

**EXPERIMENTAL EVALUATION OF
OBSERVATION BASED METHODS FOR
ASSESSING THE SENSITIVITY OF OZONE
TO VOC AND NO_x**

Research Proposal to
The United States Environmental Protection Agency

By

Gail S. Tonnesen, Co-Principal Investigator
William P. L. Carter, Co-Principal Investigator
William H. Brune, Co-Investigator

December 4, 2002

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

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Attachments

Assurances, Non-Construction Programs
 Recommended Reviewers
 Form 5700.48, Procurement System Certification
 Form 5700.49, Debarment/Suspension Certification
 Lobbying Certification and Disclosure
 Form 4700.4, Preaward Compliance Review
 Indirect Cost Rate Agreement

Abstract

The need to determine whether VOC or NO_x control strategies are more effective for attaining ozone (O₃) air quality standards has led to a search for observational based methods (OBMs) that uniquely characterize VOC sensitive versus NO_x sensitive conditions. Several different theoretical approaches have been used for designing OBMs that should identify whether O₃ is more sensitive to emissions reductions in either NO_x or VOC. Here we define OBMs to include several different methods including indicator ratios, extent parameter, and constrained steady state models. The theoretical basis for the usefulness of OBMs has been derived from analyses of the budgets of radical species termination (Sillman, 1995; Kleinman et al., 1997), radical propagation efficiency (Tonnesen and Dennis, 2000a,b) and from analyses of the variability of O₃ production efficiency as a function of total NO_y availability (Johnson, 1994; Hess et al., 1992; Chang et al., 1997). Although the OBM concept is very promising, it has not yet been evaluated in experimental studies under controlled conditions. If the OBM concept is experimentally validated it will provide a direct method for using ambient data to determine the sensitivity of O₃ to its precursors in ambient air. It also represents an extremely promising approach for performing a rigorous model evaluation because the model must correctly simulate both the O₃ concentration and the O₃ sensitivity. Thus, experimental evaluation of OBMs is a high priority.

Because OBMs predict the sensitivity of O₃ to changes in VOC or NO_x, experimental evaluation requires that O₃ concentrations be measured for a “base case” and for sensitivity cases in which emissions or concentration of VOC and NO_x are perturbed from the base case. Two different approaches can be used to accomplish this: One possibility is to perform a base case experiment, and to perform subsequent experiments with injections of VOC or NO_x to determine the effects on O₃. Another possibility is to use multiple experiments at varying VOC and NO_x levels to “map out” the O₃ isopleth diagram. In this approach one would also measure the values of each of the OBMs for each experiment and then determine empirically what values of the OBMs are associated with NO_x sensitive or VOC sensitive conditions.

The most effective approach for evaluating OBMs is to carry out experiments in environmental chambers that are characterized for model evaluation (Jeffries et al, 1992). The use of such a chamber facility provides for reproducible, well-controlled experiments in an analytical laboratory setting in which instrumentation can be carefully controlled and calibrated. Moreover, chamber facilities are specifically designed to allow for injections of VOC and NO_x that can be used to evaluate the OBMs. We propose to perform a series of chamber experiments using a wide range of VOC and NO_x levels, and to measure the concentrations of each of the species required to evaluate the proposed OBMs. Because the chemistry of free radical species is the key to the theoretical basis for several of the OBMs, we also propose that a Laser Induced Florescence instrument be temporarily moved to the UCR chamber for the purpose of this study. The chamber design and proposed experiments are listed in Section 2. The budget for this proposal includes approximately \$180,000 for carrying out experiments at UCR and approximately \$65,000 for transportation and operation of the Penn State LIF instrument at the UCR chamber. The work proposed here will include experiments with simple as well as more realistic surrogate VOC-NO_x mixtures. We will use photochemical box model simulations to design the experiments, and a modeling analysis will be performed for all completed simulations. The project report will

include an analysis of the performance of each of the OBMs and comparisons with previous modeling studies.

1. Background

OBMs including indicator ratio analysis have been derived both for the sensitivity of peak O_3 concentration (Sillman, 1995, 2000; Chang et al., 1997; Tonnesen and Dennis, 2000b; Blanchard, 1999) and for the sensitivity of the production rate of O_3 ($P(O_3)$) or of odd oxygen ($P(O_x)$) (Tonnesen and Dennis, 2000a). Table 1 lists examples of peak O_3 and $P(O_3)$ indicators. It is useful to consider both of these approaches to gain insight into the dynamics of O_3 production and to clarify the conceptual basis for OBMs. High O_3 concentrations result from the integral of O_3 formation rates and other O_3 sink and source processes over a periods of several hours or a few days. Indicators of peak O_3 sensitivity are useful for investigating the cumulative sensitivity of O_3 production over the history of an air parcel trajectory, while the indicators of $P(O_3)$ sensitivity are useful for evaluating local O_3 and O_x production sensitivity at a particular time and location. The combined use of both peak O_3 and $P(O_3)$ indicators should provide the most rigorous approach for model validation (Tonnesen and Dennis, 2000b).

Indicators of peak O_3 sensitivity include ratios of relatively long lived species such as HNO_3 and H_2O_2 . There remains considerable uncertainty in the robustness of indicators of peak O_3 sensitivity due to variability in heterogeneous chemical production of HNO_3 from N_2O_5 and because of uncertainty in the deposition rates of H_2O_2 and HNO_3 (Tonnesen and Dennis, 2000b). There is also uncertainty in the robustness of peak O_3 indicators for different geographical regions (Lu and Chang, 1998; Vogel et al., 1999). Indicators of $P(O_3)$ sensitivity may be less susceptible to biases caused by deposition and heterogeneous chemistry because these indicators make of short-lived species, yet considerable uncertainty exists in the values of $P(O_3)$ indicators because of uncertainty in the budgets of free radical species $HO_x=OH+HO_2+RO_2$ (Stevens et al., 1997; Crosley, 1997; Jacob, 1998; Carpenter et al., 1998).

Table 1 lists those indicators that have been proposed and evaluated in model simulations. There is not yet a scientific consensus about the particular forms of indicators that are most useful. For example, the extent parameter has recently been applied in California (Blanchard et al., 1999), yet Sillman (2000) concluded that the extent parameter is not useful. Moreover, Sillman (1995) has proposed the ratio of $HCHO/NO_y$ as an indicator of O_3 concentration sensitivity and this indicator has been widely used, yet Tonnesen and Dennis (2000b) found that $HCHO/NO_y$ performed poorly and that $HCHO/NO_x$ performed significantly better in model simulations in the eastern U.S. To date, indicator values have only been evaluated in modeling studies – there has been no empirical investigation of the particular values of the indicators that signify NO_x -sensitive or VOC-sensitive conditions. As a result, there remains considerable uncertainty in using indicators to determine whether O_3 is primarily NO_x -sensitive or VOC-sensitive. Empirical testing of the indicator concept can be performed in specially designed smog chamber studies to evaluate the usefulness of each of the proposed indicators and to determine the particular values of the indicator ratios that denote the transition from VOC sensitive to NO_x sensitive conditions.

The budget of HO_x is of special interest for the evaluations of OBMS. The rate of production of O_3 is controlled by the availability of reactive nitrogen oxides ($NO_x = NO+NO_2$) and the sources

Table 1. Modeling Studies of Indicator Sensitivities.

Sensitivities For	Indicator Ratios Evaluated	Reference
O ₃ Concentration	Extent parameter	Blanchard et al., 1999; Chang et al., 1997
	NO _y	Milford et al., 1994; Vogel et al., 1999
	NO _y , O ₃ /NO _y , HCHO/NO _y , O ₃ /HNO ₃ , H ₂ O ₂ /HNO ₃	Sillman et al., 1997, 1998; Kleinman et al., 1997
	O ₃ /NO _z , HCHO/NO _y , H ₂ O ₂ /HNO ₃	Lu and Chang, 1998
	O ₃ /HNO ₃ , HCHO/NO ₂ , H ₂ O ₂ /(O ₃ +NO ₂), O ₃ /NO _x , H ₂ O ₂ /HNO ₃	Tonnesen and Dennis, 2000b
<i>P</i> (O ₃), <i>P</i> (O _x)	O ₃ /NO _x	Tonnesen and Dennis, 2000a
	<i>P</i> (H ₂ O ₂)/ <i>P</i> (HNO ₃)	
	HO ₂	
	$\sum k_{OH,i}VOC_i / (k_{OH}NO_2 + \sum k_{OH,i}VOC_i)$	
	$k_{HO_2}NO / (k_{HO_2}(HO_2 + RO_2) + k_{HO_2}O_3 + k_{HO_2}NO)$	

and sinks of HO_x (Levy, 1971; Logan et al., 1981). The budgets of the hydroxyl radical (OH) and hydroperoxyl radical (HO₂) are particularly important because HO₂ is rapidly converted to OH in the presence of NO_x, and OH attack on volatile organic compounds (VOC) and carbon monoxide (CO) is the primary source of tropospheric O₃ (NRC, 1991). In addition to its importance to the production of O₃, it has also been proposed that the radical budget is the key factor in determining the sensitivity of O₃ to its precursor species VOC and NO_x. For example, Kleinman et al. (1997) used a steady-state budget analysis of HO_x and Tonnesen and Dennis (2000a) used an analysis of radical propagation efficiency to derive the theoretical basis for indicator ratios. Moreover, modeling studies have suggested that the ratio $[HO_2]^2/[OH][NO_2]$ is the best indicator of *P*(O₃) sensitivity to VOC and NO_x and that [HO₂] by itself was also an excellent indicator of *P*(O₃) sensitivity (Tonnesen and Dennis, 2000a). Thus, there is great interest in acquiring measurements of OH and HO₂ to more fully evaluate both the rate of O₃ production and the mechanistic processes that control the sensitivity of O₃ to its precursors.

