

## Technical Proposal

### *Air Quality Impacts of Low Vapor Pressure-Volatile Organic Compounds*

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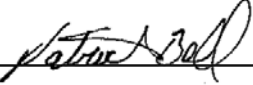
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## **Statement of Significance**

The results of experiments and modeling studies conducted with consumer products that use Low Vapor Pressure–Volatile Organic Compounds (LVP-VOCs) will determine if these compounds can contribute significantly to ozone and / or secondary organic aerosol formation in California. These findings will provide scientific support for future regulations and/or for the decision to maintain an exemption status for many LVP-VOCs. The results will strengthen the scientific basis for the emissions controls within the SIP efforts.

## Abstract

Low Vapor Pressure-Volatile Organic Compounds (LVP-VOCs) are a category of organic compounds that do not evaporate as easily as higher vapor pressure VOCs at typical ambient temperatures due to their intrinsic chemical properties. The tendency for LVP-VOCs to remain in the condensed phase is thought to reduce their efficacy in ozone production relative to VOCs, despite the fact that some LVP-VOCs actually have relatively high Maximum Incremental Reactivities (MIRs) when they are tested in a form that makes them available for chemical reactions. LVP-VOCs that were historically used in a small number of consumer products were granted an exemption from regulations designed to reduce ozone concentrations. Since that time, this exemption status has promoted the use of LVP-VOCs in a variety of consumer products with liquid and aerosol application methods that can enhance their ability to evaporate. Recent measurements have determined that several compounds classified as LVP-VOCs readily evaporate, raising the possibility that some of the consumer products that heavily use these compounds may be contributing to photochemical reactions leading to ozone formation and/or secondary organic aerosol (SOA) formation.

The objective of the proposed research is to test consumer products employing significant fractions of exempted LVP-VOCs to determine if they have the potential to contribute significantly to regional levels of ozone and/or SOA. A target list of LVP-VOCs developed in coordination with state agencies will be introduced into a photochemical reaction chamber seeded with an initial mixture of NO<sub>x</sub>, VOCs, and aerosol that represents typical conditions in California. The additional ozone and SOA that forms in the system due to the introduction of the LVP-VOCs will be measured as a function of time over 3-5 hour experiments. The sensitivity of the formation rates to the composition of the initial representative mixture, temperature, and relative humidity will be studied. Experiments that adjust the composition of the background system will be designed to probe behavior at different levels of oxidant/NO<sub>x</sub> concentrations that can often lead to different regimes of chemical reactions. Fundamental models will be developed to explain the ozone and SOA formation based on the SAPRC11 chemical mechanism combined with the Statistical Oxidation Model (SOM) while accounting for the effects of water on the partitioning of organic compounds. The regional implications of these results will be evaluated by embedding the chemical mechanism that can explain the chamber results inside one or more of the following regional chemical transport models: CMAQ, WRF-CHEM, and the UCD/CIT air quality model. Simulations will be conducted for the CALNEX study period to determine how LVP-VOCs may contribute to ozone and SOA formation.

The results of the experiments and modeling conducted for LVP-VOCs will determine if these compounds merit further research and regulation to reduce their contribution to ambient ozone and SOA production. The results will strengthen the scientific basis for the emissions controls within the SIP efforts.

## Project Objective

The objective of the proposed research is to measure the ozone and SOA formation potential of LVP-VOCs commonly used in consumer products. The implications of chamber measurements will be evaluated in the context of regional ozone and SOA formation using reactive chemical transport models. The results will provide guidance for the level of control required for LVP-VOCs in future SIPs.

## Project Tasks

Major Task 1: A list of consumer products that heavily use LVP-VOCs will be developed in coordination with state agencies. Each LVP-VOC will be ranked according to annual usage  $\times$  estimated volatility  $\times$  MIR for ozone formation. A range of experiments will be conducted with consumer products that employ LVP-VOCs with the highest ranking to test the actual ozone and SOA formation potential of these major LVP-VOCs as used in consumer products where interactions with other components of the organic mixture may modify behavior. A range of experimental conditions corresponding to different NO<sub>x</sub> concentrations and relative humidity will be explored.

Major Task 2: A mechanistic model for ozone and SOA formation associated with LVP-VOCs in consumer product mixtures will be developed based on the SAPRC11 chemical mechanism, the sequential oxidation model (SOM) for SOA formation, and our enhanced understanding of organic partitioning in the presence of different levels of RH.

Major Task 3: The regional ozone and SOA formation associated with LVP-VOCs used in consumer product mixtures will be calculated during the time-period corresponding to the CALNEX field study. The parameterizations used in the smog chamber modeling will be incorporated into regional grid models applied to California. The wide range of emissions rates for gaseous and PM pollutants across California combined with the range of meteorological conditions across the state will explore a wide range of potential ozone and SOA formation regimes.

Major Task 4: Project Deliverables. At the conclusion of the project, a draft final report and text files of all relevant data used in this study and suitable for data archiving will be submitted to the ARB. The draft final report will include a comprehensive summary and discussion of all of the topics and issues addressed in this research project. Journal article preparation will be taken up as soon as results emerge, with manuscript(s) submitted to professional journals. The draft final report will be amended into a final report based on comments from ARB staff.

## Technical Plan

### *Introduction*

Low Vapor Pressure-Volatile Organic Compounds (LVP-VOCs) are a category of organic compounds that do not easily evaporate at typical ambient temperatures due to their intrinsic chemical properties. The California Air Resources Board defines a LVP-VOC to be a compound with at least one carbon atom that (a) has a vapor pressure less than 0.1 mm Hg at 20°C, as determined by ARB Method 310; or (b) is a chemical “compound” with more than 12 carbon atoms, or is a chemical “mixture” comprised solely of “compounds” with more than 12 carbon atoms, and the vapor pressure and boiling point is unknown; or (c) is a chemical “compound” with a boiling point greater than 216°C, as determined by ARB Method 310; or (d) is the weight percent of a chemical “mixture” that boils above 216°C, as determined by ARB Method 310.

Classification as an LVP-VOC exempts the compound from California regulations that target emissions reductions designed to reduce ambient ozone concentrations. There are currently hundreds of compounds classified as LVP-VOCs that are used in consumer products in the State of California (see Table 1 for examples). Consumer products that have been reformulated in recent decades to employ exempt LVP-VOCs instead of traditional VOCs include (a) hair care products, (b) insecticide productions, (c) cleaning products, (d) fragrance products, (e) lubricant products, (f) floor polishes, and (g) carpet and upholstery products.

Ozone concentrations have decreased in California over the past 40 years (see for example <http://www.aqmd.gov/smog/o3hist-trend.pdf>) partly due to the regulations favoring the use of LVP-VOCs over traditional VOCs but also in large part due to the success of regulations focusing on major sources such as motor vehicles. Further reductions in ozone concentrations below current health-based standards will require identification and regulation of numerous small sources since virtually all major sources have now been controlled. LVP-VOCs may be one category of emissions that merit re-examination in this context. Recent measurements have determined that some LVP-VOCs readily partition to the gas phase (<http://www.aqmd.gov/prdas/Coatings/VOCs/RedefiningVOCs.pdf>). These observations are largely based on simple evaporation tests that use bulk liquid. Application of the LVP-VOCs in aerosol form may further enhance the evaporation of the LVP-VOC due to the Kelvin effect which increases the vapor pressure above small droplets. Once in the gas-phase, LVP-VOCs are highly available for chemical reaction. As gases, several LVP-VOCs actually have significant ozone formation potential as measured by the maximum incremental reactivity (MIR) scale (see for example ethylene glycol with MIR=3.13). A re-examination of the role that LVP-VOCs play in contemporary ozone production in California appears warranted at this time.

Secondary Organic Aerosol (SOA) formation is a second potential air pollution problem where LVP-VOCs may play a role. Recent studies indicate that major reductions in emissions of primary organic aerosol (POA) leave SOA as the dominant fraction of airborne particulate carbon in most locations across the US (Zhang, Jimenez et al. 2007). There are several theories describing the formation of SOA in the atmosphere that focus on different pathways, including gas-phase reactions (Kroll, Chan et al. 2007, Kroll and Seinfeld 2008), aqueous reactions in

atmospheric water droplets (Ervens, Turpin et al. 2011), condensed organic-phase reactions (Tolocka, Jang et al. 2004) and co-condensation of water (Chang and Pankow 2010). There is no consensus about the dominant pathway, but all theories agree that a LVP-VOC that somehow participates in the production of ozone is likely also to be of relevance for production of secondary organic aerosol. Any examination of the atmospheric reactions of LVP-VOCs should also consider their potential for SOA formation.

