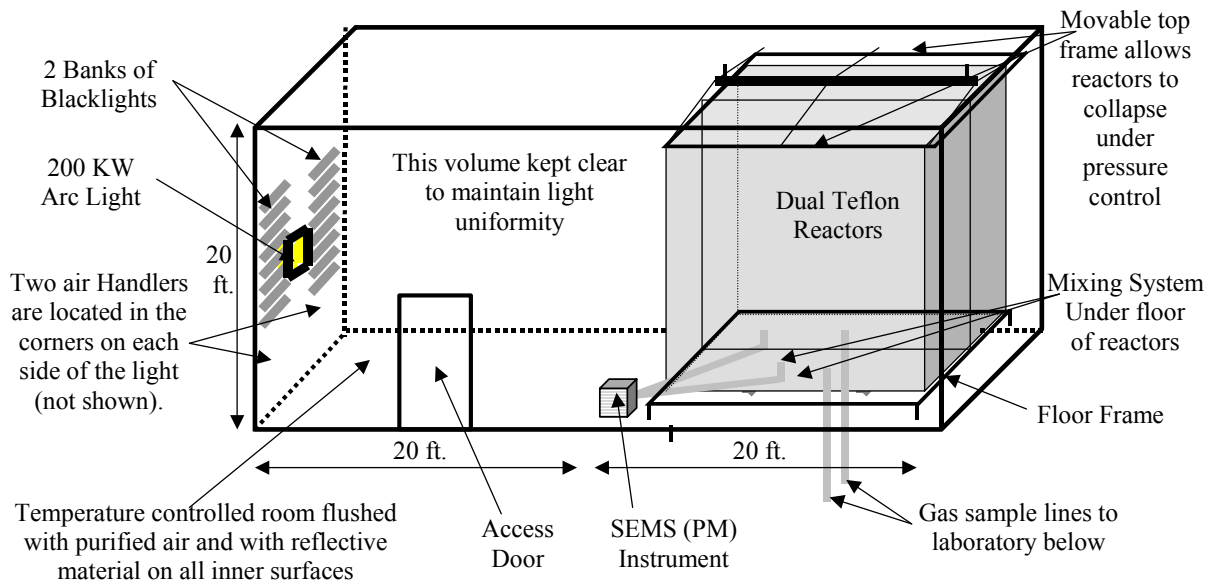


Figure 1. Schematic of the environmental chamber reactors and enclosure.

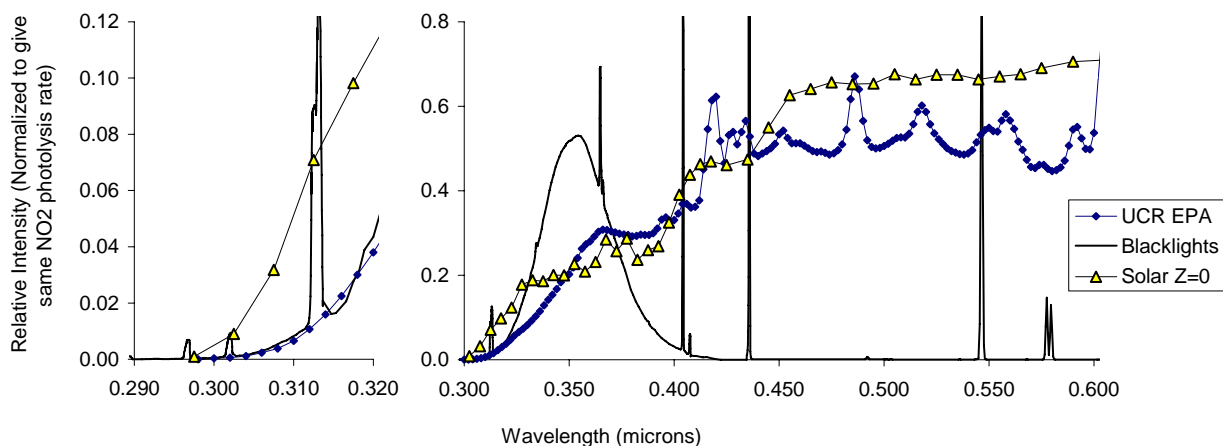


Figure 2. Spectrum of the argon arc light source used in the chamber. Blacklight and representative solar spectra, with relative intensities normalized to give the same NO<sub>2</sub> photolysis rate.

