

The UCR EPA Environmental Chamber

William P. L. Carter

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

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Abstract

The UCR EPA chamber is a new large indoor environmental chamber constructed at the University of California at Riverside (UCR) under United States EPA funding for the purpose of evaluating gas-phase and secondary aerosol mechanisms for ground-level air pollution. The major characteristics of this chamber, the results of its initial characterization for gas-phase mechanism evaluation, and examples of initial gas-phase mechanism evaluation experiments, are described. It is concluded that the chamber has lower or at most comparable background effects than other chambers previously used for mechanism evaluation, and can provide useful mechanism evaluation data at NO_x levels as low as 2 ppb. Future research directions to utilize the capabilities of this chamber are discussed.

Background

Chemical mechanisms are critical components of airshed models used for predictions of secondary pollutants such as ground-level ozone or secondary organic aerosol. Because many of the chemical reactions are incompletely understood, these mechanisms cannot be relied upon to give accurate predictions of impacts on emissions on air quality until they have been shown to give accurate predictions under realistic but controlled conditions. The most reliable way to test this 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. For this reason, environmental chambers are essential to developing predictive mechanism for compounds for which basic mechanistic information are insufficient (as is the case for aromatics), testing approximations and estimates necessary for modeling the reactions of almost all VOCs under simulated atmospheric conditions, and testing entire mechanisms under varied conditions.

However, results of environmental chamber experiments are only useful for testing mechanisms if the conditions of the experiments are sufficiently well characterized so that the characterization uncertainties are less than the uncertainties of the mechanisms being tested. As discussed by Dodge (2000), the chamber data base used to develop and evaluate current mechanisms had a number of limitations and data gaps that could affect their accuracy. 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) at the University of California at Riverside (UCR) has undertaken a program to develop a “Next Generation” environmental chamber facility for chemical mechanism evaluation and VOC reactivity assessment. 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. This project resulted in the construction of new “UCR EPA” chamber, which became fully operational in early 2003. The design features and characteristics of this chamber, the results of its initial characterization, and completed and ongoing projects in this chamber are summarized briefly below.

Facility Description

The indoor facility comprises a 20’x20’x40’ thermally insulated enclosure that is continually flushed with purified air at a rate of 1000 L min⁻¹ 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 m³ (6.1 m x 3.1 m x 5.5 m, Surface area to volume = 1.35 m⁻¹) 2 mil FEP Teflon® film reactors, a 200 kW Argon arc lamp, a bank of 72 W 4-ft blacklights, along with the light and aerosol instrumentation. A schematic of the enclosure is provided in Figure 1.

Enclosure

The interior of the thermally insulated 450 m³ enclosure is lined with reflective Everbrite® (Alcoa, PA) 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 air conditioner capable of producing a temperature range of -5 to 80 C.