Some compounds with intermediate volatilities react strongly in the gas phase leading to ozone production and also quickly forming reaction products with low volatility that form SOA. As an example, the important biogenic compound  $\alpha$ -pinene has a vapor pressure at 20°C of  $\sim 3 \text{ mm Hg} = 2 \times 10^7 \mu\text{g m}^{-3}$ , an ozone MIR = 4.51, and a relatively high SOA yield upon photooxidation. Thus, many LVP-VOCs with volatilities at the upper end of the LVP-VOC range (0.01 – 0.1 mm Hg) may have relatively large SOA formation potentials since they have vapor pressures that are lower than  $\alpha$ -pinene.

## ***Hypotheses***

The testable hypotheses listed below provide a preliminary framework for examining the ozone and SOA formation potentials of consumer products that use LVP-VOCs under representative conditions in California. The level of desired statistical significance can be targeted through the design of an experimental program with sufficiently large numbers of samples for cases where the uncertainty in each sample is predetermined. As with any hypothesis test, the most interesting answers can either be associated with the null hypothesis or the alternative hypothesis.

**Hypothesis 1a,b:** Consumer products applied in liquid form that contain LVP-VOCs can produce (a) ozone and/or (b) SOA in smog chamber experiments at representative ambient concentrations.

**Hypothesis 2a,b:** Consumer products applied in aerosol form that contain LVP-VOCs can produce (a) ozone and/or (b) SOA in smog chamber experiments at representative ambient concentrations.

**Hypothesis 3a,b:** The atmospheric relative humidity and NO<sub>x</sub> concentration affects the extents and rates of (a) ozone and /or (b) SOA production from LVP-VOCs.

**Hypothesis 4a,b:** The level of (a) ozone and/or (b) SOA production associated with consumer products that contain LVP-VOCs is significant for regional ozone and/or SOA formation in regional modeling calculations under typical California conditions.

## ***Approach***

**Identification of Key Consumer Products and LVP-VOCs for Study:** The list of target consumer products and LVP-VOCs will be developed in coordination with state agencies. LVP-VOCs and consumer products will be ranked based on their annual usage rates x their estimated volatility x their MIRs for ozone production. Table 1 illustrates a partial set of LVP-VOCs that

will be considered in this exercise. A second ranking will also be developed that considers their estimated SOA formation potentials based on published experiments with similar compounds and the expert opinions of the project team. Once rankings are established by the project team, chamber experiments will be conducted on as many as 20 consumer products and/or LVP-VOCs as allowed by the project timeline and budget. The exact number of compounds tested will depend on the final project budget and the details of the test procedure established after consultation with ARB staff.



**Table 1.** List of some of the LVP-VOC's used in California. A subset of these species (or others chosen in consultation with ARB staff) will be selected for experimental study.

Chemical Name	Chemical Formula
Dimethyl Glutarate	C7H12O4
2,2,4-Trimethyl-1,3-Pentanediol Isobutyrate (Texanol)	C16H30O4
Dibutyl Phthalate	C16H22O4
Diisopropyl adipate	C12H22O4
1-Tetradecene	C14H28
Diethylene Glycol n-Butyl Ether Acetate	C10H204
2-Methyl-2,4-Pentanediol	C6H14O2
Diethylene Glycol Monoethyl Ether Acetate	C8H16O4
Diethylene Glycol Mono(2-Ethylhexyl) Ether	C12H26O3
Propylene Glycol Phenyl Ether	C9H12O2
Tripropylene Glycol n-Butyl Ether	C13H28O4
Diethyl Phthalate	C12H14O4
Dimethyl Adipate	C8H14O4
Diethylene Glycol Monohexyl Ether	C10H22O3
Dipropylene Glycol n-Propyl Ether	C9H20O3
Triethylene Glycol Monobutyl Ether	C11H22O4
Ethylene Glycol Monohexyl Ether	C8H18O2
Tripropylene Glycol	C9H20O4
Triethylene Glycol Monoethyl Ether	C8H18O4
Diethanolamine	C4H11NO2
Triethylene Glycol Monomethyl Ether	C7H16O4
Propylene Glycol	C3H8O2
Phthalic Anhydride	C8H4O3
Triisopropanolamine	C9H18N
1,4 Butanediol	C4H10O2
Diethylene Glycol Propyl Ether	C7H16O3
Diethylene Glycol Monobutyl Ether	C8H18O3
Ethylene Glycol	C2H6O2
Diethylene Glycol Monoethyl Ether	C6H14O3
Triethylene Glycol	C3H6O2
1,3 Butanediol	C4H10O2
Diethylene Glycol	C4H10O3
Triethanolamine	C6H15NO3
Ethylene Glycol Phenyl Ether	C8H10O2
Benzyl Alcohol	C7H8O

**LVP-VOC Volatility:** An important property that governs the tendency of LVP-VOCs to exist in the gas-phase at high concentrations where they are available for photochemistry is the pure-compound vapor pressure. LVP-VOCs are generically assumed to have “low” vapor pressures, but in actual fact the selected threshold of 0.1 mm Hg @ 20°C falls close to the high-end of the intermediate volatility range (Jathar, Farina et al. 2011). Using equilibrium gas-particle partitioning theory and taking typical ambient OA mass loadings of 1-50  $\mu\text{g m}^{-3}$ , only compounds with vapor pressures  $<0.000001$  mm Hg will exist exclusively in the particle phase. By this criterion, many LVP-VOCs that enter the atmosphere (by evaporation from liquid-applied products or following use in aerosol products) will be predominantly in the gas phase and thus available for reactions that produce  $\text{O}_3$  or SOA.

In the current study, the pure-compound vapor pressure of individual LVP-VOCs will be obtained from the literature, as available, or calculated using a group contribution method, which allows for estimation of pure compound vapor pressures based on knowledge of the type of functional groups and their locations in a molecule. We will use the SIMPOL.1 group contribution method, developed by Pankow and Asher (Pankow and Asher 2008), as well as the EVAPORATION model of Campernolle et al. (Campernolle, Ceulemans et al. 2011), both of which have been shown to accurately predict vapor pressures for compounds with a variety of functional group types over the range of vapor pressures relevant to LVP-VOCs.

The volatilities of LVP-VOCs as they exist in consumer product mixtures are more difficult to predict because of the potential for non-ideal interactions with other components of the mixture. Similarly, the volatilities of individual LVP-VOCs within mixtures are difficult to measure because simple analysis of mass loss as a function of time cannot distinguish contributions from specific components of the mixture. However, the general chemical similarity between components that make up mixtures suggests that the activity coefficients of individual compounds likely do not deviate by more than an order of magnitude from unity. The range of vapor pressures of different individual LVP-VOCs is thus likely much larger than non-ideal effects, suggesting that investigation of the ozone and SOA formation potential across a range of different LVP-VOCs is a useful starting point.

In the current study, the volatility of LVP-VOCs in consumer products mixtures will be calculated using the pure-compound vapor pressures combined with Raoult's Law and unity activity coefficients. Kelvin theory applied using bulk surface tension values will be used to account for enhanced volatility of consumer products applied in aerosol form. The resulting volatilities will primarily be used to rank LVP-VOCs and consumer products for potential testing in smog chamber experiments. Further scrutiny and direct measurements of LVP-VOC volatility in consumer product mixtures will be warranted if smog chamber results indicated significant departure from ideal behavior. In this case, the actual evaporation rates of LVP-VOC compounds contained in consumer product mixtures will be measured using sorbent tube capture of air samples followed by GC-MS analysis (Kumar et al 2011). This technique is laborious, but provides excellent sensitivity and selectivity. It will primarily be pursued for those compounds demonstrated to produce significant ozone and/or SOA in smog chamber experiments when theoretical calculations cannot reproduce experimental results.

Based on the assessment of LVP-VOC volatility, we will divide compounds into two classes: those (1) likely or (2) unlikely to partition to the gas phase given the formulation and mode of application in high use consumer products. Those in the first group will be available in general for photochemical reactions and will therefore be sorted according to their ozone formation MIRs. The LVP-VOCs likely to form SOA after photochemical reaction will be those compounds with vapor pressures that are less than that of isoprene, one of the most volatile VOCs that is known to form SOA. For compounds likely to form SOA, we will further distinguish between those that are “volatile” vs. those that are “semi-volatile”, with these distinctions being based on whether their vapor pressures (related to inverse saturation concentrations) are greater than or less than 0.01 mm Hg ( $\sim 500 \mu\text{g m}^{-3}$ ), respectively. A subset of these compounds will be selected for experimental study based on the results of these calculations and in consultation with ARB staff.