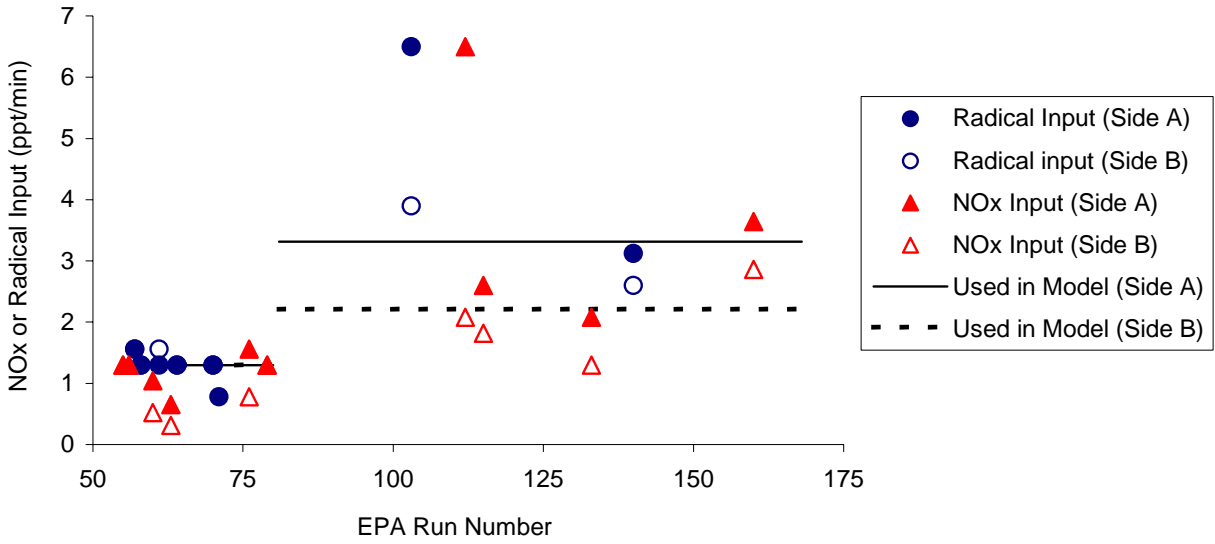


Figure 3. Plots of NO<sub>x</sub> or radical input rates necessary for model simulations to predict the experimental data against experimental run number (i.e., against the order the experiment was carried out).