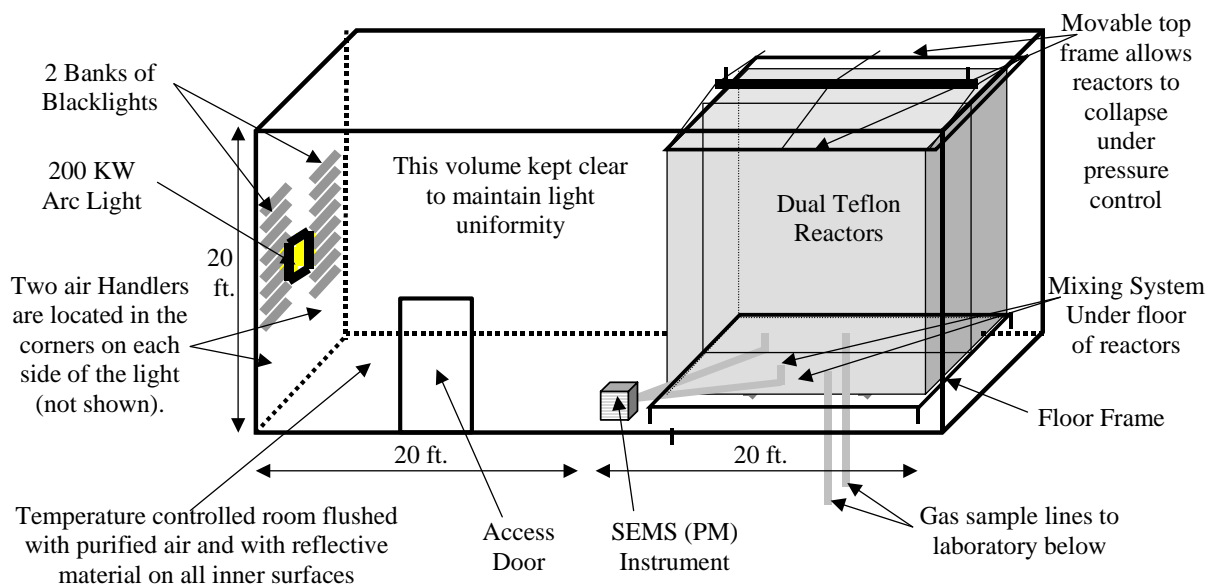


Figure 1. Schematic of the environmental chamber reactors and enclosure.

Teflon Reactors

The 2 mil (54 μm) 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 $\frac{1}{4}$ " to $\frac{1}{2}$ " for sample injection and withdrawal. The moveable top frame is raised/lowered with a motorized pulley system enabling the user to expand (during filling) and contract (during an experiment or for flushing) as necessary. The rate of contraction/expansion is set to maintain a differential pressure of 0.02 in H_2O 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 $\frac{1}{3}$ of its maximum value (typically about 10 hours). 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 a U-frame mount to the reactor ceiling and floor.

Pure Air System

An Aadco 737 series (Cleveland, Ohio) air purification system produces compressed air at rates up to 1500 L min^{-1} . 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 ($<1 \text{ ppb}$), NO_x ($<15 \text{ ppt}$), no detectable particles ($<0.2 \text{ particles cm}^{-3}$), and a dew-point below -40 C .

The reactors are cleaned between runs by reducing the reactor volume to less than 5% of its original volume while flushing the reactors with 500 L min⁻¹ purified air. The reactor is then returned to its original volume by filling with purified air. No residual hydrocarbons, NO_x, 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 to irradiate the enclosure and closely simulate the entire UV-Vis ground-level solar spectra. The arc lamp is mounted on the far wall from the reactors at a minimum distance of 20' to provide uniform lighting within both reactors. Backup lighting is provided by banks of 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 blacklights are located on the ends of the same wall of the Argon arc lamp. Figure 2 shows the spectra for each light source with a comparison to a representative ground-level outdoor solar spectrum.

Interreactor and Intra-reactor 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, when desired, 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.

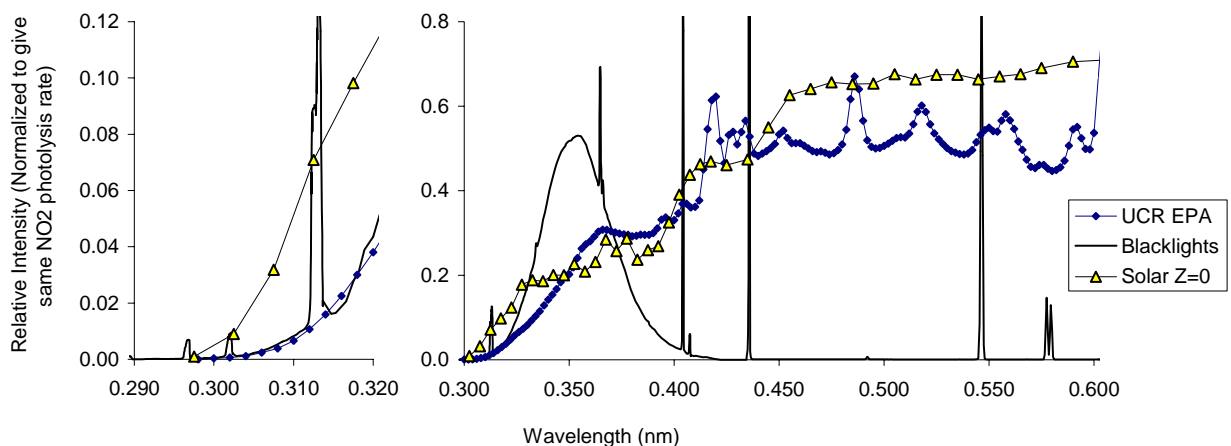


Figure 2. Spectrum of the argon arc light source used in the chamber. Blacklight and representative solar spectra, with relative intensities normalized to give the same NO₂ photolysis rate.

