DRAFT PROPOSAL

AIR QUALITY IMPACTS OF LOW VAPOR PRESSURE-VOLATILE ORGANIC COMPOUNDS

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# ABSTRACT

The College of Engineering Center of Environmental Research and Technology (CE-CERT) at the University of California, Riverside (UCR) proposes to conduct laboratory and environmental chamber experiments to develop key parameters for the evaluation of the ozone and secondary organic aerosol (SOA) formation potential of consumer products containing low vapor pressure volatile organic compounds (LVP-VOCs). The work will consist of three major tasks: 1) evaluate the emission flux of LVP-VOCs for pure components and from select consumer products; 2) perform environmental chamber analysis to better quantify potential atmospheric impacts of the LVPs; and 3) evaluate the atmospheric availability of LVP-VOCs after dilution in water (down the drain) and in the presence of real-world surfaces.

A critical component of this research will be to develop a chamber model to evaluate and predict the behavior of LVP compounds as they partition between gas-phase, chamber surfaces, and particle surfaces. This model will provide a foundational approach to analyze ozone reactivity and SOA formation potential from material that may be participating in wall sorption effects. The model will then enable future research to evaluate the relative importance of surfaces in influencing LVP availability.

The work utilizes the advanced environmental chamber facility housed at CE-CERT designed to investigate atmospheric reactivity, ozone formation, and PM formation at low atmospheric concentrations. This chamber facility is ideally suited for these studies with its precise environmental controls and the largest volume to surface area available for any indoor controlled environmental system—features essential for the development and exploration of the atmospheric impacts of LVP-VOCs.

The estimated cost of the program is $508,267 for a three-year program. (Task 0: $2,795; Task 1: $66,994; Task 2: $340,716; Task 3:$51,836; Task 4: $27,913; Task 5: $18,733)). We anticipate the possibility of co-funding additional work related to this project from industrial sponsors (Consumer Products Inc.; coatings industry; etc.) and the SCAQMD, which will broaden the scope of the program aiding the overall objectives and goals of the program. The co-funding will also provide a mechanism for participation of both the ARB and consumer product industries in providing the best science possible for effective control strategies as needed for LVP-VOC compounds. An advisory board for the program is envisioned with participation from ARB and SCAQMD scientists and industry representatives.

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# BACKGROUND AND PROBLEM STATEMENT

## Introduction

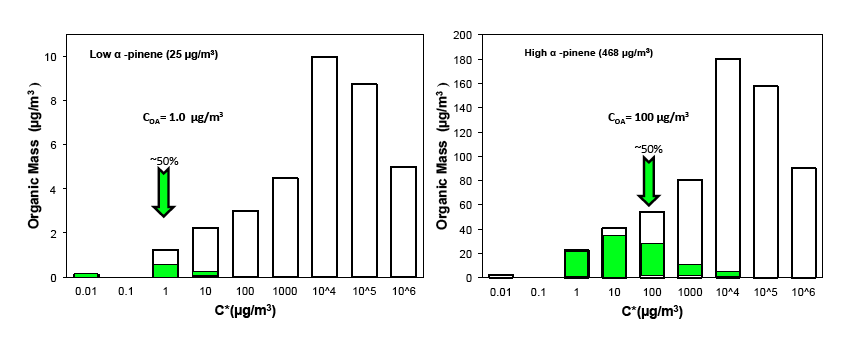
Atmospheric emissions of low vapor pressure-volatile organic compounds (LVP-VOCs) from consumer products and their impacts on ozone and secondary organic aerosol (SOA) formation are poorly understood at this time. LVP-VOCs are used in consumer products and currently receive VOC exemptions based on their vapor pressure. However, recent work (Vŏ and Morris, 2012) has demonstrated that certain compounds currently receiving VOC exemptions on the basis of vapor pressure may have greater atmospheric impacts than previously understood. Many of these compounds have high maximum incremental reactivity (MIR) (Carter et al. 1995; Carter 2008) relative to ethane and if available for atmospheric oxidation would be expected to participate in the formation of ozone (based on available MIR estimates) and SOA (based on the low vapor pressure of LVP-VOCs).

Critical insight into the availability of LVP-VOCs for atmospheric reaction is necessary to provide recommendations on the requirement for changes in regulatory strategies regarding LVP-VOCs, especially whether a LVP-VOC should be exempted or not. Questions as to their long-term atmospheric availability via slow evaporative processes must be addressed and the atmospheric chemical degradation pathways of these chemicals should be assessed.

The concept of a gas-particle partitioning model for atmospheric organic aerosol was introduced by Odum et al. (1996) using the foundations laid by Pankow (1994a,b) to describe the SOA formation by using a thermodynamic equilibrium scheme and two semi-empirically lumped compounds of different vapor pressures. This concept has been applied to over one hundred atmospherically relevant compounds including aromatics (Cocker et al. 2001; Song et al. 2005; Na et al. 2006; Ng et al. 2007; Song et al. 2007; Warren et al. 2008), alkenes (Matsunaga et al. 2009), and terpenes (Cocker et al. 2001; Na et al. 2007; Ng et al. 2007) and other compounds (Chan et al. 2009; Lim and Ziemann, 2009). More recently, Song et al. (2005) suggested that atmospheric chemistry involving both the VOC and NOx may play a pivotal role in determining SOA yield from parent compounds.

Over the last ten years, another concept, the volatility basis set (VBS), has been used to visualize the atmospheric behavior of semi-volatile organic species (Donahue et al., 2006). The VBS allows one to envision a complex mixture of organic aerosol evaporating and condensing over many orders of compound vapor pressures depending on parameters such as temperature and organic aerosol concentration. The VBS is most often constructed using basis sets with volatilities separated by one order of magnitude and spanning many orders of magnitude. The overall partitioning is given by

where (µg/m3) is the condensed-phase mass concentration of compound *i*, (µg/m3) is the total condensed-phase concentration of all compounds in condensed-phase mixture, and is defined as a partitioning coefficient for compound *i* given an effective saturation concentration under a certain . The VBS can easily be used to demonstrate how compounds volatilize based on surrounding atmospheric concentrations. Shown below are two volatility distributions for SOA from a-pinene ozonolysis (Donahue et al., 2007). Fig 1 (left) shows the volatility distribution of the same mixture of products when only 1 μg m-3 of organic aerosol is present while the Fig 1 (right) shows the distribution when 100 μg/m3 of organic aerosol is present..

**Figure 1**: Volatility distribution (pas/particle) for low vapor pressure compounds as function of organic aerosol concentration. Example is for a-pinene ozonolysis (Donahue, 2010, AAAR tutorial). Green shaded areas represent aerosol partitioned component, clear represents gas-phase.

As C\* is related to the vapor pressure of the compound,

: vapor pressure of pure compound

: activity coefficient of a compound i

It can be seen how chemicals that would be measured in the particle phase (low vapor pressure) begin to evaporate (species with C\* of 1 are now partitioned 50-50 between the gas and particle phase) when the organic aerosol concentration is lowered to 1 µg m-3 whereas the same species with C\* of 1 would be 99% in particle phase for organic aerosol concentrations of 100 µg m-3. Similarly, compounds with “low” vapor pressure with LVP-VOC exemptions may be more readily available for atmospheric degradation resulting in ozone and fine particle formation. The VBS tool therefore provides a conceptual framework for how LVP-VOCs can be released over long periods of time to participate in atmospheric chemistry.

Previous challenges for exploring the atmospheric availability and reactivity of LVP-VOCs included analytical challenges in accurate measurement of these compounds and their propensity to sorb to surfaces of chambers. These challenges prevented earlier research efforts from reducing the uncertainty of the chemical degradation mechanisms and atmospheric reactivity of these compounds. Here, we propose to use the advances in GC-inlet technology and gas-phase instrumentation to identify and more readily quantify their atmospheric concentrations. Recent work within our group has successfully demonstrated our ability to measure complex low-volatility chemicals including cresols and xylenols (Nakao et al. 2009; Nakao et al. 2011) and atmospheric amines (Silva et al. 2008; Erupe et al. 2010). Further, the recent acquisition of a selected ion flow tube mass spectrometer (SIFT-MS, Syft Technologies Ltd.) holds great promise for detection of trace, low-volatility gases within complex gas-phase mixtures.

Atmospheric chambers have been utilized for several decades as the gold standard approach toward the evaluation of atmospheric reactivity as well as ozone and SOA formation processes of atmospheric precursors. This work is often performed at concentrations far in excess of those present in the atmosphere. The UCR/CE-CERT environmental chamber (Carter al. 2005) was developed to allow for the study of these processes at more atmospherically relevant concentrations.

Work by the Ziemann group at UCR (Matsunaga and Ziemann, 2010) has challenged the conventional assumption that the highly hydrophobic Teflon surfaces used for chamber wall material do not participate in the gas-particle equilibrium achieved within the reaction mixture inside the chamber. Matsunaga and Ziemann (2010) point out that sufficiently low vapor pressure products could participate in an equilibrium process with the wall, providing a sink for VOCs during the initial part of the experiment and a possible source later in the experiment. These concerns must be addressed as the precursor VOC and atmospheric products in the environmental chamber move to lower vapor pressures, similar to those that may be experienced in this program. Therefore a chamber model to incorporate these wall effects as well as gas-particle partitioning effects is necessary when developing appropriate experiments to study the atmospheric reactivity and SOA formation of LVP-VOCs.

It is necessary to accurately define VOC and volatility when providing low vapor pressure (LVP) exemptions for organic compounds and to estimate VOC content from consumer products. Recently, the South Coast Air Quality Management District released a white paper on redefining volatile for volatile organic compounds (Vŏ and Morris, 2012). This paper summarizes the current LVP exemptions as “Currently, EPA, California Air Resources Board (CARB), and the ozone transport commission (OTC) exempt LVP solvents in consumer products with a vapor pressure less than 0.1 mmHg, a boiling point greater than 216 ºC or 12 or more carbon atoms. The European Union (EU) and Canada exempt solvents with a boiling point greater than 250 ºC. Green Seal exempts solvents with boiling point greater than 280 ºC.” However, these exemptions may not capture the true atmospheric availability of these compounds as they may evaporate over extended periods of time based in part on the gas-phase concentrations of the LVP compounds.

Vŏ and Morris (2012) evaluate a number of methods to determine VOC volatility including GC, boiling point, carbon number, and vapor pressure. They conclude that these methods provide contradictory evaluations as to whether a number of compounds currently classified as LVP-VOCs should be provided the LVP-VOC exemption. Further, Vŏ and Morris (2012) notes that many of these compounds receiving the exemption have high maximum incremental reactivities (MIRs) relative to ethane - meaning that should the species volatilize into the atmosphere they could significantly contribute to ozone formation. Given their low initial volatility, it is also expected that they will participate in fine particle formation. Therefore, it is essential as part of State Implementation Plan (SIP) development to determine the availability and impact of these LVP-VOCs as well as identify whether the LVP-VOC exemption is appropriately placed for key consumer products.

Data on SOA formation in well-characterized environmental chamber experiments representing a range of atmospheric conditions are essential to test and improve our theories and models for predicting SOA in the atmosphere. Emerging evidence obtained from such experiments demonstrates that NOx levels during atmospheric simulations impact the extent of gas-to-particle conversion measured for atmospherically relevant hydrocarbons (Chen et al., 2007; Hurley et al., 2001). Previous work widely cited and used in atmospheric airshed models are derived from atmospheric chamber simulations at elevated NOx concentrations far exceeding those typically encountered in urban airsheds (e.g., Odum et al., 1996, 1997; Griffin et al., 1999; Cocker et al., 2001; Izumi and Fukuyama, 1990; Jang and Kamens, 2001). Recent data from our group (Song et al., 2005) and at EUPHORE (Johnson et al., 2005) indicate that current environmental chamber data obtained under elevated NOx conditions may significantly underestimate SOA formation. For aromatic systems, Song et al. (2005, 2007) has performed a series of experiments demonstrating that aerosol production is elevated at low NOx concentrations and that this cannot simply be predicted by ozone (O3), hydroxyl (OH), and nitrate (NO3) concentrations present in the chamber. A significant portion of the underprediction in aerosol formation may be resulting from improperly evaluating aerosol formation at atmospherically relevant VOC to NOx ratios.

