ENVIRONMENTAL CHAMBER STUDIES OF VOC SPECIES IN ARCHITECTURAL COATINGS AND MOBILE SOURCE EMISSIONS

Proposal and Statement of Work to the
South Coast Air Quality Management District

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Summary

The College of Engineering Center for Environmental Research and Technology (CE-CERT) of the University of California at Riverside (UCR) proposes to carry out an environmental chamber study to assess the ozone and PM formation potential of selected types of VOCs emitted from architectural coatings and selected mixtures represent current mobile source emissions. This program will supplement and extend existing projects for the U.S. EPA and the California Air Resources Board (CARB) to enhance the benefit of these projects to the South Coast Air Quality Management District (SCAQMD). The EPA project is to develop and characterize a "next generation" environmental chamber for atmospheric chemistry and VOC reactivity research, and has resulted in the construction and characterization of a unique facility that is available for this project. The CARB project is to use this chamber to assess ozone impacts of selected architectural coatings VOCs. This proposed SCAQMD project will cover environmental chamber studies of VOC mixtures representative of current mobile source emissions and additional types of VOCs present in water-based architectural coatings and also chamber studies of VOC surrogate mixtures representing current mobile-source-dominated emissions, and characterization of PM formation potentials of the VOCs studied The amount requested for this one-year project is $199,547.

Introduction, Background and Objectives

As a part of the 1999 amendments to Rule 1113 – Architectural Coatings, the California South Coast Air Quality Management District (SCAQMD) Board approved a resolution, directing the SCAQMD staff to assess the reactivity and availability of solvents typically used in the formulation of architectural coatings. In addition, the SCAQMD staff desires to further understand the interactions between various architectural coating materials and other emission sources, such as on-road mobile vehicles, on ozone formation. Because of this, they initiated efforts in 1999 to conduct research on reactivity-based controls to determine whether it is feasible as an alternative compliance option. Preliminary research had found that different VOC species have varying reactive properties to form ozone under the same NO_x environment. However, the research also highlighted the need for additional effort needed to reduce the uncertainty associated with the reactivity values determined using an environmental chamber, especially for the most commonly used solvents in architectural coatings formulations, and their impacts relative to impacts of mobile source emissions. If feasible, this optional strategy could allow manufacturers to use greater quantities of less reactive solvents, and reduce the quantity of higher reactive solvents.

The environmental chambers previously used to develop the existing models have a number of limitations, particularly for evaluating effects on PM formation under controlled temperature, humidity, and lighting conditions and for evaluating secondary pollutant formation under lower pollution conditions representing near-attainment scenarios. Because of this, the U.S. EPA provided $3 million funding to CE-CERT for the design, construction and operation of a state-of-the-art, next-generation environmental chamber facility capable of obtaining the data needed for assessing the use of reactivity data as an ozone control strategy. This chamber was recently completed and is undergoing extensive validation testing to conduct reactivity-related studies. Experiments to assess surrogate - NO_x experiments for reactivity studies and to evaluate mechanisms under low NO_x conditions are now underway. The original $3 million funding used to construct and evaluate the chamber has now been spent, but an additional $200K of Federal funds is expected to support continued evaluation of the chamber and utilization for ozone impact, PM and mechanism evaluation studies.

The California Air Resources Board (CARB) has contracted CE-CERT to utilize the new chamber to improve reactivity assessments of some solvent species found in architectural coatings. The scope of the project was sufficient to conduct ozone reactivity experiments on at least seven different types of coatings VOCs, to be determined in consultation with the CARB staff and the CARB's Reactivity Research Advisory Committee (RRAC), which consists of representatives of industry and regulatory groups, including the SCAQMD. Based on discussions with the RRAC, it was decided that the CARB project will focus on experiments with Texanol®, an important compound in water-based coatings, and six different types of petroleum distillates that are utilized in solvent-based and (to a lesser extent) water-based coatings. However, the current list of solvents for testing for the CARB project does not represent all of the solvent species found, particularly those in water-based coatings. The CARB project also does not contain sufficient funds to utilize fully the equipment and expertise available at CE-CERT to assess the PM formation potential of the solvents studied, or to obtain ozone or PM reactivity data for mixtures representing current vehicle emissions for comparison purposes. Therefore, additional projects are needed to reduce the uncertainty of architectural coatings reactivity data, to compare reactivities of architectural coatings VOCs with current mobile source VOC emissions, to study the availability and reactivity of low vapor pressure solvents, and to assess PM as well as ozone formation potentials.

There is also a need to provide data to fully evaluate mechanisms for O_3 and PM formation of current ambient mixtures and mixtures representing mobile source emissions. Although there is a large environmental chamber data base for assessing O_3 impacts of ambient or mobile source mixtures at the relatively high concentration range employed in previous environmental chambers, data are needed to evaluate mechanisms at concentration ranges representative of current ambient atmospheres, and especially at atmospheres with the lower concentration representing attainment. PM formation data in highly controlled experiments representative of mobile-source dominated ambient conditions are also extremely limited and are inadequate to test models needed for planning PM attainment strategies. In addition, reactivity experiments for mobile source and coatings VOCs involve adding the test compounds to "base case" surrogates representing ambient conditions, and currently data are inadequate to characterize these base case experiments needed for reactivity studies.