**Smog Chamber Experiments:** Simple smog chamber experiments conducted with actual consumer products that employ LVP-VOCs provide the most efficient method of directly measuring the endpoints of interest: ozone and SOA formation potential. The approach in the current project is to screen a priority list of consumer products and LVP-VOCs for ozone and SOA formation and apply more detailed measurements and model calculations to the most significant compounds. This approach will focus the most expensive aspects of the study on the most important compounds yielding costs savings relative to a “blanket approach”. Simple smog chamber experiments therefore anchor the entire project and will be carried out in all three years of study. The prioritized list developed through emissions inventory estimates, volatility estimates, and ozone/SOA formation estimates in consultation with ARB staff will guide the consumer products and LVP-VOCs selected for experiments.

The ozone and SOA formation potential of consumer products containing target LVP-VOCs will be measured in  $3 \text{ m}^3$  photochemical reaction chambers at UC Davis. Each chamber experiment will start with a background concentration of pollutants representing typical urban conditions in California. The gas-phase VOC surrogate will be based on the experiments for ozone formation using the MIR scale (Carter 1994) and applied recently to study the ozone formation potential of agriculture VOCs (Howard, Yang et al. 2008) and pesticides (Kumar, Howard et al. 2011). NO<sub>x</sub> concentrations will be based on recent ambient measurements spanning the range encountered in locations where consumer LVP-VOCs are heavily used: Los Angeles, San Francisco, Sacramento, Fresno, and Bakersfield. Background primary organic aerosol (POA) in chamber experiments will be produced by addition of representative POA surrogates, such as dioctyl phthalate (Song, Zaveri et al. 2007). The resulting primary organic aerosol will be targeted for a background concentration of  $10 \mu\text{g m}^{-3}$  to act as seed particle for SOA formation. Alternatively, either no seed or an inorganic seed aerosol may be used in some experiments to investigate the influence of the background aerosol on SOA formation from the LVP-VOC's.

Chamber characterization experiments will be conducted to determine the O<sub>3</sub> and particle wall-loss rates (previous measurements in similar Teflon chambers indicate loss rates of approximately  $15\% \text{ hr}^{-1}$ ). Measurements of ozone, NO<sub>x</sub>, and SOA volume concentrations will be made periodically for each chamber as the reaction proceeds to profile the time response of the system with a minimum sample volume extracted, thereby allowing estimated experimental times up to 5 hrs (Howard, Yang et al. 2008). Ozone measurements will be made using an ozone

analyzer (Model #450, Teledyne Instruments Advanced Pollution Instrumentation, Inc., San Diego, CA); NO<sub>x</sub> measurements will be made using a chemiluminescence analyzer (Model #ML9841A, Teledyne Monitor Labs, Englewood, CO); and SOA volume measurements will be made with a scanning mobility particle size (SMPS) (TSI Model 3080). The minimum detection limits and typical uncertainties in previous photochemical measurements using these instruments are summarized in Table 2.

**Table 2.** Instrumentation detection limits and uncertainties.

Instrument	Detection Limit	Typical Uncertainty
NO <sub>x</sub> analyzer	0.5 ppb	5% accuracy
Ozone analyzer	<3 ppb	5% accuracy
SMPS	~0.1 µg m <sup>-3</sup>	±10% accuracy/±2% precision

Ozone and SOA formation experiments will be conducted simultaneously with control experiments in identical reaction chambers. Each set of chamber experiments will be conducted with one control (background surrogate only) and one consumer product (background surrogate + CP) pair. The additional ozone and SOA formation observed in chamber experiments seeded with consumer products will be interpreted as the ozone and SOA formation associated with that compound under the experimental conditions:

$$\Delta O_3 = [O_3]_{CP+background} - [O_3]_{background} - ([NO]_{CP+background} - [NO]_{background}) \quad (1)$$

$$\Delta SOA = [PM]_{CP+background} - [PM]_{background} \quad (2)$$

For consumer products that exhibit measurable O<sub>3</sub>/SOA formation, additional experiments will be performed to compare the O<sub>3</sub>/SOA formation from the pure-compound LVP-VOCs within those products to determine if the effects are linearly additive. In simple terms, we will determine if the reactivity of the consumer product could have been predicted by simply adding the reactivity of the component LVP-VOCs in the mixture. Experiments conducted using pure-compound LVP-VOC's will use either the same initial LVP-VOC concentration or will utilize a constant total initial VOC mass concentration (summed over all compounds comprising the mixture). This will allow for assessment of the SOA formation potential of a given LVP-VOC relative to that of the mixture.

The photochemical reaction system will be irradiated using black lights (Sylvania # F40BL) with total UV flux measured with a UV photometer (Model #PMA-2111, Solar Light Co. Inc., Glenside, PA). Temperature and relative humidity in chamber experiments will be adjusted to represent the range of conditions in California where ozone and SOA formation is of interest. There are experimental challenges involved with doing experiments at high RH, such as temperature fluctuations in the chamber leading to condensation on the walls. Our chambers are housed in a temperature-controlled enclosure, and thus should allow for experiments to be conducted at elevated RH. The upper-limit RH explored will be established experimentally, with a target high RH condition of 80%. The intensity of UV irradiance from black lights is a function of temperature, and so the control experiment paired with each LVP-VOC measurement

will be a critical feature of the data interpretation. Table 3 summarizes the target range of temperature and RH that will be explored.

**Table 3:** Range of experimental conditions explored during laboratory studies.

Variable	Range of Values
Consumer products / LVP-VOCs	Priority list of 20 developed with ARB staff
Background VOC	50-200ppb
Background NOx	25-75ppb
Temperature	20-40°C
Relative Humidity	20-80%

Because the focus of the study will be to provide a preliminary estimate of ozone and SOA formation potential from LVP-VOCs as used in consumer product mixtures, detailed measurements of individual gas-phase VOC compounds and particle-phase organic compounds are only planned for a subset of the experimental program. Detailed measurements will be made for up to 5 compounds that exhibit the greatest potential for SOA formation. Gas-phase samples will be collected in charcoal tubes (Orbo 32, Sigma-Aldrich, St. Louis, MO) containing 400 mg and 200 mg of activated carbon in two successive sections allowing for sample collection and breakthrough determination, respectively, for less volatile/semi-volatile organic compounds at a sampling rate of 2 liters per minute for 5 minutes (NIOSH, 2003). Individual sections of each charcoal tube and DNPH silica cartridge will be extracted in separate vials using 1.5 mL of CS<sub>2</sub> followed by 15 min of sonication. The supernatant phase of the charcoal extracted solvent will be transferred into an autosampler vial and analyzed by an Agilent 6890A gas chromatograph coupled with an Agilent 5973N mass spectrometer with a ZB-624 capillary column (Phenomenex, Torrance, CA) with dimensions 30 m × 0.25 mm × 1.4 mm. The instrument will be calibrated with a mixture of known concentration of several groups of compounds to verify the linearity of the measurements. Analyte separation will be attained in the column with the following temperature program: initial oven temperature at 35°C for 5 min, then raised to 220°C at a rate of 7°C min<sup>-1</sup>, and then held for 5 min. A second ramp of 10°C min<sup>-1</sup> to 240°C will be then applied with a holding time of 2 min. The injector will be set at 200°C.

Particle phase samples will be collected at the conclusion of selected photochemical experiments on quartz fiber filters. The total organic carbon content in the particle phase will be measured using the standard thermal-optical technique (Chow, Watson et al. 1993) for comparison to inferred organic carbon mass from SMPS measurements. The majority of the SOA formed during photochemical experiments is expected to be polar and possibly combined into a high molecular weight oligomer structure. Analysis of the true molecular structure of the majority of this SOA material (without excessive fragmentation) is an active research area not suitable for the current applied project. Particle-phase samples will be archived for possible future analysis if the mechanisms of SOA formation from LVP-VOCs are deemed to be of interest in the future. Note that the project team has access to advanced LC/MS and GC/MS instrumentation and the scope of this task can be expanded if it is of priority interest to ARB and budgets are available.

