STATE OF CALIFORNIA

AIR RESOURCES BOARD

MEETING OF THE

RESEARCH SCREENING COMMITTEE

May 11, 2012
10:00 a.m.

Air Resources Board
Research Division
Cal/EPA Building
1001 I Street
Sacramento, CA 95814
(916) 445-0753

State of California
AIR RESOURCES BOARD

Research Screening Committee Meeting
Cal/EPA Headquarters Building
1001 I Street
Conference Room 510, 5th Floor
Sacramento, California 95814
(916) 445-0753

and

University of California, Los Angeles
Terasaki Life Sciences Building, Room 1100
610 Charles E. Young Drive East
Los Angeles, California 90095

May 11, 2012
10:00 a.m.

AGENDA

I. Approval of Minutes of Previous Meeting: March 9, 2012 — iii-xi

II. Discussion of a New Research Project: — v

1) "New Car Buyers' Intentions Toward Zero-Emission Vehicles," University of California, Davis, $250,000, Proposal No. 2744-274 — 1

III. Discussion of Draft Final Reports:

1) "Toxicity of Source-Oriented Ambient Aerosol," University of California, Davis, $838,934, Contract No. 06-331 — 7

2) "Effects of GSTM1 Genotype on Ozone-Induced Allergic Airway Inflammation," University of California, San Francisco, $747,990, Contract No. 03-315 — 13

3) "Environmental Exposures in Early Childhood Education Environments," University of California, Berkeley, $417,496, Contract No. 08-305 — 19

4) "Assessment of Baseline Nitrous Oxide Emissions in California Cropping Systems," University of California, Davis, $300,000, Contract No. 08-324 27

5) "SOA Formation: Chamber Study and Model Development," University of California, Riverside, $474,229, Contract No. 08-326 33

6) "Nocturnal Chemistry in the Urban Boundary Layer of Los Angeles," University of California, Los Angeles, $409,090, Contract No. 08-318 39

7) "Source Apportionment of Carbonaceous Aerosols Using Integrated Multi-Variant and Source Tracer Techniques and a Unique Molecular Marker Data Set," University of Wisconsin-Madison, $409,963, Contract No. 07-333 45

IV. Other Business:

1) Update on Annual Research Plan

State of California
AIR RESOURCES BOARD

Research Screening Committee Meeting
Cal/EPA Headquarters Building
1001 I Street
Conference Room 510
Sacramento, California 95814
(916) 445-0753

and

California Polytechnic State University
Engineering IV, Building 192
Room Number: 206
Street location: Corner of California Blvd. and Highland Drive
San Luis Obispo, California

March 9, 2012
9:00 a.m.

MINUTES

RSC Members in Attendance

Harold Cota
Chung Liu
Forman Williams
Suzanne Paulson
Daniel Costa
Steven Japar – via teleconference
Rachel Morello-Frosch – via teleconference

The Research Screening Committee (RSC or Committee) meeting convened at 9:00 a.m. The minutes of the December 2, 2011 meeting were approved.

I. Response to a Request for Proposals

1) "Investigate the Durability of Diesel Engine Emissions Controls," University of Denver, $289,678, Proposal No. 2734-273, RFP No. 11-309

   The Committee asked about identification of selective catalytic reduction (SCR) equipped vs. non-equipped truck. Staff asserted that since license plate info will be collected, the investigators will correlate it against the Department of Motor Vehicles data to ascertain model year – which, in turn, will answer whether or not the truck is SCR equipped. Additionally, the investigators will monitor for a blue cap on top of the

Diesel Exhaust Fluid tank that should provide clues to presence (or absence) of SCR.

The Committee noted that the funds seem too low for a study of this magnitude. Staff's response was the investigators have been doing on-road measurements for a long time and have adequate experience to handle these kinds of studies within a reasonable budget.

The Committee noted that the sample size of 1500 vehicles per site per year might not be enough vehicles in each category (diesel, compressed natural gas, diesel particulate filter-only, diesel particulate filter + selective catalytic reduction). Staff clarified that ARB will re-assess the program design after the first sampling year and adjust if necessary.

The Committee suggested that particle measurement instruments (particle sizing) should be loaned to the investigators to collect size data along with measuring mass.

The Committee also asked whether the program will be able to differentiate between emissions from a malfunctioning device vs. a high-emitter (or vehicles with minimal controls certified as a part of averaging process). Staff's response was, since ARB will have emissions data along with make and model, ARB should be able to separate out vehicles with malfunctioning devices from those that are using an averaging process for certification. Staff also clarified that this is a pilot study; the results of which may be used to improve future road-side inspection techniques.

The Committee asked if the data for trucks without controls could be used to improve the emission inventory for that vehicle category. Staff responded that we are only collecting data over a single acceleration, and the data will be inadequate to estimate on-road emission rates for the inventory. The data will be used to estimate the frequency and magnitude range of high emitters arising from deterioration, malfunction, or tampering. Staff also noted that ARB is conducting other on-road studies with portable emissions monitoring equipment over a range of real-world driving conditions in order to collect data that will help improve emission inventories and improve the way they are modeled.

Motion: Move to accept subject to the inclusion of comments from staff and the Committee.

The Committee approved the proposal.

II. New Research Projects

1) "Benefits of High Efficiency Filtration to Children with Asthma," University of California, Davis, $3,350,000, Proposal No. 2735-273

   The Committee expressed overall support, and the need for a study such as this one. They also expressed the importance of utilizing the expert advisory committee

that was assembled to help with the study. One Committee member had concerns that there was no discussion of housing stock or the effects of nearby busy roadways. They also expressed concern about air sampling only once every six months, which would fail to address seasonality. Staff responded that housing stock was not a determinant for selection criteria; however, information about the physical characteristics of homes and proximity to busy roadways would be gathered for use in analyses. Staff also explained that staggered enrollment will result in all seasons being addressed. Also, one member commented that there seemed to be an over-emphasis on measurements of ultrafine particles and ozone, and expressed concern over issues such as verification that filtration is being used and is functioning properly, and issues of mold in homes. Staff clarified how ultrafine and ozone data would be collected and used; explained that site visits and quarterly phone calls during the study, and diary records and smart thermostats would be used to validate filtration function and use; and explained that the mold concern was primarily for polyurethane foam samplers in the field, which would be investigated prior to starting the main study.

Several Committee members wanted to know more about the use of mattress covers in the study. A concern was that the mattress intervention would nullify effects of filtration, potentially biasing towards the null because those with filtration first would see continued benefits from the mattress covers after the filtration was removed. Staff agreed to ask the PI to investigate the anticipated time period required for children to establish a new asthma symptom baseline after using the covers, and to assess the percentage of asthmatic children that have dust mite allergen as an asthma trigger. Staff noted that the mattress covers are intended to reduce the reaction to house dust mites so that any change due to the reduction of airborne contaminants is more discernible.

The Committee was concerned about the utility of personal sampling in the study and the feasibility of gathering meaningful personal exposure data from children ages 6-12. Staff explained that personal sampling is planned only for a subset of the participants, that children have participated successfully in previous studies, and that it is hoped that the personal sampling will provide empirical data to support the modeling of personal exposure. Also, a Committee member questioned how diary entries would be confirmed and suggested the use of medical records to try and verify the participant's symptom diary. The Committee also recommended that households with smokers be excluded from the study, as this might significantly improve the study design. It was also recommended that the pilot study be conducted in one or two Spanish speaking homes. Staff agreed to pass along these recommendations to the PI.

Several Committee members expressed the importance of recording outdoor temperature and relative humidity data throughout the study and using it to determine the comparability of the meteorological conditions during the paired periods of monitoring. A Committee member had specific questions about the last part of the discussion on Objective 1 on page 53 of the proposal. The Committee also expressed concerns about how the study would address the large number of

variables, such as different allergies, ethnicity, age, etc. Staff pointed out that temperature and humidity indoors is relatively stable; however, it would be easy to get outdoor data from local meteorological stations, and the PI plans to do so. Staff also explained that the last part of Objective 1 was largely exploratory in nature, and was intended to make a global assessment of the effectiveness of filtration in homes. The PI had provided a publication that discusses the approach, but will be asked to clarify this part of the proposal. Finally, staff reiterated that the crossover control study design makes each child his or her own control, minimizing the effects of many confounding variables.

A Committee member stressed the importance of the pre-study measurements. Another member asked regarding the number and brands of filters to be used (still to be determined), whether VOCs would be measured (not unless additional funding becomes available, but ozone and VOCs will be filtered in about one-half the homes), and whether the removal effect of the filters vs. the house itself will be measured (any effect seen will be due to the filtration, because of the case control cross-over design of the study with each child's home having a year of sham filtration and a year of true filtration).

Motion: Move to accept subject to the inclusion of comments from staff and the Committee.

The Committee approved the proposal.

2) "Quantification of the Emission Reduction Benefits of Mitigation Strategies for Dairy Silage," University of California, Davis, $400,000, Proposal No. 2736-273

The Committee expressed support for the project. The Committee asked how the measurement would proceed given the large area of the emission sources at dairies. Staff explained that the PI will divide the silage pile into two areas, the operational face and the covered area. The measurement would focus on the open face. The Committee also expressed concern about cooperation of the dairy industry. Staff responded that the PI has secured the participating dairies. Additionally, the Committee requested more information on the measurement methodologies, and the data analysis plan for non-VOCs gases.

Motion: Move to accept subject to the inclusion of comments from staff and Committee.

The Committee approved the proposal.

3) "Emissions of Potent Greenhouse Gases from Appliance and Building Waste in Landfills," California Polytechnic State University, San Luis Obispo, $299,826, Proposal 2737-273.

The Committee expressed some concern that the landfill research was a landfill cover "hot spots" research project that may not be necessary as this is a methane

emissions issue that has previously been investigated. It was noted by staff that the references to sampling hot spots in the research was simply to take emission measurements at hot spots and random surface locations to allow representative sampling of the landfill surface for the materials of concern, which are high global warming potential greenhouse gases from waste foam.

The Committee expressed disappointment and concern over the poorly written section for the project objectives, noting that the background of the issue was not clearly represented in the proposal. It was also questioned why the landfill gas combustion system required sampling to detect the chlorofluorocarbon (CFC) and other potent greenhouse gases from waste foam, when it was assumed that several studies had already ascertained that emissions from these compounds were negligible from a typical landfill. Staff noted that, while it is true that landfill gas emission studies have covered toxic compound emissions adequately, including dioxins, actual studies of CFC emissions from landfill combustion systems are extremely limited in North America, with none available for California landfills.

Motion: Move to accept subject to the inclusion of comments from staff and Committee. Hal Cota abstained from voting.

The Committee approved the proposal.

4) "Quantifying the Comprehensive Greenhouse Gas Co-Benefits of Green Buildings," University of California, Berkeley, $180,000, Proposal No. 2738-273

A Committee member asked how the percent of effort would be dedicated to the research project. Staff explained that each team member would devote one quarter of their time to the project over eighteen months, which would be accomplished by working a longer number of hours over a few days per week. A Committee member also asked if staff was satisfied with the total number of buildings the research team proposed to work with to collect measured data. Staff said yes, of the 1300 buildings surveyed in the target population, it seems reasonable to collect measured data from at least 100 randomly selected buildings that respond to the survey.

Motion: Move to accept subject to the inclusion of comments from staff and the Committee.

The Committee approved the proposal.