Because of this, on April 4 2003 the SCAQMD Board approved a proposal to authorize the SCAQMD Chairman to execute a contract to conduct Reactivity and Availability Studies for VOC Species used in Architectural Coatings and Mobile Source emissions. The language of the proposal that was approved is as follows:

> The proposed project will focus on assessing the reactivity of VOC species most commonly found in solvent-based and waterborne architectural coatings and mobile sources, including studying ozone reactivities of low volatility solvents and re-evaluating uncertainties resulting from the current data and modeling. The project will also explore the potential of the new environmental chamber to investigate availability of the low volatility solvents and coordinate the studies with other availability studies sponsored by the Reactivity Research Working Group (RRWG). The chamber will be used to conduct experiments to study specific VOC species in the absence of any other air pollutant, as well as in conjunction with urban air mixtures that include VOCs from area, stationary, and mobile sources. The urban mix will be based on current ambient measurements. The chamber will also be utilized to validate the mechanism for simulating the base case surrogate experiments at lower pollution concentrations that are more representative of ambient conditions. Lastly, this project will evaluate the formation of PM in conjunction with reactivity experiments, including VOC emissions from mobile sources.

The specific objectives and statement of work is described below. It is designed to implement this proposal based on discussions we have already had with SCAQMD staff. However, specific elements of this project may evolve based on new information obtained in this and other projects and results of ongoing discussions with the SCAQMD staff.

Objectives

The overall objectives of this project is to conduct environmental chamber studies of selected architectural coatings VOCs and mixtures representing current mobile-source-dominated emissions to assess their impacts on ground level ozone and PM formation. This project will build upon and supplement an existing EPA to evaluate and utilize the new "next generation" environmental chamber system for chemical mechanism evaluation and an existing CARB project to conduct experiments in that chamber on selected architectural coatings VOCs. All experiments will be carried out for the purpose of evaluating and/or developing chemical mechanisms for use in airshed models, and will therefore incorporate the characterization and control efforts required for this purpose. The specific objectives are as follows:

- Conduct environmental chamber experiments with reactive organic gas (ROG) surrogates representing current ambient emissions and concentrations in order to determine the most appropriate set of "base case" experiments to use in incremental reactivity assessment experiments for this and the CARB architectural coatings reactivity project. These experiments will also be useful to evaluate models for current emissions that are dominated by mobile sources.
- Conduct environmental chamber for reactivity assessment and chemical mechanism evaluation for at least 3 types of coatings VOCs selected by the SCAQMD in conjunction with discussions with the CE-CERT investigators and RRAC. It is expected that the VOCs will include at least some experiments with ethylene and propylene glycol and other VOCs used in water-based coatings.
- Conduct measurements of PM formation in reactivity assessment and mechanism evaluation experiments not only for this project but also for the CARB reactivity project. The results of these experiments can then be used to evaluate the PM formation potentials of the types of VOCs studied, and be available for developing and evaluating models for their impacts on PM formation in the atmosphere.
- Evaluate the potential utility of the CE-CERT environmental chamber system for testing models for availability of emitted VOCs to react in the atmosphere to form O_3 and secondary PM. This work will carried out in consultation with the atmospheric availability subgroup of the Reactivity Research Working Group.

The specific tasks that will be carried out to address these objectives are described in the following section.

Methods and Specific Tasks

Given below is a brief description of the facility and procedures that will be employed for the chamber experiments for this project, followed by a description of the specific tasks and their associated experiments and/or measurements. Brief justifications and background information for the various tasks are also given, where appropriate. Note that Tasks 4 and 5 consist primarily of analysis, consulting, literature review, and reporting and do not involve chamber experiments as such in the current statement of work. However, based on the analysis for Task 4 and discussions with SCAQMD staff and the RRWG availability group it may be decided to include some experiments in that task, though at the expense of experiments in the other tasks unless additional funding is obtained. This is discussed below in conjunction with the description of that task.

A separate statement of work listing the tasks for administrative purposes is given as Attachment 1 to this proposal.

Facility

All experiments for this project will be carried out in the UCR-EPA chamber located at CE-CERT/UCR. The facility and available instrumentation is described in various reports to the EPA and the RRWG and are available at the UCR EPA chamber project web site at http://www.cert.ucr.edu/~carter/epacham (Carter 2002a,b, 2003a). Briefly, it uses an indoor chamber because conditions can be controlled and characterized with much greater precision that is possible with outdoor chambers, and this is essential for model evaluation. It consists of a 40’ x 20’ x 20’ temperature-controlled “clean room” enclosure fitted with a 300 KW argon arc light source, with two ~100 m^3 reactors constructed of Teflon film fitted on specially designed moveable frameworks. The large reactors minimize background effects, permit experiments using instrumentation with high sampling requirements, and are necessary for PM research. The argon arc light source is designed to give a very close approximation to the spectrum of sunlight, and is much more representative than the blacklights that are normally used for indoor chambers. In addition to the arc light source, the enclosure now also has a set of blacklights that provide approximately the same intensity in terms of the NO_2 photolysis rate, for use in experiments where blacklights are sufficient. However, the arc light will be employed in most if not all of the experiments for this project. The enclosure is continually flushed with purified air to minimize introduction of laboratory air into the reactor due to permeation or leaks, and tests have shown that this reduces background NO_x effects to less than 1 ppb per day, significantly lower than achieved in any other currently operating indoor chambers.