2. Project Summary

2.1 Objectives

The primary objective of this project is to provide data needed to experimentally evaluate the performance of various OBMs for predicting sensitivities of O₃ concentrations and O₃ production rates to changes in precursor concentrations. A related objective will be to provide data to evaluate model predictions of indicator ratios and of radical levels. These data are needed to

evaluate the utility of indicator species and radical measurements in field studies for predicting the sensitivities of air quality to VOC and NO_x emissions changes. These data are also needed to evaluate the accuracy and completeness of the models we use to predict the effects of control strategies on air quality.

2.2 Approach

The overall approach will be to conduct well-characterized environmental chamber irradiations of VOC and NO_x mixtures in the range of concentrations that occur in ambient atmospheres, and make measurements of most of the indicator species that have been evaluated in the modeling studies listed in Table 1. This will include measurements of HO₂ radical levels to evaluate the predictions of Tonnesen and Dennis (2000a). Experiments with varying VOC and NO_x concentrations will be conducted to directly determine the particular values of the OBMs that are associated with the transition from VOC sensitive to NO_x sensitive conditions for O₃. The experiments will be conducted at several different O₃-VOC-NO_x combinations to determine if the OBMs are robust for a variety of conditions. Direct measurements of OH, HO₂ and of OH reactivity (described below) will also be made to evaluate the theoretical basis for several of the OBMs and to evaluate its consistency with model predictions.

Although most of the experiments will employ surrogate VOC mixtures designed to represent the mixtures of VOCs responsible for O₃ formation in ambient air, some experiments with simpler mixtures will also be carried out both for model evaluation with chemically simpler systems and for evaluation of the measurement methods. Specifically, the simple VOC-NO_x mixture experiments will be used to demonstrate if the radical budget can be balanced for simple chemical systems.

The experiments will be carried out in the new UCR-EPA chamber facility that was developed and is being evaluated under separate EPA funding (Cooperative Agreement 827331-01-0; see Carter et al., 1999, Carter, 2002a,b). Use of this facility provides a number of significant advantages for this project, which are described in the following section. The most important include the availability of characterization data needed for model evaluation being obtained from the existing EPA cooperative agreement, the ability to conduct well-characterized experiments at lower and more representative pollutant levels than has been possible previously, and the availability of instrumentation needed to measure all of the major indicator species listed on Table 1 except for radical species. This facility is discussed further below, and also in the "Related Programs" section of this proposal.

Because the UCR-EPA chamber currently lacks the capability for radical measurements, we will be collaborating with Dr. William Brune of Penn State University to utilize his laser-induced fluorescence (LIF) instrumentation for the OH and HO₂ radical measurements needed for comprehensive OBM evaluation. Dr. Brune's group has also developed a method to use the LIF to measure total OH reactivity of the sampled mixture (Kovacs et al, 2002), and we will take advantage of this collaboration to evaluate the consistency of these measurements with model predictions and to evaluate their utility for OBMs.

Modeling will be a critical component of this project for experimental design and analysis of the results. Modeling will be used to determine the minimum set of experiments that will provide the

most useful data for the objectives of this project. The results obtained will be compared with model predictions, both for mechanism evaluation and evaluation of the measurement methods that have not been comprehensively evaluated previously. If discrepancies between experimental and model results are obtained, then experiments with chemically simpler systems will be designed and carried out to assess whether the problem is model or measurement related. The SAPRC-99 chemical mechanism, which was developed by one of the Investigators, will be utilized for this purpose. Note that there is an ongoing project for the California Air Resources Board (CARB) to evaluate, and if appropriate, to improve the SAPRC-99 mechanism for low NO_x conditions, and the results obtained from that project should be helpful to this project, and vice-versa.

3. Methods of Procedure

3.1 The UCR-EPA Chamber Facility

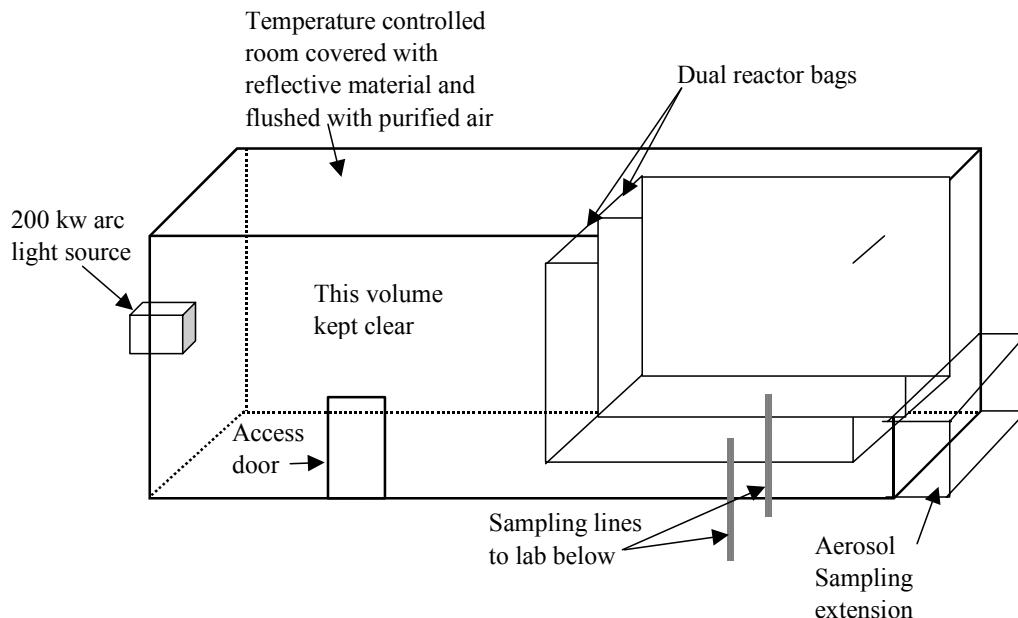
3.1.1 Facility Description

To address the need for an improved environmental chamber facility to evaluate mechanisms for O₃ and PM formation, UCR has recently completed development of a “next-generation” environmental chamber under separate funding from the U.S. EPA (Cooperative Agreement 827331-01-0; see Carter et al., 1999, Carter, 2002a,b). As discussed in the proposal for this cooperative agreement (Carter et al., 1999), the objectives are to develop an 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 budgets under more realistic and varied environmental conditions than previously has been possible. An additional objective is to develop a facility suitable for evaluating measurement methods under controlled conditions. Therefore, this chamber is well suited for the objectives of this proposal, since experiments were specifically included in the chamber design objectives.

The new chamber facility is located in a building specifically designed for this purpose. The two-story building has the chamber enclosure on the second floor and the sampling equipment, space for the analytical laboratory, support equipment, and offices on the first floor. This arrangement allows sampling directly below the chamber along the centerline between the two sides. The chamber enclosure occupies a space 20 feet wide 40 feet long and 20 feet high. A pad to the side houses the air purification system, water chiller, compressed air cylinders, and cryogenics.

Figure 1 shows a diagram of the layout of the environmental chamber enclosure. The reactors are located in a temperature-controlled housing specifically designed by a contractor specializing in refrigerated rooms and environmental enclosures. The temperature in the enclosure can be controlled to within $\pm 1^\circ\text{C}$ between $\sim 5^\circ\text{C}$ and $\sim 50^\circ\text{C}$. The enclosure is flushed with purified air to minimize contamination by pollutants by leaks or permeation through the Teflon® film reactor walls. Tests with smaller reactors has shown that this approach reduces background NO_x input rates to less than 1 ppb per day (Carter, 2002a).

Figure 1. Schematic of the temperature-controlled enclosure used for the UCR-EPA chamber.



The reactors are constructed of flexible 2 mil FEP Teflon® film attached to an upper and lower framework support system as shown on Figure 2. Tests with smaller reactor showed that this type of Teflon film performs as well or better than alternative reactor materials in terms of minimizing background chamber effects (Carter, 2002a). The support system is designed to provide a rigid framework to simplify construction of the reaction bags and to minimize leakage through difficult-to seal corners. The support system also permits the chamber to be collapsed to avoid dilution due to sample withdrawal and to expedite removal or reactants and cleaning between experiments. Pressure sensors are used to maintain the reactor at a constant slightly positive pressure, with the upper frame being lowered to increase the pressure as air is withdrawn by sampling or emptying, and being raised as the reactor is being filled with purified air. Teflon-coated valves and pipes attached to openings on the bottom of the reactors (not shown on the figures) are used to mix the air within the reactors or to exchange the air between reactors to assure equal reactant concentrations in each, when called for in the experimental plan.