5) "Modeling Household Vehicle and Transportation Choice and Usage," University of California, Davis, $300,000, Proposal No. 2739-273

A Committee member requested several clarifications on this proposal, including more details on the geography for classifying households, and whether the California subset of National Household Travel Survey data is representative of the

State (and if so, what metro areas). The member requested that residential self-selection be modeled as both a dependent and independent variable in this project. The member also inquired about the role of commute times and distance to work in vehicle ownership levels, and suggested that the vehicle ownership model should have clearer specifications on the voluntarily low vehicle ownership households, more detail on how mobility impairment plays out in household context, and explanation of the other socio-economic variables they will investigate. The member commented on page 16 of the proposal, requesting that, in addition to neighborhood, this project should consider regional factors such as location of shopping hubs and connectivity to services, and pointed out that the research team should look at existing literature on this topic. And finally, there was a request for greater clarification on how the researchers will address vehicles changing households over time, and on page 22, how the research team intends to map vehicles to households.

Motion: Move to accept subject to the inclusion of comments from staff and Committee.

The Committee approved the proposal.

6) "PIsCES: the Personal InteraCtive Eco-driving System," University of California, Davis, $297,783, Proposal No. 2740-273

The Committee expressed significant concerns about the safety of using a smartphone in the vehicle to receive eco-driving feedback, and one Committee member inquired whether there is evidence that Prius drivers (who already receive similar feedback) crash more. Staff described the safety precautions that the researchers plan to take and pointed out that eco-driving implies slower driving which is generally safer.

Motion: Move to accept subject to the inclusion of comments from staff and Committee with careful examination of the safety impacts.

The Committee approved the proposal. One Committee member voted against the proposal.

7) "Effects of Complete Streets on Travel Behavior and Exposure to Vehicle Emissions," University of California, Los Angeles, $200,000, Proposal No. 2741-273

Staff proposed that the Committee approve an addition of $50,000 (for a total of $250,000) to the proposal to analyze the exposure implications of complete street conversions for pedestrians, cyclists, and drivers. The Committee agreed that the exposure assessment of street users is important and essential for the proposed study. A Committee member asked if the investigators could collect exposure data using stationary monitors, and staff explained that personal monitors will provide more informative exposure measurements in evaluating the street users'

exposures to vehicle emissions. A Committee member suggested the title of the proposal include a reference to the exposure addition. The Committee requested that the investigators include details of the demographic criteria used and add crime rates as part of the selection criteria for matching the complete and incomplete twin streets for the difference-in-difference analysis.

Motion: Move to accept subject to the inclusion of comments from staff and the Committee, title change and the additional funds.

The Committee approved the proposal.

8) "Analyzing the Economic Benefits and Costs of Smart Growth Strategies," University of California, Berkeley, $300,000, Proposal No. 2742-273

Staff proposed to augment proposal funding by $30,000 (for a total of $330,000) to support the study team's evaluation of the economic impacts of smart growth strategies on low-income and minority communities. The Committee encouraged the study team to gather input – during the interview task – from a wide array of community-based organizations seeking to engage in local land use planning processes, and – in the case study task – to consider the impacts of changes in real estate costs on local businesses as well as households. The Committee also asked that the project's literature review include studies that evaluate the impacts of smart growth strategies on low-income and minority households, businesses and neighborhoods. Staff assured the Committee that the study's environmental justice component would include these activities.

Motion: Move to accept subject to the inclusion of comments from staff and the Committee and the additional funds. Forman Williams and Steven Japar abstained from voting.

The Committee approved the proposal.

III. Draft Final Reports

1) "Effects of Ozone Exposure on Cardiovascular Responses in Healthy and Susceptible Humans," University of California, San Francisco, $399,029, Contract No. 04-322

The Committee asked for several changes to the draft final report in addition to those requested by staff. One Committee member requested that the investigator reconsider claiming to have performed the first study on the topic. Another Committee member requested that the results for the most important endpoints be presented graphically in addition to tables. The member also noted that some of the results have large standard deviations, and asked that the investigators comment on how these standard deviations compare to those typically reported for these endpoints.

Motion: Move to accept subject to the inclusion of comments from staff and the Committee with graphical changes.

The Committee approved the report.

2) "In-Vehicle Air Pollution Exposure Measurement and Modeling," University of California, Irvine, $500,000, Contract No. 07-310

The Committee agreed that this is a comprehensive report. A Committee member suggested using "older technology" or "newer technology" instead of the age of vehicle in the report. The Committee suggested expanding the limitations and recommendations for future studies; and adding a comprehensive discussion to the report. A suggestion was made to identify the most sensitive variables and add the uncertainties for the models where they are discussed in the report. The report needs to clarify that the models will be applied to future epidemiological studies and that the current study only involved model development and validation. It was suggested to clearly state in the report that the 25 subjects involved in the collection of personal in-vehicle polycyclic aromatic hydrocarbons exposure data are from the National Children's Study cohort through National Institute of Environmental Health Sciences funding.

Motion: Move to accept subject to the inclusion of comments from staff and the Committee.

The Committee approved the report.

IV. Other Business

1) "ARB Staff Update on Annual Research Plan"

Staff provided the Committee with a status update of the 2012-2013 research planning effort. Staff are currently in the process of evaluating the 153 concepts received from the public for policy relevance and linkages to ARB's programs. Areas of particular importance in this planning cycle are: Advanced Clean Cars, ensuring effectiveness of rules, and integrating air quality and climate change programs. Staff met with ARB's Executive Office and Chiefs from other Divisions to discuss some preliminary recommendations and identify additional research gaps. A final list of projects will be presented to the Committee in May and to the Board for approval in June.

The meeting adjourned at 11:40 a.m.

DISCUSSION OF A NEW RESEARCH PROJECT
ITEM NO.: 1
DATE: May 11, 2012
PROPOSAL NO.: 2744-274

STAFF EVALUATION OF AN INTERAGENCY RESEARCH PROPOSAL

TITLE:	New Car Buyers Intentions Toward Zero-Emission Vehicles
CONTRACTOR:	University of California, Davis
PRINCIPAL INVESTIGATORS:	Kenneth Kurani, Ph.D. Thomas Turrentine, Ph.D
TOTAL AMOUNT:	$250,000
CONTRACT TYPE:	Interagency Agreement
CONTRACT TERM:	18 Months

For further information, please contact Fereidun Feizollahi at (916) 323-1509.

I. SUMMARY

New advanced light-duty vehicle technologies and designs, including those that reduce criteria pollutant and greenhouse gas emissions, continually evolve in response to consumer preferences and other market conditions. Total on-road fleet emissions and compliance with vehicle standards will therefore depend on consumers' willingness to purchase and use these advanced light-duty vehicles. This project's objective is to conduct a statewide survey and household interviews of California buyers of new vehicles to understand consumer attitudes, barriers, and motivators toward purchasing zero, near-zero, and low-emission vehicles. The project will produce a statistically robust representation of California's new car buying population to identify the factors that influence new-vehicle purchase decisions and the areas where additional policies, incentives, or outreach could be implemented to facilitate greater adoption rates of cleaner cars.

II. TECHNICAL SUMMARY

Objective

The main objective of this research is to collect information on the decision-making process and influencing factors on new light-duty vehicle buyers in California, with a particular focus on the barriers and motivations for near-zero and zero-emission vehicles (ZEV). The results of the research project will inform policy makers about the potential areas where policies, incentives, or outreach might be effective to remove significant barriers or enhance motivations for the adoption of near- or pure-ZEVs.

Background

Advanced light-duty vehicle technologies are needed to meet California's air quality and gas reduction goals. Recent amendments to ARB's light-duty vehicle emission program call for lower fleet average rates of criteria pollutants and greenhouse gases as well as an increasing zero (tailpipe) emission vehicle requirement. Manufacturers' compliance with these regulations and total emissions from the on-road light-duty fleet will depend, in part, on at least some consumers being willing to purchase new vehicles with lower emission profiles than are currently offered, including near- or pure-ZEVs. These ZEV-type vehicles include plug-in hybrid vehicles (e.g., Chevy Volt), range-extended battery electric vehicles, full-battery electric vehicles (e.g., Nissan Leaf), and hydrogen fuel cell vehicles (e.g., Honda Clarity). The production and sale of ZEVs is of special interest because these vehicles fulfill ZEV requirements while simultaneously lowering a manufacturer's fleet average emissions and can make a significant contribution to criteria pollutant and greenhouse gas emission reductions from the transportation sector.

Proposal Summary

The proposed research will enhance ARB's understanding of purchasers of new light-duty vehicles in California. The primary data collection method will be a statewide online survey, with supplemental data collected through household in-person interviews. The subcontractor will be responsible for identifying a sample of 1,700 households that is representative of the new car buying population in California; only households with a recent history of a new vehicle purchase will be eligible to participate.

The prime researchers will then develop a written survey to collect information related to the purchase process, factors and considerations influencing their ultimate purchase decision, social and environmental attitudes, consumer awareness and knowledge about ZEVs as well as basic household characteristics. The survey will be developed in a manner to allow for longitudinal analysis; both worded to maximize the number of questions to be included in potential future surveys if funding is available and as consistent as possible with prior, related surveys that would allow for additional historical data points to be included. From the survey respondents, roughly 40 volunteers representing populations of special interest, such as actual purchasers of ZEVs or purchasers of larger vehicle types that are unlikely to be offered as ZEVs in the near-term, will be interviewed in-person to provide additional details on or supplemental information to their survey responses, and richer context for their purchase decisions.

The research results will be presented in three main forms. For the survey, descriptive statistics on the responses will first be compiled, e.g., frequencies, distributions, and other summary statistics. Afterwards, multivariate analyses will be performed to correlate purchase decisions to personal, households, or contextual measures such as attitudes or socioeconomics. Lastly, interview transcripts will be analyzed and summarized to identify themes and compare the different market segments. Additionally, evaluating the combined results will help isolate any prevalent real or perceived barriers and motivators for ZEV purchases.

III. STAFF COMMENTS

Although past research has evaluated general consumer vehicle purchasing behavior or even consumer acceptance of ZEVs, those efforts occurred at a time when actual availability of ZEVs in dealer showrooms was more limited, the technology less mature, and fuel prices lower and less volatile. In addition, past research has not always emphasized consumer attitudes or other more subjective characteristics that might contribute to consumer perceptions, instead focusing on more empirical or technical metrics. Today and in the next few years, the landscape will be changing rather rapidly with greater availability of ZEVs utilizing more mature technologies offered on a greater

diversity of vehicle types and among more brands. This research project will provide an up-to-date picture of the current state of the new vehicle market in California and the consumers within that market, with a particular focus on where policy interventions may facilitate the removal of barriers or enhance motivations for consumer purchases of ZEVs.

Two prior drafts of this proposal were developed in close consultation with ARB staff and also reviewed by staff at the California Energy Commission and United States Environmental Protection Agency (U.S. EPA). Reviewers were generally positive about the need for the research and the qualifications of the research team. The main theme of the comments focused on providing additional background, description, or detail about the issues that the project would address. Notably, the discussion of the methods that would be employed to analyze the survey results seemed insufficient. The submitted proposal continues to lack details and staff recommends that this section be expanded to provide a more thorough discussion. Additionally, multiple staff expressed some skepticism on the use of the vehicle design games to gauge potential interest in ZEV technologies when many new car buyers are unlikely to be familiar enough with the various options on these technologies to respond knowledgeably. Staff had suggested de-emphasizing this component or including it only as a potential option, however the submitted proposal did not incorporate either of these suggestions. The submitted proposal provides a better justification for the design games, though to ensure that the primary objectives of this survey are met, staff recommends that this component only be included if space allows.