Instrumentation is available to measure the range of gas-phase species needed for comprehensive evaluations, including tunable diode laser absorption spectroscopy instruments for sensitive and specific analysis of NO_2, HNO_3, H_2O_2, and formaldehyde, GC’s for speciated analysis for organic reactants and toxic products, and extensive instrumentation for characterizing experimental conditions. There are also two Scanning Electrical Mobility Spectrometers (SEMS) for measuring aerosol size and number distribution and a Tandem Differential Mobility Analyzer (TDMA) for measuring aerosol responses to changes in temperature and humidity has been constructed and will be available for this project.

As discussed in the latest project report for the CARB coatings project (Carter, 2003b) the characterization experiments for that chamber have been completed and we are now conducting experiments for low NO_x mechanism evaluation and initial base case surrogate - NO_x evaluation experiments for use in VOC reactivity assessment[1]. We are also carrying out blacklight experiments in this chamber to measure aerosol formation potentials of toluene and m-xylene in this chamber, for

[1] Note that the present CARB coatings and EPA programs do not cover the cost of all the base case surrogate - NO_x experiments required for comprehensive reactivity assessment, which is why experiments of this type need to be included in the statement of work for this project, as discussed later in this section.

comparison with existing data at other laboratories. Therefore, we already have extensive experience and familiarity with operating this chamber for aerosol as well as gas-phase measurements.

Procedures

The procedures that will be employed for the experiments are based on those currently employed in the ongoing experiments for the CARB and EPA projects. Briefly they involve the following steps:

- The reactors and the enclosure are cleaned by flushing with purified air at least overnight
- Span checks are made on all applicable instruments prior to the experiment
- The reactants common to both reactors are injected and mixed. In an incremental reactivity experiment, this would consist of the base case ROG mixture and NOx.
- The reactants that are to be in only one reactor are injected and mixed. In incremental reactivity experiments this would be the test compound or mixture.
- Sampling is conducted for sufficient time to determine initial concentrations for the injected reactants and background concentrations of other species, if any.
- The lights are turned on. The light intensity is continuously monitored using a PAR spherical irradiance monitor and occasional NO_2 actinometry using the quartz tube method. Light spectra are also taken periodically during most experiments using our LiCor LI-1800 spectroradiometer.
- Sampling for the continuous instruments is taken alternative from each reactor and the enclosure, sampling for each 5 minutes from each source to allow the instruments to stabilize.
- GC samples are periodically taken from each reactor to determine consumption rates of reactant VOCs and formation of products that can be monitored by GC.
- Aerosol size and number distribution data are taken from each reactor prior to, during, and after the irradiations, using a separate SEMS instrument for each enclosure. Intercomparisons of the two SEMS instruments are carried out periodically.
- The irradiation is terminated after at least 6 hours, or longer depending on the experiment. Final samples are taken on all instruments.
- The reactors are emptied and filled several times until all injected reactants and O_3 are at background or below detection levels.
- The data are processed in Excel spreadsheets according to the procedures described in the data processing procedures documentation (Carter, 2002c)

Standard operating procedure (SOP) documents have been prepared for most of the major instruments and procedures, and work is continuing in completing the SOPs applicable for this project. A draft quality assurance project plan has also been prepared and is available at the UCR EPA project web site at http://www.cert.ucr.edu/~carter/epacham (Carter, 2002d).

Task 1. Evaluation of ROG and NO_x Surrogates

As discussed elsewhere (Carter and Atkinson, 1987; Carter, 1995, Carter et al, 1995a,b, Carter, 2000 and references therein), incremental reactivity experiments provide the most generally useful data for experiment for assessing O_3 and other impacts of VOCs and evaluating mechanisms for model predictions of these impacts. These consist of determining the effects of adding the test VOC to "base case” reactive organic gas (ROG) surrogate - NO_x experiments designed to approximate ambient pollutants. To fully evaluate the mechanisms, base case experiments representing different ROG and NO_x conditions and ratios, and different ROG surrogate compositions need to be employed. Although a standard set of base case experiments were employed in previous studies (Carter, 1995, Carter et al, 1995a,b, Carter, 2000 and references therein), they generally represent higher pollutant conditions than representative of ambient atmospheres because of limitations in the chambers and analytical instrumentation previously employed. Because the new UCR EPA chamber has the capability of running mechanism evaluation experiments at lower pollution levels, it is appropriate to employ new base case experiments representing these lower pollution levels in reactivity experiments in this chamber.