**Modeling of Ozone Formation from LVP-VOCs in Chamber Experiments:** The SAPRC11 chemical mechanism will be modified (where necessary) to explicitly describe chemical reactions of LVP-VOCs rather than lumping these compounds into broad categories which may skew reaction mechanisms and rate constants. Rate constants and reaction pathways for detailed LVP-VOCs will be obtained from the literature and/or from the Master Chemical Mechanism (MCM). The UV spectrum emitted by the black lights used in the smog chamber experiments will be translated into photochemical rate constants based on the quantum yields for each photochemically active molecule at each wavelength. UV irradiance will be set based on measured UV irradiance during each experiment. Rate constants will be adjusted for actual temperature during each experiment using standard correction methods in the SAPRC mechanism. Humidity levels measured during each experiment will be specified as the initial water vapor concentration in the reaction mechanism since water molecules can act as an important source of oxidants under conditions typical for California (Kleeman 2008).

Wall loss rates measured in chamber experiments will be added to the reaction matrix to account for the behavior observed in chamber experiments where the surface to volume ratio is significant. Typical wall loss rates for gas-phase species in  $1 \text{ m}^3$  chambers are  $15\% \text{ hr}^{-1}$  (Howard, Yang et al. 2008).

The photochemical reaction system will be integrated with respect to time using the same numerical methods and programs as those employed in the UCD/CIT airshed model. Predicted ozone concentrations and measured ozone concentrations will be compared to ensure that the reaction mechanism adequately describes dominant chemical pathways under a range of conditions. An example of results from a similar exercise conducted with animal waste VOCs is provided by Howard et al. (Howard, Yang et al. 2008, Howard, Kumar et al. 2010, Howard, Kumar et al. 2010).

**Modeling of SOA Formation from LVP-VOCs in Chamber Experiments:** SOA formation will be assessed first through determination of SOA yield curves from experiments conducted using individual LVP-VOCs, where yield is defined as the amount of SOA formed per amount of LVP-VOC reacted. Only experiments where significant SOA formation is observed will be explicitly considered for analysis. The observations will be fit to the traditional 2-product equilibrium partitioning model (Odum, Hoffmann et al. 1996) and to the static volatility basis set (VBS) model (Presto, Huff Hartz et al. 2005, Donahue, Robinson et al. 2006). The so-called semi-volatile product yields and saturation concentrations from the 2-product model are currently utilized in the simulation of SOA within air quality models such as CMAQ. In addition, the newly-developed statistical oxidation model (SOM) (Cappa and Wilson 2012) will be used to simulate the time-dependent SOA formation. The SOM provides a natural framework for the simulation of photochemical formation of SOA from individual compounds and from multi-component mixtures as it accounts for time-dependent multi-generational formation of condensable species from the gas-phase reaction of hydrocarbons. This stands in contrast to 2-product and VBS formulations, which assume static distributions of products species. The SOM has recently been shown capable of accurately simulating the formation of SOA from a suite of  $\text{C}_{12}$  alkane isomers (Cappa, Zhang et al. 2012). The SOM is currently being developed for use in photochemical air quality models (ARB Contract: 12-312). The important effects of ambient relative humidity on levels of SOA will be investigated by the approach described by Pankow

and Chang (Pankow and Chang 2008). In this approach reasonable chemical structures are assigned to the oxidation products, and the resulting levels of SOA are calculated by consideration of the co-condensation of water with full accounting for the effects of both activity coefficients and varying mean molecular weight in the SOA phase by classical Pankow theory (Pankow 1994).

For LVP-VOCs that show significant SOA formation above the background conditions, the observed aerosol yields for individual LVP-VOCs will be compared between each other and relationships will be investigated between the SOA formation potential and the LVP-VOC compound structure and volatility. Additionally, SOA formation from individual LVP-VOCs will be compared with the SOA formed during experiments conducted utilizing consumer product formulations that contain that LVP-VOC.

**Regional Modeling for the Ozone Formation and SOA Formation from LVP-VOCs in California:** The regional implications of the ozone and SOA formation potential associated with LVP-VOCs will be evaluated using a regional reactive chemical transport model. The gas-phase reactions and SOA formation mechanisms necessary to explain the smog chamber measurements will be combined with the SAPRC11 gas phase mechanism in one or more of the CMAQ, WRF-CHEM, and UCD/CIT air quality models. Each model includes a comparable framework for simulating ozone production with the SAPRC chemical mechanisms and secondary organic aerosol production with a variety of models. The WRF-CHEM model has the ability to simulate interactions and feedback effects between air pollution and meteorology but it requires longer simulation times relative to the other models. The UCD/CIT airshed model provides source apportionment information for primary and secondary pollutants and has been extensively tested with all versions of SAPRC90, 99, 07, and 11 chemistry. The CMAQ model is used in regulatory applications and therefore would have relevance for future SIP applications. The final model used for the regional calculations will be determined in consultation with ARB staff.

The regional modeling exercise will take advantage of the extensive measurement database assembled for the CALNEX field study (<http://www.esrl.noaa.gov/csd/projects/calnex/>) for the time period May/June 2010. Emissions inventories for the CALNEX study period will be obtained from the California Air Resources Board. Detailed speciation profiles for gas-phase VOCs will be applied based on the database maintained by SAPRC (<http://www.engr.ucr.edu/~carter/SAPRC/>). Detailed speciation profiles for particle phase mass will be applied based on measurements made in multiple source tests conducted by the project PI (Robert, Kleeman et al. 2007, Robert, VanBergen et al. 2007, Jakober, Robert et al. 2008, Kleeman, Robert et al. 2008). Meteorological fields will be simulated using the WRF model with assimilation of meteorological measurements.

Upwind boundary conditions for the study period will be based on measurements made during the CALNEX field campaign. A one week model initialization time will be specified so that the results are not sensitive to initial conditions. All model predictions for gas-phase and particle-phase pollutant concentrations will be compared to available surface and aircraft measurements to evaluate the accuracy of the base-case model. Standard metrics like Mean Fractional Error (MFE) and Mean Fractional Bias (MFB) will be calculated and compared to accepted

performance guidelines (Boylan and Russell 2006). Proper simulation of base-case conditions is necessary to ensure that model chemical reactions are operating in the correct regime prior to calculating sensitivity to emissions from LVP-VOC sources.

The direct contribution to regional ozone and SOA concentrations from consumer products formulated with LVP-VOCs will be calculated by conducting a sensitivity analysis where those emissions are withheld from the emissions inventory. The EIC number associated with each consumer product of interest will be tabulated so that scaling factors can be applied to emissions from these sources. The approach is similar to the analysis conducted by Hu et al. to examine the relative importance of VOCs emitted from motor vehicles and animal feed emissions on regional ozone concentrations in the San Joaquin Valley (Hu, Howard et al. 2012). Population-weighted concentrations of ozone and SOA formation associated with consumer products that employ LVP-VOCs will be calculated in each major population region in California.

The purpose of the current study is to determine if **future** emissions of LVP-VOCs in California will make significant contributions to ozone and SOA formation, thereby presenting an obstacle to the attainment of health-based standards. In the present study, the regional modeling analysis for the year 2010 described above will be repeated using emissions inventories projected for future State Implementation Plan (SIP) attainment. These inventories will be provided by state agencies. The meteorology experienced during the CALNEX field campaign will be used for this analysis under the assumption that similar meteorological patterns could occur in the future. Boundary conditions for background ozone will be increased to match future projections from global chemistry models (Vingarzan 2004). The role that consumer products containing LVP-VOCs play in future ozone and SOA concentrations relative to the health based standards will once again be evaluated.

One possible outcome of the regional modeling exercises described above is that predicted air quality fails to meet state and federal standards when LVP-VOCs emissions are allowed, but successfully meets those standards when LVP-VOCs are removed from the emissions inventory. If this possible outcome occurs, further work will be conducted to determine if a complete ban of LVP-VOCs is required, or if only the compounds that contribute most strongly to ozone and SOA production need to be controlled. Simulations will be conducted by sequentially removing individual consumer product EIC numbers from the emissions inventory, gradually moving between the base-case and complete control scenarios explored above. The point at which air quality standards are met will be used to estimate the volatility threshold of LVP-VOCs that would be appropriate moving forward in California.