Lastly, as this research project has a California statewide focus, the South Coast Air Quality Management District has expressed interest in co-funding this project to provide additional detail for their air basin. Any co-funding would be used to recruit additional respondents in the South Coast region, analyze the regional results, and provide a comparison between the regional and statewide results. Given that South Coast represents the largest new vehicle market within the state as well as the air quality improvements required in the air basin, these more detailed regional results would provide further insight into multiple policies related to market potential, incentives and

infrastructure. Staff will update the Research Screening Committee on any commitments for co-funding.

This research team has been investigating consumer behavior related to alternative fuel vehicles for decades and the PI's are recognized experts in the field. They are also involved in complementary research projects, such as household interviews of Nissan Leaf owners in the San Diego region, which will provide them with additional perspective for interpreting the results of the statewide survey and interviews. Additionally, they may be able to leverage existing partnerships with industry and other government agencies to enhance the quality of the final deliverables.

IV. STAFF RECOMMENDATION

Staff recommends the Research Screening Committee approve this proposal for a total amount not to exceed $250,000, subject to inclusion of appropriate additions and revisions in response to the staff comments, and any changes and additions specified by the Committee.

DISCUSSION OF A DRAFT FINAL REPORT
ITEM NO.: 1
DATE: May 11, 2012
CONTRACT NO.: 06-331
Link to Report

STAFF EVALUATION OF A DRAFT FINAL REPORT

TITLE:	Toxicity of Source-Oriented Ambient Aerosol
CONTRACTOR:	University of California, Davis
PRINCIPAL INVESTIGATORS:	Anthony S. Wexler, Ph.D. Kent Pinkerton, Ph.D.
TOTAL AMOUNT:	$838,934 (ARB funding $461,515)
CONTRACT TYPE:	Interagency Agreement
CONTRACT TERM:	60 Months

For further information, please contact Dr. Alvaro Alvarado at (916) 445-4843.

I. SUMMARY

Ambient particulate matter (PM) has been associated with premature death and hospitalization, but it is unknown which components are the most responsible for the adverse health effects. Ambient PM derives from a wide range of sources and experiences a range of atmospheric processes that may alter its toxicity. Direct exposures of animals to PM emissions neglects the atmospheric photochemistry that may enhance toxicity, while exposure to total ambient PM combines the effect of many sources so that it does not elucidate which source contributes to the toxicity. This study used a single-particle mass spectrometer to selectively collect and separate ambient particles with a series of biosamplers attached to a particle concentrator. Mice were exposed to biosampler contents and studied for possible toxicity. The results demonstrated that there were clear differences in the physiological responses in mice exposed to particles from different biosamplers for a number of toxicological endpoints. The driving force of this project was to develop relative toxicity indices for particles or particle components derived from different source categories.

II. TECHNICAL SUMMARY

Objective

The objective of this project is to obtain toxicity profiles of atmospherically processed source-oriented fine and ultrafine particulate emissions.

Background

Ambient PM has been associated with adverse health effects including premature death and hospitalizations. To investigate the possible mechanisms of PM-mediated toxicity, the UC Davis investigators conducted animal health effects toxicity studies in the Central Valley at the San Joaquin Valley Aerosol Health Effects Research Center (SAHERC) located in Fresno, California. For these studies, concentrated ambient particles (CAPs) were generated via the Versatile Aerosol Concentration Enrichment Systems (VACES), which concentrates large amounts of ambient air particles. Rodents were then exposed to CAPs and their toxicity relative to filtered air was determined. CAPs exposure was found to be associated with changes in cellular changes in the lung consistent with inflammation. Although these studies were informative, CAPs represent the mixture of particles present in ambient air and could not be used to elucidate the relative contribution of each source or source components to toxicity.

For this study, the investigators used a ChemVol high volume cascade impactor (CV) to collect, identify, and segregate a variety of different particle types by pairing the instrument with an ultrafine single-particle mass spectrometer (RSMS-II). RSMS-II has been previously employed at four United States Environmental Protection Agency PM supersites to determine the chemical composition of individual ultrafine particles and associate these compositions with their sources. RSMS-II analyzes single-particle spectra and then classifies and identifies individual particles through the use of chemical compositions and shape indices. Each particle analyzed possesses a mass spectrum and, in real time, these spectra are classified into similar groups indicative of their primary emissions source and the degree of their atmospheric processing. The combination of a CV and RSMS-II allowed for the real-time collection and separation of particles into “bins” for future chemical and toxicological analysis.

The principal investigators used a RSMS-II enhanced CV system to select particles based on composition and measure their toxicity in a rodent model. Both “ultrafine” (UF; less than 170 nm) and “sub-micron fine” (SMF; 170-1000 nm) samples were obtained over several weeks, under different meteorological conditions. Particles having different compositions were separated into “bins” by the RSMS-II. Mice were exposed to UF and SMF samples of PM from these separate “bins” and analyzed for toxicologically-relevant changes in both lung and systemic biomarkers of inflammation. In addition, oxidative potential and average particle sizes of some PM samples were determined. This project was jointly funded by the Electric Power Research Institute (EPRI) and ARB.

Methods

Ambient particles (UF and SMF) were collected in Fresno, California using a CV attached to an SKC BioSampler impinger. A RSMS-II ultrafine single-particle mass spectrometer and a CV were located side-by-side at the same Fresno site where the investigators collected other SAHERC ambient samples in previous studies. This was completed from funds from a separate EPRI contract.

For Task One, the investigators used the real-time categorization capabilities of RSMS-II to control the sampling of ambient particles. A 10-position rotary valve directed the output from the CV to one of the biosamplers. The RSMS-II controlled the rotary valve such that each biosampler collected particles characteristic of one source profile. The RSMS-II was first operated to characterize the range of particle types found there using an improved version of an algorithm that the investigators developed for this project. A source profile was then defined by (1) detection of a single particle type, or (2) detection of multiple particle types that often appear together. After “training” the RSMS-II, the investigators operated the RSMS-II to obtain 40 biosamples: 10 each for two seasons (winter & summer) and two size fractions (SMF and UF). The investigators submitted an interim report upon completion of task one which was approved by staff from ARB and EPRI.

Task One involved constructing the instrumentation and samplers, collecting biosamples and characterizing them. It consisted of the following subtasks:

- Improving and test the data classification algorithm.
- Updating the RSMS-II.
- Designing, building, and testing a CV system that can sample into 1 of 10 pairs of computer selectable biosamplers.
- Designing, building, and testing the interface between the RSMS-II single particle mass spectrometer and the 10-position CV.
- Collecting source-oriented biosamples for summer and winter.
- Chemically characterizing the biosamples.

Through the combination of existing protocols and a desire to maximize recovery of PM-related components, the investigators developed a method of sequential sonication, and lyophilization in three different solvents to obtain the final samples for the toxicological assays in Task Two. In this task, the investigators used BalbC mice to obtain toxicity profiles of ambient particles collected for each biosampler. A fixed concentration of biosampler material was aspirated into the mouse lungs. After 24 hours, the investigators lavaged the lungs, isolated and assayed lung tissues for indicators of pulmonary inflammation, and analyzed for systemic inflammatory biomarkers in blood samples. The following were specific assay targets:

- Bronchoalveolar lavage fluid (BALF) supernatant was analyzed for protein content and cytotoxicity.
- The cell pellet fraction of the BALF was used to determine recovered cell numbers, cell viability, phagocytic index, and cell differential.
- Blood was analyzed for red and white blood cell counts, and percentages of neutrophils, lymphocytes, monocytes, eosinophils, and basophils.
- Physical properties of the PM samples such as oxidative potential and average particle size were measured.

Results

The investigators often found that, for a set of bins of a given season and size, the samples with the greatest response were not always consistent across the various toxicological endpoints. Despite this lack of consistency in toxicological endpoints, there was clear toxicological difference between individual samples for specific endpoints:

- Based on particle size, UF PM was a more potent inducer of inflammatory and cytotoxic response compared to SMF PM on a per mass basis.
- Measured oxidative potential was significantly higher for SMF compared to UF. The highest oxidative potential was seen in samples containing metals.
- The oxidative potential was positively correlated with bronchial alveolar lavage (BAL) protein for winter and negatively correlated with lactose dehydrogenase (LDH) levels for summer and winter.
- For pulmonary inflammation and cytotoxicity, samples containing PM from vehicular sources or metals had the high biological response for summer samples, while PM from vehicular sources, regional processes background, and nighttime inversions had the highest response for winter samples.
- In general, the same PM sample produced greater inflammatory and cytotoxic responses in lung samples than in the blood samples under the conditions used in this study.
- Analysis of systemic inflammation did not reveal major differences between the collected samples.

Conclusions

This project combined aspects from the latest in engineering technology and established animal toxicological techniques to produce a unique study. Given the novelty of the project and uncertainty in establishing consistent toxicological data for many endpoints for comparing any two PM samples, the process represented a high risk–high reward project. The project did not identify any particular sources as more or less “toxic” than another, which supports the need to control all components.

III. STAFF COMMENTS

ARB staff members and staff from EPRI commented on the report. Staff noted several editorial suggestions. These were conveyed to the investigator for inclusion in the final version of the report. The draft report summarizes the results of this project on the association between PM composition and different toxicity endpoints; however, additional information based on ongoing comprehensive chemical composition analysis of the PM is expected. In addition, this project has developed a comprehensive protocol for the isolation of PM from filters that will be valuable for future toxicological and chemical analysis projects.

IV. STAFF RECOMMENDATION

Staff recommends the Research Screening Committee accept this draft final report, subject to inclusion of appropriate additions and revisions in response to the staff comments and any changes and additions specified by the Committee.

DISCUSSION OF A DRAFT FINAL REPORT
ITEM NO.: 2
DATE: May 11, 2012
CONTRACT NO.: 03-315
Link to Report

STAFF EVALUATION OF A DRAFT FINAL REPORT

TITLE:	Effects of GSTM1 Genotype on Ozone-Induced Allergic Airway Inflammation
CONTRACTOR:	University of California, San Francisco
PRINCIPAL INVESTIGATOR:	John R. Balmes, M.D.
TOTAL AMOUNT:	$747,990
CONTRACT TYPE:	Interagency Agreement
CONTRACT TERM:	95 months

For further information, please contact Dr. Alvaro Alvarado at (916) 445-4843.