It is important that the appropriate set of base case experiments be established prior to reactivity assessment experiments for different VOCs, as discussed in Task 2, below. This requires conducting experiments with different base ROG and NO_x levels with compounds with known or well established mechanisms to determine if the models can appropriately represent the results of the base case experiment and also appropriately represent the effects of adding the test compounds with established mechanisms. If reactivity experiments are to be used for PM as well as O_3 impact assessment it is important that the PM formation from the base case be established for different amounts of base case ROG reacting, since this information is needed to assess the PM impact of the added test compound (see discussion of Task 3, below.) A limited number of base case assessment experiments are being conducted for the CARB and EPA programs, but the funds in the EPA project have been exhausted and the statement and work and funding for the CARB program is not sufficient to cover the number of base case evaluation experiments that are required without impacting the number of VOCs that can be studied. Therefore, in order to adequately carry out the CARB project and also Task 2 of this project, this proposed program includes a limited number of base case assessment experiments.

Experiments with base case ROG surrogates are also highly relevant to assessing the impacts of mobile source emissions because the base case ROG mixture currently employed (Carter et al, 1995b) is based on mixtures derived ambient air analyses (Jeffries et al, 1989) that detect primarily mobile source VOCs. Therefore, providing data to evaluate mechanisms for the base case also provided needed data to test models for mobile source impacts in the atmosphere. Although there is an extensive database of experiments from previous chambers that have been used for evaluating mechanisms for mobile source VOCs (e.g., Carter, 2000 and references therein), most of the experiments were conducted at higher than current ambient concentrations and contain no information on PM impacts. The base case assessment experiments for this project would be an important addition to the mechanism evaluation database, in addition to providing the base case data needed for VOC reactivity assessment studies.

The budget for this project calls for carrying out at least 8 dual chamber experiments for the purpose of base case evaluation. Because of the limited number of experiments, all experiments will use the 8-component “full surrogate” we have used extensively in our previous reactivity studies (Carter et al, 1995b, Carter, 2000 and references therein). These experiments will consist of surrogate - NO_x experiments at different ROG and NO_x levels, with emphasis on those with ROG/NO_x ratios corresponding to maximum incremental reactivity (MIR) and maximum O_3 (MOIR) conditions.

An important aspect of assessing base case experiments for reactivity assessment is determining whether effects of adding test compounds with known mechanisms on the results of these experiments are consistent with model predictions. In addition, if incremental reactivity experiments are to be used for PM assessment it is useful to determine effects of adding compounds that don’t form PM forming products on the PM formation from the base case experiment. This information is needed to correct for these indirect effects when assessing effects of added VOCs that are PM precursors.

Based on these considerations, the test compounds employed in the base case assessment experiments for this project will be CO and formaldehyde. Both of these have simple mechanisms that are reasonably well established but yet are different in important aspects, do not form reactive products, and are not direct PM precursors. CO is of interest because it only causes NO to NO_2 conversions and has no direct radical sources or sinks, though its addition generally suppresses OH levels because it competes for reaction with OH. It is also useful for evaluation because its addition increases the O_3 level while decreasing the amount of base case VOC reacting. It will be useful for providing base case information for PM assessment because its addition may decrease the amounts of PM formation from the base case VOCs, since less of them would react in the presence of test compounds that are radical inhibitors or compete for reaction with OH. Formaldehyde is useful because it is a radical initiating species, and thus has a different effect on OH levels and amounts of base case VOCs reacting than formaldehyde, while also enhancing O_3. These experiments will complement experiments already being carried out with the remaining EPA funding using n-octane and m-xylene as the evaluation VOCs, which are used because they represent important types of reactive species in stationary and mobile source emissions.

Task 2. Reactivity Assessments for Selected Coatings and Mobile Source VOCs

The major effort for this project will be to carry out reactivity assessment experiments for selected coatings and other VOCs of specific interest to SCAQMD. This effort can be thought of as extending the current CARB coatings VOC reactivity project by increasing the number of compounds that are studied. Except as discussed in conjunction with Task 3, below, the general objectives, approach, and procedures will be the same as employed in the chamber experiments for the CARB program, which are described in the proposals for this project (Carter, 2001).

Based on our present cost estimates for operating the chamber, the budget for this program is sufficient for carrying out at least 22 dual chamber experiments for reactivity assessment. The number of experiments required to evaluate the reactivity of a compound may vary depending on the compound, the uncertainty of its mechanism, the extent to which the results of the initial experiments are consistent with model predictions, run-to-run reproducibility, and the ease or difficulty with which the compound can be quantitatively injected or analyzed. In addition, if the compound or mixture being assessed is found to have strong PM formation potential, it may be appropriate to do additional experiments to assess how its PM formation potential depends on conditions, such as amount of organic aerosol mass. At a very minimum the experiments with a given VOC should be conducted with twp different ROG/NO_x ratios and with two differing amounts of the test compound or mixtures, making a minimum of 3-4 experiments for compound. For other VOCs 6 or more experiments may be required. Based on these considerations, we expect that at least 4 or perhaps 5 types of VOCs can be studied for this project.