The light source for the experiments will consist of a 200 KW argon arc light located as indicated on Figure 1. Calculations by the light source vendor, Vortek Industries, Ltd of Vancouver Canada, indicate that the configuration shown on Figure 1 should yield a light uniformity of $\pm 5\%$ for the portion of the enclosure where the reactor is located. The light has a specially designed spectral filter that duplicates the spectrum of sunlight as closely as possible for an artificial light source. This is shown on Figure 3, which compares the spectrum of the UCR EPA chamber light source with the solar spectrum as calculated by Peterson (1976). This gives a significantly better representation of sunlight than blacklights, and is also somewhat better than the xenon arc lights used in our previous chambers (Carter et al, 1995a,b). Preliminary tests indicate that this light source gives NO_2 photolysis rates of up to $\sim 0.4 \text{ min}^{-1}$ in the enclosure, though somewhat lower intensity may normally be used in experiments to extend the lifetime of the lamp components.

Figure 2. Diagram of reactor bag support system

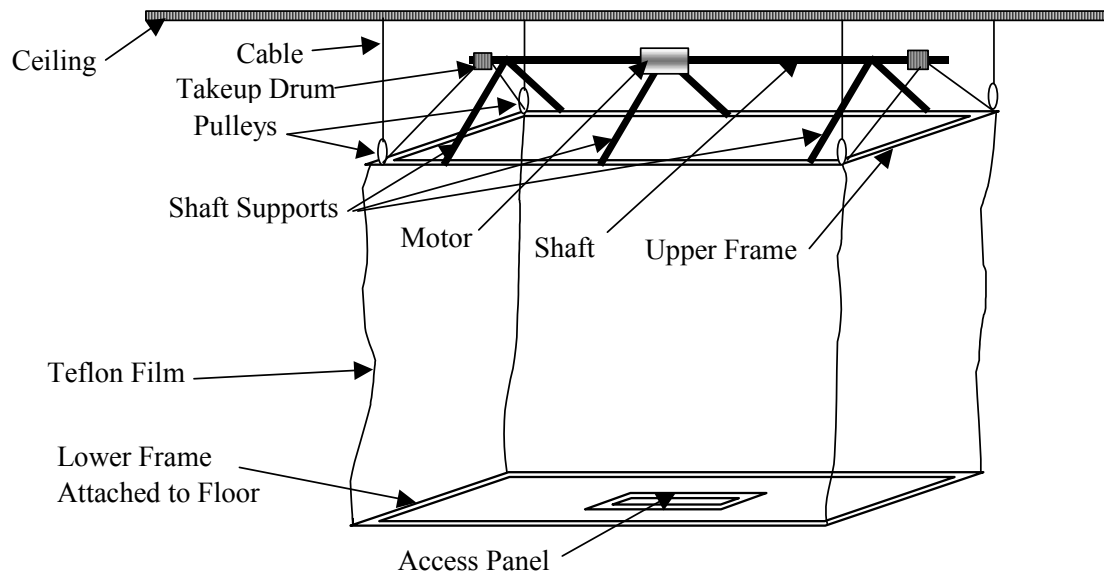
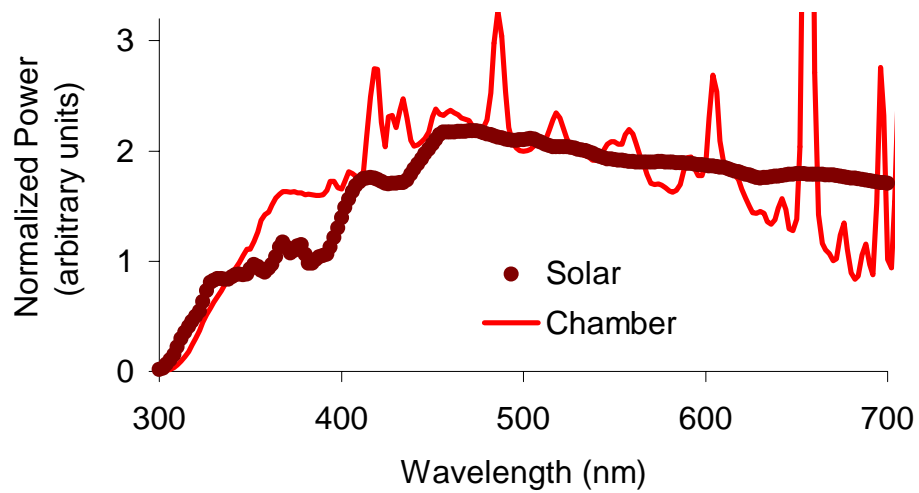


Figure 3. Comparison of a calculated ground-level solar spectrum with that of the UCR EPA chamber



We are also in the process of installing a bank of blacklights on the wall with the argon arc light, to serve as backups when the argon arc light is not functioning or for use in experiments or chamber conditioning runs where a close match to the solar spectrum is not as critical. Although the blacklight provides lower than solar relative intensities in the $\lambda \geq 400$ nm range, it gives reasonably realistic intensities in the portion of the UV that affects most photolysis reactions. However, the argon arc light will be used for most if not all of the experiments for this project.

3.1.1 Available Instrumentation

As discussed by Carter (2002a), the UCR EPA chamber has a full complement of analytical and characterization instrumentation needed for environmental chamber experiments. The instrumentation available for use for this project is listed on Table 2.

As indicated on Table 2, two tunable diode laser absorption spectroscopy (TDLAS) are available in our laboratory, one currently set up for analysis of NO_2 and HNO_3 , and the other for analysis of formaldehyde and H_2O_2 . Although the current setup works well for sensitive and highly specific analysis of NO_2 and formaldehyde, the sensitivity for analysis of HNO_3 and H_2O_2 is not adequate for the purposes of the proposed project. In particular, the diode laser currently used for HNO_3 needs to be replaced, and the path length and diode temperature range for TDLAS #2 is not optimum for sensitive analysis of H_2O_2 . Therefore, before conducting the experiments for this project we will change the H_2O_2 analysis to TDLAS #1 and obtain a diode laser for this purpose, and obtain the new diode laser for HNO_3 in TDLAS #2. Although this will yield somewhat lower sensitivity for HNO_3 than would be the case if we obtained a new laser for the first system, the sensitivity will be sufficient for this purpose. The result should yield analyses of all four species (NO_2 , formaldehyde, HNO_3 , and H_2O_2) with sufficient sensitivity for the purpose of this project.

3.2 LIF Instrument

An important component of this project is measurement of HO_2 radicals and OH reactivity ($\sum_i k_{\text{OH},i} \text{VOC}_i$), which is necessary to evaluate the indicator ratios proposed by Tonnesen and Dennis (2000a), as indicated on Table 1. Since the UCR-EPA chamber facility does not have the capability to make these measurements, we will be collaborating with Dr. William Brune of Penn State University to utilize his laser-induced fluorescence (LIF) instrumentation that can be used for this purpose. These instruments are described below.

3.2.1 Description

The technique for measuring OH and HO_2 is laser-induced fluorescence (LIF) at low pressure (often called FAGE) [Hard *et al.*, 1984, 1992; Stevens *et al.*, 1994; Mather *et al.*, 1997]. In this technique, the air sample is drawn into a low-pressure chamber with a vacuum pump. As the air passes through a laser beam, OH is both excited by the laser and detected at the $\text{A}^2\Sigma^+ (v'=0) \rightarrow \text{X}^2\Pi(v''=0)$ OH transition near 308 nm. Collisional quenching of the excited state is slow enough at the chamber pressure (4-12 hPa) that the weak OH fluorescence extends beyond the prompt scattering (Rayleigh, Mie and wall scattering) [Hard *et al.*, 1984, 1992] and is detected with

Table 2. List of analytical and characterization instrumentation available for use in this project.

Type	Model or Description	Species	Approx. Sens. (ppb)	Comments
Ozone Analyzer	Dasibi Model 1003-AH. UV absorption analysis	O ₃	2	Standard monitoring instrument
High Sensitivity Chemiluminescent NO Analyzer	Eco-Physics Model CLD 780 TR.	NO	0.04	
Conventional NO – NO _y Chemiluminescent Analyzer	ThermalEnvironmental Instruments Model 42C with external converter.	NO	1	Useful for NO and initial NO ₂ monitoring. NO _y data may be useful if scrubbers are used to remove HNO ₃ .
		NO _y	1	
Luminol Gas Chromatograph	Developed and fabricated at CE-CERT.	NO ₂	0.2	
		PAN	< 0.5	Suitability for PAN analysis still being evaluated
CO Analyzer	Dasibi Model 48C. Gas correlation IR analysis.	CO	50	Standard monitoring instrument
TDLAS #1	Unisearch model TAMS-150	NO ₂	0.5	These instruments will be reconfigured for this project. See text.
		HNO ₃	~50	
TDLAS #2	Unisearch model EMS-100	HCHO	0.1	
		H ₂ O ₂	≥5	
Continuous Formaldehyde Analyzer	Alpha Omega Power Technologies, Model MA-100. Continuous wet chemical analysis	HCHO	1	Suitability for routine use still being evaluated.
GC-FID #1	HP 5890 GC with dual columns, loop injectors and FID detectors. Various megabore GC columns available.	VOCs	10 ppbC	Different columns can be used for different sets of VOCs. Loop injection suitable for low to medium volatility VOCs that are not too "sticky". Trap analysis for increased sensitivity.