Analytical Instrumentation

The instrumentation used to monitor gas-phase species in this chamber are described by Carter. (2002). Briefly, ozone, CO, NO, and NO_y are monitored using commercially available instruments. Two Tunable Diode Laser Absorption Spectroscopy (TDLAS) are available for monitoring NO₂, HNO₃, H₂O₂ and formaldehyde. 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. Two GC-luminol instrument based on previous work by Gaffney et al (1998) are used to monitor PAN and higher PAN analogues. It 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 those species. Organic reactants other than formaldehyde are monitored by gas chromatography with FID detection.

Instrumentation was also available to measure aerosol size distributions, from which aerosol number and volume can be calculated. This is described by Cocker (2004), and also by Carter (2002). The use of this chamber for aerosol studies is discussed by Cocker (2004).

Characterization Results

Light Characterization

Argon Arc Light. Although the intensity of the argon arc light can be varied by varying the lamp power, normally it is operated at 80% of maximum. Information about trends in light intensity with time is available from data from the spectral radiometer and PAR radiation instruments (Carter et al, 2002), and from results of NO₂ 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. Actinometry experiments with the quartz tube located inside the reactors yielded an NO₂ photolysis rate of 0.26 min⁻¹.

Blacklights. The light intensity inside the reactors with blacklight irradiation was measured in a series of experiments 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 min⁻¹, respectively. The light intensity measured in the enclosure during blacklight experiments indicated a gradual decreasing trend in light intensity during the experiments that was consistent with the differences between these two measurements.

Spectra. The spectrum of the arc light sources were measured using a LiCor LI-1800 spectroradiometer, and are shown on Figure 2. No appreciable change in the light source spectrum was observed in the first 18 months of operation.

Characterization of Contamination by Outside Air

Contamination of the reactor by leaks and permeation of laboratory air contaminants is minimized by continuously flushing the enclosure that houses the reactors with purified air. NO_x and formaldehyde levels in the enclosure before or during irradiations were generally less than 5

ppb and PM concentrations are below the detection limits of our instrumentation. 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, so 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. No appreciable CO (below the 50 ppb detection limit) was obtained for this experiment.

Chamber Effects Characterization

It is critical to characterize 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. The most important of these for mechanism evaluation include background offgasing of NO_x and other reactive species, offgasing or heterogeneous reactions that cause “chamber radical sources” upon irradiation (e.g., see Carter and Lurmann, 1990, 1991), and ozone losses to the reactor walls. 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. The chamber effects that have been assessed and the types of experiments that have been utilized for assessing these effects in this chamber are summarized on Table 1 and discussed further below.

Note that 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 and thermal rate constants calculated using the light characterization data, the measured temperatures of the experiments, and assuming no dilution for reasons discussed above. The rates of heterogeneous reactions not discussed below, such as N₂O₅ hydrolysis to HNO₃ or NO₂ hydrolysis to HONO, were derived or estimated based on laboratory studies or other considerations as discussed previously (e.g., 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.

NO_x offgasing

NO_x offgasing is the main factor limiting the utility of the chamber for conducting experiments under low NO_x conditions. Although this can be derived by directly measuring increases in NO_x species during experiments when NO_x is not injected, the most sensitive measure is the formation of O₃ in irradiations when VOCs but not NO_x are initially present. The NO_x offgasing rate is not determined directly, but derived by determining the NO_x offgasing rates in model simulations of the experiments that fit the O₃ yields obtained. The NO_x offgasing can be represented in the model as inputs of any species that rapidly forms NO_x in atmospheric irradiation systems, such as NO, NO₂, or HONO (which rapidly photolyzes to form NO, along with OH radicals), but for reasons discussed below it is represented in our chamber effects model as offgasing of HONO, e.g.,



Table 1. Summary of types of characterization experiments and types of chamber effects parameters derived from these experiments.