## ***Data Management Plan and Statistical Analysis of Results***

Each set of experiments involving a control measurement and a LVP-VOC measurement will be used as a sample point in a paired t-test. Confidence intervals for the difference between the measured ozone/SOA in the control experiment vs. the LVP-VOC experiment will be developed following standard statistical methods. As a starting point in this exercise, each consumer product or pure LVP-VOC identified on the initial prioritized study list will be tested once under standard conditions representing Los Angeles. The measured ozone and SOA formation potential in this initial test will be used to update the MIR/estimated SOA formation potential in the ranking exercise to produce a second prioritized study list. Subsequent experiments will then be carried out over a range of conditions appropriate for locations in California including (but not limited to) Bakersfield, Fresno, Sacramento, and San Francisco. Multiple experiments under different conditions will be conducted for those consumer products and LVP-VOCs that exhibit significant variability under different conditions.

If the difference between ozone/SOA formation in the control experiments and consumer product experiments given by eqs 1-2 is tabulated in  $N$  experiments ( $d_1, d_2, d_3, \dots, d_N$ ), then the uncertainty in the average difference ( $\bar{D}$ ) is the standard deviation of the experimental points ( $S_d$ ) divided by the square root of the number of sample points ( $S_d/\sqrt{N}$ ). This uncertainty is significantly smaller than the uncertainty derived from treating each measurement as an individual sample point. Paired experiments will be strongly correlated because the variability introduced by different NOx and background VOC conditions is dominant. If 90% of the experimental variability comes from changing the NOx/background VOC conditions and 10% of the variability comes from actual measurement error, then the width of the confidence interval derived from the paired t-test measurements will be approximately 75% tighter than the corresponding unpaired confidence interval assuming a total of 5 experiments.

## **Expected Outcomes**

**Benefits:** The results of experiments will provide an understanding of the O<sub>3</sub> and SOA formation potential of LVP-VOCs. The experimental results and analysis of the chamber experiments will allow for simulation of O<sub>3</sub> and SOA formation from emission of these compounds within regional air quality models that are used for SIP analysis and an assessment of the potential air quality impacts if they are to continue to be exempted for use in consumer products. The regional modeling analysis will provide information to determine if LVP-VOCs should continue to receive exemptions from emissions control programs, or if the definition of LVP-VOCs should be adjusted.

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Vingarzan, R. (2004). "A review of surface ozone background levels and trends." Atmospheric Environment **38**(21): 3431-3442.

Zhang, Q., J. L. Jimenez, M. R. Canagaratna, J. D. Allan, H. Coe, I. Ulbrich, M. R. Alfarra, A. Takami, A. M. Middlebrook, Y. L. Sun, K. Dzepina, E. Dunlea, K. Docherty, P. F. DeCarlo, D. Salcedo, T. Onasch, J. T. Jayne, T. Miyoshi, A. Shimono, S. Hatakeyama, N. Takegawa, Y. Kondo, J. Schneider, F. Drewnick, S. Borrmann, S. Weimer, K. Demerjian, P. Williams, K. Bower, R. Bahreini, L. Cottrell, R. J. Griffin, J. Rautiainen, J. Y. Sun, Y. M. Zhang and D. R. Worsnop (2007). "Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes." Geophys. Res. Lett. **34**(13): L13801.

## Project Schedule

**Task 1:** Select LVP-VOCs for study

**Task 2:** Compare theoretical and actual volatility of LVP-VOCs in consumer product formulations

**Task 3:** Measure ozone formation potential of LVP-VOCs in consumer product formulations

**Task 4:** Measure SOA formation potential of LVP-VOCs in consumer product formulations

**Task 5:** Model ozone and SOA formation from LVP-VOCs in smog chamber experiments

**Task 6:** Model regional ozone and SOA formation from LVP-VOCs in California

**Task 7:** Project Deliverables

Year 1	PERIOD	1	2	3	4	5	6	7	8	9	10	11	12	
TASK														
1														
2														
3														
4														
5														
6														
7														
		m		p		m		p		m		p		

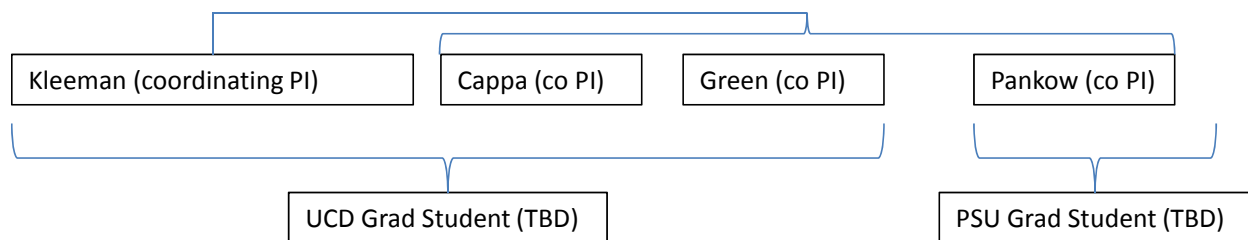
Year 2	PERIOD	1	2	3	4	5	6	7	8	9	10	11	12	
TASK														
1														
2														
3														
4														
5														
6														
7														
		m		p		m		p		m				

Year 3	PERIOD	1	2	3	4	5	6	7	8	9	10	11	12	
TASK														
1														
2														
3														
4														
5														
6														
7														
		m		p		m		p		m				F

p = Quarterly progress report; f = Deliver final report; m = Meeting with ARB staff

## Project Management Plan

### a. Organizational Chart



### b. Summary of responsibilities

Kleeman will act as coordinating PI. He is an expert at regional modeling of ozone and SOA formation. He will incorporate smog chamber models for ozone and SOA formation from LVP-VOCs into regional models for ozone and SOA formation in California. Kleeman will be responsible for one co-supervising one graduate student who will work on chamber experiments and regional modeling.

Cappa is an expert on SOA formation from parent hydrocarbons and soot generation with flames. He will be responsible for the generation of background aerosols in the smog chamber experiments, and measurement of SOA formation rates in smog chamber experiments. Cappa is also an expert on SOA formation predictions. He will be responsible for one of the models used to predict SOA formation in chamber experiments.

Green is an expert on ozone formation from VOCs contained in pesticides. He will be responsible for conducting smog chamber experiments over a range of NO<sub>x</sub> concentrations and under different RH conditions.

Pankow is an expert on SOA prediction using advance models that consider the effects of mixtures on SOA partitioning. He will be responsible for one of the models used to predict SOA formation in smog chamber experiments.

### c. Management

Funds will be administered through the UC Davis Office of Sponsored Research and the Department of Civil and Environmental Engineering staff. Monthly project meetings will be held to discuss sampling approaches, logistics of sample collection, laboratory analysis, and final data analysis in preparation for publication of results in peer-reviewed journals.

## d. Curriculum vitae for key personnel

**MICHAEL J. KLEEMAN, Professor**

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[mjkleeman@ucdavis.edu](mailto:mjkleeman@ucdavis.edu); <http://cee.engr.ucdavis.edu/faculty/kleeman/>; 530-752-8386**PROFESSIONAL PREPARATION:**

University of Waterloo, Ontario, Canada	Mechanical Engineering	B.A.Sc. 1993
California Institute of Technology, CA	Environmental Engineering Science	M.S. 1994
California Institute of Technology, CA	Environmental Engineering Science	Ph.D. 1998

**APPOINTMENTS:**

University of California, Davis	Assistant Professor	Jan 1999 – June 2003.
University of California, Davis	Associate Professor	July 2003 – June 2006.
University of California, Davis	Professor	July 2006 – present.

**Honors**

1993-1994	California Institute of Technology Knapp Fellowship
2007	California Air Resources Board Silver Superior Accomplishment Award
2008	US Environmental Protection Agency Scientific and Technological Achievement Award Level III

**Professional Service**

2010 - Editorial Advisory Board, Atmospheric Environment

**5 RELATED PUBLICATIONS**2001 Kleeman M.J., G.R. Cass. A 3D Eulerian source-oriented model for an externally mixed aerosol. *Environmental Science & Technology* 35: 4834-4848.2003 Aw J., M.J. Kleeman. Evaluating the first-order effect of intraannual temperature variability on urban air pollution. *Journal Of Geophysical Research-Atmospheres* 108: 4365.2006 Ying Q, M.J. Kleeman. Source contributions to the regional distribution of secondary particulate matter in California. *Atmospheric Environment* 40: 736-7522009 Hixson, M., A. Mahmud, J. Hu, S. Bai, D. Niemeier, S.L. Handy, S. Gao, J.R. Lund, D. Coe Sullivan, and M.J. Kleeman. Influence of Regional Development Policies and Clean Technology Adoption on Future Air Pollution Exposure. *Atmospheric Environment*, 44, 552-562.2010 Chen, J., C. Jakober, S. Clegg, and M.J. Kleeman. Theoretical vs. Observed Gas-Particle Partitioning of Carbonyl Emissions from Motor Vehicles. *Journal of the Air and Waste Management Association*, accepted for publication.