I. SUMMARY

Epidemiological data suggest that asthmatics may be more sensitive to Ozone (O_3) exposure than nonasthmatics, although the basis for this difference is largely unknown. Animal and human exposure studies have shown that O_3 exposure can enhance allergic inflammatory and bronchoconstrictor responses in the lungs, both of which are features of asthma. Several studies suggest that variant forms of the antioxidant gene that produces glutathione S-transferase 1 (GSTM1) may influence responses to inhaled O_3. A variant form of the GSTM1 gene (GSTM1 null), which occurs in 30 to 50 percent of the population, produces an inactive form of GSTM1 that has no antioxidant properties. It has been hypothesized that individuals with the inactive form of the GSTM1 gene would be more responsive to O_3 than individuals with the active form of the gene. This study compared the lung function and airway inflammatory responses of ten adult allergic asthmatics to allergen challenge. The subjects underwent four-hour intermittent exercise exposures to filtered air (FA) or 0.16 ppm O_3, which were followed twenty hours later by an allergen challenge (dust mite). Lung function, airway

inflammation and allergic responses were measured four hours after the allergen challenge. O_3 exposure induced the expected decrease in lung function, as well as larger decrements following the allergen challenge compared to FA exposure. There was a small, non-significant increase in lung inflammatory cells in response to the allergen challenge after O_3 compared to FA exposure, but unexpectedly, the levels of most inflammatory biomarkers were lower after the O_3 than the FA exposure. There were no significant differences in lung function response to O_3 between subjects with the two forms of the GSTM1 gene, but the inflammatory mediator response to allergen was consistently lower in the subjects with the inactive form of the gene, contrary to expectations.

II. TECHNICAL SUMMARY

Objectives

The project investigated two questions: 1) whether O_3 exposure enhances airway inflammatory responses of asthmatic subjects during late-phase reactions to allergen challenge, and 2) whether asthmatic subjects with the GSTM1 null genotype have greater allergic inflammatory responses than subjects who have GSTM1 present.

Background

Asthma is a disease characterized by airway inflammation, particularly during the late-phase response to allergen, and the degree of airway inflammation is an important predictor of asthma severity. Epidemiological evidence suggests that people with asthma are at increased risk for exacerbation when exposed to elevated levels of ambient O_3. However, controlled human exposure studies have not consistently shown subjects with asthma to have greater lung function responses to O_3 than non-asthmatics, although the neutrophilic airway inflammatory response in asthmatics does appear to be greater compared to non-asthmatics. However, lung function and airway inflammatory responses to O_3 are not well-correlated in healthy subjects. Thus, one possible explanation for the epidemiological findings is that O_3 exposure may enhance the inflammatory response to allergen. Animal toxicological data provide evidence that O_3 exposure can enhance allergic inflammatory responses in the lungs.

Controlled human exposure studies have confirmed that O_3 exposure can enhance both the early and late bronchoconstrictor responses to inhaled antigen in some, but not all allergic asthmatic subjects.

Oxidative stress, with the formation of reactive oxygen species (ROS) is a key component of inflammation. Although antioxidant defenses are available to detoxify ROS in the airway, individuals differ in their ability to deal with an oxidant burden, such as inhaled O_3, and such differences are, in part, genetically determined. Decreased ability to detoxify ROS may lead to enhanced airway inflammation, and thus potentially to increased bronchoconstriction and asthma symptoms. The glutathione S-transferase (GST) family of enzymes produces antioxidant enzymes that are critical to the protection of cells from ROS. GSTM1, one of the enzymes in this family, is produced by a gene that has a common variant form. Between 30 and 50 percent of the general population has the GSTM1 null form, which produces an inactive enzyme, while the rest of the population has the wildtype form of the gene, which produces the active form of the enzyme. Several studies have suggested that individuals who are GSTM1 null have enhanced lung function responses to O_3 exposure, and one study using a high concentration (0.4 ppm) showed an enhanced airway inflammatory response compared to subjects having the wildtype of the GSTM1 gene.

This study sought to address the literature inconsistencies and gaps described above as to whether the allergen interacts with O_3 exposure to enhance airway inflammatory responses in asthmatics, and whether GSTM1 genotype modifies airway inflammatory responses to O_3 exposure. The experiment used a repeated-measures design, each subject completing both exposures within the experiment, with the order of the exposures counter-balanced. Subjects were screened prior to beginning the experimental protocol so that 50 percent had the GSTM1 null genotype. Ten asthmatic subjects with specific sensitization to the house dust mite, *Dermatophagoides pteronyssinus* (DP), were exposed on separate occasions to 0.16 ppm O_3 and FA control for 4 h with intermittent exercise. At 20 h post-exposure, subjects underwent a challenge bronchoscopy during which DP allergen was instilled in a

sub-segmental bronchus of the right middle lobe and saline was instilled in a sub-segmental bronchus of the right upper lobe. Six hours later, a sampling bronchoscopy was performed to collect samples of airway lining fluid from each challenged bronchus for analyses of cellular and biochemical markers of non-specific and specific allergic inflammatory responses. Subjects underwent lung function testing pre- and immediately post-exposure, 18 h post-exposure, prior to and then hourly after the challenge bronchoscopy until the sampling bronchoscopy. The differences in lung function, airway cells, and airway inflammatory proteins after O_3-allergen exposure and FA-allergen exposure were compared.

The results of this study suggest that O_3, at least at the concentration (0.160 ppm) and exposure duration (4 h) tested, appears to have mixed effects on allergen-induced airway inflammation. O_3 exposure significantly enhanced the lung function response to allergen at 3 h-post allergen challenge, as expected. However, while airway neutrophils were non-significantly increased after O_3-allergen exposure compared to FA-allergen exposure, airway concentrations of most inflammatory mediators (interleukins 1b, 4, 5, 6, 8, 10, 13, tumor necrosis factor-α, granulocyte macrophage colony-stimulating factor) assayed were non-significantly lower after O_3-allergen exposure. Also contrary to expectations, the inactive form of GSTM1 was associated with a smaller, rather than larger, inflammatory cytokine response to allergen challenge after O_3 exposure. These results must be interpreted with caution, however, given the small sample size (n=10).

III. STAFF COMMENTS

The investigator submitted a previous draft of the final report, which was reviewed by ARB staff. The revised report sent to the Committee was reviewed by staff from ARB and OEHHA. Overall, the reviews concluded that the study had been well conducted, and that the report was well presented. The reviewers had some suggestions for improving clarity at several points in the report, particularly in the background and introduction sections. Reviewers also noted several typos and formatting inconsistencies that should be corrected in the final draft of the report. All of the comments and suggested revisions are minor in nature.

The original research proposal had planned for a larger sample size (n=30), but multiple problems contributed to the investigator's inability to meet this goal. First, the UCSF Committee on Human Research (CHR) expressed considerable concern about the safety of the protocol, and it took almost 2 years before the CHR concerns were addressed so that the project had CHR approval to go forward. CHR approval required many iterations of the protocols to address committee concerns related to the number of bronchoscopies, the allergen challenge, and the unexpected requirement that the investigator obtain approval from the United States Food and Drug Administration to administer the dust mite allergen. Second, the multiple bronchoscopies and allergen challenge procedure made recruitment and retention of subjects exceptionally difficult. The investigators screened over 500 potential subjects to find 10 who were willing and able to complete the study. Finally, one of the subjects experienced a severe anaphylactic reaction after his initial allergen exposure, which required CHR review of the study and changes to the allergen exposure protocol, adding to project delays. Fortunately, this subject recovered without long-term sequelae. Third, mechanical problems developed in the exposure chamber that prevented chamber control sufficient to allow for safe human exposures. Replacement parts for the chamber control system were no longer commercially available; therefore, the investigator had to redirect some monies to alteration and updating the exposure chamber control system, further delaying the project. Although the investigator was unable to meet all of the original goals of the project, the investigator anticipates that there will be two publications based on this work.

IV. STAFF RECOMMENDATION

Staff recommend the Research Screening Committee accept this draft final report, subject to inclusion of appropriate additions and revisions in response to the staff comments and any changes and additions specified by the Committee.

DISCUSSION OF A DRAFT FINAL REPORT
ITEM NO.: 3
DATE: May 11, 2012
CONTRACT NO.: 08-305
Link to Report

STAFF EVALUATION OF A DRAFT FINAL REPORT

TITLE:	Environmental Exposures in Early Childhood Education Environments
CONTRACTOR:	University of California, Berkeley
PRINCIPAL INVESTIGATOR:	Asa Bradman, Ph.D.
TOTAL AMOUNT:	$417,496
CONTRACT TYPE:	Interagency Agreement
CONTRACT TERM:	38 Months

For further information, please contact Peggy Jenkins at (916) 323-1504.

I. SUMMARY

This study sought to characterize the exposures of children to contaminants in child care centers and the potential risks posed by those exposures. The environmental characteristics of 40 California early childhood education (ECE) facilities and the contaminant levels in their air and dust were examined. The results showed that the highest concentrations of volatile organic compounds were d-limonene (from cleaning products) and decamethylcyclopentasiloxane (found in personal care products). For most chemicals, health-based dose or exposure benchmarks were not available, but when they were available, estimated exposures were usually below levels of concern. However, formaldehyde levels exceeded the California eight-hour reference exposure level (REL) and chronic reference exposure level (cREL) in 87.5 percent of facilities, and acetaldehyde concentrations exceeded the United States Environmental Protection Agency (U.S. EPA) reference concentration (RfC) in 30 percent of facilities. Levels of formaldehyde, acetaldehyde, chloroform, benzene, and ethylbenzene exceeded child-specific Safe Harbor Levels for cancer, based on Proposition 65 guidelines, in

several facilities. Child dose estimates for two brominated flame retardants (BDE-47 and BDE-99) exceeded the non-cancer U.S. EPA reference doses (RfDs) for children <1 year old in 10.3 percent of facilities. Concentrations for indoor PM10 collected over eight hours exceeded the level of the 24-hour California PM10 Ambient Air Quality Standard in 46 percent of the facilities. PM2.5 collected over eight hours exceeded the level of the U.S. EPA 24-hour PM2.5 standard in 11 percent of the facilities. Overall, the findings suggest that contaminant levels in ECE environments are similar to those measured in homes and schools in previous studies, but that mitigation strategies may be warranted to reduce exposures to some chemicals, especially formaldehyde, that exceed health benchmarks. This information will help ARB and other agencies better protect children's health by identifying key exposures that can be reduced through regulations, guidelines, or other approaches.

II. TECHNICAL SUMMARY

Objective

The objectives of this project were to: 1) measure levels of selected volatile organic compounds (VOCs), aldehydes, phthalate esters, flame retardants, perfluorinated compounds, pesticides, and particulate matter in the indoor air and floor dust of 40 ECE facilities located in urban and agricultural California communities, and 2) estimate the potential health risks associated with the indoor contaminant levels found. Outdoor air samples were collected at a subset of the facilities. Dust samples were collected and analyzed to quantify phthalates, perfluorinated compounds, flame retardants, pesticides, and lead. Questionnaires and detailed facility inspections were conducted to identify building characteristics and potential sources of exposure. Finally, child exposures were estimated and compared to health-based benchmarks and to results from other studies.

Background

It is estimated that around 1.1 million children ages five years or younger attend child care and preschool centers in California, and many infants and young children spend as much as 10 hours per day, 5 days per week, in child care and preschool centers. By the time they enter kindergarten, over 50 percent of all California children have attended some type of licensed child care facility. California has the largest number of licensed

child care centers in the United States at 49,000, 80 percent of which are family-based centers located in homes. Additionally, 146,000 staff work in California's licensed child care facilities.

Collectively, (ECE) facilities are varied and include home-based child care providers, centers operated like private schools, and programs run by government agencies (e.g., preschool in school districts or Head Start) or religious institutions. Recent studies indicate that ECE environments may contain lead, pesticides, allergens, and other contaminants hazardous to children's health. Because children exhibit exploratory behaviors that place them in direct contact with surfaces that may have contaminants present such as floors, walls, table tops, plastic toys etc., they are more likely to be exposed to those contaminants than adults. Children have proportionately higher exposures than adults because they breathe more air, eat more food, and drink more water per unit of body weight compared to adults. They are also less developed immunologically, physiologically, and neurologically and therefore may be more susceptible to the adverse effects of chemicals and toxins. Although several studies have looked at exposures in residential and school environments, this is the first large-scale study to examine exposures in early childhood education facilities.

