

AIR RESOURCES BOARD SPONSORED BIOGENIC RESEARCH THE STRATEGIC PLAN

1. BACKGROUND

To determine the effects of emissions control strategies identified in the State Implementation Plan (SIP), future concentrations of ozone and aerosols at ground level have to be modeled. To simulate ozone and aerosol concentrations properly, Cal/EPA Air Resources Board (ARB) and other concerns have sponsored research into plants' emissions of ozone forming hydrocarbons (Table 1). Even in the highly urban South Coast Air Basin (SoCAB), the biogenic ozone forming hydrocarbon emissions are an increasing fraction of total hydrocarbon emissions (~15%-20%). Biogenic hydrocarbons can also form constituents of Particulate Matter 2.5 micrometer in diameter and less (PM_{2.5}).

The Biogenic Working Group (BWG), comprised of ARB, academicians, Environmental Protection Agency, and the California air quality management districts is the group primarily responsible for guiding the development of tools and means in biogenic ozone and aerosol research.

Table 1

Contract Name	Funding	Funding Source	Contractor	Status
Investigation of the Role of Natural Hydrocarbons in Photochemical Smog Formation in California	\$266	Research	UC Riverside	Final-1983
Hydrocarbon Emissions from Vegetation Found in Central Valley	\$170K	Research	UC Riverside	Final-1989
Inventory of Leaf Biomass and Emission Factors for Vegetation in the South Coast Air Basin	-	SCAQMD	Valley Research	Final-1991
Leaf Biomass Density for Urban, Agricultural, and Natural Vegetation in California's San Joaquin Valley	-	SJV Study Agency	Valley Research	Final-1992
Development of a Natural Source Emission Inventory	-	SJV Study Agency	DRI	Final-1992
Determination of Variability in Leaf Biomass Densities of Conifers and Mixed Conifers under Different Environmental Conditions in the San Joaquin Valley Air Basin	\$116K	Research	UC Riverside	Final-1995
Critical Evaluation of a Biogenic Emission System for Photochemical Grid Modeling in California-UCLA Phase I	\$100K	PTSD	UCLA-STI	Final-1995
Ventura County Leaf Biomass	\$50K	Ventura APCD	Sonoma Tech	Final-1996
Biogenic Hydrocarbon Inventories for California: Generation of Essential Databases-UCLA Phase II	\$298K	Research	UCLA	Final-1998
Methodology, Databases and Biometric Relationships for Estimating Leaf mass in California Airsheds	\$20K	PTSD	UC Coop Extension	Final-1998
Development & Validation of Databases for Modeling	\$258K	Research	UCLA	Active

Biogenic Hydrocarbon Emissions in California Airsheds-UCLA Phase III				
Leaf Area Index Derived from Satellite Spectral Observation – Finer Resolution & Updated with newer Satellite Scenes	\$25K	Forest Service	Oak Ridge Nat Lab	Proposed Never Funded
Whole Ecosystem Measurements of Biogenic Hydrocarbon Emissions-UC Berkeley Phase I	\$150K	Research	UC Berkeley	Active

*This list does not include Biogenic Emissions in a Mediterranean Atmosphere (BEMA) by European Union. This list does not include substantial work by NCAR & EPA.

2. INTRODUCTION

Biogenic Research Workshop was held at Cal/EPA headquarters

December 13th to 14th, 2000 to develop a plan to meet requirements of the near and long term ozone and PM2.5 SIP's. Participants included:

Professor Arthur Winer (University of California Los Angeles)
 Professor Allen Goldstein (University of California Berkeley)
 Professor Paul Ziemann (University of California Riverside)
 John Karlik (University of California Cooperative Extension)
 Tom Pierce (Environmental Protection Agency)
 Mark Rosenberg (California Department of Forestry (CDF))
 Brian Schwind (United States Forest Service (USFS))
 Tony VanCuren (ARB),
 Luis Woodhouse (ARB),
 Klaus Scott (ARB),
 Bart E. Croes, Research Division Chief (ARB),
 John Holmes, Science Advisor to the Chair (ARB),
 Michael Benjamin (ARB), Organizer
 James Pederson (ARB), Moderator
 Ash Lashgari (ARB), Organizer
 Eileen McCauley (ARB), Atmospheric Processes Section Manager
 Cheryl Young (ARB), Recorder

We explained the short-term need for statewide emission inventories for updating the ozone SIP due in six months and the requirements of PM2.5 SIP due in the next five years. We presented a preliminary simulation of the Biogenic Emissions Inventories through Geographic Information Systems (BEIGIS); the participants then discussed methods to evaluate and to improve BEIGIS. We focused on twelve key points needed for a reliable California biogenic emissions inventory:

1. Methods for Using Historical Emissions Rate (ER) Data
2. Leaf to Branch to Regional Scaling Approaches for Emission Rates, Leaf Data, and Vegetation Maps
3. Simulation Inputs and Platform Flexibility to Cope with Changes in Plant Species, Density, Climate, and Land Use

4. Extending Taxonomic Methods used for Isoprene to Other Hydrocarbon Emissions (Terpenes & Oxygenated species) & Leaf Mass – Through the Taxonomic Method, we use the plant classification relationships to estimate isoprene emission rates for plants with no emission rates
5. Validation of Emission Inventory and Photochemistry Models
6. Field Studies
7. Trans-Pacific Transport of Ozone and PM2.5 and the Effect on Simulation Boundary Conditions
8. Net Effects of Plants on Ozone and PM2.5 Ambient Concentrations
9. Emissions from Green Waste Recycling
10. Improving Emission Inventory Simulation Inputs
11. Policy Development at ARB and EPA
12. Funding Sources

3. Simulation Platform Inputs Consensus

Photochemical modelers have found biogenic emissions from the agricultural and urban vegetation have the highest impact of all biogenic emissions on ambient ozone concentrations. Urban vegetation that is routinely irrigated can have a disproportionate effect on ozone levels. We need to understand agricultural and urban forests better for ozone photochemistry; we need to study oak woodlands and pine forests better for ozone and PM2.5 chemistry. We arrived at consensus on some key points and on others we developed elements of key points whose resolution would be necessary for arriving at consensus at a later date. Our consensus can be viewed through the lens of the “wish list” for BEIGIS development or through the prism of short-term (six months) to long-term (five years) SIP requirements.

3.1 Historical & Other ER Data

With at least 5,682 different species in the California’s natural plant community, no ER program can ever hope to provide empirical measurements for all the species present. We do need the historical ER data and ER data collected elsewhere. There are inconsistencies in the quality and completeness

of accompanying information such as light intensity and ambient temperature for the historical ER databases. There are questions on proper plant identification and proper use of chemical standards in historical measurements; the same species of plants may emit differently in a different ecosystem. Nevertheless, we need reasonable means to incorporate the best and latest ER measurements, as well as exploit the wealth of historical ER databases properly reviewed in a collection or compendium. The Hewitt database (United Kingdom) that is available via the Internet is a good model to start with; Hewitt and his team should be praised. But, a more dynamic database with critical peer reviewed inputs and periodic reappraisal would receive even wider acceptance in the biogenic research community. To exploit the synergies between California and national ER measurement programs and to avoid the problems affecting the Hewitt program, we have to build an ER clearinghouse securing opportunities for review and publication. To build these peer-reviewed collections of ER and leaf mass databases, the Biogenic Working Group representing the biogenic research community should take the lead (Short and Long-Term).

3.2 Scaling Approaches for ER, Leaf Data, and Vegetation Maps

California has some of the most diverse topography and heterogeneous ecology in the world. Although such variability is less evident at the county level, BEIGIS grid cells still have to incorporate substantial diversity. To manage, we need to take advantage of our systematic knowledge of botany and use such tools as the taxonomic method to estimate ER and leaf mass particularity from family and genera generalities. In other words, our landscape calibration techniques rely on relating to plant communities. Current BEIGIS leaf mass relies on a leaf area index (LAI) database is available on a seasonal basis but offers fairly low values. It is not clear if that is because California forests and woodlands are not as dense as eastern United States or the trees do not have as many leaves due to the semi-permanent drought conditions here. BEIGIS LAI database has received limited validation using ground level LAI instruments; we need to continue and to expand these validation experiments keeping issues of scaling in mind (Short and Long-Term).

BEIGIS addresses some canopy level scaling problems by using branch level ER data to incorporate shading effects. But, orientations of leaves and needles are critical for ER's and may need to be considered as a separate calibration effect; methyl butenol ER's are generally leaf level measurements and canopy models may have to be considered for proper determination of light attenuation effects on such ER's (Short and Long-Term).

While we need landscape scale data generated from species scale data; we need to acknowledge the dynamics of seasonal changes that are not easily apparent but have significant impact on how emissions inventory models work; for example, ground level vegetation changes during growing season in hardwood forests (Short-Term). We also need to be able to reconcile higher isoprene emissions data from satellites that are derived from averaging over large areas; calibration factors for such satellite data may have to be considered (Long-Term).