Type	Model or Description	Species	Approx. Sens. (ppb)	Comments
GC-FID #2	HP 5890 GC with dual columns and FID detectors, one with loop sampling and one set up for Tenax cartridge sampling. Various megabore GC columns available.	VOCs	10 ppbC	Different columns can be used for different sets of VOCs. Loop injection suitable for low to medium volatility VOCs that are not too "sticky". Trap analysis for increased sensitivity.
		VOCs	1 ppbC	Tenax cartridge sampling can be used for low volatility or moderately "sticky" VOCs that cannot go through GC valves but can go through GC columns.
Gas Calibrator	Model 146C Thermo Environmental Dynamic Gas Calibrator	N/A	N/A	Used for calibration of NO _x and other analyzers.
Data Acquisition System	Windows PC with custom LabView software, 16 analog input, 40 I/O, 16 thermo-couple, and 8 RS-232 channels.	N/A	N/A	Used to collect data from most monitoring instruments, control sampling solenoids, and carry out initial data processing.
Temperature sensors	Thermocouples, radiation shielded thermocouple housing	Temp	0.1°C	
Humidity Monitor	General Eastern HYGRO-M1 Dew Point Monitor	Humidity	Dew point range: -40 - 50°C	
Spectroradiometer	LiCor LI-1800 Spectroradiometer	300-850 nm Light Spectrum	Ade-quate	Resolution relatively low spectral resolution (4nm)

Type	Model or Description	Species	Approx. Sens. (ppb)	Comments
Thermal Converter NO ₂ Analysis	Thermal converter interfaced to a specific NO ₂ analysis system as described by Day et al. ¹⁴	Total PANs and Total organic nitrates	Not determined	Complements TDLAS and GC-luminol NO ₂ instruments
Spherical Irradiance Sensors	Biospherical QSL-2100 PAR Irradiance Sensor Responds to 400-700 nm light.	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. May give more precise measurement of light intensity trends than NO ₂ actinometry.

time-gated microchannel plate (MCP) detectors. HO₂ is detected by chemical titration to OH through the reaction with NO followed by LIF detection of OH.

The Penn State ground-based tropospheric hydrogen oxides sensor (GTHOS) instrument will be transported to UCR to make these measurements. It is a custom-built HO_x measurement system and partitioned into 3 subsystems: detection axes, laser system and electronics. The detection axes will be mounted in the access panel under the chamber reactor (Figure 2, above) through a 1.0 mm diameter inlet, down a 20-cm long, 5-cm diameter tube, into a low-pressure (4.7 mbar) detection chambers by a vacuum pump. Detection occurs in the detection chambers at the intersections of the airflow, the laser beams that are passed through multipass White cells (typically 32-36 passes), and the detector fields-of-view. A successive pair of White cells will be used. The first detection cell encountered by the air stream is for OH. The second cell for HO₂ is 10 cm downstream of the first. An injector loop positioned between the axes is used to add ascarite-filtered NO for converting HO₂ to OH. Because of the two-axis arrangement, the detection of OH and HO₂ will be simultaneous.

The laser is a combination of a Spectra-Physics T40-X30S-432Q diode-pumped frequency-doubled Nd:YAG laser (532 nm, 3 kHz repetition rate, 25 ns pulse width, 3 watts average power) which pumps a Harvard-modified Chromatix frequency-doubled dye laser [Wennberg et al., 1994]. The dye used was Pyrromethene 597 (Lambda Physik) in isopropanol. This dye laser has an intracavity etalon that both narrows the laser line width to 3.5 GHz, about the OH Doppler line width of the Q₁(2) line used for excitation, and allows for tuning on and off the OH resonance. The OH transition usually used was the Q₁(2) line near 308 nm. The UV laser power was totally about 15-20 mW. The UV laser beam was delivered via the 0.270 mm diameter optical fibers (ThorLabs, Newton, NJ) to OH and HO₂ cells with UV power of about 6.0 and 2.0 mW, respectively.

A reference cell containing OH made on a hot filament indicates when the laser is on-line and off-line with the OH transition [Stevens et al., 1994]. The off-line position alternates between a longer and a shorter wavelength than the on-line position to test the flatness of the background signal. A spectral scan taken once every hour is used to identify the laser line and measures the background shape.

The OH fluorescence and background signals were determined when the laser is tuned on and off resonance with the OH transition (called on-line and off-line) every 10 seconds. Collection optics gathered about 8% of the fluorescence and sent it to detectors behind narrow-band 308 nm interference filters. The MCP-PMT detectors (Hamamatsu) were gated on for approximately 300 ns to detect the OH fluorescence ~ 60 ns after each laser pulse had cleared the detection cells. Two counter gates were used for each detector: one counts the OH fluorescence signal; a second counts the Rayleigh and chamber scattering for 50 ns during the laser pulse when the detector gate was off. Sampling occurred 5 times a second.

3.2.2 OH Reactivity Measurement

Details concerning the OH reactivity measurements are given elsewhere (Kovacs et al, 2002), and are summarized here. Measurements of the OH reactivity are obtained with a technique similar to the laboratory kinetics discharge-flow technique (Kaufman, 1984; Donahue et al, 1996). A large abundance of OH is introduced through a moveable injector into a flow tube in which a flow of ambient air has been established at a known velocity. This mixture is sampled downstream of the injector with a detection axis similar to those used to detect atmospheric OH. By changing the distance between the OH detector and the OH injection point, the OH reactivity (s^{-1}) is measured.

A diagram of the system used for OH reactivity measurement is shown on Figure 4. Air is pulled into a diameter flow tube with an air speed of $0.4\text{--}0.8 \text{ m s}^{-1}$, as measured by a hot wire anemometer. OH and HO₂ are created in a stainless steel tube by photolysis of water vapor in nitrogen, using the 185 nm radiation from a mercury lamp that is shielded from the airflow. The OH and nitrogen are then injected into the flow tube through holes that were drilled radially in a Teflon endcap. Typical OH mixing ratios are 10–100 ppt, which is high enough to avoid influences from reactor OH and HO₂ levels, and low enough to avoid complications from radical self-reactions and the depletion of OH reactants. The injected OH mixes rapidly across the flow tube and reacts with the chemicals in the ambient air that was pulled into the flow tube. At the flow tube's end, OH is detected by laser-induced fluorescence in a low-pressure detection chamber. After ~ 20 s, the injector is pulled back. The reaction time is increased because the mixture now has to travel farther down the tube at a constant velocity before it is sampled. Measurements are made in 10 steps of 1–2 cm each, giving a total reaction time of 0.15–0.4 s. The time to measure each decay is approximately 4 min. For typical conditions, the OH signal decays a factor of 10–20 in this reaction time. The OH reactivity, $\Sigma_i k_{\text{OH}\cdot\text{Reactant}_i}$, is ideally determined by the slope of the logarithm of the OH signal, SOH, as a function of time minus the first order rate of OH loss to the flow tube's. Corrections need to be made for loss of OH on the walls, recycling of OH to HO₂, and other factors as discussed by Kovacs et al (2002).

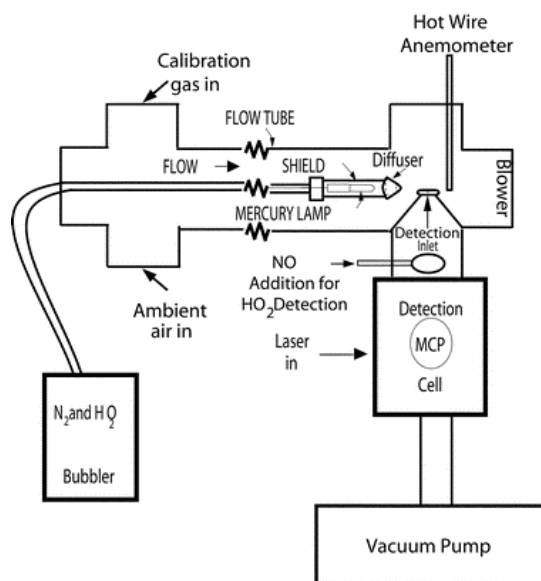


Figure 4. Schematic of the total OH loss-rate measurement instrument (TOHLM). The detection system consists of a laser beam crossed with a detection axis that includes a microchannel plate detector that detects the OH fluorescence in the lower pressure detection chamber. The hot wire anemometer monitors the air speed in the flow tube. The zigzags indicate that the flow tube is longer relative to the diameter.

OH reactivity measured using this method were consistent with calculated values using VOC, CO, and NO_x reactant measurements in a Nashville tunnel and their corresponding OH rate constants (Kovacs et al, 2002). OH reactivity measurements in ambient air during the Nashville summer 1999 SOS campaign were ~1.4 times higher than expected from measurements, as might be expected considering that not all reactive oxidized organic species in ambient air can be measured using current methods. Comparisons in a chamber system such as proposed for this project will provide useful evaluation data in this regard.

3.2.3 Calibration

The GTHOS instrument will be calibrated before, during and after its use in each chamber experiment. To determine the sensitivity (*C*) of the instrument, known amounts of OH and HO₂ were generated through the photolysis of water vapor at 184.9 nm with the subsequent reaction with O₂.