Run Type	No. Runs	Sensitive Parameters	Comments
Ozone Dark Decay	4	O ₃ wall loss rate	The loss of O ₃ in the dark is attributed entirely to a unimolecular wall loss process.
CO - Air	8	NO _x offgasing	Insensitive to radical source parameters but O ₃ formation is very sensitive to O ₃ offgasing rates. Formaldehyde data can also be used to derive formaldehyde offgasing rates.
CO - HCHO - air	2	NO _x offgasing.	Insensitive to radical source parameters but O ₃ formation is very sensitive to NO _x offgasing rates. Also can be used to obtain formaldehyde photolysis rates
CO - NO _x	6	Initial HONO, Radical source	O ₃ formation and NO oxidation rates are very sensitive to radical source but not sensitive to NO _x offgasing parameters. Formaldehyde data can also be used to derive formaldehyde offgasing rates.
n-Butane - NO _x	1	Initial HONO, Radical source	O ₃ formation and NO oxidation rates are very sensitive to radical source but not sensitive to NO _x offgasing parameters.

Where k_1 is the light intensity as measured by the NO₂ photolysis rate, and RN is the 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 NO_x offgasing rates that fit the results of relevant experiments carried out in the first eight months of operation of this chamber are shown as the diamond symbols on Figure 3. It can be seen that the rates were around 1.5 ppt/min up to around run 85, then increased to 2-7 ppt/min after that, being somewhat higher in the “A” 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_x offgasing rates are discussed further below.

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_x -air irradiations of compounds, such as CO or alkanes, which are not radical initiators and do not form radical initiating products to a sufficient extent to

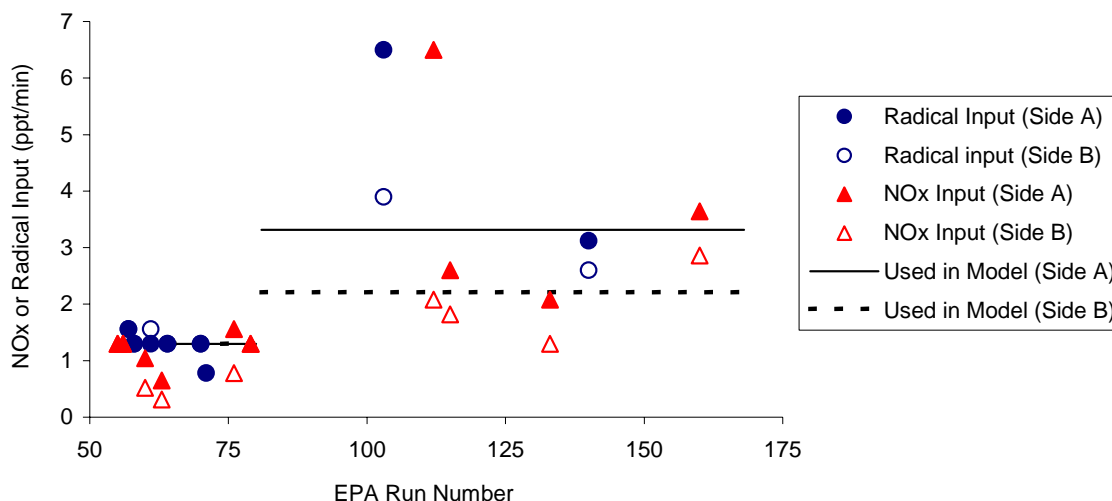


Figure 3. Plots of apparent NO_x or radical input rates against run number.

significantly affect their photooxidations. In some chambers at least part of the chamber-dependent radical source can be attributed to formaldehyde offgasing (Simonaitis et al, 1997, Carter, 2004a), but as discussed below the magnitude of the formaldehyde offgasing in this chamber is not sufficient by itself for the model to simulate radical-source characterization experiments. For this chamber, assuming HONO offgasing at a similar magnitude as the apparent NO_x 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 on Figure 3 shows plots of the HONO offgasing rates that are adjusted to fit the radical-source sensitive CO - NO_x and n-butane - NO_x experiments that were carried out in January-October of 2003. Note that since these experiments had initial NO_x levels ranging from 10 - 200 ppb, they were not sensitive to NO_x offgasing as such. However, from Figure 3 it can be seen that the magnitudes of the NO_x 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_x offgasing to increase around the time of run 85 caused the same increase in the apparent radical source.