MIRs are used by the state of California to evaluate the reactivity of VOCs and their propensity to form ozone. MIR estimates have been developed for many compounds relevant for consumer products by Carter et al, 2008. However, in this earlier work, mechanism development and accurate MIR representations were difficult to achieve due to challenges in analytical instrumentation for measuring these low-volatility compounds and the lack of a chamber wall model to account for the partitioning of these species between the chamber surfaces, fine particles, and the gas-phase (Carter, 2008).

More recent work in our environmental chamber on improving analytical methods has yielded new techniques to measure directly the gas-phase concentrations of challenging LVP-VOCs. This includes measurement of amine precursors using sorption tubes followed by thermal desorption and the use of online gas-phase mass spectroscopy. Further, other low volatility precursors (e.g., sesquiterpenes, xylenols, etc.) have been successfully measured using this system within the environmental chamber. Therefore, it is encouraging that with proper sorption tube composition and GC-column selection many LVP compounds can be accurately quantified using flame ionization detection (FID). Further, real-time measurements of these species become possible with the use of online mass spectroscopy.

A wealth of data on ozone formation and fine particle formation have been obtained and analyzed for use in ozone and PM model development from the UCR/CE-CERT environmental chamber including many of the LVP compounds discussed in the current RFP. This work serves as a foundation for developing the necessary protocols to handle these challenging compounds that are discussed within the proposal.

# OBJECTIVES

*Task 0: Form a project advisory board*

We propose to create an advisory board for this program that includes both ARB and SCAQMD staff along with industrial representatives of the consumer products industry and other stakeholders impacted by the scientific outcomes of this program. Further, it is envisioned that co-funding (ongoing conversations with the consumer products industry, for example) will be provided to broaden the scope of the program and address additional concerns about the atmospheric impact of LVPs. The advisory board would provide guidance on the LVP-VOC and consumer products selected with final task decisions for this program between ARB staff and UCR PIs.

*Task 1: Investigate LVP-VOCs volatilization rates*

This task includes evaluation of ambient evaporation rates of pure LVP-VOCs as well as from their LVP-VOC evaporation from consumer products. Parallel experimental approaches will be used to characterize and quantify ambient emission rates. During this task, UCR researchers will consult with the project advisory board and CARB staff to identify the LVP-VOCs and consumer products chosen for this work. This task further includes a thorough literature review of existing vapor pressure data for LVP-VOCs identified through the initial consultation with the advisory board and CARB staff. Once identified, the volatility measured as the atmospheric flux of the species, will be experimentally determined using three separate analytical approaches. Evaporation of pure LVP-VOCs will provide upper bounds on atmospheric availability while evaporation from their complex mixtures due to chemical interactions may be considerably slower. These results will be critical toward assessing the availability of LVP-VOCs for ozone and PM formation and will provide insight into the need to modify LVP-VOC exemption rules based on their atmospheric availability.

*Task 2: Environmental Chamber Studies of Ozone and SOA Impacts of LVP-VOCs*

A state-of-the-art environmental chamber will be utilized to explore ozone and SOA formation from LVP-VOCs. The focus will be on LVP-VOCs identified in consultation with the stakeholder advisory board from Task 0. A series of at least 120 environmental chamber experiments (including characterization runs) has been budgeted for this work. Successful completion of this task will include (1) new method development for injection of LVP-VOCs and consumer products into the environmental chamber while minimizing thermal degradation of the compounds studied; (2) development of a chamber model to account for partitioning of LVP-VOCs to surfaces within the chamber (walls or particles); and (3) development of chemical mechanisms necessary to more accurately estimate MIRs and PM formation from the LVP-VOCs. It is noted that a select subset of experiments will involve whole consumer products. Further, this program will evaluate SOA impacts through direct partitioning of LVP-VOCs to particulate matter as well as through condensation of lower volatility oxidation products.

Task 2 will provide the critical inputs necessary to evaluate the atmospheric impacts of LVP-VOCs and provide the baseline data necessary to evaluate whether changes are necessary to the LVP-VOC exemptions.

*Task 3: Investigate environmental fate of LVP-VOCs in select consumer products*

This task will focus on the atmospheric availability of the LVP-VOCs when they are diluted in water. Many LVP-VOCs will be at least partially hydrophilic, which may limit their ability to be released back into the atmosphere once poured down the drain. Therefore, studies similar to task 1 will be conducted on highly diluted consumer products to assess the ability of the LVP-VOC to be released from dilute systems. Graduate students involved in this program will be assigned on their committee a water treatment expert within the UC Riverside Chemical and Environmental Engineering Water Quality Faculty ([www.cee.ucr.edu/](http://www.cee.ucr.edu/)ceepeople/departmentfaculty.html) to guide the student on practical water treatment steps and additional information needed to evaluate the ability of the LVP-VOCs to escape water treatment facilities. It is noted that this is a highly complex task in itself given chemical and biological interactions at water facilities. The scope of the current project will be to evaluate the ability of the LVP-VOC to escape from dilute water systems.

Further, several environmental chamber studies will be conducted with “real” surfaces added to the reactor to assess changes in atmospheric availability due to partitioning to nearby surfaces. These surfaces will be identified in consultation with the stakeholder advisory board and may include both masonry and/or plant material. The surface evaluation will build from the chamber model developed in task 2 and will be meant as an exploratory task for future research needs on LVP atmospheric availability.

## TECHNICAL APPROACH

### Task 1: Investigate LVP-VOCs Volatilization Rates

As mentioned in the objectives, there will be three approaches employed as part of task 1 to provide the best estimate of atmospheric availability of LVP-VOCs in consumer products while providing the greatest flexibility to investigate influences of environmental parameters.

Approach 1: Gravimetric analysis (pure compounds only)

This approach is based on the recent work by SCAQMD scientists (Vŏ and Morris, 2012). Evaporation rates of the pure compounds will be evaluated gravimetrically from miniature environmental chambers operating as continuous stirred tank reactors (CSTRs). The mass flux of the pure compound will simply be determined through a mass balance approach with the pure compounds being placed on Teflon® filters or in aluminum boats and weighed following 2010 federal protocols for gravimetric analysis. The general guidelines used as part of the 2010 regulations including filter holders and filter handling procedures will be implemented to ensure the greatest mass accuracy due to compound volatilization. These losses will be evaluated as a function of residence time of air within the chamber. Samples will be weighed ***daily*** for first week and then weekly thereafter for compounds with slow evaporative rates for a period of six months.

As part of ongoing emissions work at CE-CERT, a blank Teflon® filter has been regularly measured allowing for correction due to evaporation losses of the Teflon® filter itself over long periods of time. Additionally, a field blank will be used as a control for the duration of the experiment. Best weighing procedures as outlined by the Code of Federal Regulations and best practice approaches developed at CE-CERT as part of its PM testing from vehicles will be utilized. It is noted that this approach will not be as effective for compounds with high hygroscopicity as water will attach to the test compound biasing the gravimetric weights upwards and offsetting losses due to volatilization (although this influence is minimized by the very low dew point of our clean air system).

The residence time of the chambers will initially be set to 1 exchange of air per hour with the ability to change the air exchange rate as deemed necessary based on evaporation rates measured. Exchange rates will be controlled by metering the flow of dilution air into the CSTR. The air entering the chambers will be purified (see pure air system description as part of task 2) with very low humidity (dew point < - 60 ºC) to reduce the impacts of water sorption by the LVP compounds measured. The temperature of the system will be maintained at room temperature, which is tightly controlled in the environmental chamber building. Fluctuations in temperature will be recorded.

It is envisioned that a bank of 12 of these systems will be utilized in parallel. A hydrophobic, well characterized, low volatility control compound will be used in one of the 12 reactors while a non-volatile (e.g., salt) will be used in a second system to account for field bias during measurement of the samples. The system will also have the flexibility to change the humidity of the surrounding air. The number of LVPs analyzed will be dictated by the number of atmospheric parameters (e.g., dilution rate, humidity) explored. Should approach 2 prove successful, the environmental parameters will be explored more rapidly using approach 2.

Approach 2: (pure compounds and mixtures)

Chemical concentrations of many of the chemicals may be measured directly from the atmosphere using a selected ion flow tube mass spectrometer (SIFT-MS, Syft Technologies Ltd.) capable of rapid quantification at sub ppb detection limits for single compounds. This coupled with steady-state loss rates for systems in CSTR mode will allow real-time evaluation of chemical evaporation. Should this method prove successful when compared to gravimetric analysis, it will allow the evaporation rate to be explored as a function of temperature and ambient humidity.

Further, the SIFT-MS has the capability to identify a single compound from a complex mixture (e.g., consumer product) based on selected mass spectra. This enables evaluation of the evaporation rate of LVP-VOCs as present in consumer products thereby allowing for evaluation as to the role of liquid-liquid interaction on LVP-VOC evaporation. A mass balance will be performed for the pure compounds with the gravimetric losses to provide a critical quality control check.

Approach 3: Sorptive sampling followed by thermal desorption GC-FID analysis

A third approach for measuring flux of the LVP compounds from the microchambers described above will be to use sorption tubes to capture the LVP compounds as they are released from the system. This will allow total capture (depending on system flow rate) of LVPs as they evaporate. This approach requires analytical development to ensure proper elution of the LVPs from the GC-column and quantitative transfer of the compounds onto the GC-column. This approach will be similar to approaches implemented in our laboratory on other LVP compounds (e.g., dibenzylamine, diphenylamine, sesquiterpenes, etc.) and will provide the highest analytical sensitivity of the approaches above. It is expected that this approach will readily work on pure compounds, while partial flow sampling will be necessary for complex mixtures as other components in consumer products will block active sites of the sorption tube. This approach will only be used as a back-up and calibration for Approach 2 should Approach 2 be proven successful for the LVP-VOCs studied.

For all approaches, the number of LVPs measured will be decided in consultation with CARB staff. Should approach 2 prove effective, this method will provide the greatest potential for understanding evaporation of LVP compounds from complex matrices and looking at the impact of various environmental parameters. It is anticipated that resources will be available for evaluation of 10 – 30 LVP compounds depending on sensitivity of SIFT-MS to LVP-VOCs of interest. Figure 2 is a schematic of the system.

**Figure 2:** Schematic for LVP-VOC volatilization measurement

### Task 2: Laboratory chamber experiments on LVP-VOCs

More details on experimental procedures for these laboratory chamber studies is located at the end of the task section and includes details of facility and summary of instrumentation.

Task 2.1: Experimental Design and Development of Chamber Model

LVP commercial products present a unique challenge to environmental chamber studies due to their inherent low volatility. Environmental chamber surfaces are traditionally composed of fluorinated ethylene propylene (FEP) Teflon® film due to the transparency of the film to UV irradiation necessary to drive photochemical degradation reactions as well as its large hydrophobicity, which limits the deposition of VOCs onto the chamber surfaces. Further, the relative low atmospheric abundance of the LVP compounds requires advanced chamber designs to enable the study of these species within an environment with minimal background effects.