The specific compounds or types of VOC mixtures to be studied will be determined in consultation with SCAQMD staff and the CARB's RRAC. Based on initial discussions, we would expect that studies of additional water-based coatings VOCs would provide the best complement to the existing CARB coatings project. The top compound on the water-based coatings emissions list is Texanol®, which is already being studied for the CARB project. Ethylene and propylene glycols are also high on the water-based coatings emissions list, but are not covered by the CARB project. Although ethylene glycol is expected to have a simple mechanism and not be a PM precursor, there are no chamber data to validate model predictions of its impacts, so at least 3-4 experiments with this compound would be useful. Propylene glycol has been studied by us previously (Carter et al, 1997), but depending on the ethylene glycol results it may be appropriate to further evaluate its mechanism at the lower concentrations attainable in the new chamber. The other compounds to be studied will be determined based on the results of discussions and results of ongoing experiments.

Although most of the experiments with this task are expected to focus on coatings VOCs, for comparison purposes it may be appropriate to conduct reactivity experiments using surrogate mixtures representing current or estimated future mobile source emissions. Separate experiments in this regard may be appropriate if the mobile source profiles are different from the base case ROG surrogate mixtures. The mixture(s) studied and the number and types of such experiments to be conducted for this program will be determined in consultation with the SCAQMD staff.

Task 3. PM Measurement Support for Reactivity Experiments

Although the focus of current regulatory efforts for VOCs (other than toxics) concerns their ozone impacts, at least some types of VOCs play a significant role in the formation of secondary PM. Since the South Coast Air Basin is a non-attainment area for PM as well as O_3, eventually the SCAQMD will need to know how emissions of different types of VOCs will contribute to PM formation, and how to take into account the significant differences among VOCs in PM forming potential in its planning to attain PM standards. Although assessments of O_3 impacts may be the priority for VOC regulations at the present, assessments of PM impacts may well be the priority in the not-too-distant future, especially since PM impacts of VOCs are much less well understood and quantified than is the case for O_3 impacts.

It should be noted in this regard that if PM formation potential assessments are to be carried out for the VOCs to be studied in this and the CARB project, it would be far more cost effective to do this in conjunction with the O_3 reactivity experiments, rather than carry out separate experiments for this purpose at a later time. Essentially the same type of experiment can serve both purposes, since the objective is to simulate the effect of adding the test compound on irradiations of realistic mixtures under a representative variety of conditions. Therefore, for the most part all that is needed to conduct PM assessments in conjunction with gas-phase mechanism evaluation experiments is to make PM measurements during the experiments, and analyze the data. Since we already have the necessary PM instrumentation and PM expertise as a result of the EPA project, including PM measurements with our experiments Involves primarily supporting a postdoctoral researcher or graduate student to maintain and operate the instrument and analyze the data. We estimate the incremental cost for this additional effort is about $500 per experiment, which is only about 10% the total cost of carrying out a UCR EPA chamber experiment according to our present estimates.

In view of this, this proposed task involves making the necessary PM formation measurements in conjunction with the surrogate evaluation and incremental reactivity experiments carried out under Task 1 and 2 for this project, and also for at least 20 of the reactivity experiments to be carried out for the CARB project. The results will be analyzed in order to obtain an indication of the PM formation potentials of the test compounds studied. Note that the results of the base case evaluation experiments will be important to assess the effects of added VOCs on PM formation resulting from their effects on the amount of the base ROG mixture that has reacted.

Taking full advantage of the PM data obtained in the reactivity and the surrogate evaluation experiments will require carrying out at least some control and characterization experiments designed specifically to characterize PM formation in our chamber, to characterize and evaluation the instrumentation employed, and to obtain data that can be compared with PM measurement studies in other laboratories. The specific types of control experiments will be determined in consultation with Dr. David Cocker of the UCR College of Engineering and CE-CERT. Dr. Cocker is a Co-Investigator on this project who is an expert on PM studies in environmental chamber systems, developed the indoor chamber for PM studies at Caltech (Cocker et al, 2001a), and used it a number of PM assessment studies (Cocker et al, 2001b,c). We may also consult with Dr. John Seinfeld of Caltech, an internationally recognized expert on aerosol studies who was a collaborator on our original EPA chamber project.

The current statement of work calls for at least 5 dual chamber experiments for control or characterization purposes to support the PM studies. These probably will include aerosol yield studies for m-xylene for comparison with existing data (e.g., Cocker et al, 2001c).

Task 4. Assessment of Potential of Chamber for Availability Studies

In order for emitted VOCs to react in the atmosphere and form O_3 and secondary PM, it is necessary for them to exist in the gas phase. The tropospheric concentrations of emitted VOCs depend not only on their gas-phase reaction rates, but also on removal through a variety of competing processes such as deposition and re-emissions from various types of surfaces. These competing deposition processes can affect the “availability” of emitted VOCs to react in the gas phase, and are therefore a factor to consider in assessing their overall atmospheric reactivity (Kurland et al, 1999 and references therein).