The calibration system was carried to the top of the scaffolding tower. 50 slpm of ultra-zero air was run from the base of the tower up to the calibration system and a small flow was passed through a HPLC grade water bubbler. A variable air bypassed to the water bubbler allowed the generation of a range of different water concentrations (0-2%). The water concentration is detected by a LICOR LI-6969 H₂O/CO₂ instrument (LICOR Instruments, Lincoln, NE). A low-

pressure Hg lamp generated the actinic flux in a 3.8×1.3 cm irradiation region at the outlet of the calibration system to photolyze the water. The UV flux at 184.9 nm was measured with a solar blind Cs-I photodiode tied to a NIST-calibrated photodiode at the University of Colorado. The produced OH and HO₂ concentrations are then calculated out of the flow rate of the air, the mixing ratio of the water in the air [H₂O], the absolute cross section of water $\sigma_{\text{H}_2\text{O}}$ [7.2×10^{-20} cm², *Cantrell et al.*, 1997], the quantum yield of OH Φ_{OH} [1.0, *DeMore et al.*, 1997], and the integrated actinic flux field $F_{\lambda=184.9 \text{ nm}}$:

$$[\text{OH}] = [\text{HO}_2] = [\text{H}_2\text{O}] \sigma_{\text{H}_2\text{O}} \Phi_{\text{OH}} F_{\lambda=184.9 \text{ nm}}$$

Currently the upper-limit of the absolute calibration uncertainty is estimated at $\pm 32\%$ (at the 95% confidence level). The sensitivity of instrument (*C*) is then obtained from:

$$C = \frac{\Delta S}{[\text{OH}]P}$$

where ΔS is the difference between on-line and off-line signals (counts per second), [OH] is the calculated concentration from equation (1) (ppt), and P is the laser power monitored at the output of the White cell (mW). Hourly diagnostic tests and real time monitoring of key parameters like laser power, temperature and pressure at various positions of the instrument ensure the stability of the calibration in between calibrations [*Stevens et al.*, 1994]. The chamber measurements of [OH] are then calculated from simply inverting equation (2). The minimum detectable [OH] we define as the OH derived from twice the standard deviation of the background signal is:

$$[\text{OH}]_{\text{min}} = \frac{(S/N)}{C} \sqrt{\frac{2\sigma_b}{t}}$$

The detection limits (with 2σ confidence and 1 min integration time) were estimated to be in the order of 3×10^5 cm⁻³ for OH and 2.5×10^6 cm⁻³ (0.1 pptv) for HO₂.

3.3 Environmental Chamber Experiments

Addressing the objectives of this project will involve conducting several types of environmental chamber experiments. A summary of the various types of experiments to be carried out for this project is given in Table 3. As indicated there, these include characterization runs for the LIF instrument, experiments with simplified chemical conditions, and experiments with surrogate VOC and NO_x mixtures representing various types of ambient conditions. The purpose and types of experiments are discussed below. Note that the number of experiments for each type is an initial estimate and is subject to revision as the project progresses, and the numbers of characterization or simple chemical conditions runs does not include experiments carried out under other funding that may be useful to the data analysis or modeling for this project.

Since the UCR-EPA chamber is currently set up with dual reactors, more than one experiment can be conducted at a time, and thus each of the experiments listed on Table 3 actually consist of irradiations of two mixtures. This will permit two different concentration ranges or types of mixtures to be studied at once. However, it is not yet clear whether it will be feasible to interface the LIF instrument to two reactors at once, and the currently projected numbers of experiments

Table 3. Summary of types of environmental chamber experiments to be carried out for this project.

Runs	Description
8	Characterization Experiments
1	Actinometry
2	Radical Source and background evaluation
2	Control experiments
1	Side equivalency tests
2	Other
8	Simple Chemical Systems
2	Propene + n-Butane - NO _x
2	Formaldehyde + n-Butane - NO _x
2	Isoprene - NO _x
2	Aromatic - NO _x or Other
17	Surrogate VOC - NO _x
3	Initial tests to evaluate surrogate suitability for project objectives
7	VOC and NO _x conditions (2 replicates per condition – 14 runs total)
3	Additional surrogate tests or simple chemical condition experiments as needed
36	Total number of dual reactor experiments

listed on Table 3 is based on the assumption that this will not be the case. Under this assumption, experiments in the one reactor will be used for the radical balance determination, and the experiments in the other will be to provide reproducibility information for the indicator species measurements or for characterization and control experiments. Note that the characterization experiments will include side equivalency tests to assure that equivalent results are obtained in each reactor. If the LIF can be used to evaluate radical balances in both reactors, the numbers of simple mixtures or VOC and NO_x conditions for the surrogate experiments with radical balance data will be significantly increased.

3.3.1 Characterization Experiments

One of the principal objectives for conducting the chamber experiments for this project is to determine consistency of measurements with model predictions. In order for the experiments to be useful for this purpose it is essential that the experimental conditions be appropriately represented in the model simulation. If the conditions of the experiments are uncertain, then poor model performance in simulating the results may be attributable to characterization uncertainties, or, worse, apparent good performance of the model in simulating the data may be due to compensating errors between characterization errors and errors in the underlying mechanism being evaluated (Jeffries et al, 1992). Characterization experiments are needed to minimize these uncertainties and possibilities for compensating errors, so the results can be used for meaningful model evaluations.

As discussed elsewhere (e.g., Carter and Lurmann, 1991; Jeffries et al, 1992; Carter et al, 1995a; Carter, 2002a), characterization experiments include at a minimum the following:

- Actinometry experiments to measure light intensity;
- Dark decay runs to measure wall losses of O₃ and other species that may be destroyed or absorbed on the walls, such as formaldehyde, H₂O₂ or low volatility species;
- Pure air, NO_x – air, or VOC – air runs to evaluate background effects;
- CO - NO_x or n-butane - NO_x runs to assess chamber radical sources;
- Formaldehyde - NO_x to evaluate light characterization and some background effects;
- Standard propene - NO_x experiments to evaluate overall performance of the chamber model and measurement methods;
- Control experiments with standard VOC surrogate - NO_x mixtures to assure side equivalency in the dual reactors and consistency and reproducibility of results; and
- Experiments with other simple chemical systems (whose mechanisms are reasonably well known) for testing for appropriate representation of experimental conditions or evaluating uncertain measurement methods.

These various types of characterization experiments have been developed over the years in our use of chamber experiments for mechanism evaluation (e.g., Carter and Lurmann, 1991; Jeffries et al, 1992; Carter et al, 1995a, 1997), though new types of experiments are being developed as needed for the lower background conditions of the new UCR-EPA chamber (Carter, 2002a).

Much of the basic characterization effort for the UCR-EPA chamber is already covered by the existing EPA cooperative agreement that funded the development of this facility, though the funding for that cooperative agreement will not be sufficient for the standard characterization and control experiments that must be carried out as part of any ongoing chamber experimental program. This includes periodic actinometry experiments, experiments to assure that the chamber radical source and background effects are in the normal range for the chamber, and occasional control experiments with standard systems. However, some of the cost of these ongoing characterization and control experiments can be shared by other experimental programs utilizing the chamber during the time period of the study, such as our current CARB study of architectural coatings VOCs (see Related Programs, below). For example, although more than one actinometry experiment would be necessary to adequately characterize trends in light intensity, because of experiments for the CARB project only one additional experiment of this type will probably need to be charged to this project.

The number and types of characterization experiments listed on Table 3 are based on the considerations discussed above. However, they may be subject to change based on the results of the initial characterization study of the UCR-EPA chamber that is currently underway for the existing EPA cooperative agreement, and the characterization protocol that is being developed as a part of this effort.

Although the radical measurements with the LIF system are not necessary to obtain the characterization data required for these experiments, most will be carried out after the system is interfaced to the chamber to assure that any perturbation it may have on the overall system is reflected in the results of the characterization runs.

3.3.2 Experiments with Simplified Chemical Systems

Experiments with simplified chemical systems, where the mechanisms of the reactions are believed to be reasonably well characterized, will be carried out to evaluate whether the observation based methods performed as expected and whether the radical budget can be balanced under these well understood conditions. These will be particularly important if there are discrepancies between model predictions and the results of the more realistic experiments, and the number of such experiments may be increased if this is found to be the case. These experiments will also be useful to evaluate the reliability of the radical and other measurements to be carried out for this project as they are implemented in our chamber system.

The specific types of simplified chemical systems to be examined will be determined based on the results of modeling analyses to be carried out for this project, as discussed in the following section. The types of experiments that might be chosen based on this analysis are indicated on Table 3. To be useful, the experiments should not be dominated by chamber effects (which means that they must have species, such as formaldehyde and propene, that have radical sources in their mechanisms), and they should have the VOC and NO_x levels and reactivity characteristics that generate O₃ and radical levels representative of ambient conditions. At least two types of simplified chemical conditions will be examined, and at differing VOC and NO_x levels to assess how the results are affected by the results of such conditions.

As indicated on Table 3, experiments with isoprene may also be carried out to evaluate the performance of the model to simulate indicator species and radical balances under conditions dominated by biogenic. The extent to which such experiments are conducted may depend on whether isoprene is included in the ambient VOC surrogate used in the more complex mixture experiments, discussed in the following section.

Table 3 also indicates that experiments with single aromatics may also be carried out if appropriate. Such experiments would be indicated if it is found that the model performs quite differently in simulating surrogate VOC experiments (whose reactivity characteristics are significantly influenced by aromatics) than in the simple systems not containing aromatics. Aromatics have significant uncertainties in their mechanisms, and problems with their mechanisms may affect model predictions of radical balances and indicator species.