The CE-CERT environmental chamber facility has several key advantages toward the study of these LVP compounds. First, it is the world’s largest indoor environmental chamber allowing for precise atmospheric controls with the best volume-to-surface area ratio necessary toward the minimization of chamber wall effects. Further, its unique collapsing elevator design provides a slight positive pressure differential between the reaction mix within the chamber and its surroundings. (The design will be modified to maintain maximum volume to surface area should Teflon wall losses prove large for this study). This pressure differential coupled with the chamber enclosure being flushed with purified air allows one to study atmospheric effects at the lowest VOC and NOx concentrations possible.

Despite these advances, it is likely that at least some of the LVP products will partition between the surfaces of the chamber, the particle surfaces and the gas-phase. This will have the effect of reducing VOC availability during ozone and SOA formation experiments at the onset of the experiment as LVP injected prior to commencing the experiment. Later in the experiment, as concentrations of the LVP parent compound decrease, the wall and particles may then become a source of the LVP. Similarly, these effects may occur with partitioning into fine particulate within the chamber (Figure 3).

 **Figure 3**: Schematic of LVP distribution in chamber to be modeled

Such effects were observed in previous work by Carter (2008) where concentrations of LVP-VOC consumer products injected in the chamber were seen to increase during the course of the reaction despite the obvious consumption of the VOC based on observed ozone formation. Development of the chamber model allows one to address these surface effects (sources/sinks), thereby improving our understanding of processes occurring within the chamber, which in turn allow for appropriate interpretation of chamber data to understand chemical mechanisms leading to ozone and SOA formation.

Further, careful analysis of these chamber effects provides the foundation for evaluation of atmospheric availability of the LVP compounds. The following experiments will be conducted to identify these effects:

Characterization experiments: Each of the selected LVP-VOCs will be introduced into the chamber and the concentrations of the LVP-VOC will be monitored relative to an inert tracer gas (n-perfluorohexane) to account for dilution. The chamber temperature will then be cycled from 5 to 40 ºC to evaluate the partitioning of the LVP-VOC of interest onto and off of the chamber surfaces. Once stabilized, an inert seed (ammonium sulfate) will be injected into the chamber and changes in the LVP-VOC concentration will be monitored. Finally, an extremely low-volatility organic aerosol (e.g., dioctylphthalate) will be injected to evaluate gas-particle partitioning of the LVP-VOC in the absence of photochemical oxidation processes. Mass balance between injected mass of the LVP-VOC and measured LVP-VOC concentrations as well as LVP-VOC concentration versus time with and without the seed aerosol will be used as a foundation to evaluate surface effects and sorptive partitioning effects of the LVP prior to gas-phase oxidation.

Further, the tandem differential mobility analyzer (TDMA) present in the environmental chamber facility will be used to directly evaluate the uptake of LVPs onto particle surfaces. The TDMA will be operated in “organic” mode (o-TDMA) which enables the measurement of organic sorption to particle surfaces based on the increase in particle size. This technique is very similar to that of a “hygroscopic” TDMA or h-TDMA where water is allowed to surround a particle surface and the hygroscopicity is reported as the ratio of the final diameter to initial diameter (McMurry and Radar, 1986; Cocker et al., 2001). This method is deemed exploratory and has not been demonstrated for such compounds in the literature. Should it be proven successful, this will further insight into the relative uptake of the LVP onto different particle surfaces as particle composition and size is easily varied prior to injection into the TDMA. Successful characterization of the chamber will be aided by this tool, but is not dependent on it in its entirety.

The chamber wall model developed will be used to estimate LVP surface losses during photochemical oxidation experiments as well as their propensity to repartition back to the gas-phase. Therefore, by evaluating these surface effects carefully, the input concentration of LVP over the course of the experiment can be best estimated.

Task 2.2: Method Development for Chamber Studies

***LVP analysis*:** Many of the LVP chemicals proposed for this study are analytically challenging to accurately measure. For this work, we propose a multi-faceted approach toward this problem by using thermal desorption GC-FID as a standard for measurement of these compounds as well as development of online measurement of these compounds by selected ion flow tube mass spectrometry (SIFT-MS).

GC-FID is the standard for measurement of many organic compounds due to the robustness of the measurement and the relative ease of calibration. However, challenges of using this technique remain, including injection methods to transfer LVP-VOCs onto GC-columns as well as chromatographic challenges. For this work, we propose using sorption tubes to capture the LVP-VOC at the exit of the chamber (thereby minimizing sample line losses of the LVP-VOC). These tubes provide several advantages including the ability to concentrate the gas-phase samples on the sorption tubes thereby increasing the number of molecules sampled and the lower detection limit of the sample.

The exact material used for the thermal sorption tubes will be determined in coordination with Dynatherm (we use ACEM model 9305) who we have worked with closely while developing methods for amine analysis and xylenol analysis. Column selection will be made in consultation with Agilent technologies (former J&W staff) and the method optimized following standard GC optimization procedures. An example of a related successful LVP compound is dibenzoamine (b.p. > 300 C).

For some LVP-VOCs, GC may become impractical due to volatility/boiling point issues. For these circumstances, we will capture the LVP-VOC and perform liquid chromatography (LC) analysis with UV-Vis detection. An accurate mass time-of-flight mass spectrometer will be used to confirm the identification of the eluting compounds.

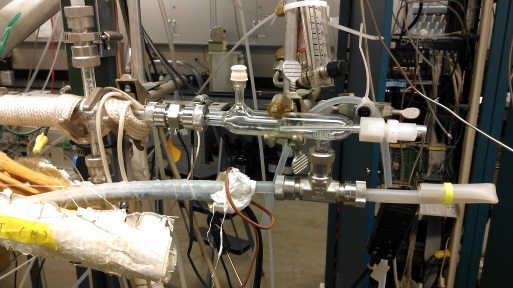
SIFT-MS is a promising new analytical tool available at our chamber facility. The instrument, constructed by Syft Technologies Ltd., has greatly enhanced the sensitivity over earlier SIFT-MS instruments through advances in quadruple technology. The current instrument achieves sub ppb sensitivity for a number of atmospherically relevant species. The technique works by ionizing sample gas molecules through collision with a focused beam of either H3O+, NO+, or O2+ to provide quantitative collisional activation of the analytes. This ionization is considered “soft” because it reduces the break-up of the parent molecule and provides unique spectra for the analyte of interest.

Advantages of the SIFT-MS system include high-sensitivity with fast signal response. Theoretical calculations as to the collisional efficiencies within the instrument allow for estimation of the response factors of the instrument. Calibration factors will be routinely obtained using GC-FID methods described above to further the quantitative accuracy of the instrument. (Should the GC-FID approach fail for select LVP-VOCs, a realtime FID will be used to identify VOC concentrations for calibration OR calibration will be performed based on gravimetric analysis). Real-time monitoring of the evolution of the LVP-VOCs provides critical information into the behavior of the LVP-VOCs and will allow the exploration of many more parameters impacting LVP-VOC atmospheric availability (see task 3).

**LVP injection**: Due to their inherent low-volatility, the injection of LVP-VOCs into atmospheric chambers is challenging. The CE-CERT group has extensive experience in this area having worked with a number of LVP-VOCs including many of those expected to be targeted as part of this work (in coordination with ARB staff). Challenges include vaporization of the LVP-VOCs without thermal degradation (especially into smaller, reactive VOCs) and transport losses during injection into the environmental chamber.

To overcome concerns of thermal degradation, we propose to inject the LVP compounds in situ with the chamber. The injections will be accomplished by (other ideas exist, these will be the first attempted)

1. For compounds that still have relatively “high” vapor pressures, above 10 ppm (or 0.00076 torr), the compounds will be gently heated (35-40C, in a small oven (if needed) and evaporated into a nitrogen stream (~5 LPM). The chamber atmosphere will be scanned for light degradation molecules/impurities prior to commencing an experiment. (Figure 4)



**Figure 4**: Injection system currently used (valid for methods 1 and 2)

1. For compounds with very low vapor pressures (<10 ppm), the compounds will be heated (oven temperature approx.. 160C) and injected through a heated transfer line into the chamber (55 C, adjustable higher as needed). A mass balance will be performed between the amount injected and the known chamber volume to assess the injection ability of the compound. Further, degradation compounds will be scanned for using the scanning mode of the SIFT-MS. Should thermal degradation be seen during this injection method (or if losses >25% are seen) we will move to injection method#3.
2. The LVP-VOC will be dispersed over a very large hydrophobic surface. The LVP-VOC will then be injected into an evacuated chamber as the fill air of the chamber passes over the surface, providing up to 85 cubic meters of dry purified air to evaporate the LVP-VOC into during chamber filling. This has the advantage of not needing to heat the LVP-VOC (no thermal degradation). Further, by flowing large volumes of air past the LVP-VOC during injection, the airborne concentration of the LVP-VOC will remain below the vapor pressure of the compound reducing the risk of LVP-VOC loss during transport into the chamber. Again, a mass balance on the LVP-VOC will be performed to ensure proper injection of the LVP-VOC into the reactor as well as a scan by SIFT-MS to ensure that impurities do not influence the chemistry to be studied in the chamber.
3. Atomization of the LVP. A nebulizer will be used to provide a fine mist of the LVP-VOC compound which can be directly introduced into the chamber. This requires that the LVP-VOC or consumer product to be in liquid form and allows direct transfer into the chamber with very little loss. The LVP-VOC will then evaporate to establish an equilibrium within the chamber.

To minimize transfer losses during injection, one of several approaches will be used. First, we currently have heated transfer lines to minimize losses during transport of low-volatility VOCs. These will be used to transfer LVP-VOCs for injection method 1 or 2 above. Should losses of the LVP-VOCs be noted (based on mass balance between injection and measured chamber concentrations), the injection system will be moved immediately adjacent to the chamber reducing the potential for transfer line losses.

For LVP-VOCs with even lower vapor pressures, the injections will be made by either highly diluting the analytes prior to injection (achieved in injection method 3) or by injecting the analytes without transfer lines directly in the chamber through an access port in the chamber.

Task 2.3: Environmental chamber experiments

Well-characterized environmental chamber experiments are critical to the development of chemical models with predictive capability, particularly for processes whose chemical details are not well understood. They also provide important information on how best to model these processes, which in turn provides clues on the chemical reactions that occur under atmospheric conditions. The experimental effort will have three major components, each of which is important and necessary to the overall effort. These are discussed below.

*Summary and Review of Existing Chamber Data*. In order to take full advantage of work that has already been carried out, existing environmental chamber studies involving LVP chemicals including those from consumer products will be reviewed. This includes the work of Carter et al. (2008). For this earlier work, analytical instrumentation now available at the UCR CE-CERT chamber was not available limiting the usefulness of these earlier estimates. However, this data will still provide insight into chamber and experimental design for this program.

Characterization of Effects of Chamber Walls on Aerosol Formation

A potentially significant parameter that must be accounted for is the role of the chamber walls in aerosol formation. The importance of characterizing and appropriately representing chamber effects in evaluations of mechanisms against chamber data has been recognized for some time in the context of gas-phase mechanism development (e.g., Carter et al, 1982; Jeffries et al, 1992), but to date it has received inadequate attention in evaluations of SOA models. We have observed, even in our remarkably clean chamber system, that some background aerosol formation occurs in the presence of only purified air (Carter et al, 2005a,b). Therefore, an important component of this project will be to develop and evaluate a chamber effects model for background PM formation in the UCR EPA chamber.