Methods

For this study, levels of specified contaminants were measured in the air and floor dust of 40 ECE facilities located in Monterey (n=20) and Alameda (n=20) counties. Air samples were collected over an entire school day, for a typical sampling duration of 8-10 hours. Airborne VOC samples were collected using tubes with Tenax-TA sorbent, and then thermally desorbed and analyzed by gas chromatography/mass spectrometry (GC/MS). Aldehydes and other low molecular weight carbonyl compounds were derivatized to Dinitrophenylhydrazine (DNPH) on the XPoSure Aldehyde Sampler, eluted, and subsequently analyzed by high-performance liquid chromatography (HPLC). Gravimetric analysis was used to determine the mass of airborne PM2.5 and PM10 fractions using Teflon filters, and ultrafine particle numbers were determined using condensation particle counters. Semi-volatiles were collected on polyurethane foam

substrates and then analyzed by GC/MS/MID. Finally, dust samples were collected with a special vacuum device according to ASTM D 5483-94 and analyzed with the appropriate downstream method for the target analytes. Dust samples are particularly important for semi-volatile compounds because dust serves as a reservoir, or sink, for such compounds, and children experience a greater exposure to the dust contaminants than adults.

The screening risk assessment involved several steps. Measured concentrations of indoor air pollutants were compared to California chronic or acute reference exposure levels (RELs) or, for particulate matter, to the California 24-hour PM10 ambient air quality standard and the 24-hour PM2.5 national ambient air quality standard. Child exposure-dose estimates were calculated based on air concentrations, assumptions about inhalation and absorption, dust concentrations, non-dietary ingestion from house dust, and dermal absorption. For non-cancer causing compounds, exposure-dose estimates were compared to appropriate health-based benchmarks, such as U.S. EPA reference doses (RfDs). For potentially carcinogenic compounds, California's Proposition 65 "No Significant Risk Levels" (NSRLs) were used to define Safe Harbor Levels that account for the increased sensitivity of very young children. Age-adjusted NSRLs were calculated for four age groups (i.e., <1 year; 1 to <2 years; 2 to <3 years; and 3 to <6 years). The NSRL is defined as the daily intake level posing a one in 100,000 risk of cancer, assuming lifetime exposure. Child exposure estimates were compared to the age-specific NSRL benchmarks. The risk assessment presented in the final report provides preliminary information on the potential cancer and non-cancer health risks associated with documented exposures.

Results

Of the VOC compounds analyzed in air, d-limonene and decamethylcyclopentasiloxane were found to have the highest air concentrations, with median (range) values of 33 $\mu g/m^3$ (0.8-82 $\mu g/m^3$) and 51 $\mu g/m^3$ (2.6-88 $\mu g/m^3$) respectively. D-Limonene is a common solvent that is found in cleaning products, and decamethylcyclopentasiloxane is often used as a lubricant in personal care products. The median (range) concentrations for formaldehyde and acetaldehyde were 17.8 $\mu g/m^3$ (0.7-48.8 $\mu g/m^3$)

and 8.5 $\mu g/m^3$ (0.7-23.3 $\mu g/m^3$), respectively. Levels of formaldehyde exceeded the California eight-hour REL and chronic REL in 87.5 percent of the facilities. In several facilities, child inhalation exposure estimates for five VOC compounds (benzene, chloroform, ethylbenzene, acetaldehyde and formaldehyde) exceeded age-specific NSRL Safe Harbor Levels for carcinogenicity based on Proposition 65 guidelines.

For the semi-volatile compounds, phthalates were detected in 100 percent of the air and dust samples. Diethyl phthalate, diisobutyl phthalate, and butyl benzyl phthalate concentrations were significantly higher indoors than outdoors, and the highest concentrations found in dust were for those for diethylhexyl phthalate and butyl benzyl phthalate. Exposures to the phthalates were all below levels of concern. Analysis of flame retardants revealed that levels of organophosphate flame retardants in dust were higher than several polybrominated flame retardants and median levels of brominated flame retardants in dust were lower than those found in other studies that examined residential environments. Based on dust measurements, child dose estimates for non-dietary ingestion of polybrominated diphenyl ethers (PBDEs) in children ages birth to <1 year exceeded the non-cancer U.S. EPA RfDs for two brominated flame retardants (BDE-47 and 99) in 10.3 percent of facilities. Air concentrations for PBDEs did not exceed health based benchmarks. With respect to pesticides, pyrethroid pesticides were detected in all of the ECE facilities. Diazinon and chlorpyrifos, which are organophosphate pesticides (OPs), were frequently detected in dust (>90 percent). Although these pesticides are no longer approved for indoor use, they persist indoors for long periods; however, no pesticide exposures exceeded health-based benchmarks. Perfluorinated compounds (PFCs) were measured; however, measurements of PFCs in air were not successful. Ten PFC compounds were measured in dust from ECEs. Perflurooctanoic acid (PFOA) and perfluorooctane sulphonate (PFOS), the most common PFC breakdown products, were detected in 72 percent and 54 percent of facilities, respectively. Although PFCs are now ubiquitous in the environment and can be immune toxicants, liver toxicants, carcinogens, and even endocrine disruptors, there are currently no health-based benchmarks available for evaluating risk from PFC exposures.

Levels of lead were also examined in the dust collected from ECE facilities. Lead was detected in 95 percent of the samples, and child lead exposure estimates exceeded age adjusted NSRL benchmarks based on carcinogenicity in more than 80 percent of facilities for all the age groups concerned. However, the primary concern for children's exposure to lead is developmental toxicity. Based on the levels observed in the study, which is typical of levels found in homes, it is unlikely that the levels of lead in ECE facilities would contribute significantly to cases of childhood lead poisoning.

Examination of indoor and outdoor particle levels for ECE facilities revealed that median indoor and outdoor levels of PM2.5 were 15.0 and 16.2 $\mu g/m^3$, respectively, and indoor and outdoor PM10 levels were 47.6 and 28.9 $\mu g/m^3$, respectively. Indoor PM10 concentrations exceeded the level of the 24-hour CAAQS in 46 percent of the facilities. Ultrafine particle (UFP) numbers were also measured. Though generally stable, the indoor UFP number increased by as much as six orders of magnitude during cooking with gas stoves. The median indoor UFP number level in center-based facilities was 12,000/cm^3, whereas the median for home-based facilities was 39,000/cm^3.

Finally, temperature, humidity, and air exchange rates were also examined. The average indoor temperatures for all childcare facilities were within the American Society of Heating, Refrigerating and Air Conditioning's (ASHRAE) standard for acceptable temperatures. Relative humidity exceeded ASHRAE standards in only five percent of the facilities, and only a few facilities had air exchange rates below recommended ventilation levels.

Conclusions

Over the course of this study, extensive environmental measurements of dozens of toxicants in air and dust were made for 40 ECE facilities. The levels of contaminants found in these facilities were generally similar to the levels found in other indoor environments, and most of the measures were below available health-based benchmarks. However, the screening risk assessment identified five VOC compounds and one metal in dust that exceeded Proposition 65 Safe Harbor Guidelines for cancer.

Exposure to formaldehyde, acetaldehyde, PM10 and PM2.5, and two flame retardants (BDE-47 and BDE-99) all exceeded their respective non-cancer health benchmarks in some ECE facilities as well. These findings underscore the need for additional research and actions to identify strategies to reduce indoor sources of these chemicals, and to assess the potential health risks of elevated ultrafine particulate levels, and define standards if needed.

II. STAFF COMMENTS

ARB staff reviewed and commented on the draft of the final report. Also, staff from both ARB and OEHHA reviewed the health risk characterization section of the report, which went beyond the contract requirements. Staff provided a number of comments to the investigator on the presentation and interpretation of the results, along with editorial comments, and the appropriate changes were made. Staff anticipates that there will be additional editorial comments that will need to be addressed in the revised report provided to the Committee.

III. STAFF RECOMMENDATION

Staff recommends that the Research Screening Committee accept this draft final report, subject to inclusion of appropriate additions and revisions in response to the staff comments and any changes and additions specified by the Committee.

DISCUSSION OF A DRAFT FINAL REPORT
ITEM NO.: 4
DATE: May 11, 2012
CONTRACT NO.: 08-324
Link to Report

STAFF EVALUATION OF A DRAFT FINAL REPORT

TITLE:	Assessment of Baseline Nitrous Oxide Emissions in California Cropping Systems
CONTRACTOR:	University of California, Davis
PRINCIPAL INVESTIGATOR:	William Horwath, Ph.D.
TOTAL AMOUNT:	$300,000
CONTRACT TYPE:	Interagency Agreement
CONTRACT TERM:	36 Months

For further information, you may contact Dr. Dongmin Luo at (916) 324-8496.

I. SUMMARY

Nitrous oxide (N_2O) is a potent greenhouse gas (GHG) that contributes to global warming. Agriculture is the major source of N_2O on both the global scale and in California, accounting for about 60 percent of anthropogenic N_2O emissions, most of which is derived from agricultural soils. Because N_2O is produced in soil through microbiological processes involving nitrogen (N) compounds, its emission is closely related to soil N content and influenced by numerous variables that govern microbial activities such as soil properties, meteorological conditions, and crop management practices. As a result, N_2O fluxes from agricultural fields are highly variable and subject to large uncertainties in N_2O emissions estimates. Thus, characterization of N_2O fluxes from agricultural fields is important in determining both baseline N_2O emissions and mitigation potentials of N_2O. This project measured N_2O fluxes from five major California crops (tomatoes, wheat, alfalfa, lettuce, and rice) representative of a large acreage of the state's crop land, evaluated impacts of soil conditions and N fertilizer rate on N_2O

emissions, and established crop-specific emission factors. The project provided the most comprehensive and robust dataset of N_2O monitoring so far from California crop systems, which will serve as critical inputs to an ongoing modeling study for the development of statewide baseline N_2O emissions from agricultural soils in California.

II. TECHNICAL SUMMARY

Objective

The objectives of this project were to (1) determine annual N_2O emissions for five California major crops: tomato, wheat, lettuce, alfalfa, and rice under typical management practices; (2) develop optimum N application rates, or the economic N yields, for the crops; and (3) evaluate key environmental conditions affecting N_2O fluxes.

Background

The California Global Warming Solutions Act of 2006 (AB 32) requires the reduction of statewide GHG emissions to the 1990 level by 2020. Due to the irregular nature of N_2O emissions from cropping systems, however, the estimate of N_2O emissions from agricultural soils is subject to significant uncertainties. To address AB 32 mandates, it is important to improve this estimate and identify mitigation potentials associated with soil emissions. Given the diversity of California's crop profiles, as well as environmental conditions, determining baseline N_2O emissions from California agricultural soils is especially challenging. This project was initiated as part of the AB 32 Early Actions in a statewide research effort to enable monitoring of N_2O emissions at multiple crop sites in different regions of the State.