## **5 OTHER PUBLICATIONS**

1998 Kleeman, M.J., J.J. Schauer, and G.R. Cass. Size and Composition Distribution of Fine Particulate Matter Emitted from Wood Burning, Meat Charbroiling and Cigarettes. *Environmental Science, and Technology*, 33:3516-3523.

2000 Kleeman, M.J., J.J. Schauer, and G.R. Cass. Size and Composition Distribution of Fine Particulate Matter Emitted from Motor Vehicles. *Environmental Science, and Technology*, 34:1132-1142.

2001 Chung A., J.D. Herner, M.J. Kleeman. Detection of alkaline ultrafine particles at Bakersfield California. *Environmental Science, and Technology*, 35: 2184-2190.

2006 Jakober, C.A., M.J. Charles, M.J. Kleeman, P.G. Green. LC-MS Analysis of Carbonyl Compounds and Their Occurrence in Diesel Emissions. *Analytical Chemistry*, 78: 5086-5093.

2007 Riddle, S., M.A. Robert, C.A. Jakober, M.P. Hannigan, M.J. Kleeman. Size Distribution of Trace Organic Species Emitted from Heavy-Duty Diesel Vehicles. *Environmental Science and Technology*, 41: 1962-1969.

## **SYNERGISTIC ACTIVITIES**

- My research group recently completed a study of how climate change may affect air quality in various locations throughout the United States. (CARB Project #04-349; EPA Project #RD83337201). This project involved extensive downscaling of GCM results to the regional scale using the WRF model. The findings from this study helped quantify the inter-annual variability of air quality in California relative to the changes induced by climate.
- I am PI for a project funded by the US EPA (#RD-83184201) to study how future patterns of urban growth and in the San Joaquin Valley will affect air quality. The insights gained from future emissions in California will be contrasted against the results of the diesel emissions program studied in the current project.
- My research group is participating in the San Joaquin Valley Health Effects Research Center sponsored by the USEPA (EPA Project # R832414-010). This effort includes a large modeling component including extensive meteorological simulations using the WRF model. The resources available for this project provide a support network for the modeling exercises proposed in the current research.
- I am PI for a project funded by the US EPA (#R833372) to construct a source-oriented version of the WRF –CHEM model and to apply this model using emissions profiles for transportation sources using biofuels (ethanol, biodiesel) under different climate conditions. The source-oriented WRF-CHEM model created under project #R833372 is central to the proposed simulations in the current project. Project #R833372 will also improve the quality of the basecase emissions inventory produced for current and future climate periods.



## **CHRISTOPHER DAVID CAPPA**

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### **EDUCATION**

- Ph.D., Physical Chemistry, University of California, Berkeley, 2005 (with Ronald C. Cohen and Richard J. Saykally)
- B.S. with Honors, major in Chemistry, minor in Environmental Science, 2000, Hope College

### **RESEARCH EXPERIENCE**

- Post-doctoral Research Associate, University of Colorado Cooperative Institute for Research in Environmental Sciences and National Oceanic and Atmospheric Administration-Earth System Research Laboratory Chemical Sciences Division, 2005-2007 (with A. R. Ravishankara)

### **TEACHING EXPERIENCE**

- Assistant Professor, University of California, Davis (2007-...)  
Courses taught include: Global Climate Change (ECI 289A), Air Pollution Control System Design (ECI 150), Air Pollution (ECI 149), Aerosols Lab (ECI 247L)
- Graduate Student Instructor, University of California, Berkeley,  
Chemistry 1A, General Chemistry (2000)  
Chemistry 4B, General Chemistry and Quantitative Analysis (2002)  
Chemistry 125, Physical Chemistry Laboratory (2003)
- Teaching Assistant, Hope College  
Inorganic Chemistry (1998)

### **HONORS AND AWARDS**

- ACCESS participant (2005)
- Advanced Light Source Doctoral Fellowship in Residence (2004-2005)
- National Defense Science and Engineering Graduate Fellowship (2001-2004)
- NASA Earth System Science Fellowship (2001, Declined)
- Berkeley Atmospheric Sciences Center Fellowship (2001)
- AMS/DOE ARM Program Graduate Fellowship (2000-2001)
- NSF Graduate Research Fellowship Honorable Mention (2000, 2001)
- Phi Beta Kappa, Hope College Chapter (2000)
- Pharmacia-Upjohn Research Award at Hope College (2000)
- Gene Van Tamelen Award for Creativity in the Sciences at Hope College (2000)
- Sigma Xi (2000)
- Junior Chemistry Journal Award at Hope College (1999)
- Jaeker Chemistry Scholarship at Hope College (1998-2000)

## FIVE RELATED PUBLICATIONS

Cappa, C. D., Zhang, X., Loza, C. L., Craven, J. S., Yee, L. D., Seinfeld, J. S.; "Application of the Statistical Oxidation Model (SOM) to secondary organic aerosol formation from photooxidation of C12 Alkanes." *Accepted, Atmospheric Chemistry and Physics*.

Ruehl, C. R.; Chuang, P. Y.; Nenes, A.; Cappa, C. D.; Kolesar, K. R.; Goldstein, A. H.; "Strong evidence of surface tension reduction in microscopic aqueous droplets." *Geophys. Res. Lett.*, **2012**, 39, L23801, doi:10.1029/2012GL053706.

Cappa, C. D. and Wilson, K. R.; "Multi-generation gas-phase oxidation, equilibrium partitioning and the formation and evolution of secondary organic aerosol." *Atmospheric Chemistry and Physics*, **2012**, 12, 9505-9528, doi:10.5194/acp-12-9505-2012.

Cappa, C.D. and Wilson, K.R.; "Evolution of organic aerosol mass spectra upon heating: Implications for OA phase and partitioning behavior." **2011**, *Atmospheric Chemistry and Physics*, *11*, 1895-2011.

Cappa, C.D.; "A Model of Aerosol Evaporation Kinetics in a Thermodenuder." *Atmospheric Measurement Techniques*, **2010**, 3, 579-592.

**Peter G. Green, Associate Research Engineer**

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**Education**

1984	B.S.	Chemistry	Stanford University
1989	Ph.D.	Physical Chemistry	Massachusetts Institute of Technology

**Positions**

1989-1992	Post-doctoral Researcher, California Institute of Technology
1992-2000	Senior Scientist (staff), Environmental Engineering Science, Caltech
2000-2007	Assistant Research Engineer, CEE, UC Davis
2007-present	Associate Research Engineer, CEE, UC Davis

**Honors**

Undergraduate degree earned with university distinction as well as departmental honors  
Phi Beta Kappa and NSF Pre-doctoral fellowship

**Affiliations**

Society for Environmental Toxicology and Chemistry  
UC Davis John Muir Institute for the Environment  
UC Davis Agricultural and Environmental Chemistry graduate group  
2004-2006 Air Quality Advisory Committee, for California ARB, reviewing ozone and NO<sub>2</sub> standards UC Davis Air Quality Research Center

**Five Related Publications**

Reactive Organic Gas Emissions from Livestock Feed Contribute Significantly to Ozone Production in Central California. Cody J. Howard, Anuj Kumar, Irina Malkina, Frank Mitloehner, Peter G. Green, Robert G. Flocchini, and Michael J. Kleeman. Environmental Science and Technology 44, pp2309-2314 (2010).

Identification and Quantitation of Volatile Organic Compounds Emitted from Dairy Silages and Other Feedstuffs. Malkina Irina L.; Kumar Anuj; Green Peter G.; Mitloehner Frank M., Journal of Environmental Quality, Volume: 40 Issue: 1 Pages: 28-36 (2011).

Volatile organic compound emissions from green waste composting: Characterization and ozone formation. Kumar Anuj; Alaimo Christopher P.; Horowitz Robert; Mitloehner Frank M.; Kleeman Michael J.; and Green Peter G. Atmospheric Environment 45:10 1841-1848 (2011).

Determination of Volatile Organic Compound Emissions and Ozone Formation from Spraying Solvent-based Pesticides. Kumar Anuj; Howard Cody J.; Derrick Doniche; Malkina Irina L.; Mitloehner Frank M.; Kleeman Michael J.; Alaimo Christopher P.; Flocchini Robert G.; and Green Peter G. Journal of Environmental Quality, 40: 5, Pages: 1423-1431 (2011).