One example of wall effects is the production of background aerosol during a pure air irradiation. A ten-hour pure air (with added NOx) irradiation leads to production of several hundred particles per cubic centimeter of air with a mass of nearly one-tenth of a microgram per cubic centimeter. While this background is lower than found in most aerosol forming experiments conducted in the chamber, it still may play a non-negligible role in aerosol formation for experiments with low starting hydrocarbon concentrations. The addition of CO or NOx to the system is found to suppress this background aerosol formation. This suggests that the background PM formation is due to the presence of some precursor that reacts with OH radicals to form PM products, since both CO and NOx suppress OH levels in this system. Examples of background PM data in the UCR EPA chamber are given by Carter et al (2005a,b).

The loss of particles to chamber walls is another chamber effect that needs to be taken into account. The large volume to surface area of the UCR chamber reduces the overall losses of these particles, but even in the large chamber the particle wall loss half life is on the order of 4 hours. The standard wall loss correction of Cocker et al (2001) appears to be adequate for this chamber, and will be used to estimate total aerosol formation from the LVP-VOCs studied in this project.

It should be noted that although it would be beneficial to have a complete understanding of effects of chamber walls on PM formation, this is unlikely to occur during the course of this project, and this understanding, in itself, is not the major objective of this task. For the purpose of this project it is sufficient to have estimates that can appropriately take these chamber wall effects into account when testing for SOA formation. Parameterized models that are consistent with the available data will probably be necessary, and if appropriately evaluated, should be sufficient for the objectives of this project.

This chamber background and PM wall loss model will be used when evaluating the mechanism developed using the data obtained for this project. This is analogous to the use of chamber wall effects models when evaluating gas-phase mechanisms (e.g., Carter et al., 2005). These effects include LVP-VOC chamber surface and particle loss effects

*Chamber Experiments to study ozone and PM formation*: The major effort for this project will be to carry out environmental chamber experiments to support evaluation of ozone and SOA formation from LVP-VOCs. We have budgeted into this program a minimum of 120 chamber experiments (including characterization runs) conducted over a two-year period using the UCR EPA environmental chamber. Actual LVP-VOCs to be tested will be determined in consultation with the program advisory board and CARB staff.

Experiments will be conducted on both pure components and on mixtures (actual consumer products) to elucidate the impact of LVP-VOCs on ozone and PM formation. By modifying the concentration of LVP-VOCs in the consumer product, we can explore the influence of the VOC exempt species.

**SOA formation:** These experiments represent classical SOA formation potential studies of single hydrocarbons. Prior to a typical VOC/NOx experiment, the chamber will have been flushed with purified air. NO will be injected to the chamber through a heated gas-manifold system while the LVP-VOC of interest will be injected (see Task 2.2) into the chamber. The system will be allowed to mix sufficiently such that two measurements of the initial hydrocarbon are consistent. The reaction commences by turning on the blacklights, where the gases, partial oxidation products, and aerosol evolution are then tracked versus time. The experiments will be conducted for a minimum of six hours.

**Ozone formation:** These experiments represent classical ozone MIR studies of single hydrocarbons. Prior to a typical experiment, the chamber will have been flushed with purified air. NO will be injected to the chamber through a heated gas-manifold system while the LVP of interest will be injected (see task 2.2) into one of the dual chambers. The Carter surrogate mixture (comprised of n-butane, n-octane, ethene, propene, trans-2-butene, toluene, m-xylene and formaldehyde) mimics a typical atmospheric reactive mix, will be added to both chambers. The system will be allowed to mix sufficiently such that two measurements of the initial hydrocarbon are consistent. The reaction commences by turning on the blacklights, where the gases, partial oxidation products, NOx, and ozone evolution are then tracked versus time. The experiments will be conducted for a minimum of six hours.

**Mixtures:** For these experiments, whole consumer products will be injected into the chamber (see Task 2.2). These experiments will follow the typical SOA/ozone experiments described above. For select experiments, the actual consumer product may be “placed” into the chamber prior to filling and allowed to evaporate into an atmospheric surrogate mixture.

A well-characterized chamber system with tight quality assurance/quality control practices and an extremely low background of trace atmospheric species must be employed for the work to be successful. Our previous results demonstrate the ability of our two new reactors to perform high-quality SOA work at low NOx and hydrocarbon concentrations (Carter et al., 2005, Song et al., 2005, Song et al., 2007a,b). Nevertheless, we believe that with improved characterization of run conditions and improved understanding of factors affecting PM formation in our chamber we can obtain data of even higher quality than obtained previously.

**Mechanism and Model Development**

The general approach that will be followed will be similar to that used in developing the gas-phase SAPRC mechanism (Carter, 2010). Mechanisms will be developed based on considerations of the chemistry involved and available laboratory and chemical characterization data, and then tested and refined using the chamber data. The mechanism development and evaluation process will also provide the driving force for the experiments to be conducted for this project, as discussed above. The close interaction of chamber experimentation and mechanism development has been a feature and strength in the development of the SAPRC gas-phase mechanisms for many years. PM formation will be adjusted for particle wall loss and reported as a fractional yield.

The objective in the mechanism development will be to derive a mechanism that is sufficiently detailed to appropriately predict ozone formation from LVP-VOCs under a variety of conditions and have predictions that are consistent with available chamber data, but be sufficiently condensed to be appropriate to use in the 3-D airshed models used in regulatory and research applications. It is expected that models with variable levels of detail will be developed for this project.

### Task 3: Environmental Fate of LVP-VOCs

A critical question into LVP-VOC impacts relates to their atmospheric availability – to what extent do LVP-VOCs eventually enter the atmosphere and are available for atmospheric reaction? This question is partially addressed as part of Task 2 as the partitioning of these compounds is evaluated between the gas-phase, particulate-phase, and chamber walls. For this task, we propose to build on the chamber wall model and provide additional surfaces (e.g., masonry, cement, plants, etc.) within the chamber that can compete for the LVP compounds. It can be assumed (will be experimentally verified) that the uptake (reactive or sorptive) of these surfaces will far exceed that of the FEP Teflon walls. By introducing these additional surfaces within the chamber one can identify the feasibility of the release of these compounds.

Task 3.1: Water-LVP-VOC Interactions

It is necessary to evaluate the emissions of LVP-VOCs from water systems—will the LVP compounds, especially those with higher hydrophilicity, still partition into the atmosphere from a dilute water solution. This question will be addressed using a similar approach to Task 1 and will utilize the SIFT-MS to evaluate the flux of identified LVP-VOCs from dilute water solutions. The specificity of the SIFT-MS will help identify key species as they are released into the environment and provide an upper bound as to their availability once they enter a dilute water system. The dilution of the consumer product containing the LVP-VOCs will be varied over several orders of magnitude based on the atmospheric availability observed for the species at 100:1 water dilution. (This dilution is much less than expected and is used to set upper boundaries on emission rates—should the LVP-VOCs not be released at this dilution, it is unlikely to participate at greater dilutions seen in environment).

The PI of the project will also consult with water quality faculty within his Chemical and Environmental Engineering department to discuss the atmospheric availability of the LVP-VOCs and discuss relevant design parameters based on water quality systems. This will provide insight into the concentrations (dilutions) to explore. It is expected that the concentrations of the consumer products will vary widely in water treatment facilities and the presence of lagoons, aeration, ozonation, biology, and other water treatment unit operations will have influences on the flux of these compounds. This work will focus most directly on the reduction (if any) of atmospheric availability due to hydrophilic interactions of the LVP components of consumer products.

Should the SIFT-MS not work as anticipated for this program, the loss of the LVP components of consumer products could be measured by sorbent trapping of the LVP-VOCs as they are released into the atmosphere followed by thermal desorption gas chromatography with flame ionization detection. This method has been demonstrated to be effective for measurement of several LVP-VOCs within our atmospheric chamber laboratory including amine based and aromatic based species.

Task 3.2: Atmospheric Availability Developmental Models

The atmospheric availability of LVP-VOCs drives their atmospheric impacts. For this task, we propose a very limited number of experiments to explore the impact of introducing a masonry surface into the environmental chamber (see Task 2) to evaluate its influence on the atmospheric availability (and therefore O3 and SOA formation potential) of the LVP-VOCs studied. Here, it is assumed that the material added into the chamber will have a far greater uptake than that of the chamber wall surface. These tests will provide preliminary information on atmospheric availability in the presence of real-world surfaces. The selected surfaces will be chosen in consultation with the program advisory committee (e.g., masonry, plant material, etc.).

## Experimental Methods

### Environmental Chamber Facility

The environmental chamber experiments will be carried out using the UCR EPA chamber, which is described in more detail elsewhere (Carter, 2002, 2004; Carter et al, 2005a,b). This chamber was constructed under EPA funding to address the needs for an improved environmental chamber database for mechanism evaluation (Carter et al., 1999). The objectives, design, construction, and initial evaluation of this chamber facility are described in more detail elsewhere (Carter et al, 1999, Carter, 2002, 2004). This chamber was successfully utilized in our “low NOx” mechanism evaluation study for the CARB (Carter, 2004), for experiments to reduce uncertainties in reactivities of coatings VOCs (Carter and Malkina, 2005; Carter et al, 2005c), pesticides (Carter and Malkina, 2007; Carter, 2007c), and amines (Carter, 2007b), and is being continuously utilized for ongoing PM studies (Carter et al, 2005c; Song et al, 2005, 2007a-c). Descriptions of the chamber and procedures generally are given in the references cited above, but are briefly summarized below.

The UCR EPA chamber consists of two ~85,000-liter Teflon® reactors located inside a 16,000 cubic ft temperature-controlled “clean room” that is continuously flushed with purified air. The clean room design is employed in order to minimize background contaminants into the reactor due to permeation or leaks. The primary light source consists of a 200 KW argon arc lamp with specially designed UV filters that give a UV and visible spectrum similar to sunlight. Banks of blacklights are also present to serve as a backup light source for experiments where blacklight irradiation is sufficient, which will be the case for many of the experiments to be carried out for this project (see below). The interior of the enclosure is covered with reflective aluminum panels in order to maximize the available light intensity and to attain sufficient light uniformity, which is estimated to be ±10% or better in the portion of the enclosure where the reactors are located (Carter, 2002). The reactors are attached to a semi-flexible moveable framework that allows the reactors to be emptied between experiments and reduces the volume under positive pressure control to prevent dilution due to sampling or leaks during experiments. A high-volume mixing system with Teflon® pipes and Teflon®-coated flanges is used to mix the reactors and to exchange reactants between the reactors to achieve equal concentrations when desired. A diagram of the enclosure and reactors is shown on Figure 5, and the spectra of the light sources are shown on Figure 6.

An AADCO air purification system that provides dry purified air at flow rates up to 1500 liters min-1 is used to supply the air to flush the enclosure and to flush and fill the reactors between experiments. The air is further purified by passing it through cartridges filled with Purafil® and heated Carulite 300® which is a Hopcalite®-type catalyst and also through a filter to remove particulate matter. The measured NOx, CO, and non-methane organic concentrations in the purified air were found to be less than the detection limits of the instrumentation employed.

The chamber enclosure is located on the second floor of a two-floor laboratory building that was designed and constructed specifically to house this facility (Carter, 2002). Most of the analytical instrumentation (except for the PM instrumentation) is located on the ground floor beneath the chamber, with sampling lines leading down as indicated on Figure 5. The PM instrumentation that needs to be at the same temperature as the air being sampled is located inside the enclosure, between the reactors and the entry door, as also indicated on Figure 5.

The experiments for this project will be carried out in the large, state-of-the-art UCR EPA environmental chamber facility. That facility has been described in detail elsewhere (e.g., Carter, 2004, Carter et al, 2005a), and its major features will only be summarized here. A schematic of the chamber is shown on Figure 5.