Comparison of Radical Source and NO_x Offgasing with Other Chambers

Although HONO is not measured directly in our experiments, the fact that both the radical-sensitive and NO_x-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 Kleffmann et al (2003), 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

(Brauers et al, 2003) at rates comparable to those observed in the earlier experiments in this chamber. The SAPHIR chamber is similar in design to the chamber discussed here, except it is larger in volume and is located outdoors. In particular, like our chamber it has Teflon walls and uses a dual-reactor configuration to minimize contamination by outside air. Therefore, it would be expected to have similar chamber NO_x and radical sources, and this appears to be the case.

Figure 4 shows plots of the NO_x 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 (Kleffmann et al (2003). In addition to this UCR EPA chamber, 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 (1990, 1991) for the University of North Carolina (UNC) outdoor chamber (e.g., Jeffries et al, 1982, 1990), and those derived by Carter (2004a) 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 on Figure 3, including a few runs at reduced temperature.) The figure shows that the radical source and NO_x 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_x 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 all indicate that the radical source and HONO or NO_x offgasing rates all increase with temperature.

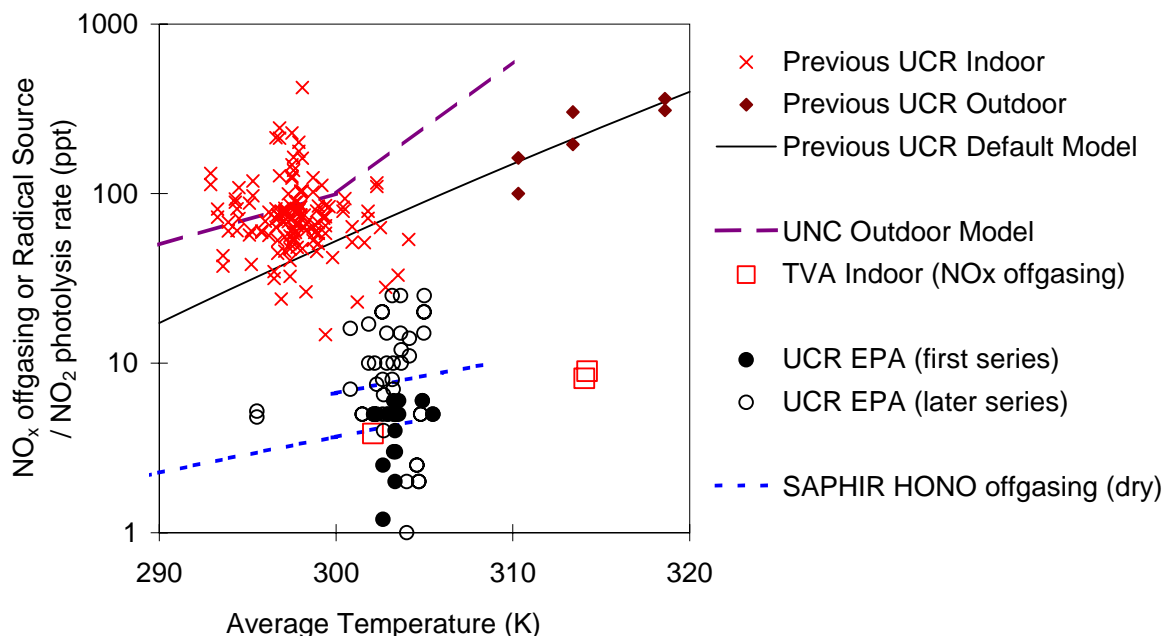


Figure 4. Plots of ratios of NO_x offgasing or radical source to the NO_2 photolysis rates derived from modeling characterization runs for various chambers.