Because of the potential for these availability issues affecting the overall atmospheric impacts for at least some types of VOCs, the Reactivity Research Working Group (RRWG) has been funding studies in for integrating environmental fate and availability models into airshed models. Although this has not yet been fully assessed, it may be that the UCR EPA chamber may serve as a resource for testing such models. This will be investigated as part of this project by conducting discussions with the RRWG availability group and the contractors working on their project and carrying out a review of available information and methods employed to test such models. We will then report back to the SCAQMD staff and the RRWG concerning the potential utility of this chamber for availability studies, and if appropriate develop a proposed research plan for consideration by the SCAQMD, RRWG participants, or perhaps other agencies or groups interested in availability research.

The present budget does not include any provisions for any chamber experiments related to availability. However, if the assessment indicates that a limited number of experiments may be useful for assessing the utility of this chamber for this purpose, some such experiments may be conducted for this program. This will be done only after discussions with the SCAQMD staff and obtaining their approval to redirect resources from other tasks for this project.

Task 5. Analysis and Reporting

The results of the experiments will be analyzed in terms of their implications concerning the ability of the current SAPRC-99 mechanism to predict the impacts of the test VOCs or base case mixtures on O_3 formation and other gas-phase processes, using procedures employed in our previous reactivity studies (see Carter and Carter et al. references listed below). Modifications may be made to the mechanism or representation of the VOCs if appropriate and indicated by the results of the experiments. The results will also be analyzed in terms of the impacts of the VOCs on PM formation, using procedures developed previously (e.g., see Cocker et al, 2001a,b and references therein) with appropriate modifications for incremental reactivity experiments. Since most previous PM formation potential chamber studies are based on analysis of experiments where the VOC of interest is the only reactive VOC present, it probably will be necessary to develop new analysis methods for analyzing effects of added VOCs when added to base case experiments that also form secondary PM. Although such analysis may be more complex, the results will be more atmospherically relevant because such experiments are much more representative of atmospheric conditions.

The results of the analyses of the experiments will be included in the final report for this project and, where applicable, also in the final report for the CARB coatings project. The final report for this project will also describe the objectives, methods, results, analysis, and conclusions drawn for the experiments for this project, and discussions of their implications concerning models or methods for deriving the atmospheric O_3 and PM impacts of the compounds and mixtures that were studied. The results of the availability assessment in Task 4 will also be described in the final report, along with recommendations for future work, if applicable.

Since Task 2 includes conducting PM measurements in conjunction with the CARB experiments, a discussion of the results of these measurements and the associated analysis and conclusions will also be included in the report to the CARB on the coatings project. SCAQMD staff will receive this report for review at the same time it is submitted to the CARB, and the SCAQMD contribution to this project will be noted in the acknowledgements.

Schedule

An estimated schedule for this project is given with the Statement of Work in Attachment 1 to this proposal. The experiments and measurements for this project will be carried out within the one year period of performance of this project, with the evaluation of the ROG and NO_x surrogates (Task 1) being carried out first. Task 2 will be carried out following the completion of Task 1, but probably following the initial experiments for the CARB project, which will be using lower volatility VOC mixtures that are expected to be easier to work with. We will then work with the RRAC and SCAQMD staff, participating with the RRAC, to schedule the ordering of VOCs to study for the CARB coatings project and Task 2 of this project. Task 3 will be carried out concurrently with Tasks 1 and 2, except that the PM control and characterization experiments will probably be carried out in conjunction with or immediately following the experiments for Task 2. Task 4 will be initiated around the beginning of the program, though the schedule for completion may depend on ongoing projects at other laboratories. The analysis of the data (Task 5) will be carried out concurrently with the experiments because the results will be used in part to plan the best approach for subsequent experiments, and determine the number of experiments necessary for particular tasks or types of VOCs. The other major effort for Task 5 will be preparation of the final report, which will be carried out around the end of the period of this project.

Deliverables

The major deliverable for this program will be the final report, which will be submitted for review by SCAQMD and RRAC participants approximately 11 months after the beginning of this project. SCAQMD staff and RRAC participants will have at least 30 days to provide comments for consideration when preparing the final version. The final version of the report will also be posted on the Principal Investigator's web site at http://www.cert.ucr.edu/~carter/bycarter.htm, probably also with links to it at relevant project web pages such as that for the UCR EPA chamber and the CARB coatings project. In addition, periodic reports summarizing work on this project and its current status and plans will be prepared and submitted to the SCAQMD and the RRAC approximately quarterly. These reports will probably not contain detailed analyses (unless this is needed for consultations for planning modifications or ongoing work), but will have sufficient information so SCAQMD staff and others can assess progress on the program and provide appropriate input where needed.