Recent work by Warren et al. (2008) indicates that aromatic SOA formation is more sensitive to light intensity than light spectra. Therefore, it is anticipated that the experiments will be conducted with blacklights; which are simpler and more cost-effective to perform and permit more experiments to be conducted with the available funding. The blacklights have a sufficiently good representation of the spectrum of sunlight in the near UV region that is most important for photolysis reactions. For most reactions the effects of differences in the spectra on photolysis rates are known, and can be taken into account when modeling the experiments.

Modifications to the facility to increase the light intensity by increasing the number of blacklights and other approaches were made as part of a project to the CARB carried out for gas-phase mechanism evaluation (see Related Programs, below). These were completed and evaluated in 2010, permitting SOA formation to be evaluated over a wider range of light intensities than previously possible.

### Analytical Methods

A summary of the instrumentation available for use for this project is given in Table 1. That table also indicates the compounds, parameters, or properties measured and typical sensitivities. The gas-phase and particle-phase analysis and data analysis methods are discussed in more detail below.

**Gas-phase Analysis**

Decay of the aromatic species will be monitored using dual Agilent 6890 (Palo Alto, CA) gas chromatographs (GC) equipped with flame ionization detectors (FID). A Thermal Environmental Instruments Model 42C chemiluminescence NOx analyzer will be used to measure NO, NO2 and NOx. Ozone concentration will be monitored by a Dasibi Environmental Corp. Model 1003-AH O3 analyzer. We will use the SYFT SIFT-MS to monitor volatile oxygenated reaction products (and in some cases parent hydrocarbons for comparison with GC- FID analyses), complimenting the real time aerosol analysis capabilities of the high resolution time-of flight aerosol mass spectrometer (HR-ToF-AMS) discussed below. These species include glyoxal and methyl-glyoxal, two species identified as potential precursors to oligomer formation. Additional gas-phase equipment for this system is available and will be used as needed for specific experiments. This includes tunable diode lasers, a cavity ring down spectrometer, and other nitrogen specific analyzers.

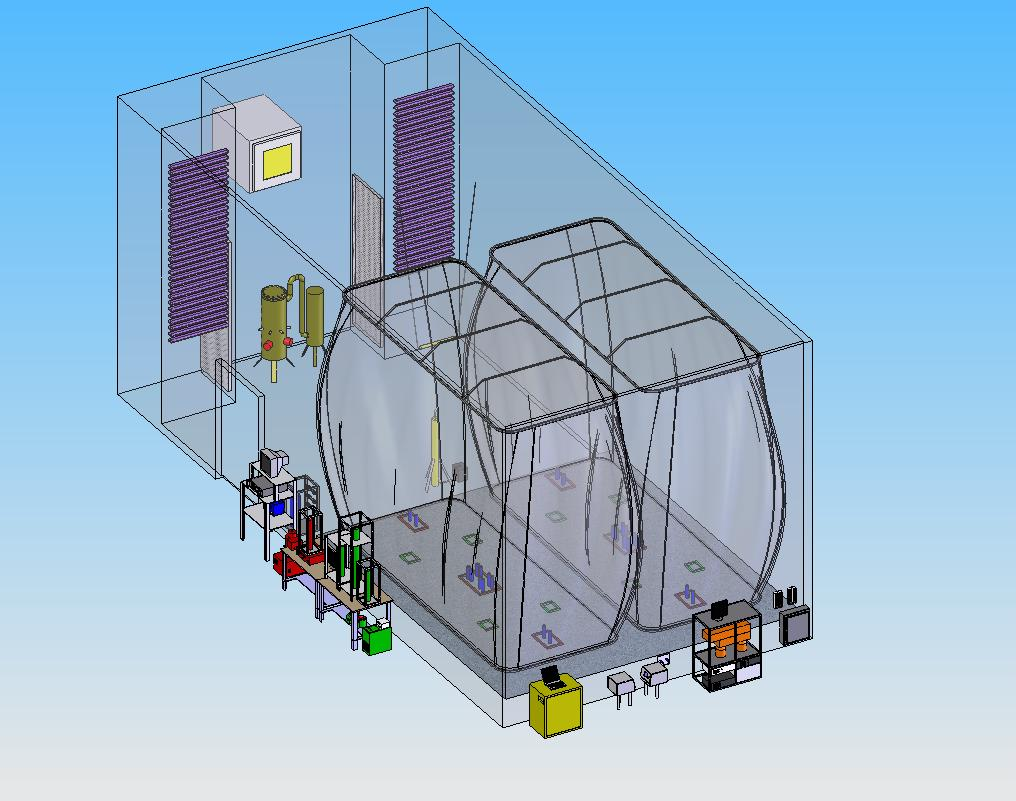


Figure 5. Schematic of the UCR EPA chamber, showing the two side-by-side 90 m3 Teflon bags (right), the light source (upper left), and the area flushed with pure air to control temperature and humidity.



Figure 6. Comparison of blacklight, argon arc-lamp, and ground-level outdoor spectra

Table 1. List of analytical and characterization instrumentation

| Type | Model or Description | Species | Sensitivity | Comments |
| --- | --- | --- | --- | --- |
|  |  |  |  |  |
| Gas Calibrator | Model 146C Thermo Environmental Dynamic Gas Calibrator | N/A | N/A | Used for calibration of NOx and other analyzers. |
| Data Acquisition Sytem | 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 and control sampling solenoids. In-house LabView software. |
| Temperature sensors | Various thermocouples, radiation shielded thermocouple housing | Temper-ature | ~0.1 oC | Primary measurement is thermocouples inside reactor. Corrections made for radiative heating effect with arc light irradiation. |
| Ozone Analyzer | Dasibi Model 1003-AH. UV absorption analysis. Monitor Labs Chemiluminescence Ozone Analyzer Model 8410 | O3 | 2 ppb | Standard monitoring instruments. |
| NO - NOy Analyzer | Teco Model 42 C with external converter. Chemiluminescent analysis for NO, NOy by catalytic conversion. | NO | 1 ppb | Useful for NO and initial NO2 monitoring. Converter close-coupled to the reactors so the “NOy” channel should include HNO3 as well as NO2, PANs, organic nitrates, and other species converted to NO by the catalyst. |
| NOy | 1 ppb |
| CO Analyzer | Dasibi Model 48C. Gas correlation IR analysis. | CO | 50 ppb | Standard monitoring instrument |
| GC-FID #1 | HP 6890 Series II GC with dual columns, loop injectors and FID detectors. Various megabore GC columns available. Controlled by computer interfaced to network. | VOCs | ~10 ppbC | Equipped with: 30 m x 0.53 mm GS-Alumina column used for the analysis of light hydrocarbons and 30 m x 0.53 mm DB-5 column used for the analysis of C5+ alkanes and aromatics. Loop injection suitable for low to medium volatility VOCs that are not too “sticky” to pass through valves. |
| GC-FID #2 | HP 6890 Series II GC with dual columns and FID detectors, one with loop sampling and one set up for cartridge sampling. Various megabore GC columns available. Controlled by computer interfaced to network. | VOCs | ~10 ppbC | 30 m x0.53 mm GSQ column. Loop injection suitable for low to medium volatility VOCs that are not too “sticky”. Not used as primary analysis for most of these experiments. |
| VOCs | 1 ppbC | Sorption cartridge sampling will be used for low volatility or moderately “sticky” VOCs that cannot go through GC valves but can go through GC columns. Equipped with a 30 m x 0.53 mm DB-1701 column. Uses Dynatherm ACEM model 9305 . |
| Humidity Monitor | LiCor Li-840 | Humid-ity | Dew point range: -60 - 50oC | Used for determination of RH in system. RH for dry experiments often below detection limit (<0.1% RH). |
| Spectro-radiometer | LiCor LI-1800 Spectroradiometer | 300-850 nm Light Spect-rum | Adequate | Resolution relatively low but adequate for its purpose. Used to obtain relative spectrum. Also gives an absolute intensity measurement on surface useful for assessing relative trends. |
| Spherical Irradiance Sensors | Biospherical QSL-2100 PAR Irradiance Sensor or related product. Responds to 400-700 nm light. Spectral response curve included. | Spherical Broad-band Light Intensity | Adequate | Provides a measure of absolute intensity and light uniformity that is more directly related to photolysis rates than light intensity on surface. Gives more precise measurement of light intensity trends than NO2 actinometry, but is relatively sensitive to small changes in position. |
| Scanning Mobility Particle Sizer (SMPS) | Uses matrix inversion program. Consists of TSI 3081L differential mobility analyzer, TSI 3077 85Kr neutralizer, TSI 3760A condensation particle counter. | Aerosol Number and Volume concen-tration | Adequate | Provides information on size distribution of aerosols in the 28-730 nm size range, which accounts for most of the aerosol mass formed in our experiments. Data can be used to estimate secondary PM formation. |
| Tandem Differential Mobility Analyzer (TDMA) | Comprised of two TSI 3081L differential mobility analyzer, TSI 3077 85Kr neutralizer, TSI 3760A condensation particle counter and temperature conditioning chamber | Aerosol volatility | Adequate | Provides information on the volatility of SOA produced during the reaction. |
| APM-SMPS | Kanomax APM coupled to custom SMPS similar to that described above | Aerosol Density | Requires ~5 ug m-3 PM | Used to obtain real time (every 100 sec) density data necessary to convert aerosol volume (from SMPS) to aerosol mass |
| SIFT-MS | SYFT Voice200 single ion flow tube mass spectrometer | VOCs | Sub ppb | Online, real time (1 hz) acquisition of VOC data including critical oxidation products such as formaldehyde and glyoxal. |
| HR-ToF-AMS | Aerodyne High Resolution (W and V-mode) time of flight aerosol mass spectrometer | PM chemical composition | Requires ~5 ug m-3 PM | Online measurement of aerodynamic particle mobility and EI mass fragmentation pattern from chamber aerosol. |
| LC-ToFMS | Agilent 1200 series high performance liquid chromatograph coupled to accurate mass ® time of flight mass spectrometer | PM chemical composition | Varies by species | Used for offline chemical analysis of SOA formed. Will be applied to a very limited subset of SOA experiments, as needed, to aid in determination of chemical structures of select SOA products. |

**Particle-Phase Analysis**. Aerosol growth will be monitored using a pair of scanning mobility particle sizers (SMPS). The particle sampling equipment is located inside the enclosure to ensure that instrumentation temperature is identical to the reaction temperature. Total particle concentration within the chamber will be monitored by additional model 3776 condensation particle counters used to track ultrafine particle concentrations >2.5 nm up to 3x105 particles cm-3. These values will be used to correct the total number concentrations obtained by the SEMS and account for any biases due to particle charging efficiencies. Furthermore, the total number counts will be used to correct for particle wall losses assuming a first order wall loss decay as described in Cocker et al. (2001). A tandem differential mobility analyzer (TDMA) also will track routinely the evolving volatility of SOA produced within the reaction chamber. The system will routinely monitor the volatility of the aerosol particles. The system was designed following the original work of Stolzenburg and McMurry (1989) and is quite similar to that reported in Cocker et al. (2001). Furthermore, an organic TDMA option can be pursued by directly injecting the aerosolized LVP compounds into the TDMA in order to determine the organic uptake of LVP-VOCs. Particle density will be obtained using the Kanomax APM. This analyzer classifies the mass of a single aerosol based on the balance between centrifugal and electrostatic forces. When coupled to an SMPS, this method provides for a rapid, accurate determination of particle density within the chamber. Density can also be calculated by analysis of simultaneous SMPS and HR-ToF-MS data; this method will provide comparison for the APM-derived value. These methods provide insight into the changing nature of the aerosol produced within the chamber and allows for direct conversion of SMPS data into particle mass. We have used the APM to measure accurately the density of *m-*xylene oxidation products (Song et al., 2007).