Since obtaining radical balance as well as other indicator species information for these simplified chemical systems is a primary objective for these experiments, most if not all of these experiments will be conducted after the LIF system is interfaced to the chamber.

3.3.3 Ambient VOC Surrogate - NO_x Experiments

The major portion of this project is expected to consist of carrying out experiments using surrogate VOC - NO_x mixtures designed to simulate the mixture of compounds present in polluted ambient atmospheres, with initial reactant concentrations varied to assess how indicator species and radical balances vary with initial VOC and NO_x levels.

The VOC surrogate employed in this study will be designed to represent the major classes of reactive organics that contribute to radical cycles and O₃ formation. The specific composition

will be determined in consultation with the EPA project officer. The recommended and most cost-effective approach is to employ the same VOC surrogate that will be employed in our reactivity studies to be carried out for the CARB (see Related Programs), which we expect to be the same 8-component surrogate we employed in previous studies (e.g., Carter et al, 1995a,c, 1997). This surrogate, which consists of n-butane, n-octane, ethene, propene, trans-2-butene, toluene, m-xylene, and formaldehyde, was derived to have approximately the same level of chemical detail as condensed molecular-based mechanisms used in ambient modeling [such as RADM2 (Stockwell et al, 1990) or fixed-parameter SAPRC-99 (Carter, 2000a,b)], with one actual compound corresponding to one model species. The relative concentrations of each are derived to give the same ozone reactivities as the all-city average mixture derived by Jeffries et al (1989) and as used in the reactivity scale calculations of Carter (1994, 2000a). Model calculations indicate that this should give the same results in reactivity experiments as use of much more complex mixtures (Carter et al, 1995c).

For simulations of rural atmospheres, it may be appropriate to also include surrogates dominated by biogenic VOCs such as isoprene or terpenes. However, employing more than one ambient ROG surrogate will significantly increase the number of experiments required for an adequate evaluation of each, or reduce the number of VOC and NO_x conditions that can be studied. Experiments with the urban surrogates are given priority because it is urban conditions where the uncertainty of relative effects of VOC and NO_x controls are most uncertain – rural conditions are already considered to be most responsive to NO_x controls in most cases. The determination of whether to include experiments with a “rural surrogate” will depend on the results of the experiments with the urban surrogate, and the number of experiments required to obtain definitive results. The latter will also depend on whether radical measurements can be made from more than one reactor at a time.

The VOC and NO_x conditions for the ambient surrogate experiments will be chosen to represent the range of conditions relevant to ozone formation, and to provide sufficient data to determine the sensitivity of the results to changes in VOC and NO_x levels. The specific conditions will be determined by model analysis, and predictions of how O₃ and radical levels depend on VOC and NO_x. In terms of an O₃ isopleth diagram, shown in Figure 5, experiments will be designed to “map out” the O₃ response surface, ideally as illustrated by the crosses in Figure 5. In practice it may not be feasible to completely map out the isopleth, particularly if radical measurements cannot be made simultaneously in both reactors. In that case, a subset of conditions will be chosen to represent the various conditions, and adequately characterize the “ridgeline” of VOC and NO_x conditions that defines the border between VOC and NO_x-sensitive regions. An example of a possible subset of 7 conditions is shown by the circles on Figure 3. Although this limited number of experiments will obviously not be sufficient to exactly locate the ridgeline, a comparison of the results with model predictions should be sufficient to evaluate how well the ridgeline can be predicted by the model. Note that radical measurements are not necessary to determine the ridgeline, and even if such measurements can be made in only one reactor, the experiments in the other reactor with different VOC or NO_x levels can provide useful evaluation data for model prediction of the ridgeline location.

Since obtaining radical balance as well as other indicator species information for these ambient surrogate systems is a primary objective for these experiments, most if not all of these experiments will be conducted after the LIF system is interfaced to the chamber. However, if

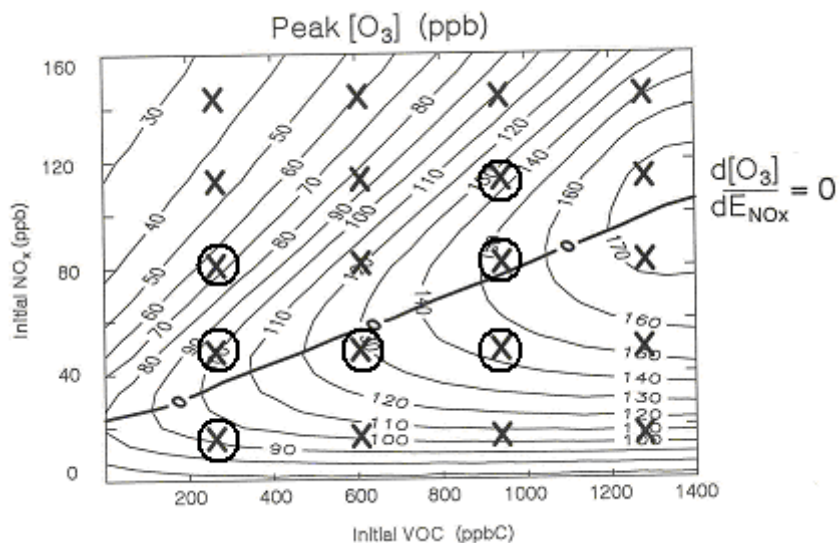


Figure 5. O_3 isopleth diagram showing isolines of model simulated peak O_3 concentration as a function of initial VOC and NO_x concentrations. The bold line shows the ridgeline of maximum O_3 concentration defined by $\partial[O_3]/\partial E_{NO_x} = 0$, and the crosses and circles illustrate VOC and NO_x concentrations that might be utilized in chamber experiments.

necessary experiments to better map out the VOC - NO_x - O_3 surface may be carried out after the LIF has been removed if this is needed and sufficient funding is available for this purpose.

3.3 Modeling and Analysis of Experimental Results

Modeling of the photochemical reactions in the chamber experiments will constitute an important component of this project. A standard box model (Gery and Crouse, 1991) using a Gear solver will be used to simulate the chamber experiments. The model is capable of representing dilution of chamber and has a flexible mechanism reader to allow for changes in the photochemical mechanism and also includes process analysis outputs that can be used for evaluating the radical budgets in model simulations as discussed below. An extensive set of model simulations will be run prior to the experimental stage to select the concentrations levels of VOC and NO_x to be used in the chamber experiments. The model simulations will be used to setup a suite of experiments that will cover a range of conditions from NO_x limited (with high HO_2/OH ratios) to low VOC/ NO_x , radical limited conditions (with low HO_2/OH ratios). After completing the experiments, times-series of species measured in the chamber experiments will be compared with the model predicted results, and additional model simulations will then be performed to attempt to obtain better fits to the experimental data by modifying the chemical mechanism as appropriate. This comparison of model results and chamber results will constitute an important test of the accuracy of current photochemical mechanisms and will likely lead to improvements in the photochemical mechanisms.

In addition to evaluating the species concentration time-series, two kinds of model simulations will be used to provide a more detailed evaluation of radical budgets.

First, radical concentrations will be calculated using a constrained, steady-state calculation (e.g., Kleinman et al., 1994). This approach has been used in previous field studies (Stevens et al., 1997), and most recently in the 1999 Nashville field study (Frost, 2000), and it is useful for assessing whether the model correctly represents radical sink and source terms. The results from previous field studies have shown that there sometimes exist large inconsistencies in the radical budgets (Cantrell et al., 1997, Stevens et al., 1997; Carpenter et al., 1998). Preliminary results for the Nashville 1999 field study presented at a data analysis workshop (Frost, 2000; Cohen, 2000) indicated that the high NO_2 concentrations did not significantly inhibit O_x production. This result would contradict our current understanding of radical and oxidant photochemistry, and hence it raises concern over the accuracy with which current photochemical mechanisms characterize radical budgets.

Second, model simulations will also be used to balance the radical budgets in terms of the production and sinks of HO_x radicals. Rates of new radical initiation must be balanced by radical termination, and the primary sinks for radical species are believed to be the production of radical termination products: HNO_3 , PAN, organic nitrates, hydrogen peroxide (H_2O_2), and organic peroxides. This budget analysis will be performed by calculating the integrated rates of the radical initiation reactions in the model simulations, and then comparing integrated radical initiation with the concentrations of radical termination products. Because species such as HNO_3 and H_2O_2 may also be deposited on surfaces or consumed in subsequent reactions, it will be necessary to use model simulations that include wall deposition to provide a full accounting for the budget of each of these species, and then to compare the budgets for radical initiation and termination. The ability to compare radical initiation rates with accumulation of radical termination products represents an important advantage of studying radical budgets in a chamber – in ambient field studies the radical termination products are dispersed by advective or turbulent transport processes and hence cannot be easily compared with the radical initiation rates.

Finally, the concentration of HO_2 is believed to be a useful indicator of O_x production sensitivity to changes in VOC and NO_x , where an HO_2 concentration of 20 ppt is strongly associated with conditions of equal O_x production sensitivity to VOC and NO_x (Tonnesen and Dennis, 2000a). The suite of chamber experiments to be performed in this study will bracket the conditions in which O_x production transitions from being VOC sensitive to NO_x sensitive for a range of O_3 levels and VOC/ NO_x ratios, and this will provide an opportunity to test whether the HO_2 concentration is a robust indicator of O_x production sensitivity. Because this indicator also represents a component in the theoretical basis for other photochemical indicators of O_x production and O_3 concentration sensitivity (Tonnesen and Dennis, 2000a,b) this analysis will be useful in evaluating the potential usefulness of photochemical indicators more generally.