Budget

The total cost for this project is approximately $199,547. A cost breakdown by task is given in Table 1, along with a brief discussion of the origins of the costs. The costs for the UCR EPA chamber experiments are based on costs for laboratory personnel as currently employed, some Principal Investigator time for overseeing the runs and processing the data, laboratory supplies, repairs, and replacement Teflon film for the reactor. The cost for PM support is based on assuming a postdoctoral researcher needs to spend 100% of his or her time during periods when experiments with PM measurements are being made. The costs for given numbers of experiments are computed based on the cost per year for operating the chamber divided by the amount of time required to carry out the experiments, based on an assumed productivity rate of approximately one experiment every two days. Often we have a productivity of up to 4 experiments per week, but that rate cannot be maintained too long without creating a backlog of data to process, and there are often periods when runs cannot be conducted because of problems with equipment or other reasons. Based on this, the approximate cost per experiment without PM measurements is estimated to be approximately $4,400 per run, with experiments with PM measurements costing approximately $500 more per run. As indicated on Table 1, the costs for Tasks 5 and 6 are primarily personnel costs.

Table 1. Breakdown by task for costs for the proposed project.

Task	Cost	Description	Budget Discussion
1	$35,140	Evaluation of ROG and NO_x Surrogates	Cost for 8 chamber runs, not counting PM support
2	$96,635	VOC Reactivity Assessment for Selected VOCs	Cost for 22 chamber runs, not counting PM support
3a	14,953	PM Measurement Support for Task 1 and 2 experiments	Cost for postdoctoral researcher to operate PM instrument and analyze results for the 30 Task 1 and 2 experiments and for at least 18 experiments for the CARB project, respectively.
3b	8,972	PM Measurement Support for CARB Coatings Reactivity Experiments	
3c	24,169	Control Experiments for PM Assessment.	Cost for 5 chamber runs, counting PM support.
3	$48,095	Total for Task 3	Sum of 3a+3b+3c
5	$5,116	Assess Potential of Chamber for Availability Studies	Approximately 0.3 months of effort for the Principal Investigator, plus some student time to help with literature searches.
6	$14,561	Analysis and Reporting	One month of the Principal Investigator’s time plus some office expenses.
	$199,546	Total Cost	

References

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ATTACHMENT 1

STATEMENT OF WORK FOR THE REGENTS OF THE UNIVERSITY OF CALIFORNIA, RIVERSIDE ON BEHALF OF THE COLLEGE OF ENGINEERING CENTER FOR ENVIRONMENTAL RESEARCH AND TECHNOLOGY

The College of Engineering Center for Environmental Research and Technology (CE-CERT) of the University of California at Riverside (UCR) proposes to carry out an environmental chamber study to assess the ozone and PM formation potential of selected types of VOCs emitted from architectural coatings and selected mixtures represent current mobile source emissions. This program will supplement and extend existing projects for the U.S. EPA and the California Air Resources Board (CARB) to enhance the benefit of these projects to the South Coast Air Quality Management District (SCAQMD). The EPA project is to develop and characterize a “next generation” environmental chamber for atmospheric chemistry and VOC reactivity research, and has resulted in the construction and characterization of a unique facility that is available for this project. The CARB project is to use this chamber to assess ozone impacts of selected architectural coatings VOCs. This proposed SCAQMD project will cover environmental chamber studies of additional types of VOCs present in water-based architectural coatings and also chamber studies of VOC surrogate mixtures representing current mobile-source-dominated emissions, and characterization of PM formation potentials of the VOCs studied

The amount requested for this one-year project is $199,547.

<u>Task 0- Work Plan</u>

0.1) CONTRACTOR shall determine sets of surrogate ROG and NO_x concentrations that are the most useful for evaluation to serve as the base case in reactivity assessment experiments.

0.2) CONTRACTOR shall determine appropriate sets of test compounds and incremental reactivity experiments for use in evaluating experimental methods for experiments for assessing O_3 and PM impacts of VOCs.

0.3) CONTRACTOR shall, in consultation with the SCAQMD, identify ROG compositions that represent current and potential future mobile source emissions and will develop a work plan for conducting environmental chamber experiments to evaluate their O_3 and PM impacts

0.4) CONTRACTOR shall, in consultation with the SCAQMD and the California Air Resources Board (CARB)’s Reactivity Research Advisory Committee (RRAC), determine the most appropriate set of VOCs to test to assess O_3 and PM impacts of architectural coatings emissions, taking into account the compounds already being studied in an existing project for the CARB.

0.5) CONTRACTOR shall write a work plan describing the experiments to be performed and the analyses to be conducted.

Task 1 – Evaluation of ROG and NO_x Surrogates

1.0) CONTRACTOR shall conduct a minimum of 8 dual chamber experiments using the UCR EPA chamber for the purpose of base case evaluation. All experiments will use the 8-component “full surrogate” we have used extensively in our previous reactivity studies. These experiments will consist of surrogate - NO_x experiments at different ROG and NO_x levels, with emphasis on those with ROG/NO_x ratios corresponding to maximum incremental reactivity (MIR) and maximum O_3 (MOIR) conditions. The test compounds will be carbon monoxide and formaldehyde. Both of these have simple mechanisms that are reasonably well established but yet are different in important aspects, do not form reactive products, and are not direct PM precursors.