Mobile Source & Livestock Feed Contributions to Regional O<sub>3</sub> Formation in Central California. J.Hu, C.J.Howard, F.Mitloehner, P.G.Green, and M.J.Kleeman. Environmental Science & Technology, 46 p2781-2789 (2012).

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**PROFESSIONAL PREPARATION:**

1973 State University of New York (SUNY) at Binghamton (B.A. in Chemistry with Honors)  
1976 California Institute of Technology (M.S. in Environmental Engineering Science)  
1979 California Institute of Technology (Ph.D. in Environmental Engineering Science)

**APPOINTMENTS:**

1973-1978 California Institute of Technology, Pasadena, California. Department of Environmental Engineering Science, Graduate Research and Teaching Assistant.  
1978-2008 OGI/OHSU, 20000 NW Walker Rd., Beaverton, OR 97006. Department of Environmental & Biomolecular Systems, Instructor to Professor.  
2008-present Professor, Portland State University, Portland, Oregon.

**HONORS & AWARDS**

2009 Elected, National Academy of Engineering  
2005 Haagen-Smit Prize (<http://geo.arc.nasa.gov/sgg/singh/winners5.html>)  
1999 Creative Advances in Environmental Science and Technology, American Chemical Soc.  
1993 John Wesley Powell Award (U.S. Geol. Survey National Citizen Achievement Award).

**PROFESSIONAL SERVICE**

Reviewer: Numerous peer reviewed journals; NSF, NIH, California Tobacco Related Diseases Research Program (TRDRP).  
Past Associate Editor, *Environmental Science and Technology*.

**FIVE RELATED PUBLICATIONS**

Pankow JF (1994) An absorption model of gas/particle partitioning in the atmosphere. *Atmos. Environ.*, 28, 185-188.  
Pankow JF (2003) Gas/particle partitioning of neutral and ionizing compounds to single and multi-phase aerosol particles. 1. Unified modeling framework. *Atmos. Environ.*, 37, 3323-3333.  
Pankow JF, Chang EI (2008) Variation in the sensitivity of predicted levels of atmospheric organic particulate matter (OPM). *Environ. Sci. Technol.* 42, 7321-7329.  
Pankow JF (2010) Organic particulate material levels in the atmosphere: Conditions favoring sensitivity to varying relative humidity and temperature, *Proc. Nat. Acad. Sci.*, 107, 6682-6686. doi:10.1073/pnas.1001043107.  
Pankow, J.F. (2013) Equations for the sensitivity of the equilibrium mass concentration of organic particulate matter with respect to changes in ambient parameters: A technical note. *Atmospheric Environment*, 64, 374-379.

## **FIVE OTHER PUBLICATIONS**

- Pankow JF (1994) An absorption model of the gas/aerosol partitioning involved in the formation of secondary organic aerosol. *Atmos. Environ.*, 28, 189-193.
- Erdakos GB, Pankow JF (2004) Gas/particle partitioning of neutral and ionizing compounds to single and multi-phase aerosol particles. 2. Phase separation in liquid particulate matter containing both polar and low-polarity organic compounds. *Atmos. Environ.*, 38, 1005-1013.
- Pankow JF, Luo W, Melnychenko AN, Barsanti KC, Isabelle LM, Chen C, Guenther AB, Rosenstiel TN (2011) Volatilizable Biogenic Organic Compounds (VBOCs) with Two Dimensional Gas Chromatography-Time of Flight Mass Spectrometry (GC×GC-TOFMS): Sampling Methods, VBOC Complexity, and Chromatographic Retention Data, *Atmos. Meas. Tech.*, 5, 345-361 (<http://www.atmos-meas-tech.net/5/345/2012/amt-5-345-2012.pdf>).
- Perraud, V, Bruns EA, Ezell MJ, Johnson SN, Yu Y., Alexander, L, Zelenyuk, A, Imre D, Chang WL, Dabdub D, Pankow JF, Finlayson-Pitts BJ (2012) Nonequilibrium atmospheric secondary organic aerosol formation and growth. *Proc. Nat. Acad. Sci.*, 109, 2836-2841.
- Rosenstiel, T.N., Shortlidge, E.E., Melnychenko, A.N., Pankow J.F., Eppley, S.M. (2012) Sex-specific volatile compounds influence microarthropod-mediated fertilization of moss. *Nature*, 489, 431-433.

## **SELECTED SYNERGISTIC ACTIVITIES**

- My research group is actively engaged in the study of how water affects predicted organic PM levels in (EPRI). This project involves both box and regional modeling with CMAQ.
- My research group is also working to provide a general framework for how amines used in post combustion CO<sub>2</sub> capture may behave in the atmosphere as a consequence of unintended release (EPRI).
- I am PI for a project funded by the US Geological Survey Research to design and build an autonomous stream water sampler for a study to be conducted between March 1, 2013 and February 28, 2014 by staff of USGS and EPA. PSU will also be providing logistical support to researchers using the PSU Autonomous Stream Water Sampler (PSU-ASWS).

## Related Research

### Kleeman:

**California Regional PM<sub>10</sub>/PM<sub>2.5</sub> Air Quality Study (CRPAQS) Modeling Analyses of Data Captured during the CRPAQS Field Program.** Funded by the California Air Resources Board. This project aimed to apply source-oriented photochemical models to the data collected during the CRPAQS field program to (1) demonstrate the models are able to predict the measured pollutant concentrations, and (2) use the source-oriented features of the model to identify regional source contributions to wintertime airborne particulate matter.

**Regional Development, Population Trend, and Technology Change Impacts on Future Air Pollution Emissions.** Funded by the US EPA. This project aims to determine if local policies enacted in California's San Joaquin Valley can significantly impact air quality in the region. Policies considered include landuse (smartgrowth), agricultural development, transportation policies, and climate-change policies.

**Impact of Global Change on Urban Air Quality via Changes in Mobile Source Emissions, Background Concentrations, and Regional Scale Meteorological Feedbacks.** Funded by the US EPA. This project aims to understand the changes to the emissions inventories and the feedbacks between meteorology and air quality that will determine how PM<sub>2.5</sub> responds to climate change. Emissions from mobile sources powered by biofuels (ethanol and biodiesel) were measured over a range of temperature and humidity. A source-oriented version of the WRF-CHEM model is being created that can better represent aerosol optical properties and cloud interactions when particles from different sources are tracked separately through the atmosphere.

**Enhanced Air Pollution Epidemiology using a Source-Oriented Chemical Transport Model.** Funded by the US EPA. This project will use air quality model predictions as inputs to epidemiology studies. The goal is to use model results to fill in the gaps for missing measurement information (both space and time). Simulations of surface-air quality over California are being analyzed for the years 2000-07.

**Kleeman Completed Research (10 most recent projects out of a total of 14)**

1. “Advanced Modeling of Airborne Particulate Matter in the San Joaquin Valley - 2000-05PM” PI for a project funded by the California Air Resources Board, July 2000 – December 2004. Total Funding: \$666,629
2. “Assessing Changes in PM<sub>2.5</sub> Due to Changes in Temperature - R 82824201”. PI for a project funded by the Environmental Protection Agency, April 2000 – December 2003. Total Funding: \$142,816
3. “Advanced Data Analysis for the Central California Ozone Study (CCOS)-01-3CCOS” PI for a project funded by the California Air Resources Board, June 2001 – June 2003. Total Funding: \$115,009
4. “Source Apportionment of Fine and Ultrafine Particles in California”. PI for a project funded by the California Air Resources Board, May 2003 – May 2006. Total Funding: \$429,904
5. “Source Apportionment of Fine and Ultrafine Particles in California: Extended Heavy Duty Diesel Measurement of Ultrafine Particles”. PI for a project funded by the Coordinating Research Council, May 2003 – May 2006. Total Funding: \$36,611
6. “Air Pollutants: Cardiovascular Effects and Mechanisms”. Co-PI for a project funded by the Environmental Protection Agency, December 2003 – December 2005. Total Funding: \$373,750
7. “Photochemical Ozone Formation Potential of Agricultural VOC Emissions”. Co-PI for a project funded by the US Department of Agriculture, March 2004 – June 2005. Total Funding: \$356,594
8. “Source-Oriented Chemical Transport Model for Primary and Secondary Organic Aerosol” PI for a project funded by the Environmental Protection Agency, January 2003 – December 2008. Total Funding: \$450,000
9. “Agriculture Pesticide VOC Sources and their Photochemical Ozone Formation Potential” Co-PI for a project funded by the US Department of Agriculture, March 2005 – June 2008. Total Funding: \$374,099
10. “Impact of climate change on meteorology and regional air quality in California”. PI for a project funded by the California Air Resources Board, July 2005-June 2010. Total Funding: \$300,415

**Cappa:**

**Organic Aerosol Volatility, Phase and Partitioning.** Funded by NSF. This project aims to understand the relationships between organic aerosol composition and physical properties.