3.4 Expected Benefits

The results of the research program proposed here will be experimental data and model simulations that will provide empirical evaluation of OBMs. The project will compare each of the proposed OBMs and will rank their specificity, universality for diverse VOC- NO_x mixtures and rank their robustness and usefulness for characterizing O_3 sensitivity to VOC and NO_x . This work will determine the suitability of OBMs both for a direct measure of O_3 sensitivity and for evaluation the chemical mechanisms and air quality models that are used in designing air quality

attainment strategies. Results may identify compounds that are especially useful in OBMs and could be used as the basis for suggesting new ambient measurements to be collected in routine monitoring or in intensive field studies. These results will directly benefit state and local air quality managers by providing more confidence in the accuracy of air quality models. The results of this work will ultimately benefit public health by helping to develop more effective and better optimized attainment strategies. It will also benefit commercial and economic interests by avoiding ineffective control strategies.

4. General Project Information

4.1 Standard Operating Procedures for Data Collection

The standard operating procedures for carrying out UCR-EPA chamber experiments are being developed and documented as part of our existing EPA cooperative agreement¹. A draft document describing standard procedures for carrying out experiments in this facility, and a separate document describing in detail the data processing procedures, have been submitted to the EPA project officer for this cooperative agreement, and is available at the project's web site². SOP documents for the major analytical instruments and the operation of the major components such as the arc light or enclosure are also being developed and will be provided to the EPA project officer.

The LIF instrument is not a normal component of the UCR-EPA chamber facility, so standard operating procedure documentation is not among those for this facility. This instrument will be operated by Penn State personnel who are familiar with its operation and who have familiarity with operating it in the field and in their laboratories. The procedures employed are documented in a report that is on file with Dr. Volker Mohnen, the QA-Officer for EPA Supersite PMTACS-NY, which is led by Professor Kenneth Demerjian, SUNY Albany. Any adaptations to the instrument or modifications to the procedures involved in interfacing it to the chamber will be described in the final report for this project and as appropriate in journal articles describing the results of this project. CE-CERT staff will work with the visiting Penn State researchers to assure that the instrumentation is interfaced to the chamber in a way that is needed for proper operation of the radical instrumentation, without adversely impacting the chamber characteristics and data quality for the UCR-EPA chamber instrumentation, or adversely affecting safety of the CE-CERT and Penn State personnel.

4.2 Quality Assurance

A draft comprehensive quality assurance project plan (QAPP) has been prepared for the UCR-EPA chamber and is available at the UCR-EPA chamber project's web site. This plan covers all aspects of data collection and management relevant to normal operation of the facility, and includes the SOP documents referenced above as appendices. It has been reviewed by the EPA and is now being revised by the CE-CERT Quality Assurance officer and other CE-CERT

¹ EPA Cooperative agreement number CR 827331-01-0, Dr. Deborah Luecken, EPA project officer. See Related Programs section.

² <http://www.cert.ucr.edu/~carter/epacham>

personnel to incorporate the EPA's comments and the evolving procedures for the facility as they are being developed. This should be in the form required by the EPA by the time the experiments for this project are begun.

The CE-CERT quality assurance officer, who is included in the budget for this project, is responsible for assisting the Principal Investigators in assuring that the quality assurance procedures are being appropriately carried out. Periodic audits will be carried out as outlined in the draft QAPP.

The Penn State personnel will be responsible for assuring that appropriate quality assurance procedures are carried out in conjunction with the operation of the LIF and associated data work-up and analysis. Penn State is working with Professor Kenneth Demerjian, SUNY Albany, on his EPA Supersite grant, PMTACS-NY, and has generated a quality assurance report entitled "Data Quality Assessment for OH and HO₂ Measurements during PMTACS-NY2001". This report is on file with Dr. Volker Mohnen, the QA-Officer for PMTACS-NY. The CE-CERT Quality Assurance officer and as appropriate other CE-CERT personnel will review these procedures and advise the investigators of any concerns they may have about the quality assurance procedures employed with these measurements, and if necessary corrective action will be taken.

Likewise, the Penn State personnel will be encouraged to provide CE-CERT personnel input about any concerns they may have about quality assurance practices we employ at the UCR-EPA facility. Such independent input is often useful to provide a perspective on matters that might otherwise be overlooked. Such input will be objectively evaluated and if necessary corrective action will be taken.

It should be pointed out that the modeling analyses of results of experiments with well-characterized chemical systems will prove an important quality-assurance component to this project, and that this is incorporated in the overall design of the project. Although unexpected or anomalous results may be due to true mechanism problems, our experience has shown that such problems more frequently turn out to be due to instrumentation or quality assurance problems. Appropriate steps will be taken to diagnose the problem that may be due to quality assurance failures, and modifications to the procedures or data work-up methods may be made as necessary to eliminate or at least reduce recurrence of such problems.

4.3 Relationship to Other Projects

This project benefits significantly from other CE-CERT environmental chamber and modeling projects, as described in the "Related Programs" section, below. The primary benefit is from the EPA cooperative agreement to develop this facility, which will also fund the initial characterization experiments that will be used to develop the characterization procedures to be used when modeling the runs for the project. The CARB projects on architectural coatings reactivity and low NO_x mechanism evaluation will also benefit this program by supporting useful characterization experiments around the period of these experiments, and for evaluating and characterizing the surrogate mixture to be used. The modeling and mechanism development projects at CE-CERT will benefit the modeling analysis for this project,

This project fits perfectly with the Penn State measurements of OH, HO₂, and OH reactivity in urban and rural regions. These studies show us that, while the basic concepts of atmospheric oxidation in these environments has been confirmed to within a factor of two or so, significant differences remain for OH, HO₂, and OH reactivity, particularly in HO_x sources, OH reactivity, and the variation of ozone production as a function of NO_x. We have proposed controlled laboratory studies to NSF in order to study these differences and will build a small reaction chamber to study them. These controlled experiments at UC Riverside will give us excellent insight into the processes that we have observed in the atmosphere. We see tremendous synergy between these studies and our continuing atmospheric measurements.

On the other hand, this project will use resources and facilities that are also needed for other current and possible future CE-CERT projects. Because this project requires Penn State LIF equipment and key personnel will need to be located at CE-CERT when the experiments are being conducted, this equipment and personnel will not be available for other Penn State laboratory or field projects where they will be required. To minimize the travel expenses involved for the Penn State personnel and the period of time that their equipment will not be available for other projects, it will be necessary that essentially all the experiments for this project be carried out during a single time period, with few if any experiments for other projects being carried out. Therefore, if the needed CE-CERT personnel, and the Penn State personnel and equipment needed for this project are not required for other projects. We currently expect that the facility and personnel should be available for this purpose in the summer of 2003, and we will adjust the schedules for our other projects to accommodate this as needed.

4.4 Schedule

As discussed above, the nature of this project is such that most of the experiments need to be carried out about the same time, which is tentatively planned for the summer of 2003. This may be delayed if there are delays in obtaining the funding from the EPA, in characterizing the UCR EPA chamber or if conflicts arise for other projects at UCR or Penn State, though the latter two eventualities are currently not believed to be likely. At least three months after the completion of the experiments will be required for data analysis and preparation of the final report and any journal articles. Assuming there are no delays, the project should be completed in one year after funding is available.

4.5 Reporting and Deliverables

A draft final report describing all the work on this project will be submitted to the EPA prior to the end of this project, and a final version will be submitted to the EPA within 30 days after receiving comments from the Project Officer. Once finalized the report will be made available on the CE-CERT web site used for reports in which Dr. Carter is involved³. At least one journal article is expected to result from this project, and a copy of the article will be provided to the EPA project officer at the time it is submitted. Periodic reports briefly describing the status and progress on the project will be submitted to the EPA project officer when requested, or approximately quarterly. The results of the UCR EPA chamber experiments conducted for this

³ <http://www.cert.ucr.edu/~carter/bycarter.htm>

project will be included with the UCR EPA chamber database that will be made available to other researchers on the CE-CERT web site.

5. Key Personnel

The CE-CERT principal investigators for this project are Dr. Gail S. Tonnesen and Dr. William P. L. Carter. Dr. Tonnesen will be primarily responsible for the experimental design and for the analysis of the results in terms of radical balance and indicator species. Dr. Tonnesen is the leader of the CE-CERT modeling projects, has conducted significant research on chemical process analysis and the theoretical basis for use of indicator species and radical analysis in development of observational based methods. Her biographical sketch is attached.

Dr. Carter will be responsible for the conduct of the UCR EPA chamber experiments and the data processing and quality assurance, and for determining the appropriate procedures for modeling the experiments for model testing. He will also work closely with Dr. Tonnesen in the experimental design and the analysis of the results, particularly in regards to experimental representation, chamber model, and details of the chemical mechanism. Dr. Carter has been involved in environmental chamber research and chemical mechanism development for a number of years, and has extensive experience in both generating and using environmental chamber data for mechanism evaluation. He is the Principal Investigator for the EPA cooperative agreement for developing the UCR EPA facility, and for the current CARB project to utilize it for reactivity assessment. He is also the developer of the SAPRC-99 chemical mechanism that will be used in the analysis of the results, and has a project with the CARB to evaluate and improve this mechanism in its ability to represent low NO_x conditions. His biographical sketch is attached.