Task 2 – Reactivity Assessments for Selected Coatings and Mobile Source VOCs

2.1) CONTRACTOR shall conduct 22 dual chamber experiments using the UCR EPA chamber for reactivity assessment. The types of experiments and specific VOCs to be studied will be determined as part of the development of the work plan (Task 0). The number of VOCs to be studied will depend on the number of experiments required per VOC, to be determined in Task 2.2, but shall be at least 4.

2.2) CONTRACTOR shall determine the most appropriate number of experiments to conduct for each compound, based on consistency of the results of the initial experiments with model prediction, whether the compound has significant PM impacts, measurement and handling difficulties, and reproducibility. At a very minimum the experiments with a given VOC should be conducted with twp different ROG/NO_x ratios and with two differing amounts of the test compound or mixtures, making a minimum of 3-4 experiments for compound. For other VOCs 6 or more experiments may be required.

Task 3 – PM Measurement Support for Reactivity Experiments

3.1) CONTRACTOR shall determine the most appropriate and useful methods for analyzing PM data from base case surrogate and incremental reactivity experiments to assess PM formation potentials of VOCs in the atmosphere.

3.2) CONTRACTOR shall conduct PM measurements using Scanning Electrical Mobility Spectrometers (SEMS) on the base case and incremental reactivity environmental chamber experiments carried out for this project in the UCR EPA chamber and for at least 20 experiments conducted under CARB funding in the UCR EPA chamber for coatings reactivity assessment. The results shall be analyzed according to the procedures developed under Task 3.1.

3.3) CONTRACTOR shall determine the most useful set of control experiments that will enhance the value of the PM measurements made under Task 3.2.

3.4) CONTRACTOR shall carry out at least 5 such experiments with PM measurements in the UCR EPA chamber, and analyze the results and incorporate them in the analysis of the results of the other experiments where PM measurements are made.

Task 4 – Assessment of Potential of Chamber for Availability Studies

4.1) CONTRACTOR shall conduct discussions with the RRWG availability group and the contractors working on their project and carrying out a review of available information and methods employed to test such models

4.2) CONTRACTOR shall report back to the SCAQMD staff and the RRWG concerning the potential utility of this chamber for availability studies, and if appropriate develop a proposed research plan for consideration by the SCAQMD, RRWG participants, or perhaps other agencies or groups interested in availability research.

4.3) CONTRACTOR shall make recommendations to SCAQMD as to whether it may be beneficial to incorporate availability experiments into this project and what other tasks, if any, would need to be scaled back to carry out such experiments without additional funding. Based on this, SCAQMD can then determine whether a modification of the statement of work to incorporate such experiments may be appropriate.

Task 5. Analysis and Reporting

5.1) CONTRACTOR shall analyze the results of the experiments for this project in terms of their implications concerning the ability of the current mechanisms to predict the impacts of the test VOCs or base case mixtures on O_3 formation and other gas-phase processes, using procedures employed in our previous reactivity studies. Modifications may be made to the mechanism or representation of the VOCs if appropriate and indicated by the results of the experiments.

5.2) CONTRACTOR shall analyze the results of the experiments for this project and the CARB experiments with PM data in terms of the impacts of the VOCs on PM formation, using procedures developed for Task 3.

5.3) CONTRACTOR shall write a final report for this project that will describe the objectives, methods, results, analysis, and conclusions drawn for the experiments for this project, and discussions of their implications concerning models or methods for deriving the atmospheric O_3 and PM impacts of the compounds and mixtures that were studied. The results of the availability assessment in Task 5 will also be described in the final report, along with recommendations for future work, if applicable.

5.4) CONTRACTOR shall include a discussion of the results of the experiments in Task 3 and the associated analysis and conclusions in the report to the CARB on the coatings project. SCAQMD staff will receive this report for review at the same time it is submitted to the CARB, and the SCAQMD contribution to this project will be noted in the acknowledgements.

Schedule

The proposed project will last 12 months and is assumed to begin on June 1. The estimated schedule for work on the tasks is given below.

Project Schedule and Milestones

Task	Month											
	Jun ‘03	Jul	Aug	Sep	Oct	Nov	Dec	Jan ‘04	Feb	Mar	Apr	May
0	x	x										
1	x	x										
2			x	x	x	x	x	x	x	x		
3		x	x	x	x	x	x	x	x	x		
4		x [a]	x						x	[b]		
5			x	x	x	x	x	x	x	x	[c]	[d]

[a] Status of availability work will be discussed at upcoming RRWG meeting scheduled for July 9-10.

[b] RRWG meeting anticipated in early Spring of ’04.

[c] Submission of draft final report end of April or early May of ‘04

[d] Completion of final report by end of May ’04.