Therefore, the radical source and NO_x 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_x 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_x, or other experiments where no formaldehyde or formaldehyde precursors were injected. Some formaldehyde formation is expected from the reactions of methane in the matrix air, since the methane removal catalyst was not operational during the period of these experiments, but formaldehyde formation in this reaction in the CO experiments 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 7.5 ppb/day at the light intensity of these experiments. This is a relatively low offgasing rate that could not be detected with formaldehyde analyzers used in most previous UCR and other chamber experiments, and is 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 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 or changes in formaldehyde offgasing with time. The data are best modeled by assuming only direct formaldehyde offgasing, as opposed to some formaldehyde precursor being formed from light-induced reactions of some undetected contaminant, as is apparently important in the TVA chamber (Simonaitis et al, 1997; Carter, 2004a).

Representative Results of Initial Evaluation Experiments

Table 2 gives a summary of the initial experiments carried out in this chamber for chamber and mechanism evaluation. The characterization and single organic - NO_x experiments and some of the ambient reactive organic gas (ROG) surrogate - NO_x experiments were funded by the EPA cooperative agreement used to fund the construction and initial characterization of this chamber. The lowest concentration ambient ROG surrogate - NO_x experiments were carried out by a separate California Air Resources Board project to obtain additional data for low NO_x mechanism evaluation, and a number of surrogate - NO_x experiments at varying initial ROG and NO_x levels at a were carried out for a separate program to obtain data to evaluate observationally based methods. Not shown on Table 2 are a number of “incremental reactivity” experiments, where various compounds or VOC mixtures were added to standard ambient ROG - NO_x

Table 2. Summary of initial chamber and mechanism evaluation experiments.

Run Type	Runs	NO _x Range (ppb)	VOC Range (ppm)	Avg. Model Bias #	Avg. Model Error #
Characterization	32	0 - 200	Varied	-3%	28%
Formaldehyde - NO _x	2	8 - 25	0.35 – 0.50	-23%	23%
Formaldehyde - CO - NO _x	2	15 - 20	HCHO: 0.4 – 0.5 CO: 15 - 80	-10%	10%
Ethene - NO _x	2	10 - 25	~0.6	-15%	15%
Propene - NO _x	2	5 - 25	0.4 – 0.5	16%	16%
Toluene or m-Xylene - NO _x	4	5 - 25	Toluene: 0.6 – 0.16 m-Xylene: 0.18	10%	10%
Aromatic - NO _x + CO	6	5 - 30	CO: 25 – 50	-17%	18%
Ambient Surrogate - NO _x	61*	2 - 315	0.2 – 4.2 ppmC	-10%	13%

* Includes experiments carried out for subsequent programs.

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.

surrogate irradiations to provide data to test mechanisms for their relative ozone impacts. The results of these experiments are still being analyzed.

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_x 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_x levels than previously available. The formaldehyde + CO - NO_x 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_x experiments were carried out because aromatic - NO_x 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_x experiments were carried out to test the ability of the mechanism to simulate ozone formation under simulated ambient conditions at various ROG and NO_x levels.

The ROG surrogate used in the ambient surrogate - NO_x experiments consisted of a simplified mixture of 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, 1995b, for a discussion of the derivation of this surrogate).

The ability of the SAPRC-99 mechanism to simulate the total amount of NO oxidized and O₃ formed in the experiments, measured by $([O_3]_{\text{final}} - [NO]_{\text{final}}) - ([O_3]_{\text{initial}} - [NO]_{\text{initial}})$ or $\Delta([O_3] - [NO])$, is summarized for the various types of experiments on Table 2 and shown for the individual runs on Figure 5. This gives an indication of the biases and run-to-run variability of the mechanism in simulating ozone formation. Note that in experiments with excess NO the processes responsible for O₃ formation are manifested by consumption of NO, so simulations of $\Delta([O_3] - [NO])$ provides a test of model simulations of these processes even for experiments where O₃ is not formed.