Dr. William H. Brune of Penn State University will be a collaborating co-investigator on this project. He, and engineer Robert Leshner, and a postdoctoral researcher Xinrong Ren working under his supervision will be responsible for the implementation of the LIF system at the UCR EPA facility and its proper operation, calibration, and data processing. He will also contribute to the experimental design and analysis of the results as they relate to the instrumentation. The Penn State group developed the first viable OH and HO₂ instrument using LIF in detection chambers at low pressure starting in 1992. Since 1996, the Penn State group has produced high quality OH and HO₂ measurements on 5 NASA DC-8 aircraft missions and 7 tower-based field studies for NOAA, NSF, EPA, and has invitations to participate in two other studies in 2003. In 1998, the Penn State group used their original instrument to measure, for the first time, the total OH reactivity. They have more than 10 peer-reviewed publications on these measurements and more than twice that many in preparation. The biographical sketches for William Brune, Robert Leshner, and Xinrong Ren are attached.

6. Related Projects

Given below are summaries of related projects at CE-CERT and Penn State that are relevant to this project.

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

Agency: United States Environmental Protection Agency
Period: 6/1/99 - 6/30/03
Amount: \$2,925,000
Status: Funded. EPA Cooperative Agreement No. CR 827331-01-0

Objectives and progress: The objectives are to develop the next-generation environmental chamber facility needed for evaluating gas-phase and gas-to-particle atmospheric reaction mechanisms, for determining secondary aerosol yields, and for measuring VOC reaction products indicator species under more realistic and varied environmental conditions than previously has been possible. The facility will then be employed to provide data that are most relevant to today's pollution problems and control strategy issues.

Information about the status and project is available at <http://www.cert.ucr.edu/~carter/epacham>. The new chamber facility has been designed and constructed and housed in a new building designed for this purpose, and the major analytical equipment was acquired. These are currently being evaluated. A successful international workshop on chamber research was held and a draft research plan was developed and submitted to the EPA and the Reactivity Research Working Group. A number of experiments were carried out to evaluate chamber effects that need to be minimized, and methods to conduct experiments at very low NO_x levels were developed. Experiments with the reactor and light source in near-final configuration were carried out beginning in February, 2002, and construction of the final configuration and a second reactor should be completed by September.

As with most complex development projects, the level of effort required to construct and evaluate the new facility was somewhat greater than initially hoped, and additional funding will be needed to complete the research plan. However, the remaining funding should be sufficient to complete chamber characterization, so experiments from the CARB projects can be used for model evaluation.

Title: **EVALUATION OF ATMOSPHERIC IMPACTS OF SELECTED COATINGS VOC EMISSIONS.**

Agency: California Air Resources Board

Period: 6/30/01 – 6/29/04

Amount: \$300,113, of which about \$205 K is available for ~50 chamber runs

Status: Funded. CARB Agreement No. 00-333

Objectives: The purpose of this three-year project is to carry out priority research needed to reduce uncertainties in ozone reactivity estimates for selected major types of Coatings VOCs. The project will be carried out in consultation with the CARB staff and the CARB's Reactivity Research Advisory Committee. The specific tasks include the following:

- Further develop and evaluate the direct reactivity method developed under the current ARB and ACC projects so they can be applied to low volatility materials.
- Utilize the new environmental chamber facility being developed for the EPA to investigate the ozone and other atmospheric impacts of 2,2,4-trimethyl-1,3-pentanediol isobutyrate (trade name Texanol®), which is widely used in water-based coatings. This will require developing procedures for conducting environmental chamber experiments for low volatility materials such as this.
- Develop improved procedures for estimating ozone impacts of various types of petroleum distillates and quantifying uncertainties of reactivity estimates for these materials in cases where limited data are available.

Conduct environmental chamber experiments to determine the effects of at least five selected types of coatings constituents on ozone and PM formation under a range of reactant concentrations. At least four of these would be selected types of petroleum distillates representing different reactivity ranges, but an additional water-based coatings constituent may also be studied. The results will then be used to evaluate the predictions of existing and updated atmospheric reaction mechanisms or reactivity estimation methods for this compound or mixture.

- Apply the direct reactivity screening method to the full range of compounds and petroleum distillates being used or considered for use in architectural coatings in California.

The priorities for specific compounds or mixtures to be studied will be determined as part of the overall project, in conjunction with discussions with the CARB staff and the CARB Reactivity Research Advisory Committee. The procedures to be developed under CARB contract 00-333 to assess reactivities and uncertainties in petroleum distillates, along with results of market surveys and input from industry groups, will be used to guide the selection of specific types of petroleum distillates chosen for study.

Title: **DEVELOPMENT AND EVALUATION OF A GAS-PHASE
ATMOSPHERIC REACTION MECHANISM FOR LOW NO_x
CONDITIONS**

Period: 12/1/01 - 11/30/04

Amount: \$79,884, of which about \$35 K is available for 7-9 chamber runs

Status: Funded. CARB Agreement No. 01-305

Objectives: The purpose of this project is to evaluate and improve the performance of the SAPRC chemical mechanism for simulating atmospheric transformations under low and very low NO_x conditions. The specific objectives will include the following:

- Complete the development of the “Low NO_x” version of the SAPRC-99 mechanism that is designed to more accurately predict organic product formation under very low NO_x conditions.
- Evaluate the performance of both the standard and the low NO_x versions of the SAPRC-99 mechanism in simulating available environmental chamber simulating low NO_x conditions, including TVA and CSIRO chamber experiments not used previously in SAPRC mechanism evaluation.
- Utilize the new environmental chamber facility being developed under EPA funding to carry out selected low NO_x mechanism evaluation experiments deemed to be the most useful for mechanism evaluation in the near term.
- Update or modify the mechanisms as appropriate based on the results of the evaluation against chamber data and other data that may become available.

The results of this study will then be used to develop recommendations concerning mechanisms to use when modeling low NO_x conditions in regional model simulations, and priorities for future research aimed at reducing uncertainties in chemical mechanisms used in regulatory and research applications.

Title: **TROPOSPHERIC OXIDATION CHEMISTRY: ATMOSPHERIC OBSERVATIONS AND LABORATORY STUDIES OF OH, HO₂, RO₂, AND OH REACTIVITY, AND THE RESPONSE OF ATMOSPHERIC AIR TO PERTURBATIONS**

Period: 09/01/02 – 08/31/07

Amount: \$963,276

Status: Funded by NSF Atmospheric Chemistry ATM-0209972

Objectives: The purpose of this grant is to improve the understanding of tropospheric oxidation chemistry with a combination of atmospheric measurements of OH, HO₂, RO₂, and total OH reactivity and laboratory studies. The specific objectives will include the following:

- Determine the cause of the observed nighttime OH and HO₂ signals, why some instruments see nighttime HO_x and others do not;
- Determine the cause of the observed slower decrease in HO₂ at greater NO, which leads to unexpected ozone production;
- Develop indicators of instantaneous O₃ production to NO_x and VOC sensitivity by using measurements of OH, HO₂, RO₂, NO, NO₂, O₃, and the OH and HO₂ reactivity.
- Develop RO₂ measurement capability as an add-on to the HO_x instrument;
- Develop techniques that use the OH reactivity measurement techniques to probe other aspects of atmospheric oxidation.

Publication of peer-reviewed papers on the results of this research will add to the body of knowledge about atmospheric oxidation. These results will contribute to the scientific underpinnings for observational strategies and regulatory policies.

7. Budget

The total amount requested for this project is **approximately \$240,000**, of which **approximately \$175,000** is for work at UCR and **approximately \$65,000** is for a subcontract to Penn State University. The work at UCR consists of the cost of conducting the ~35 proposed experiments in the UCR EPA chamber, Dr. Tonnesen and Dr. Carter's time in designing the study and analyzing the results, and upgrading the TDLAS system to improve the analysis for H₂O₂ and HNO₃. The subcontract to Penn State is to cover the cost to transport the LIF instrument to UCR, travel, lodging, and salary for the postdoctoral researcher to interface the instrument to the chamber and operate it, for processing the results, and data analysis. An itemized budget for this project is attached.

Research at CE-CERT is charged an off-campus overhead rate of 25.4%. The first \$25,000 of the Penn State subcontract is also charged overhead at that rate. Because this is an off-campus facility, it is necessary to have a separate facility charge, which is based on the amount of CE-CERT permanent staff time required. This facility charge makes the total overhead rate comparable to the on-campus rate (about 48%) making the total cost to this project to the EPA approximately the same if it were carried out on campus.

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Personnel

Benefits

Travel

Equipment

Supplies

Contractual

Construction

None.

Other Direct Costs

Indirect Costs

Attachments

- Assurances, Non-Construction Programs
- Recommended Reviewers
- Form 5700.48, Procurement System Certification
- Form 5700.49, Debarment/Suspension Certification
- Lobbying Certification and Disclosure
- Form 4700.4, Preaward Compliance Review
- Indirect Cost Rate Agreement

Recommended Reviewers