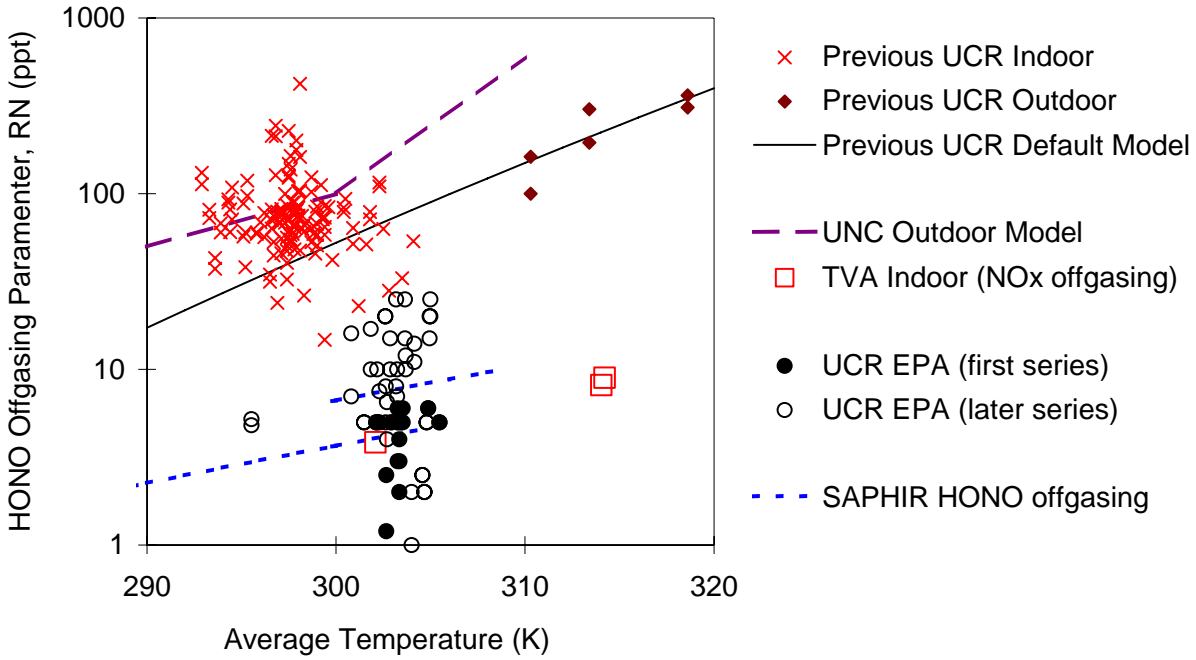


Figure 4. Plots of the HONO offgassing parameter, RN (ratios of the HONO offgassing rates the NO<sub>2</sub> photolysis rates) derived from modeling characterization runs for various chambers. Data shown are for unhumidified experiments except for the UNC outdoor and TVA chambers.

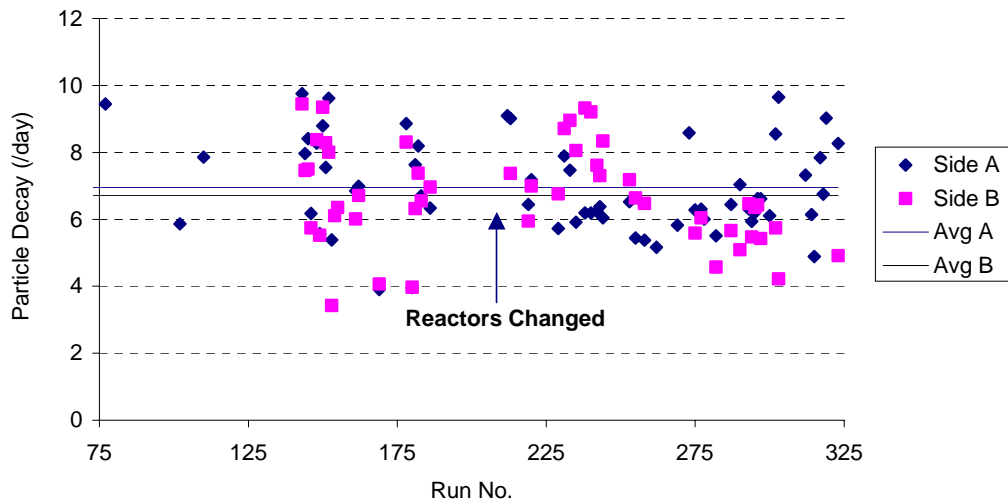


Figure 5. Plots of particle loss rates against time for experiments from February 2003 through June of 2004