Note that the characterization runs were modeled using the default characterization parameters used when modeling the mechanism evaluation runs, not with the values that were adjusted to fit the individual experiments. Therefore, the relatively large variability and average model error for the model simulations of $\Delta([O_3] - [NO])$ in those experiments provides a measure of the variability of the chamber effects parameters (e.g., HONO offgassing) 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_x or VOC - CO - NO_x experiments, the model is able to simulate the $\Delta([O_3] - [NO])$ 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

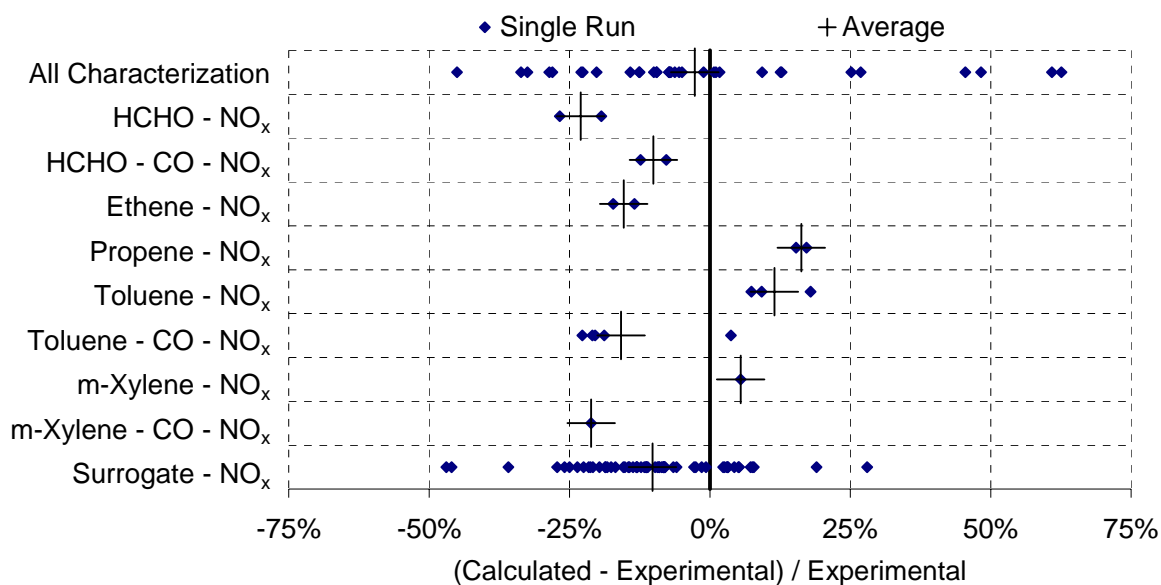


Figure 5. Fits of experimental $\Delta([O_3] - [NO])$ measurements to SAPRC-99 model calculations for the initial chamber and mechanism evaluation experiments.

magnitude of the chamber effects may make the run-to-run scatter in the model performance may be less than in the simulations of the previous data, and this tends to make relatively small biases in the model performance more evident. There are, for example, definite biases in the model to underpredict O₃ formation and NO oxidation in the surrogate - NO_x experiments carried out at lower ROG/NO_x ratios. These cases are discussed further elsewhere (Carter, 2004b).

As indicated on Table 2, the initial evaluation experiments included runs with NO_x 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_x levels greater than 50 ppb, and even the “low NO_x” TVA and CSIRO experiments had NO_x levels of ~20 ppb or greater, except for a few characterization runs (Carter, 2004a, and references therein). However, there is no indication in any difference in model performance in simulating the results of these very low NO_x experiments, compared to those with the higher NO_x levels more representative of those used in the previous evaluation.

For example, Figure 6 shows concentration-time plots for selected measured species in ambient surrogate - NO_x experiment carried out at the lowest NO_x levels in the initial evaluation runs. To indicate the sensitivity of the experiments to NO_x 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 O₃ simulations are somewhat affected when the HONO offgasing rate is varied within this somewhat extreme range, the sensitivity is not so great that the uncertainty in this parameter significantly affects