The high resolution time-of flight aerosol mass spectrometer HR-ToF-AMS is a real-time chemical aerosol analyzer capable of quantitatively sampling, sizing, and chemically analyzing aerosol with fast time resolution and sufficient mass spectral resolution to directly distinguish elemental composition of ions having the same mass (DeCarlo, 2006). The V-mode offers high sensitivity (0.04 g m*-*3) for all species with mass to charge (m/z) resolving power of approximately 2100, while the W-mode offers sensitivity of 0.4 g m*-*3 for all species with m/z resolving powers approaching 5000. It is especially suited for quantification of CxHy, CxHyOz, CxHyNz, and CxHyOzNp with direct identification of organonitrogen and organosulfur content (DeCarlo et al., 2006). Mass fragmentation patterns obtained in the chamber will be compared to those obtained from ambient air at UCR. This will be used to understand how well the atmospheric simulations being performed compare with ambient conditions. This will be done using the method developed by Zhang et al. (2007), which separates organic aerosol into hydrocarbon-like organic aerosol (HOA) and oxygenated organic aerosol (OOA) subcategories, with HOA linked to primary or freshly emitted organic aerosol and OOA representative of photochemically processed (aged) aerosol.

Additional chemical characterization will be obtained using a high performance liquid chromatograph coupled to a time of flight mass spectrometer (LC-ToFMS) for offline analysis of samples taken from selected experiments.

**Gas-Phase Chemical Analysis.** When needed to help address model predictive capabilities, detailed gas-phase chemical analyses capabilities are also available as part of the APL environmental chamber system. This includes an online SIFT-MS that utilizes soft ionization techniques with the hydronium, oxygen, or NO+ ion Typical sensitivities for the instrument are sub part per billion.

### Data management

A significant amount of data will be generated from each experiment. Basic instrumental data such as hydrocarbon, ozone, NOx, and PM concentrations are compiled together through an already existing data network. Mass spectral responses (e.g., AMS, SIFT-MS) are stored as native files and are backed up periodically. These data sets require special analysis programs that are routinely applied to small subsets of the data. Each AMS file for an experiment can contain up to 1 GB of unprocessed data. The AMS data will typically be used to track specific mass fragments over the duration of an experiment, especially when compared to isotopically labeled species with respect to aerosol formation. Igor macros provided by the manufacturer are routinely used to analyze the mass spectral and size data provided by this instrument. The TDMA data and APM-SMPS data are stored separately on each device. A MatLab program developed at UCR allows for each scan (~ every 100 sec) to be curve fitted with the final diameter in order to calculate volatility or density. All data is compiled together on a server for access to each individual researcher as part of the program and is stored as .txt, .dat, and .xls files.

The aerosol instrumentation is routinely calibrated using PSL spheres (NIST traceable) to confirm particle sizing. The TDMA calibration is checked periodically by injecting a non-volatile aerosol and not turning on the thermodenuder and ensuring that the particles sized in the second analyzer match those transmitted by the first analyzer. The APM-SMPS performance is verified by periodically measuring the density of known aerosol (e.g., PSL). The AMS is additionally calibrated, per manufacturer specifications, using ammonium nitrate aerosol for determination of ionization efficiency.

Gas-phase analyzers are calibrated using a standard certification cylinders or by injecting known liquid volumes into a fixed volume (for selected hydrocarbons for GC). A gas-divider is used to periodically span the NOx analyzers while the SIFT-MS often uses the internal calibration based on ion drift velocities in the tube. The SIFT-MS will be further calibrated against GC-FID responses for LVP compounds when possible. A calibration worksheet for all critical instrumentation is maintained at UC Riverside.

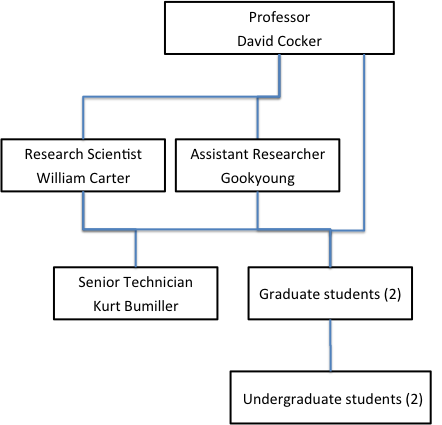
# PROJECT MANAGEMENT, SCHEDULE, AND DELIVERABLES

## Project Management

The Principal Investigator will be Professor David R. Cocker, who will be responsible for the overall management of the project and also will work on the development of analytical methodologies for measuring LVP-VOC volatilization/availability, chamber modifications for LVP-VOC studies, directing experimental work and data analysis, and the PM and chemical characterization studies. Dr. William P.L. Carter and Dr. Gookyoung Heo will serve as key researchers in developing the chamber model and ozone reactivities for the LVP-VOCs. At least two Ph.D. graduate students will work with Dr. Cocker in conducting the experiments and data analysis and work with Drs. Heo and Carter in the mechanism development and evaluation. Mr. Bumiller is a senior technician familiar with the daily operation of the chamber facility and will provide chamber maintenance and upgrade design.

## Qualifications of key researchers

As shown on **Error! Reference source not found.**, the major CE-CERT researchers working on this project will be Dr. William P. L. Carter, Dr. David R. Cocker III, and Dr. Gookyoung Heo. Dr. Carter is the developer of the SAPRC chemical mechanisms and will play the major role in adapting his SAPRC-07 gas-phase mechanism for predictions of SOA formation. He has also had extensive experience in management of environmental chamber projects for mechanism development and evaluation, and that experience will be applied to this project. Dr. Cocker has extensive experience in using environmental chambers for PM research and is the PI on a number of projects using the UCR EPA chamber for PM research. He is also the leader of the Keck instrumentation grant to utilize advance instrumentation for PM research at this facility. Dr. Heo has collaborated with developers of two chemical mechanisms dominantly used in the U.S. for photochemical air quality modeling (the Carbon Bond and SAPRC chemical mechanisms) since year 2007 and has extensive experience in developing and evaluating mechanisms for air quality research and applications. He also has significant experience in analyzing emissions data and carrying out air quality modeling.



**Figure 7:** Organizational chart for proposed project.

Although these investigators have extensive experience and track record in gas-phase mechanism development and environmental chamber experimentation, their experience in water quality and treatment is limited.. Therefore, faculty from the Chemical and Environmental Engineering Department will be utilized to discuss water-air interactions at water facilities and will serve as members of the Ph.D. dissertation committees of the graduate students working on this program.

## Reporting and Deliverables

The primary deliverable for this project will be the final report, which will describe all the work carried out as part of this program. Additional deliverables are expected to be peer-reviewed journal articles arising from the research carried out for this project, and presentations made to the CARB and others concerning the project results.

Quarterly or periodic reports will be submitted to the CARB project officer briefly summarizing the work carried out for this project since the previous reporting period, problems encountered, and progress anticipated for the coming period. The draft final report summarizing the major results of this project, which will be independent of the quarterly or periodic reports, will be submitted at the end of the second year of this project (see Schedule, below). Following the CARB review, revisions will be made to the report as appropriate based on their comments or other new information, and itemized responses to the comments will be submitted indicating how the comments were addressed. The finalized report will be made available on the Principal Investigator's web site. The support of the CARB will be appropriately acknowledged in any journal articles prepared as a result of this project, and the CARB staff will be provided with copies of any manuscripts that are submitted at the time they are submitted, and will be given sufficient time to comment on the manuscripts prior to the final modifications prior to publication. The format and content of the reports will be consistent with CARB contract guidelines.

The data obtained in the experiments carried out for this project will be made available to the CARB staff and interested researchers upon request.

## Schedule

The schedule for this proposed project is shown below. Most of the work is envisioned as being carried out over a two year period, with a third year being available for review and completion of the final report and journal articles arising from this work. The initial phases of the project will focus on review of previous LVP-VOC experiment conducted at the UCR facility and formation of an advisory board that will aid in the selection of the LVPs/consumer products to be studies. Once LVP-VOCs have been selected, implementation of task 1 to observe volatilization of the pure and mixed component LVP-VOCs. Additionally, chamber work will immediately commence to characterize the chamber surface—LVP-VOC interactions. This will include development and implementation (as needed) of appropriate injection systems and analytical system development for accurate study of the LVP-VOCs. Once the chamber model is developed and injection/analytical methods confirmed, studies of ozone and PM formation within the chamber will commence. The draft final report will be submitted at the end of the second year of the project. It is expected that the CARB's comments on the draft report should be received by the end of the first quarter of the third year and if so the report will be finalized shortly after that. The project can continue for a third year if necessary to account for delays and provide ample time for review of the final report and preparation of journal articles, but for budgeting purposes we assume that the major efforts will be completed by the end of the second year. The Gantt chart for deliverables by task is shown on the next page.

Task 0: Form a project advisory board

Task 1: Investigate LVP-VOCs volatilization rates

Task 2: Environmental chamber studies of ozone and SOA impacts of LVP-VOCs

Task 2.1: Experimental Design and Development of Chamber Model

Task 2.2: Method development for chamber studies

Task 2.3: Environmental chamber experiments

Task 3: Investigate environmental fate of LVP-VOCs in select consumer products

Task 3.1: Water-LVP-VOC interactions

Task 3.2: Atmospheric Availability Developmental Models

Task 4: Draft Final Report

Task 5: Final Report

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| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | Q1 | Q2 | Q3 | Q4 | Q5 | Q6 | Q7 | | Q8 | | Year 3 |
| Task 0 |  |  |  |  |  |  |  | |  | |  |
| Task 1 |  |  |  |  |  |  |  | |  | |  |
| Task 2.1 |  |  |  |  |  |  |  | |  | |  |
| Task 2.2 |  |  |  |  |  |  |  | |  | |  |
| Task 2.3 |  |  |  |  |  |  |  | |  | |  |
| Task 3.1 |  |  |  |  |  |  |  | |  | |  |
| Task 3.2 |  |  |  |  |  |  |  |  |  | |  |
| Task 4 |  |  |  |  |  |  |  | |  |  |  |
| Task 5 |  |  |  |  |  |  |  | |  | |  |

# BUDGET

Notes: EDP, Subs, Equip, Analyses, Mail/Phone/Fax categories not showing ($0)

Misc.: 26% facilities charge

# RELATED PROGRAMS

Brief summaries of recently completed, current, or pending projects by Dr. Cocker or Carter that are related to this proposed project are given in this section. Dr. Carter's related projects are discussed first, followed by those of Dr. Cocker

Title: Advanced Chemical and Particle Instrumentation Suite

Agency: W.M. Keck Foundation

PI: David R. Cocker, III

Co-PI's: William P.L. Carter, Roger Atkinson, Paul Ziemann, Janet Arey

Status: Funded 1.5 million dollars. Equipment acquired, installed, and characterized

Description:

This is a 1.5 million dollar instrumentation gift from the W.M. Keck foundation designed to vastly improve the UCR chamber’s ability to perform detailed chemical characterization of secondary organic aerosol. This program has led to the installation of an Agilent accurate mass LC-ToFMS, an Aerodyne high resolution (W-ToF) aerosol mass spectrometer, an Ionicon proton transfer reaction mass spectrometer, a tandem differential mobility analyzer, a Kanomax aerosol particle mass monitor – scanning mobility particle spectrometer, a pair of TSI ultrafine particle counters and gas chromatographs, and a cavity ringdown spectrometer (CRDS- still under construction). The instrument suite provides online chemical composition and physical characterization information for SOA and it’s gaseous precursors. The program has provided the necessary infrastructure for ongoing efforts to advance aromatic chemical mechanisms development. . Dr. Cocker has led the acquisition and installation of the equipment.