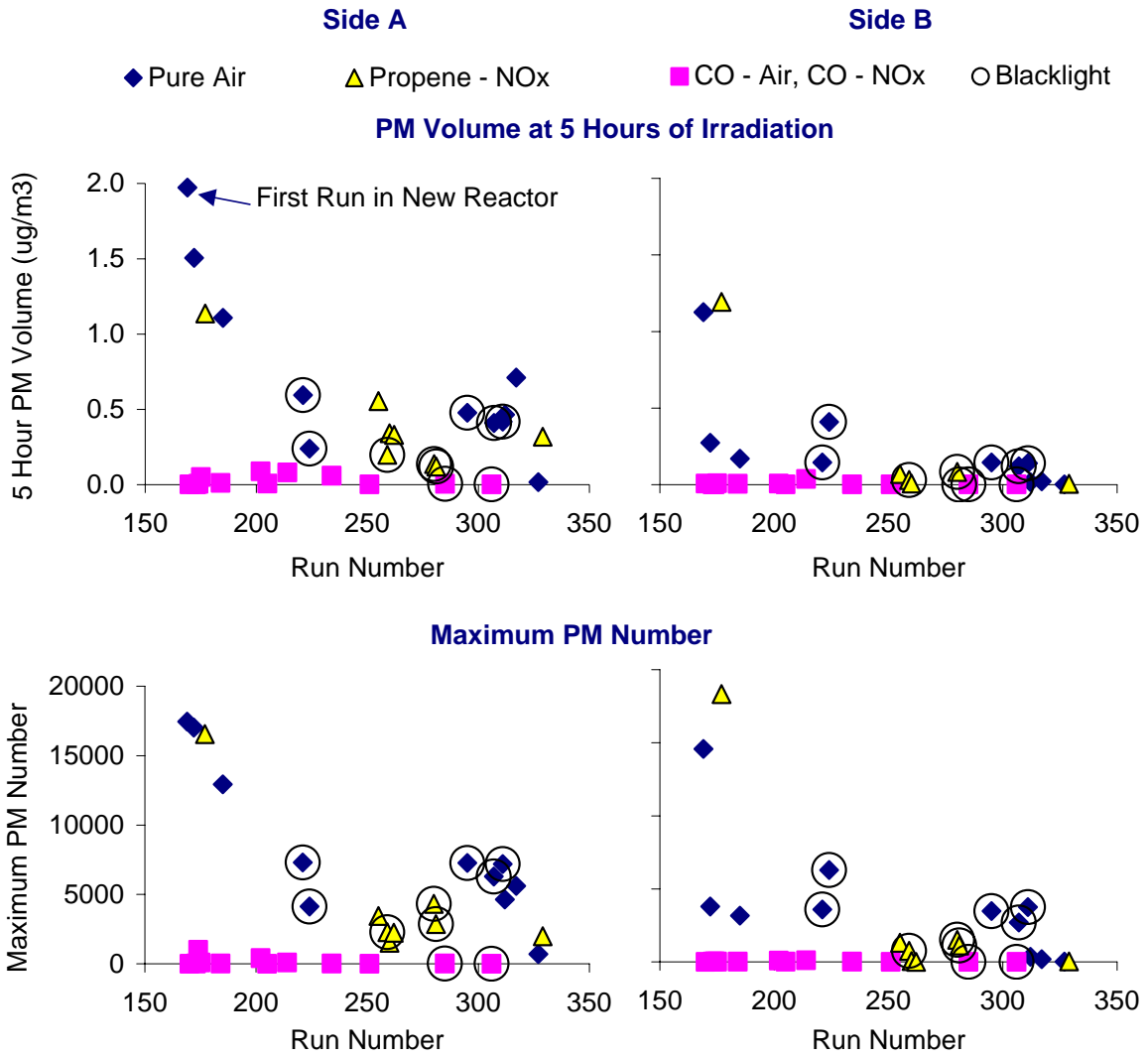


Figure 6. Plots of 5-Hour PM volume and maximum PM number data in PM background characterization experiments in the reactors installed before run 169.

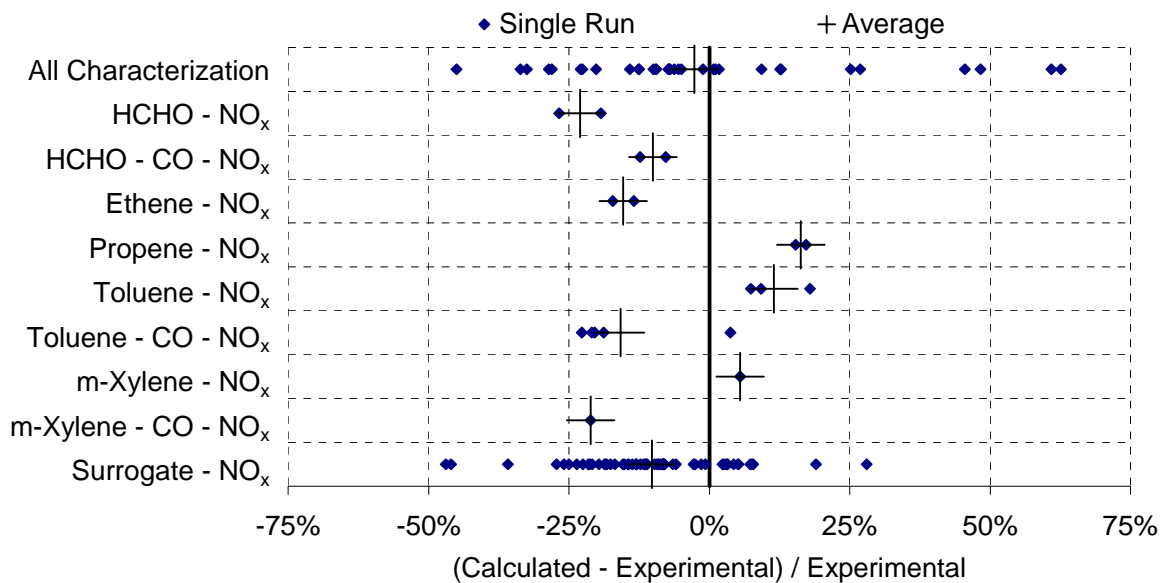


Figure 7. Fits of experimental O<sub>3</sub> formed and NO oxidized,  $\Delta([\text{O}_3]-[\text{NO}])$ , measurements to SAPRC-99 model calculations for the initial chamber and mechanism evaluation experiments.