N_2O emissions from agricultural soils are part of the natural N cycling process, driven by soil microbial activities. Due to variation of environmental conditions that affects soil microbial activities, N_2O fluxes from agricultural soils are highly irregular both spatially and temporally. In intensively managed cropping systems, spikes of N_2O fluxes are often associated with soil management events such as application of N fertilizers, irrigation, tillage disturbance, and incorporation of plant residues. Precipitation events, which change soil moisture conditions dramatically, can also induce substantial N_2O

fluxes. The results obtained from this project will provide critical California-specific information for an ongoing modeling study for the development of baseline N_2O emissions from agricultural soils in California.

Project Summary

The project measured N_2O emissions in cropping systems representative of a large acreage of California's cropland: tomato, lettuce, wheat, alfalfa and rice, under typical management practices. In addition, N_2O emissions in response to varying amounts and types of fertilizer N applications in tomato, lettuce, wheat, and rice were evaluated. N_2O fluxes were measured using static flux chambers of 10 cm height. Gaseous samples of 20 mL were taken from the chamber at regular intervals (0, 20, 40 minutes) and were analyzed for N_2O by gas chromatography. Environmental variables that potentially affect N_2O emissions such as nitrate (NO_3^-) and ammonium (NH_4^+) concentrations in the soil, soil water content as water-filled pore space (WFPS), soil organic carbon content, and soil and air temperatures, were also measured. The emission data obtained were then used to develop emission factors that characterize the amount of N_2O emitted as a function of fertilizer N inputs. To identify the "economic N yield," defined as the maximum economic return to N rate, yields and N content of the harvested crop were determined.

<u>Tomatoes:</u> The tomato experiments were conducted at University of California, Davis. N fertilizers were applied at five rates: 0, 75, 162, 225, or 300 kg N ha^{-1} before planting and during growth by side dressing in the form of ammonium sulfate (AS) or urea ammonium nitrate (UAN32). Elevated N_2O fluxes were observed after side dressing and irrigation events, with maximum N_2O fluxes reaching 20 mg N_2O-N m^{-2} day^{-1} at the highest N rate of 300 kg N ha^{-1}. Annual emission rates were estimated to range from 0.7 to 4.7 kg N_2O-N ha^{-1}, corresponding approximately to the N application rates. The calculated emission factors ranged from 0.92 to 2.08 percent, with a mean of 1.5 percent. The economic N yield was calculated to be 162 kg N ha^{-1} because tomato yields above this level did not increase significantly.

Wheat: Monitoring of N_2O emissions from wheat was conducted in Dixon, Yolo County. Five N fertilizer rates, ranged from 0 to 266 kg N ha^{-1}, were applied in 2 different combinations: anhydrous ammonia (AA) with urea or AS with urea. The bulk of the N_2O emissions occurred during the growing season with N_2O fluxes measured as high as 6 mg N_2O-N m^{-2} d^{-1}. N_2O fluxes from plots receiving AA, which has the highest N grade (>82 percent N) among all fertilizer types, were much stronger than those with AS. Overall, the emission factors in the wheat systems varied from 0.2 to 0.98 percent, with a mean of 0.57 percent, lower than that of tomatoes (1.5 percent). This is partially due to the lower temperature during the wheat growing season (November to May). The economic N yield for wheat could not be determined because the wheat yield did not differ among N treatments, suggesting high fertility in the monitored fields. Residual N from previous crops, such as alfalfa and tomato, may have contributed to the lack of fertilizer N response.

Alfalfa: The alfalfa study was conducted near Winters, Yolo County. Alfalfa is a legume crop with a biological capacity to fix atmospheric N_2, adding additional N to the soil. N_2O emission rates were compared for two alfalfa systems: one-year stand and 5-year stand. Both systems received a single application of ammonium phosphate at 17 kg N ha^{-1} during the 2-year trial. The measured annual N_2O emission rate for the 5-year stand was 5.2 kg N_2O-N ha^{-1}, which is much higher than that of the 1-year stand (2.0 kg N_2O-N ha^{-1}), equivalent to an emission factor of 12 percent, 3 times that (4.2 percent) of the latter. Higher emissions from an older stand field has previously been reported, and was probably due to the accumulation of more alfalfa residue, mainly roots, in the soil, providing additional carbon and N to microorganisms.

Lettuce: The monitoring of N_2O emissions for lettuce was conducted at the Hartnell College Farm in Salinas County, covering two crop cycles from June 2009 to March, 2011. Five N fertilizer rates: 11, 84, 168, 252, and 336 kg N ha^{-1} were evaluated. The N fertilizer was applied as urea ammonium nitrate (UAN32) via fertigation through irrigation water during lettuce growth. Detectable N_2O fluxes were clustered between July and October but peaked following the first irrigation event in the fall. The annual emission rates were estimated to range from 0.59 to 1.47 kg N ha^{-1}, which were

consistent with the N application rates. The measured emission factor was 0.54 percent across the five N application rates. The optimum N fertilizer rate based on yield was determined to be 84 kg N ha^{-1}.

Rice: Two experimental sites were chosen for the rice study: the California Rice Experiment Station (RES) near Biggs in Butte County and a grower field near Arbuckle in Colusa County. The rice was either water-seeded or drill-seeded into the field with or without additional weed control management. Three N fertilizer rates (0, 168, and 224 kg N ha^{-1}) at the RES and two rates (100 and 140 kg N ha^{-1}) at the Arbuckle site were tested. N fertilizer was applied as aqua ammonium (water-seeded) or urea (dry-seeded) before or after flooding. Significant emission fluxes of N_2O were detected for all fertilizer treatments. Annual emission rates for water-seeded conventional treatment was estimated to be around 0.26 kg N_2O-N ha^{-1} regardless of fertilizer rates, but increased to about 0.47 kg N_2O-N ha^{-1} for water-seeded no till treatment, and further to 0.59-1.2 kg N_2O-N ha^{-1} for dry-seeded treatment. The overall emission factor of N_2O was 0.38 percent for water-seeded treatment, and 0.84 percent for dry-seeded treatment. Rice yields did not differ significantly between the N application rates of 168 and 224 kg N ha^{-1}.

III. STAFF COMMENTS

The study provided the first comprehensive and robust N_2O emission monitoring dataset for California's major cropping systems, and identified optimum N application rate, where applicable or possible. The specific emission factors measured for the five crops (0.2-12 percent), which differed from the Intergovernmental Panel on Climate Change default value of one percent (a global average for all crops) and provide a more accurate estimation of N_2O emissions from the five California cropping systems. The information collected from this and other projects will be fed into a modeling study for assessing statewide baseline N_2O emissions from agricultural soil management in California.

ARB reviewed the report and requested the Principal Investigator to elaborate the discussion by cross-referencing existing literature on N_2O emissions from agricultural

soils, which was addressed in the current revision. The report is being distributed to stakeholders of industrial groups, other local, state and federal government agencies, academics, and environmental groups for review, and any comments will be reported to the Research Screening Committee and addressed properly in the final report.

IV. STAFF RECOMMENDATION

Staff recommend the Research Screening Committee approve this final report pending inclusion of appropriate additions and revisions in response to the staff comments and any changes and additions specified by the Committee.

DISCUSSION OF A DRAFT FINAL REPORT
ITEM NO.: 5
DATE: May 11, 2012
CONTRACT NO.: 08-326
Link to Report

STAFF EVALUATION OF A DRAFT FINAL REPORT

TITLE:	SOA Formation: Chamber Study and Model Development
CONTRACTOR:	University of California, Riverside
PRINCIPAL INVESTIGATOR:	William P. L. Carter, Ph.D.
TOTAL AMOUNT:	$474,229
CONTRACT TYPE:	Interagency Agreement
CONTRACT TERM:	36 Months

For further information, please contact Dr. Dongmin Luo at (916) 324-8496.

I. SUMMARY

Secondary organic aerosol (SOA) is an important component of airborne particulate matter (PM) which has a significant impact on public health, visibility, and climate change. SOA is formed through atmospheric reactions from reactive precursors, including volatile organic compounds (VOC) and nitrogen oxides (NO_X). However, the photochemical processes involved in SOA formation are poorly understood, and current air quality models often seriously under-predict ambient SOA levels. To develop reliable and effective PM control strategies, an improved SOA mechanism is needed for use in air quality models, which in turn requires a better understanding of SOA formation processes. In this project, environmental chamber experiments were conducted in order to develop a chemical mechanism to predict SOA formation from aromatic compounds, which are an important class of SOA precursors for which existing models perform poorly. Current and alternative aromatic mechanisms were evaluated, and SOA yields and partitioning parameters were optimized to simulate the available data. The results indicate that the model simulated most of the data without large biases, but with more

run-to-run variability in model performance than is seen in ozone mechanism evaluations. It is concluded that this reflects the current state-of-the-science and represents significant progress toward the eventual development of a chemical model to predict SOA from anthropogenic emissions. Such a model is essential to developing cost-effective control strategies for fine PM.

II. TECHNICAL SUMMARY

Objective

The objective of this project was to carry out experimental and mechanism development work needed to enhance existing gas-phase mechanisms so they can predictively model SOA formation from the reactions of aromatics under well-defined conditions.

Background

Airborne PM impacts public health, visibility, and climate. SOA can be responsible for most of the fine PM burden in California cities in the summer, when sunlight is most intense. However, the photochemical mechanism of SOA formation is not well understood and the air quality models used to predict SOA formation involve many highly uncertain assumptions. Previous models have under-predicted ambient SOA formation by as much as an order of magnitude. More recent models have been able to better predict ambient SOA formation but at the cost of drastically increasing the number of input variables that lead to SOA formation.

Air quality models currently treat SOA formation processes much less explicitly than gas-phase mechanism due to limited knowledge of chemical speciation and processes involved in SOA. In 2007, with ARB funding, the SAPRC-99 chemical mechanism was updated to SAPRC-07, which better represents gas-phase processes and reactivity estimates. SAPRC-07 is well-suited for adaptation to models for SOA prediction because of its ability to represent different VOCs and its improved capabilities for predicting important SOA precursors such as hydroperoxides. At that time, a preliminary model was developed that showed promise for predicting SOA formation, but significant

development and experimental evaluation was needed for regulatory modeling applications.

Thousands of smog chamber experiments have been conducted to study gas-phase photochemistry with respect to ozone formation. In contrast, SOA has rarely been speciated in smog chamber studies and its formation depends on diverse factors such as NO_X and VOC concentrations, relative humidity, and temperature. Additional data on SOA formation in well-characterized experiments representing a range of atmospheric conditions are necessary to test and improve theories and models for predicting SOA levels. Accurately predicting SOA formation is essential to developing cost-effective control strategies for fine PM, and assessing how proposed ozone control strategies may impact PM levels.

Project Summary

A total of 158 dual-chamber environmental chamber experiments were conducted to provide data on PM formation in both the presence and absence of NO_X. The 14 aromatic compounds studied (benzene and all C_7-C_9 alkylbenzene isomers) represent major types of aromatics. In addition, several phenolic products of aromatic photo-oxidation (phenol, cresols, dimethylphenols, and catechols) were studied. The experiments used varying reactant levels and, in some cases, differing light sources and addition of other reactants. Models were developed and evaluated to represent gas-particle absorption and partitioning processes, and to represent nucleation and chamber effects when modeling the experimental results. The results were used to derive mechanisms and parameters to predict SOA formation from the studied compounds, and to develop mechanisms for lumped aromatic model species for airshed models.