This project is relevant to this proposal as it provides the key characterization tools to be used in conjunction with the UCR environmental chamber system.

Title: CAREER: Evaluating Secondary Organic Aerosol Formation Processes

Agency: National Science Foundation (ATM-0449778)

PI: David R. Cocker III

Status: Funded, 5 years, $400,000 with $52,500 total supplements. Final Report Accepted, 2009

Description:

This research program investigates processes leading to the formation of secondary organic aerosol (SOA). The program focuses on the impact of oxides of nitrogen (NOx) on SOA formation potentials, experimentally investigates SOA formation from mixtures of aerosol forming precursors, and experimentally evaluate the impact of temperature and relative humidity for a discrete number of systems. The research uses the unique UCR environmental chamber for investigation of SOA processes at low NOx and hydrocarbon concentrations that had not been possible previously. The program has advanced our understanding of gas-particle equilibria and provide a critical database for evaluation of other current and future SOA predictive models. The results of this work are providing critical insight into and advances in the prediction of aerosol formation processes within the atmosphere. This research has provided a robust, well characterized dataset to evaluate the role of NOx, temperature, and humidity on SOA formation processes for select hydrocarbons including m-xylene. The data are expected to be used to improve current models predictive capabilities for SOA formation within the atmosphere. Without such data, we cannot rely on the accuracy of model predictions of effects of control strategies on the formation of this important component of fine PM. To date, we have made significant progress on elucidating a number of critical SOA formation processes, which strongly influence the SOA production from aromatic systems. Further work is ongoing on extending these effects to include temperature and humidity. Thus far, we have published seven peer-reviewed papers as part of this program with three other papers currently under review. The program has also provided extensive Ph.D. and undergraduate training opportunities and has received additional supplements of $52,500 total over four years for research experiences for undergraduates.

The project is relevant to this proposal as it has funded a significant number of m-xylene experiments to be used to aid in the development of PM-SAPRC. These experiments will be the primary emphasis for data review for the mechanism development outlined in Task 1.

Title: Ammonia – Organic Chemistry and Secondary Organic Aerosol Yield in the Troposphere

Agency: National Science Foundation

PI: David R. Cocker III

Status: Funded, 2 years, $177,000.Final Report accepted, 2006.

Description:

This work provided critical experimental insight into the role of ammonia in the production of secondary organic aerosol. Prior to this work, it was generally assumed that ambient ammonia could not directly participate in *organic* aerosol formation. Additionally, experiments conducted in this program were aimed at identifying whether organoamines could be formed through direct or indirect reaction with ammonia. This program focused on styrene and pinene as model aromatic precursors for this system. It was conclusively demonstrated that ammonia could react with secondary organic aerosol altering the total aerosol formed in the system. This work has been published in two peer reviewed journal articles.

This project is relevant to this program as it provided some initial characterization experiments for aerosol formation in the UCR chamber including several surrogate-NOx experiments that may be relevant to Task 1.

Title: Secondary organic aerosol formation from amines

Agency: National Science Foundation

PI: David R. Cocker

Co-PI's: Phil Silva (Utah State/USDA), Katie Purvis-Roberts (Claremont Colleges)

Status: Final Report Accepted, 2012

Description:

Dr. Cocker has served on a collaborative NSF study on aerosol formation from amine precursors. This work quantified the secondary aerosol formation from select primary, secondary, and tertiary amines delineating between the inorganic salt and secondary organic aerosol formation. As part of this program chemical mechanisms for the degradation of amines leading to particle formation were proposed and a number of atmospheric oxidation products identified. In collaboration with Co-PIs, the chamber investigations were compared with field studies of agricultural amines (both primary and secondary emissions). This work has led to a number of manuscripts under development and required the development of analytical tools for the study of some low vapor pressure and “sticky” VOC precursors and products, relevant to some of the LVP-VOCs expected to be studies in this program.

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Title: Atmospheric Aerosol Formation From Oxidation of Aromatics

Agency: National Science Foundation

PI: David R. Cocker

Co-PI's: William P.L. Carter, Robert Griffin (Rice)

Status: Final year of project

Description:

This program investigates aromatic secondary organic aerosol formation with the aim to improve mechanistic understandings of SOA formation for implementation into the CACM/MPMPO chemical modules for prediction of SOA formation from aromatic aerosol formation. This work is relevant to this program as many of the current methodologies used in the SOA chamber studies at UCR were developed as part of this program. Further, analytical methods were developed to measure and inject lower vapor pressure VOCs such as first and second generation of aromatic oxidation products.

Title: Title: Secondary Organic Aerosol Formation: Chamber Study and Model Development

Agency: California Air Resources Board

PI: William P.L. Carter

Co-PI's: David R. Cocker III (as senior scientist)

Status: Final report accepted, 2012

Description:

This program conducted environmental chamber and chemical mechanism and model development studies that led to the development and evaluation of models for prediction of secondary organic aerosol (SOA) formation from aromatic and other compounds. This program coupled careful controlled experimental investigations of secondary organic aerosol (SOA) formation with SOA model development using the SAPRC-07 gas-phase mechanism as the starting point. The program included SOA experiments designed to elucidate critical chemical mechanisms leading to SOA formation from aromatic precursors. The experiments, coupled to a review of earlier experimental databases obtained for various compounds in various chambers, was be utilized to develop and refine PM-SAPRC model as a tool for SOA formation from aromatic precursors.

Title: Development of the SAPRC-07 Chemical Mechanism and Updated Reactivity Scales

Agency: CARB

PI: William P. L. Carter

Status: Completed

Description:

A completely updated version of the SAPRC-99 chemical mechanism, designated SAPRC-07, has been developed and documented. This includes a complete update of the rate constants and reactions based on current data and evaluations, reformulated and less parameterized aromatics mechanisms, a representation of chlorine chemistry, a reformulated method to represent peroxy reactions that is more appropriate for modeling secondary organic aerosol formation, and improved representations for many types of VOCs. This mechanism was evaluated against the result of ~2400 environmental chamber experiments carried out in 11 different environmental chambers, including experiments to test mechanisms for over 120 types of VOCs. The performance of the mechanism in simulating the chamber data was comparable to SAPRC-99, with generally satisfactory results for most types of VOCs but some increases in biases in simulations of some mixture experiments. The mechanism was used to derive an update to the MIR and other ozone reactivity scales for over 1100 types of VOCs. The average changes in relative MIR values was about 10%, with >90% of the VOCs having changes less than 30%, but with larger changes for some types of VOCs, including halogenated compounds. Recommendations were given for future mechanism development research.

This project is relevant to this proposal because the SOA mechanism to be developed for this project will use SAPRC-07 as the starting point. One of the recommendations of the SAPRC-07 documentation report included adapting the mechanism for SOA formation. The expertise used for developing SAPRC-07 will be available for this project.

Title: Environmental Chamber Studies of Ozone Impacts of Coatings VOCs

Agency: CARB

PI: William P. L. Carter

Status: Funded for $200,041. Project beginning.

Description:

This project involves conducting environmental chamber studies to reduce uncertainties in ozone impact estimates for volatile organic compounds (VOCs) in coatings, and to develop improved experimental methods to evaluate mechanisms for predicting ozone impacts for VOCs in general. This project has two major tasks. The first is to develop and test modifications to our incremental reactivity environmental chamber experiments that will give results that give better correlations with incremental reactivities in the atmosphere. The second is to reduce uncertainties in reactivity estimates for coatings VOCs of concern for which mechanisms and reactivity estimates are either highly uncertain or do not exist. Existing chamber experiments are not as sensitive to mechanisms for secondary reactions of VOC oxidation products as is calculated to be the case for the atmosphere, and therefore do not provide adequate evaluations of this aspect of their ozone impact mechanisms. Addressing this will require developing experiments where integrated OH radical levels are comparable to those calculated for atmospheric scenarios, and approaches will include increasing overall light intensity or duration of the experiments and/or conducting experiments with added radical initiators. The new procedures will be utilized to test mechanisms for selected important representative coatings VOCs. The specific compounds to be studied will be determined in consultation with the CARB staff and the Technical Advisory Committee of the ongoing "Paints and Architectural Coatings Environmental Study" being carried out by the Environmental Research Institute at UCR.

This project is relevant to this proposal because the improvements made to the UCR EPA chamber facility to make reactivity experiments more representative of ambient conditions will enhance the capability of the chamber for this project. The improved light intensity will be particularly useful for the objectives of this project. This is also an example of ongoing support of our chamber and facility for mechanism evaluation research. Some of the characterization and control runs carried out for this project will be applicable to the characterization needed for this project, and vise-versa. This makes both projects more cost effective to the CARB.

Title: Implementation of Updated Chemical Mechanisms for Airshed Model Applications

Agency: CARB

PI: William P. L. Carter

Status: Funded for $50,000. Project beginning.

Description:

The California Air Resources Board is undertaking a peer review of the SAPRC-07 chemical mechanism prior to its use for regulatory modeling. This project is to carry out work needed to address any concerns raised by the peer review of the existing SAPRC-07 mechanism, to develop condensed versions of this mechanism, and to carry out additional work needed for implementing the mechanisms in models, such as deriving emissions assignments. Additional work may include implementing improvements to the aromatics mechanisms that could not be incorporated into SAPRC-07.As part of this project a postdoctoral researcher or Assistant Research Scientist will receive training in the development and maintenance of the SAPRC mechanisms.

This project is relevant to this proposal because any improvements made to this mechanism as a part of this project will also be applicable to the gas-phase portion of the mechanism developed in this proposed program. Any improvements made to the aromatics mechanism will be particularly relevant because the focus of the proposed project is SOA for aromatics. The training of the postdoctoral researcher or Assistant Research Scientist will also be applicable for training for SOA modeling for this proposed project.

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Warren, B., C. Song, et al. (2008). "Light intensity and light source influence on secondary organic aerosol formation for the m-xylene/NO x photooxidation system." Environmental Science & Technology **42**(15): 5461-5466.

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# BIOGRAPHICAL SKETCHES

Short biographical sketches and lists of selected relevant publications and reports are given in this section for the three senior scientists working on this project. These are Dr. William P. L. Carter and Dr. David R. Cocker III of the University of California at Riverside, and Dr. Robert J. Griffin at Rice University. Additional information about these researchers is available on the web at the following locations.

Dr. David R. Cocker III: <http://www.cert.ucr.edu/~cocker>

Dr. William P. L. Carter: <http://www.cert.ucr.edu/~carter>

Dr. Gookyoung Heo, <http://www.linkedin.com/pub/gookyoung-heo/9/13a/b39>

## William P. L. Carter

***Research Chemist***

CE-CERT 022, University of California, Riverside, CA 92521-0434 carter@cert.ucr.edu

***Professional Preparation***

|  |  |  |
| --- | --- | --- |
| University of California, Riverside | Chemistry | B.A., 1967 |
| University of Iowa, Iowa City | Physical Chemistry | Ph.D., 1973 |

***Current Appointments***

1973-present. University of California, Riverside, College of Engineering Center for Environmental Research and Technology. Research Chemist 1987-2005. Research Chemist Emeritus 2005-present.

***Research Summary***

Develops chemical mechanisms for urban and regional airshed models. Develops methods for evaluating atmospheric ozone impacts of volatile organic compounds (VOCs) and VOC reactivity scales. Conducts environmental chamber experiments to evaluate mechanisms VOC reactivity, and PM impacts. Conducts kinetic or mechanistic studies related to photochemical smog formation.