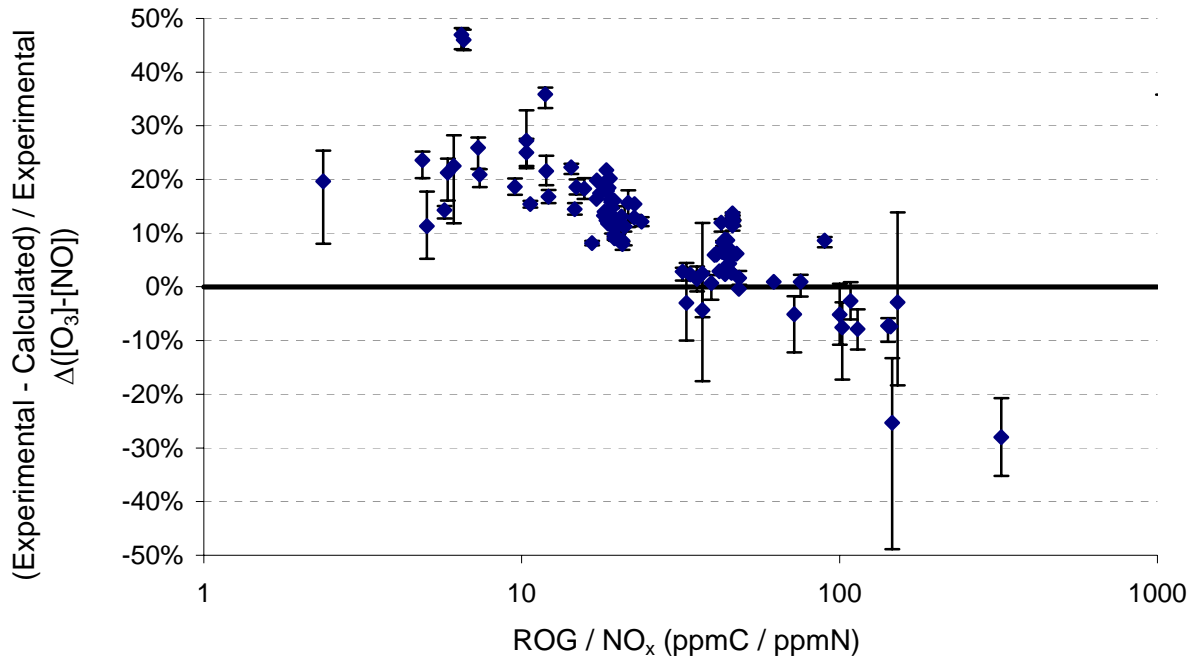


Figure 8. Plots of the tendency of the SAPRC-99 mechanism for underpredicting ozone formed and NO oxidized,  $\Delta([O_3]-[NO])$ , against the initial ROG/NO<sub>x</sub> ratio in the surrogate - NO<sub>x</sub> experiments. Error bars show the effect of varying the HONO offgassing chamber effects parameter within its uncertainty.