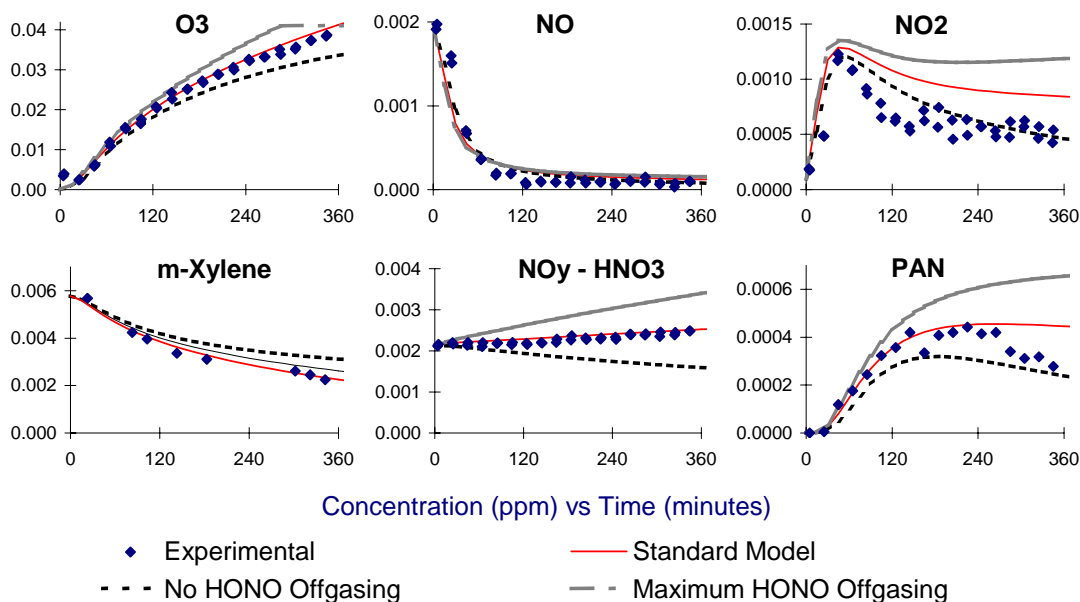


Figure 6. Concentration-time plots of selected compounds in the lowest NO_x ambient ROG - NO_x surrogate experiment in the initial evaluation experiments (NO_x ≈ 1 ppb, ROG ≈ 300 ppbC).

conclusions one can draw about the ability of the model to simulate this low NO_x experiment. However, the sensitivity would increase as the NO_x levels are reduced, and ~2 ppb NO_x probably represents a reasonable lower limit for NO_x 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_x 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_x conditions as such, but do reveal problems with the mechanisms for aromatics and the ambient ROG surrogate. This is discussed further in our companion presentation (Carter, 2004b).

Future Research Directions

The future research directions for the UCR EPA chamber will of course depend on funding availability and the interests of the funding agencies, but we would expect the research would be designed to take full advantage of its capabilities. In any case, we expect to continue the ozone reactivity and gas-phase mechanism studies that are currently underway, with the mechanism evaluation being focused on aromatics, whose mechanism are the most uncertain and where the new data indicate mechanism problems (Carter, 2004a,b), and ozone reactivities of VOC source categories of interest. We will also be utilizing the chambers for initial experiments to investigate temperature effects on O₃ formation and other measures of gas-phase reactivity, taking advantage of the temperature control capabilities of this chamber, which has not yet been fully exploited. We hope in the future to obtain instrumentation needed for NO₃, N₂O₅, HO_x, and other trace species in order to improve capabilities and utility of this facility for mechanism evaluation.

As discussed in more detail by Cocker (2004), we will also utilize the chamber for well-characterized experiments needed to develop and evaluate models for secondary organic aerosol (SOA) formation. The temperature control capabilities of this chamber permit systematic studies of temperature and humidity effects that are not possible with existing outdoor chambers or with indoor chambers using blacklights (whose intensities are temperature-dependent). The established capabilities of this chamber for *gas phase* mechanism evaluation is an important characteristic in this regard, since the model cannot properly simulate SOA formation if it does not also properly simulate the formation of the SOA precursors from the gas-phase reactions.

To be fully utilized, this chamber should also serve as a resource for *collaborative studies* where environmental chamber measurements under highly controlled conditions would be useful. We encourage collaboration with other researchers who have instrumentation that we lack that would be useful for various studies, such as our collaboration with William Brune of Penn State University, whose HO and HO₂ radical measurement instrumentation was used with the surrogate - NO_x experiments carried out for the observational based methods study. This facility would also be useful as a test bed for evaluating analytical instrumentation for use in

ambient monitoring, since it can produce realistic but highly characterized simulated pollution conditions for instrument evaluation and intercomparisons.

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