The most recent SAPRC gas-phase aromatics mechanism (SAPRC-11, as recently reported for Contract No. 07-730) was the starting point to develop a mechanism for predicting aromatic SOA. Data simulations led to significant findings that were incorporated into the new aromatic mechanism for SOA formation. For example, hydroperoxides were found to be important in predictions of aromatic SOA formation.

They are formed from peroxy radicals that result from hydroxyl radical addition to the aromatic ring. Therefore, the new mechanism includes a process for condensable hydroperoxides. In addition, experiments with phenolic products (hydroxy-benzenes) of aromatic photo-oxidation reactions indicate that secondary reactions of these products are very important SOA sources. Therefore, the new mechanism uses three phenolic species: phenol, cresols, and xylenols.

The mechanism predicts that much of the SOA formed from aromatics comes from the reactions of phenolic products, with the remaining SOA derived from hydroperoxide formation and from secondary reactions of non-phenolic aromatic oxidation products. The SOA model has a level of detail similar to that in the gas-phase mechanism, and represents five SOA formation processes using 11 new model species, with yields and partitioning parameters based on simulations of chamber data. Alternative mechanism formulations and partitioning parameter values were examined in test calculations, with the results used to select a chemically reasonable baseline mechanism, and to fit the available data with the least bias. The mechanism was evaluated by conducting model simulations of the SOA mechanism evaluation experiments developed for this project, and no significant problems emerged.

III. STAFF COMMENTS

ARB reviewed earlier versions of the report and provided comments, which were addressed in the current revision. Some types of experiments described in the original proposal were not included in the report, because during the course of the study, staff agreed with Dr. William Carter that the project should emphasize the mechanism development and evaluation (with a focus on aromatic compounds, as discussed in this report). Therefore, we agreed to a re-scoping for this purpose in which 158 chamber experiments (instead of the 120 proposed) were conducted.

Dr. Carter explained that he decided to conduct more chamber experiments (158, instead of 120 proposed) with a focus on the mechanism development and evaluation as discussed in this report, since otherwise the amount of effort required would exceed the time and resources available.

Dr. Carter recently completed a companion project report entitled, “Development of Revised SAPRC Aromatics Mechanisms” (Contract No. 07-730), funded by ARB’s Planning and Technical Support Division. It includes additional details on the experiments conducted for the SOA contract, and interpretation of the resulting data, that may be of interest to RSC members. This draft final report is accessible at: http://www.cert.ucr.edu/~carter/misc/arb.

The original proposal also included the evaluation of a state-of-the-science atmospheric chemical mechanism (PM-SAPRC) that could be used in airshed models for predicting SOA formation from anthropogenic emissions. While the investigators did not succeed in developing a PM-SAPRC mechanism for airshed models, they greatly advanced the scientific base necessary to achieve this difficult goal, and provided a mechanism that will enable modelers to obtain improved predictions of SOA formation.

IV. STAFF RECOMMENDATION

Staff recommend the Research Screening Committee accept this draft final report, subject to inclusion of appropriate additions and revisions in response to the staff comments and any changes and additions specified by the Committee.

DISCUSSION OF A DRAFT FINAL REPORT
ITEM NO.: 6
DATE: May 11, 2012
CONTRACT NO.: 08-318
Link to Report

STAFF EVALUATION OF A DRAFT FINAL REPORT

TITLE:	Nocturnal Chemistry in the Urban Boundary Layer of Los Angeles
CONTRACTOR:	University of California, Los Angeles
PRINCIPAL INVESTIGATOR:	Jochen Stutz, Ph.D.
TOTAL AMOUNT:	$409,090
CONTRACT TYPE:	Interagency Agreement
CONTRACT TERM:	36 Months

For further information, please contact Dr. Eileen McCauley at (916) 323-1534.

I. SUMMARY

This project addressed one of the least well-understood areas in the atmospheric chemistry of urban areas – nocturnal atmospheric chemical processes and their impact on daytime ozone and aerosol concentrations. Field measurements were made in the greater Los Angeles (LA) area using a remote sensing technique, Long Path Differential Optical Absorption Spectroscopy (LP-DOAS), which recorded trace gas concentrations in 4 height intervals over distances ranging from 5 to 7 kilometers. This work was carried out as part of the CalNex 2010 field study that was organized by ARB and the National Oceanic and Atmospheric Administration (NOAA) to study processes at the intersection of climate change and air quality in California. Professor Jochen Stutz, the Principal Investigator (PI) for the nocturnal chemistry project, took the lead in organization and set up of a comprehensive field site on the CalTech campus for CalNex 2010; this site attracted over 40 research groups and gave the most detailed insight into gas- and particle-phase chemistry in a large urban area to date. Two important results, among many, from the project are: 1) nocturnal NO_X loss is comparable to its daytime loss due to OH chemistry and is primarily due to N_2O_5 aerosol

uptake; 2) a currently unknown source of daytime nitrous acid (HONO) contributes significantly to hydroxyl radical OH formation and hence ozone (O_3) formation. The likely source of this HONO is photo-enhanced conversion of NO_2 on the ground. Concentration profiles and results from this project will help constrain and improve models for nocturnal atmospheric chemistry, and lead to more accurate predictions of O_3 and particle formation in urban areas.

II. TECHNICAL SUMMARY

Objectives

The research addressed several objectives concerning the atmospheric chemistry in urban areas:

1. Measurement of vertical profiles of important nocturnal trace gases – O_3, NO_2, NO_3, steady state N_2O_5, and HONO – and of several other gases – HCHO and SO_2 – throughout the day and night.
2. Quantification of O_3 and NO_X budgets at night, and estimation of NO_3 and N_2O_5 aerosol uptake coefficients in the greater Los Angeles area (using observations and a 1-D chemical transport model).
3. Estimation of the impact of HONO formation chemistry on the HO_x radical budget.
4. Evaluate the impact of nocturnal chemistry on daytime O_3 formation.

Background

Atmospheric chemistry switches from the photochemistry of hydroxyl radical-driven reactions during the day to the dark chemistry of nitrate radical-driven reactions during the nighttime. Simultaneously, surface cooling suppresses mixing and generates a highly-stratified atmosphere. This coupling between chemical and meteorological processes on similar time scales presents many challenges to atmospheric researchers and requires altitudinal measurements of key nocturnal chemical species.

Nocturnal chemical reaction pathways differ in significant ways from daytime pathways. For example, NO_3 preferentially reacts with oxygenated volatile organic compounds (VOC) and alkenes and is less reactive towards alkanes and smaller aromatic compounds. These nighttime reactions essentially scavenge NO_3 and depress its

ambient concentrations. An important nocturnal storage route for NO_3 is its reaction with NO_2 to form dinitrogen pentoxide (N_2O_5). N_2O_5 is thermally unstable and decomposes back to NO_2 and NO_3 on a similar timescale, and equilibrium is quickly established between NO_3 and N_2O_5. An important removal route for N_2O_5 is heterogeneous hydrolysis to nitric acid (HNO_3) on water droplets and aerosols; but because of the heterogeneous nature of the process, its rate is highly dependent on the substrate composition. Therefore, the efficiency of NO_3 as an oxidant depends on the rate of hydrolysis: significant hydrolysis of N_2O_5 limits NO_3 oxidation. Another poorly understood process is that of HONO formation. HONO is an important primary source of OH radicals in the early morning in urban areas, and hence affects the formation of O_3 and particles and the oxidation of pollutants. Although various mechanisms for HONO generation have been proposed, most recently photo-enhanced surface reactions, further measurements of the vertical distribution of HONO during the night and day are critically needed to help constrain models.

This research formed an integral part of CalNex 2010, a major field campaign that was jointly planned by NOAA and ARB to address interrelated issues at the nexus between climate change and air quality in California. These areas are closely linked through atmospheric chemical, radiative, and dynamical processes which operate at multiple length scales. Professor Stutz took the lead in organizing the Los Angeles supersite for this study on the campus of the California Institute of Technology. To help with the expenses involved in trailer rental, power installation and other associated setup costs, ARB augmented funding for the project by $200,000 from the original $289,090. Through these efforts, over 40 research groups were attracted to the site; they collected one of the most comprehensive data sets of aerosol, gas-phase and meteorological measurements ever in an urban area.

Project Summary

The central component of the project was the setup of an urban field site in the LA region during the 2010 CalNex study. Professor Stutz's long-path DOAS instrument provided continuous measurements of the vertical distribution of O_3, NO_2, NO_3, HONO, HCHO, glyoxal, SO_2, and meteorological in-situ sensors placed at different altitudes

supplemented the DOAS measurements during the study period May 15 – June 16, 2010. This suite of measurements was used as constraints in Professor Stutz's 1D chemical transport model, which provided insights into various aspects of coupling between chemistry and meteorology that occur in the South Coast Air Basin at night.

Specific results from the project are summarized below.

1. *Measurements of vertical concentration distributions of O_3, NO_2, NO_3, and HONO, as well as HCHO, SO_2, and glyoxal in the lowest 200 – 300 m of the atmosphere.*

   The LP-DOAS instrument operated continuously during the CalNex field study; although during certain times low clouds and fog blocked some of the light paths. These measurements provided a fairly complete data set that allowed all scientific questions posed in the original proposal to be addressed.

   During the study, O_3 mixing ratios varied from near 0 to ~100 ppb. The lowest NO_X mixing ratios, ~1 ppb, were observed in the upper height interval; the highest NO_X mixing rations, up to 40 ppb, were observed in the lowest interval during the night. NO_3 mixing ratios were highest during the night in the upper levels and reached 150 ppt during the night; during the day, mixing ratios were near zero. HONO levels ranged from 20 ppt during the day up to 1.5 ppb during the night.

2. *Nocturnal loss of NO_X.*

   The average nocturnal loss of NO_X was determined to be between 0.7 and 1.3 ppb/h in the lowest 550 m of the atmosphere, which is comparable to the daytime loss rate due to OH chemistry. From an analysis of observations and model results, the primary pathway for this loss was identified as N_2O_5 aerosol uptake.

   This particle-phase N_2O_5 may then be hydrolyzed to form HNO_3 (which is eventually deposited), or if the particle contains sodium chloride (NaCl), reacts

with chloride ions Cl^- to form nitryl chloride ($ClNO_2$), which is a radical precursor in the morning.

Model performance of the gas-phase Regional Atmospheric Chemistry Mechanism (RACM) was improved by adjusting parameters so that model vertical profiles of NO_2 and O_3 more closely matched measurements. This constrained values for the N_2O_5 aerosol uptake coefficient and $ClNO_2$ yield.

3. *Daytime and nighttime formation of HONO in the South Coast Air Basin.*

Nocturnal mixing ratios of HONO were observed to decrease very rapidly with altitude. At the surface, concentrations reached ~1.2 ppb; above 200 m, concentrations were typically below 0.25 ppb. Using the highly vertically resolved model RACM and a HONO formation parameterization, the PI was able to describe observations. From such comparisons, the PI determined that the predominant HONO formation path during the night is NO_2 conversion on surfaces with water. This analysis also yielded the results that aerosol mediated NO_2 to HONO conversion and direct HONO emissions play minor roles in HONO formation.

Daytime HONO concentrations were observed to be much greater than those predicted by a steady state analysis based on OH + NO chemistry. This observation points to another active daytime source for HONO that is not currently considered in air quality models. Similar to nighttime, the daytime HONO concentrations near the surface are extremely elevated in comparison to those aloft. These high surface concentrations may be explained by a photolytic source on surfaces. This source is as important as O_3 and formaldehyde photolysis as a precursor of primary OH radical formation. These results demonstrate that it is critical to add an additional daytime HONO formation mechanism to models used to simulate atmospheric chemistry in the LA basin.