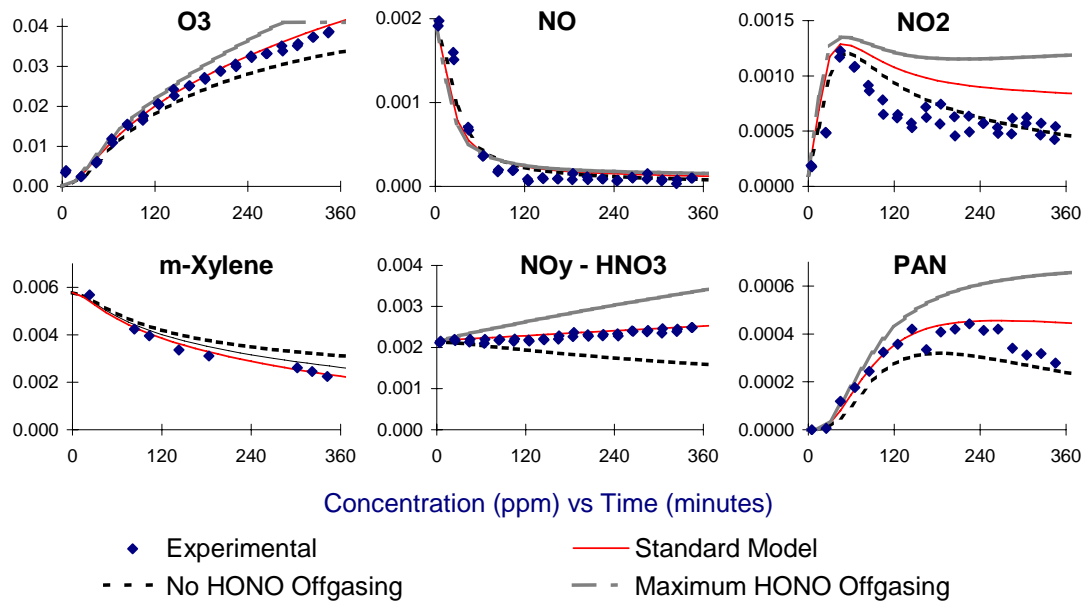


Figure 9. Concentration-time plots of selected compounds in the lowest  $\text{NO}_x$  ambient ROG -  $\text{NO}_x$  surrogate experiment in the initial evaluation experiments ( $\text{NO}_x \approx 1$  ppb,  $\text{ROG} \approx 300$  ppbC).

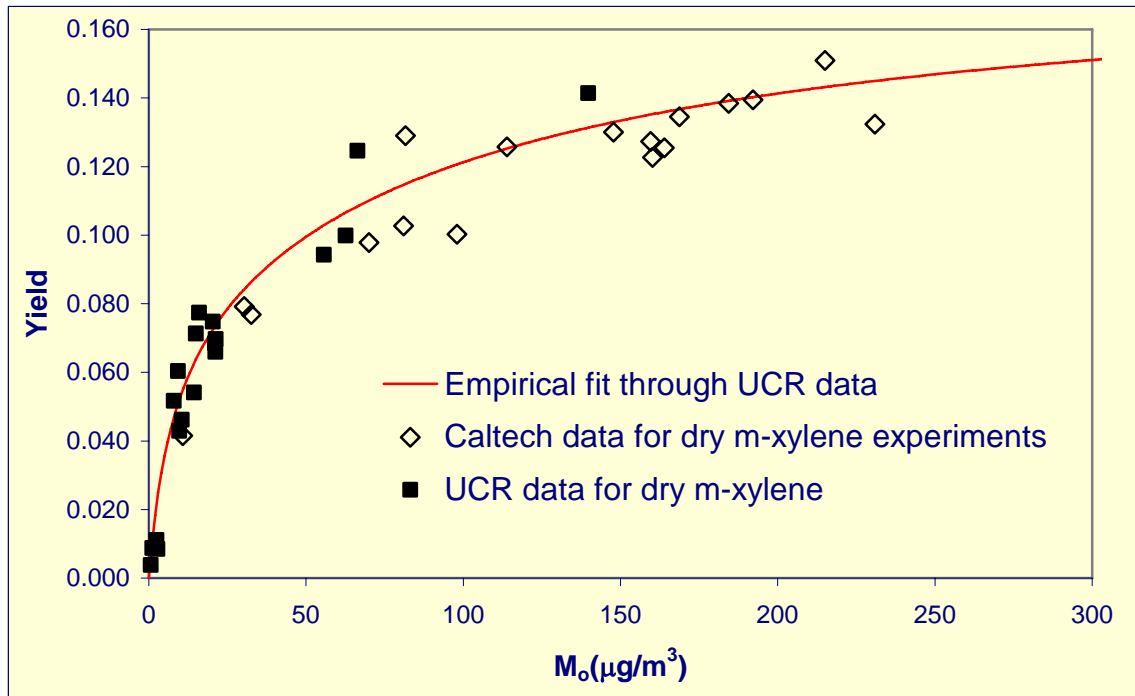


Figure 10. Comparison of yield data obtained for m-xylene/NO<sub>x</sub> system with blacklight irradiation. Solid squares represent data obtained in this reactor (UCR); open diamonds are for dry experiments conducted in the Caltech reactor (Cocker et al., 2001b); the solid line represents the best-fit two-product model for the current UCR data set.