**Characterizing and Understanding Aerosol Optical Properties: CARES.** Funded by DOE. This project is focused on analysis of ambient measurements of aerosol optical properties and establishing how they depend on chemical composition.

**Characterization of Particulate Emissions from Ships from in situ Measurements,** Funded by U.S. EPA. Atmospheric aerosol particles have important influences on global climate, precipitation, visibility and human health. Direct emissions of particulate matter from commercial ships are a growing concern, yet emissions inventories for ships are based on an extremely limited data set. This project aims to significantly expand our understanding of particulate matter (PM) emissions from large ocean going vessels, especially container ships, by combining measurements made using the UCD MW-PAS/CRD instrument with a variety of measurements made by other researchers.

**Observations and interpretation of aerosol optical properties from field measurements: from the Arctic (ICEALOT) to California (CalNex),** Funded by NOAA. Aerosol particles play a crucial role in regulating Earth's climate, yet there remains a high level of uncertainty regarding radiative forcing by aerosols. This uncertainty must be reduced if we are to predict with confidence future climate and the societal impacts of climate change at increasingly smaller spatial scales. Of particular importance is the role played by absorbing aerosols, as they influence the surface radiation budget and the distribution of heat between the surface and the atmosphere. This project has two primary objectives associated with the characterization and quantification of light absorption by atmospheric aerosols: 1) analysis of data collected as part of the 2008 ICEALOT campaign and 2) preparation for and participation in the 2010 CalNex campaign. The proposed analysis and measurements will help to advance our understanding of the influence of atmospheric aerosols on the Earth's climate.

**Heterogeneous OH Chemistry and Aerosol Optical Properties: Direct and Indirect Connections,** Funded by NSF. This project aims to characterize how the optical properties and hygroscopicity of model organic aerosol evolve as they are oxidized through heterogeneous chemical reactions. The primary instrumentation used in this project is the UCD MW-PAS/CRD.



## Publications List

### Kleeman:

Howard, C., A. Kumar, I. Malkina, P. Green, R. Flocchini, **M.J. Kleeman**. Reactive Organic Gas Emissions from Livestock Feed Contribute Significantly to Ozone Production in Central California. *Environmental Science and Technology*, 44, 2309-2314, **2010**.

**Kleeman, M.J.**, Riddle, S.G., Robert, M.A., Jakober, C.A., Fine, P.M., Hays, M.D., Schauer, J.J. and Hannigan, M.P. Source Apportionment of Fine (PM<sub>1.8</sub>) and Ultrafine (PM<sub>0.1</sub>) Airborne Particulate Matter During a Severe Winter Pollution Episode. *Environmental Science and Technology*, DOI: 10.1021/es800400, **2008**.

**Kleeman, M.J.**, S.G. Riddle, and C.A. Jakober. Size Distribution of Particle-Phase Molecular Markers During a Severe Winter Pollution Episode. *Environmental Science and Technology*, 42, pp4697-4703, **2008**.

Riddle, S., M.A. Robert, C.A. Jakober, M.P. Hannigan, and **M.J. Kleeman**. Size-resolved Source Apportionment of Airborne Particulate Matter in a Roadside Environment. *Environmental Science and Technology*, 42, pp6580-6586, **2008**.

**Kleeman, M.J.**, S.G. Riddle, M.A. Robert, and C.A. Jakober. Lubricating Oil and Fuel Contributions to Particulate Matter Emissions from Light Duty Gasoline and Heavy Duty Diesel Vehicles. *Environmental Science and Technology*, 42, pp235-242, **2008**.

### Cappa:

**Cappa, C. D.**, Zhang, X., Loza, C. L., Craven, J. S., Yee, L. D., Seinfeld, J. S.; "Application of the Statistical Oxidation Model (SOM) to secondary organic aerosol formation from photooxidation of C<sub>12</sub> Alkanes." *Accepted, Atmospheric Chemistry and Physics*.

Ruehl, C. R.; Chuang, P. Y.; Nenes, A.; **Cappa, C. D.**; Kolesar, K. R.; Goldstein, A. H.; "Strong evidence of surface tension reduction in microscopic aqueous droplets." *Geophys. Res. Lett.*, **2012**, 39, L23801, doi:10.1029/2012GL053706.

**Cappa, C. D.** and Wilson, K. R.; "Multi-generation gas-phase oxidation, equilibrium partitioning and the formation and evolution of secondary organic aerosol." *Atmospheric Chemistry and Physics*, **2012**, 12, 9505-9528, doi:10.5194/acp-12-9505-2012.

**Cappa, C.D.** and Wilson, K.R.; "Evolution of organic aerosol mass spectra upon heating: Implications for OA phase and partitioning behavior." **2011**, *Atmospheric Chemistry and Physics*, 11, 1895-2011.

**Cappa, C.D.;** "A Model of Aerosol Evaporation Kinetics in a Thermodenuder." *Atmospheric Measurement Techniques* , **2010**, 3, 579-592.

**Green:**

Quinone Emissions from Gasoline and Diesel Motor Vehicles. Chris A. Jakober, Peter G. Green, M. Judith Charles, Michael A. Robert, Sarah G. Riddle, Hugo Destailats and Michael J. Kleeman, ENVIRONMENTAL SCIENCE & TECHNOLOGY 41 (13): 4548-4554 JUL 1 2007

Cody J. Howard, Wenli Yang, Peter G. Green, Frank Mitloehner, Irina L. Malkina, Robert G. Flocchini, Michael J. Kleeman. Direct Measurements of the Ozone Formation Potential from Dairy Cattle Emissions Using a Transportable Smog Chamber. *Atmospheric Environment*, Vol 42, issue 21, pp 5267-77. 2008.

Chris A. Jakober, Michael A. Robert, Sarah G. Riddle, Hugo Destailats, M. Judith Charles, Peter G. Green and Michael J. Kleeman. Carbonyl Emissions from Gasoline and Diesel Motor Vehicles. *Environmental Science and Technology* v42 pp4697-4703 (2008).

Kumar A, Yang W, Howard CJ, Kleeman MJ, Derrick D, Green PG. Assessment of the Ozone Formation Potential from Pesticide Solvents Using a Mobile Ozone Chamber Approach *J ASTM Intl*, 2008 (5) 7.

Direct Measurements of the Ozone Formation Potential from Livestock and Poultry Waste Emissions. Cody J. Howard, Anuj Kumar, Frank Mitloehner, Kimberly Stackhouse, Peter G. Green, Robert G. Flocchini, and Michael J. Kleeman. *Environmental Science and Technology* 44, pp2292-2298 (2010).

## PROJECT ESTIMATED COST BY TASK

Task	Labor	Emp. Fringe Benefits	Subs, Consults	Equip	Travel Subsist	EDP	Copy Print	Mail Phone Fax	Materials Supplies	Analyses	Misc.	Overhead	Total
1	\$84,488	\$19,302	\$10,000	\$0	\$0	\$0	\$0	\$0	\$44,200	\$0	\$27,464	\$14,799	<b>\$200,253</b>
2	\$47,761	\$13,781	\$40,000	\$0	\$0	\$0	\$0	\$0	\$2,900	\$0	\$5,654	\$8,944	<b>\$119,040</b>
3	\$23,501	\$3,171	\$50,000	\$0	\$0	\$0	\$0	\$0	\$2,900	\$0	\$17,812	\$7,957	<b>\$105,341</b>
4	\$13,125	\$3,035	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$1,616	<b>\$17,776</b>
5	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$	<b>\$0</b>
<b>Total</b>	<b>\$168,875</b>	<b>\$39,289</b>	<b>\$100,000</b>	<b>\$0</b>	<b>\$0</b>	<b>\$0</b>	<b>\$0</b>	<b>\$0</b>	<b>\$50,000</b>	<b>\$0</b>	<b>\$50,930</b>	<b>\$33,316</b>	<b>\$442,410</b>

### Breakdown of Labor (%) assigned by Task:

**Task 1: 50%**

**Task 2: 28%**

**Task 3: 14%**

**Task 4: 8%**

**Task 5: 0%**