***Honors and Awards***

* University of California, Riverside Non-Senate Distinguished Researcher Award, 1992.
* Institute of Scientific Information “Highly Cited” researcher, 2003
* California Air Resources Board Haagen-Smit Clean Air Award, 2005
* Atmospheric Environment Haagen-Smit Prize, 2005

***Selected Publications and Reports***

* Carter, W. P. L. (2008). Development of a Condensed SAPRC-07 Chemical Mechanism. Report to CARB Contract 05-750, July 4.
* Carter, W. P. L. (2008). Development of the SAPRC-07 Chemical Mechanism and Updated Ozone Reactivity Scales, Final report to CARB Contract no. 03-318. May 28. Available at www.cert.ucr.edu/~carter/SAPRC.
* Sarwar, G., D. Luecken, G. Yarwood, G.Z. Whitten and W. P. L. Carter (2008). Impact of an Updated Carbon Bond Mechanism on Predictions from the Community Multiscale Air Quality (CMAQ) Modeling System: Preliminary Assessment, J*. of Appl. Met. and Climat.,* 47, 3-14
* Czader, B. H., D, W. Byun, Soon-Tae Kim, and W. P.L. Carter (2008). A study of VOC reactivity in the Houston-Galveston air mixture utilizing an extended version of SAPRC-99 chemical mechanism, *Atmos. Environ.*, in press.
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* Carter, W. P. L. (2000). Documentation of the SAPRC-99 Chemical Mechanism for VOC Reactivity Assessment, Report to the California Air Resources Board, May 8.
* Wang, L.; J. B. Milford, and W. P. L. Carter (2000). Reactivity Estimates for Aromatic Compounds 1. Uncertainty in Chamber-Derived Parameters. Atmos. Environ. 34:4337-4348.
* W. P. L. Carter, D. Luo, I. L. Malkina (1997). Investigations of the Atmospheric Reactions of Chloropicrin. *Atmos. Environ*, 31, 1425-1439
* Carter, W. P. L. (1996). Condensed Atmospheric Photooxidation Mechanisms for Isoprene, Atmos. Environ., 30, 4275-4290.
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* Carter, W.P.L. (1995). Computer Modeling of Environmental Chamber Measurements of Maximum Incremental Reactivities of Volatile Organic Compounds. *Atmos. Environ*. 29:2513-2527.
* Carter, W.P.L. (1994). Development of Ozone Reactivity Scales for Volatile Organic Compounds. J. *Air & Waste Manage. Assoc*. 44:881-899.
* Carter, W. P. L. (1990): A Detailed Mechanism for the Gas-Phase Atmospheric Reactions of Organic Compounds. *Atmos. Environ*. 24A, 481-518.

## David R. Cocker III

***Professor***

Department of Chemical and Environmental Engineering

UC Riverside

Riverside, CA 92507

***Education***

UC Riverside Environmental Engineering; Chemistry B.S., 1996

Caltech Environmental Engineering Science M.S., 1998

Caltech Environmental Engineering Science Ph.D, 2001

***Appointments***

Professor, Department of Chemical and Environmental Engineering 2011-present

Associate Professor, Department of Chemical and Environmental Engineering 2006-2011

Assistant Professor, Department of Chemical and Environmental Engineering 2001-2006

Graduate Researcher, Caltech 1996-2000

***Five Relevant Publications***

Nakao, S., Clark, C., Qi, L., Cocker, D.R., “Secondary Organic Aerosol Formation From

Phenolic Compounds in the Absence of NOx”, *Atmospheric Chemistry and Physics*, 11:10649-10660, 2011.

Sato, K., Nakao, S., Clark, C.H., Qi, L, Cocker, D.R., “Secondary Organic Aeorosol Formation

from the Photooxidation of Isoprene, 1,3-Butadiene, and 2,3-Dimethyl-1,3-butadiene Under High NOx Conditions”, *Atmospheric Chemistry and Physics*, 11:14, 7301-7317, 2011

Qi, L., Nakao, S., Tang, P. Cocker, D.R., “Temperature Effect on Physical and Chemical

Properties of Secondary Organic Aerosol from m-Xylene photooxidation. *Atmospheric Chemistry and Physics*, 10:8, 3847-3854, 2010.

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W.P.L. Carter, D.R. Cocker, D.R. Fitz, I. Malkina, K. Bumiller, C. Sauer, J. Pisano, C. Bufalino,

C.Song, ''A New Environmental Chamber for Evaluation of Gas-Phase Chemical Mechanisms and Secondary Aerosol Formation,'' *Atmospheric Environment*, 39, 40, 7768-7788, 2005.

***Five Other Significant Publications***

Warren, B., Austin, R., Cocker, D.R., “Temperature Dependence of Secondary Organic Aerosol”,

*Atmospheric Environment*, 43:22-23, 3548-3555, 2009.

Malloy, Q., Nakao, S., Li, Q., Austin, R., Stothers, C., Hagino, H., Cocker, D.R., “Real-time

Aerosol Density Determination Utilizing a Modified Scanning Mobility Particle Sizer Aerosol Particle Mass Analyzer”, *Aerosol Science and Technology*, 43:7, 673-678, 2009

C. Song, K. Na, B. Warren, Q. Malloy, “Secondary Organic Aerosol Formation from the

Photooxidation of *p*- and *o*-Xylene,” *Environmental Science and Technology*, 41:21, 7403-7408, 2007.

Warren, B., Song, C., Cocker, D.R., “Light Intensity and Light Source Influence on Secondary

Organic Aerosol Formation for the m-Xylene/NOx Photooxidation System”, *Environmental Science and Technology*, 42:15, 5461-5466

C. Song, K. Na, B. Warren, Q. Malloy, D. Cocker, ''Secondary Organic Aerosol Formation from

m-Xylene in the Absence of NOx,'' *Environmental Science and Technology*, 41:21, 7409-7416, 2007.

***Synergistic Activities****:*

* Co-investigator in the development and operation of the “Next-Generation” atmospheric chamber at CE-CERT, lead investigator for SOA studies in chamber.
* Co-Investigator in the development and operation of CE-CERT’s on-road heavy-duty emissions measurement laboratory, lead investigator for particulate emissions sampling and chemical analysis efforts.
* Co-investigator for investigation of impact of goods movement on air quality, a multiagency multiinvestigator program.
* Co-PI on Keck Foundation award with Roger Atkinson, Paul Ziemann, Bill Carter, and Joe Norbeck for development of chemical instrumentation for CE-CERT atmospheric chamber

***Collaborators and Co-authors:***

CE-CERT: A. Asa-Awuku, W.P.L. Carter, J. Norbeck, J.W. Miller, T. Durbin, G. Tonnesen; Caltech: J. Seinfeld, R. Flagan; UC Riverside: J. Zhang, P. Ziemann, R. Atkinson, J. Arey, H. Jung; DRI: J. Watson, H. Moosmuller, H. Kuhns; Rice: R. Griffin; Texas A&M: H.Gong, D. Diaz-Sanchez, R. Schiestl.; VA Hospital: L. Fechter; USDA: P.Silva; JARI: Hiroyuki Hagino; NIES: Kei Sato; Portland State: J. Pankow; University of Montana: Bob Yokelson; UCLA: A. Cho, J. Froines; UC Irvine, M. Kleinman; USFS: D. Weise, W. Hao.

***Graduate Advisor:***John H. Seinfeld and Richard Flagan, California Institute of Technology.

***Thesis Advisor and Postgraduate Scholar Sponsor:*** Ph.D. students: Sandip Shah\*, Aniket Sawant\*, Chen Song\*, Abhilash Nigam\*, Bethany Warren\*, Quentin Malloy\*, Ajay Choudhary\*, Harshit Agrawal\*, Qi Li\*, Kent Johnson\*, Christopher Clark\*, Shunsuke Nakao\*, Ehsan Hosseini\*, Maryam Hajbajaei, Yusuf Khan, Poornima Dixit, Taofeng Cao, Nick Gysel, Ji Luo, Ping Tang, Xiaochen Tang, Derek Price, Chia-Li Chen, Mary Kacarab, Sara Li

PostDoc: Kwangsam Na

\* awarded Ph.D.

## Gookyoung Heo

***Assistant Researcher***

CE-CERT, University of California, Riverside, CA 92521 gookyoung@engr.ucr.edu

***Professional Preparation***

|  |  |  |
| --- | --- | --- |
| Seoul National University, South Korea | Chemistry | BA, 1997 |
| Seoul National University, South Korea | Environmental Planning | MCP, 2001 |
| University of Texas at Austin | Civil Engineering | PhD, 2009 |

***Current Appointments***

2010-present. University of California, Riverside, College of Engineering Center for Environmental Research and Technology. Postdoctoral Scholar (9/2010-11/2012), Assistant Research Engineer (12/2012-present).

***Research Summary***

Gookyoung Heo is a chemical mechanism developer at the University of California at Riverside (UCR), Center for Environmental Research and Technology. His main research interest is developing and using chemical mechanisms for air quality research and applications, and he has closely worked with Dr. William Carter since his joining UCR in 2010. He participated in developing and evaluating chemical mechanisms such as CB05-TU, CB6, SAPRC-11 and PM-SAPRC. Previously, he had worked with Dr. David Allen at the University of Texas at Austin.

***Selected Publications and Reports***

* **Heo**, G., McDonald-Buller, E., Carter, W.P.L., Yarwood, G., Whitten, G.Z., Allen, D.T. (2012). Modeling ozone formation from alkene reactions using the Carbon Bond chemical mechanism. *Atmospheric Environment* 59, 141-150, <http://dx.doi.org/10.1016/j.atmosenv.2012.05.042>.
* **Heo**, G., Carter, W. P. L., Yarwood, G. (2012). Developing chemical mechanisms that are more robust to changes in atmospheric composition. Presented at the 11th Annual CMAS Conference, Chapel Hill, NC, October 15-17, 2012. (<http://www.cmascenter.org/conference/2012/agenda.cfm>).
* **Heo**, G., Yarwood, G. (2012). Gas-phase chemistry in air quality models - research needs and recommendations. EM (A&WMA’s magazine), September, 2012, p. 42-44.
* Carter, W.P.L., **Heo**, G., Cocker, D.R., Nakao, S. (2012). SOA formation: chamber study and model development. Final Report to the California Air Resources Board, Contract 08-326, May 21. Available at <http://www.cert.ucr.edu/~carter/SAPRC/pmchrpt.pdf>.
* Carter, W.P.L., **Heo**, G. (2012). Development of revised SAPRC aromatics mechanisms. Final Report to the California Air Resources Board, Contracts No. 07-730 and 08-326, April 12. Available at <http://www.cert.ucr.edu/~carter/SAPRC/saprc11.pdf>.
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* Whitten, G.Z., **Heo**, G., Kimura, Y., McDonald-Buller, E., Allen, D.T., Carter, W. P. L., Yarwood, G. (2010). A new condensed toluene mechanism for Carbon Bond: CB05-TU. *Atmospheric Environment* 44, 5346-5355.
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* Yarwood, G., Whitten, G.Z., Jung, J., **Heo**, G., Allen, D.T. (2010). Development, evaluation and testing of version 6 of the Carbon Bond chemical mechanism (CB6). Final Report to the Texas Commission on Environmental Quality, Work Order No. 582-7-84005-FY10-26.
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* Faraji, M., **Heo**, G., Kimura, Y., McDonald-Buller, E., Allen, D., Yarwood, G., Whitten, G., Carter, W. (2007). Comparison of the Carbon Bond and SAPRC photochemical mechanisms. Report to the Texas Commission on Environmental Quality, Work Order No. 582-04-65588-07.
* **Heo**, G., Allen, D.T. (2006). Effects of uncertainties in the biogenic emission inventory on gas phase oxidant and particle formation in Texas. Proceedings of the 99th Annual Conference of the Air & Waste Management Association, New Orleans, LA, June 20-23, 2006. (Paper 352).