III. STAFF COMMENTS

ARB Staff reviewed an earlier version of the report and provided comments to the investigator; these concerns were addressed in the current revised report. Staff would like to note the critical role Professor Stutz played in making the CalTech field site for CalNex 2010 an outstanding success. He spent many months in planning, organizing and setting up the field measurement site; his efforts produced an ideal scientific venue for the study of multifaceted problems in atmospheric chemistry, aerosols and climate science by a vast array of research groups. These additional datasets and studies will provide an unprecedented picture of and insights into urban atmospheres of California.

IV. STAFF RECOMMENDATION

Staff recommend the Research Screening Committee accept this draft final report subject to inclusion of appropriate additions and revisions in response to any changes and additions specified by the Committee.

DISSCUSSION OF A DRAFT FINAL REPORT
ITEM NO.: 7
DATE: May 11, 2012
CONTRACT NO.: 07-333
Link to Report

STAFF EVALUATION OF A DRAFT FINAL REPORT

TITLE:	Source Apportionment of Carbonaceous Aerosols Using Integrated Multi-Variant and Source Tracer Techniques and a Unique Molecular Marker Data Set
CONTRACTOR:	University of Wisconsin-Madison
PRINCIPAL INVESTIGATOR:	James Schauer, Ph.D.
TOTAL AMOUNT:	$409,963
CONTRACT TYPE:	Standard Agreement
CONTRACT TERM:	48 months

For further information, please contact Elizabeth Scheehle at (916) 324-0621.

I. SUMMARY

Organic carbon (OC) and elemental carbon (EC) are important contributors to fine particle concentrations throughout the State of California. As such, this carbonaceous material is important to human health, visibility, and regional climate forcing. A comprehensive year-long data set was collected to provide information to assess, inform, and compare modeling tools designed to apportion emission sources to individual OC and EC sources. Improved characterization of individual sources, such as gasoline powered vehicles, diesel engine exhaust, and primary and secondary organic aerosols (biogenic and anthropogenic) in California will help the state develop effective particulate matter control strategies and support health and climate forcing studies.

A year-long time series of hourly particulate matter 2.5 (PM2.5), daily OC and EC measurements, daily PM2.5 molecular marker measurements, and daily PM2.5 measurements of bulk fine-particle parameters (including water soluble organic carbon, water soluble nitrogen, and ultrafine particle number) were generated. Data generated

during the first portion of the project were used as inputs for source apportionment models. Results from these models were compared to determine if the commonly used source apportionment models differ significantly. Lastly, statistical analyses were performed on the data to characterize trends in day-of-the-week, time-of-day, and wind trajectory analysis was employed to identify the strengths and weaknesses of the models.

Results from the Chemical Mass Balance (CMB) and Positive Matrix Factorization (PMF) receptor models were compared, and found to show good agreement for the contributions of mobile sources and biomass smoke to PM2.5 OC of 30 percent and 10 percent, respectively. The Iterative Confirmatory Factor Analysis (ICFA) modeling results are also in reasonable agreement with mobile sources contributing 23 percent to the total PM2.5 OC. However, the CMB model estimates indicate that secondary organic carbon (SOC) dominated the remaining OC with a contribution of 60 percent while the PMF modeling results indicate that 40 percent of the remaining OC was from SOC and 20 percent was from primary biogenic material (e.g. forest fires and possibly cooking).

Overall, this study shows: 1) the importance of year-long data sets in accurately quantifying OC emissions and source apportionment, particularly seasonal trends; 2) that source apportionment techniques are sufficiently accurate for certain source contributions, but may generate substantially different results for other emission sectors; and 3) the diesel/gasoline exhaust PM split remains difficult to accurately quantify using all tested receptor models and molecular markers.

II. TECHNICAL SUMMARY

Objective

The major objectives of the project were: 1) to generate a full year of daily OC and EC measurements and daily molecular marker measurements at a central site in the Los Angeles (LA) Basin and to generate one in six day measurements at a site downwind of LA; 2) to use the data set to apportion the contributions of primary and secondary sources to carbonaceous aerosol concentrations; and 3) to compare the results of different source apportionment models.

In addition, the dataset will be made public and thus available to validate emerging source apportionment receptor models and source-oriented air dispersion models.

A secondary objective of the project was to quantitatively determine the viability and uncertainty of using measured compounds, such as water soluble carbon and nitrogen, as well as organic molecular markers as source tracers in the LA Basin.

Project Summary

Four-hundred fine particulate matter samples from two sites in the LA Basin were collected and analyzed for molecular marker source tracers. The results were used in three main source apportionment models (molecular marker chemical mass balance modeling (MM-CMB), molecular marker positive matrix factorization (MM-PMF) modeling, and molecular marker iterative confirmatory factor analysis (MM-ICFA)) to obtain daily, monthly, and annual average source contributions to fine particle OC.

Southern California experiences a number of days with very high OC concentrations that result from local biomass burning, forest fires, and secondary organic aerosols. During the one-year sampling program, high OC concentrations (greater than 8.0 µg per cubic meter of OC) were recorded on 13 days. Of these 13 days, eight were determined to be high wood smoke days, three were impacted by forest fires, and only two of these days were not associated with forest fires or high wood smoke events. Although forest fires can be considered outside the scope of local air quality regulation, public health could benefit from improved tracking and issuance of health warnings during extreme PM2.5 events due to wood smoke in Southern California. These occasional emission events can be challenging for speciation models to correctly allocate.

On an annual average, the MM-CMB and MM-PMF models show good agreement for the contribution of mobile sources and biomass smoke to PM2.5 OC of 30 percent and 10 percent, respectively. However, the remaining 60 percent of the OC was distributed differently in the two models. The MM-CMB model predicted that secondary organic carbon (SOC) dominated the remaining OC while the MM-PMF model estimated that 40 percent of the remaining OC was from SOC, and 20 percent was from primary

biogenic material (e.g. forest fires and possibly meat cooking). It is important to note that the primary biogenic source, which peaks in days with large forest fires, is very different from the biomass burning source (e.g., fireplaces). The SOC estimates, from the MM-PMF model, were in good agreement with non-biomass burning water soluble organic carbon (WSOC), which has been shown to be a robust estimate of SOC. In addition, the MM-CMB model was able to quantify vegetative detritus, which was only a very small component of the primary biogenic source.

Although the total mobile source contribution was similar among models, the split between gasoline and diesel engine exhaust emissions within the mobile source contribution warrants further investigation.

A key finding of the U.S. Department of Energy Gasoline/Diesel PM Split Study (http://www.nrel.gov/vehiclesandfuels/nfti/feat_split_study.html) was that the CMB modeling split between gasoline and diesel engine exhaust emissions is very sensitive to the input profiles used in the CMB model but that the total mobile source contribution was reasonably stable. Similar results were seen in the current study, and the multi-variant receptor models (MM-CMB and MM-PMF) were used to further investigate the drivers of model sensitivity. In the current study, MM-CMB, MM-PMF, MM-ICFA, and another receptor model (UNMIX) were investigated as a means to split the mobile source contributions between gasoline and diesel engines, but these models were unable to achieve a suitable split. However, the dataset provides a unique opportunity to test the ability of other multi-variant models to achieve a robust split between the emissions from gasoline and diesel engines. Previous molecular marker receptor models have differentiated tailpipe emissions from diesel engines, gasoline engines, and smoking engines with the use of EC, hopanes, steranes, and polycyclic aromatic hydrocarbons (PAHs) as tracers. The current study demonstrated with principal component analysis (PCA) and MM-PMF that PAH concentrations in the LA Basin are significantly impacted by biomass burning as well as tailpipe emissions, making them difficult to use as tracers for diesel.

Given the uncertainty in the split between gasoline, diesel, and smoking vehicles in MM-CMB models, it is difficult to fully evaluate the accuracy of the MM-ICFA results but the MM-ICFA results appear to agree with some previous estimates of the gasoline and diesel split. Similar to the MM-PMF model, the MM-ICFA model appears to reasonably apportion anthropogenic and biogenic SOC to total OC; but, it can also perform the gasoline-diesel split in a similar manner as the MM-CMB model. However, these MM-ICFA results appear to be preliminary and require additional validation. Future sensitivity analyses and the application of the multi-variant models are needed to better evaluate the accuracy and stability of the MM-ICFA results obtained in the current study. Nonetheless, the results demonstrate the viable pathway to further advance the relative understanding of gasoline and diesel engine contributions to PM2.5.

Analysis of the SOC results demonstrates that the models predict different overall contributions of SOC to total OC. Only the MM-PMF model predicts a seasonal trend in SOC concentrations, with a maximum contribution to OC about 60 percent occurring in late spring and summer and a minimum of around 20 percent in December. The MM-PMF model identified two SOC sources with different seasonal trends. One of the SOC sources, which has more biogenic components, dominated in the late spring and summer. The second SOC source, which had more anthropogenic molecular markers, was higher in summer and fall. In the late spring and summer, the biogenic SOC made up about 50-70 percent of the SOC but in the fall it only contributed about 20-25 percent of the SOC.

In summary, the MM-CMB, MM-PMF, and MM-ICFA modeling results were generally in good agreement, and predicted similar contributions of OC from mobile sources and biomass burning. However, the modeling results did have differences. For example, the MM-PMF model was able to provide estimates of primary biogenic emissions, whereas the MM-CMB model could not. The MM-PMF apportionment results demonstrate seasonal patterns in the split between SOC and primary OC, which were not previously shown because of the short term, intensive nature of previous studies, demonstrating the utility of this unique, year-long data set. The MM-PMF model also provided new insight into the impacts of forest fires and wintertime wood burning events. However, all

the studied receptor models were unable to separate PM source contributions between diesel and gasoline engines with a high degree of certainty.

Overall, this study shows: 1) the importance of year-long data sets in accurately quantifying OC emissions and source apportionment, particularly seasonal trends; 2) that source apportionment techniques are sufficiently accurate for certain source contributions, but model results can vary substantially for other emission sectors; and 3) the diesel/gasoline exhaust PM split remains difficult to accurately quantify using all tested receptor models and molecular markers.

III. STAFF COMMENTS

These measurements provide a unique dataset that informs scientists regarding various air quality issues. The current study provides an updated source apportionment analysis of organic aerosols in the LA Basin. The study demonstrates that past source apportionment results from short, intensive source apportionment studies were not able to represent the annual average source contributions and the seasonal trends in source contributions. The research demonstrates the bias of current MM-CMB model estimates of SOC, which result from the inability of the model to accurately represent primary biogenic materials. This is because SOC source profiles have yet to be characterized. The MM-PMF results of the study are able to effectively capture primary biogenic sources that are impacted by forest fires. All of the multi-variant receptor models used in the study were unable to separate the gasoline/diesel split within the mobile source category. The MM-ICFA results appear to agree with some previous estimates of the gasoline and diesel exhaust split; however, due to associated modeling uncertainty, no gasoline and diesel exhaust split results were provided in the report. Finally, reviewers suggest that the draft final report needs additional technical editing.

IV. STAFF RECOMMENDATION

Staff recommends that the Research Screening Committee accept this draft final report, subject to inclusion of appropriate revisions in response to the staff comments and to any additional changes specified by the Committee.