3.3 Changes in Species, Density, Climate, and Land Use

We need to emphasize that with lower anthropogenic emissions of hydrocarbon and nitrogen oxides, the influence of biogenic emissions in ozone and aerosol formation will continue to expand. California is subject to rapid urban growth that replaces agricultural and natural plants with urban and ornamental vegetation. CDF & USFS offer California Land Cover Mapping and Monitoring products including vegetation maps that document land use changes in wilderness areas. Similar developments for urban foresters are still in planning stages. We need to encourage mapping these changes in plant species and density brought about by urbanization. We also need to use such tools as the taxonomic method to estimate ER and leaf mass data from the more general knowledge of changes in plant species distribution and density. We may need to develop LAI validation techniques and procedures for urban forests.

Given the pressures of urbanization, we need to begin research into the net effects of vegetation to equitably assign to agricultural practices and to wild land management the beneficial effects of ozone and aerosol deposition and the beneficial effects of cooling and carbon dioxide uptake. On the other hand, we

need to consider the effects of higher temperatures due to global warming on biogenic emissions and regional air pollution. In light of potentially higher temperatures, we should also consider effect of these changes on partially oxidized chemical intermediaries of biogenic photochemistry. BEIGIS needs to remain flexible to address changes in species distribution and land use (Short & Long-Term) and to incorporate net effects processes (Long-Term).

3.4 Extending Taxonomic Methods to Other Hydrocarbons & Leaf Mass

Taxonomic method (at genus/family level) works best when confined to a particular geographic area and when there exists a critical mass of measurements already available. Under these conditions, we have successfully used the taxonomic method for isoprene ER's in California. Because we need for a critical mass of measurements, we need to find a way to integrate data ER data from branch enclosure measurements (branch level) with ER data from leaf cuvette measurements (leaf level)(Short-Term).

Most emission inventory models do not consider methyl butenol or other oxygenated hydrocarbon biogenic emissions and thus perhaps underestimate total emissions by 30%-40%. Terpene emissions that form aerosols are another important example. We need to safely extend the taxonomic method to terpenes and to methyl butenol (Short-Term). A similar taxonomic method extension can cover leaf weight values that compliment LAI values for determination of leaf mass in BEIGIS (Short-Term). BEIGIS should remain flexible to also consider oxygenated hydrocarbon emissions including acetone, alcohols, and other species of concern to global photochemistry and climate change (Long-Term).

3.5 Model Validation – Emissions Models or Photochemical Models or both?

Current BEIGIS framework produces a chemically speciated inventory of biogenic hydrocarbons to serve as inputs to photochemical models that incorporate generalized atmospheric chemistry mechanisms including reactivities of these hydrocarbons to produce ozone and aerosol concentrations. For example, photochemical modelers working with atmospheric chemistry experts decided to have BEIGIS generated methyl butenol emissions, with reactivities

perhaps half as high as isoprene, be coupled with its own chemical mechanism. We believe in this dialog between atmospheric chemists, emission inventory specialists, and photochemical modelers to better understand simulation results and to avoid labeling emission inventory as the cause of all or even most modeling difficulties.

Building validation exercises for ozone simulation requires assessment of both isoprene concentrations and ozone concentrations; this level of integration means validating all input databases such as ER's, leaf mass data, and vegetation maps (Short-Term). We also need both ecosystem scale and regional air quality model validation and we need to locate field measurements for isoprene and terpenes away from hot spots and where uniform concentrations would be expected (Short & Long-Term). BEIGIS character of beginning at plant level is helpful because it aids in landscape level validation. Regional or statewide application of BEIGIS is helpful because it would capture canopy level effects. BEIGIS evaluation should focus on input databases, landscape and ecosystem speciated hydrocarbon outputs, and final ozone and aerosol outputs from the photochemical models.

For organic aerosols, we first need to agree on the selection and structure of a Secondary Organic Aerosol (SOA) module for biogenic and anthropogenic aerosols formed from gaseous emissions (Short-Term). We need much better terpene ER's (Short & Long-Term); we believe that terpene emissions are understated. Moreover, during summer, these emissions are driven by temperature; and in winter, when background emissions are low, these emissions increase ten-fold with the first rains. Seasonality of emissions Input in aerosol formation must be considered and validation exercises tailored accordingly (Long-Term). Similar to BEIGIS validation through comparison of expected and measured ozone concentrations, we also need to account for seasonal changes in background aerosol concentrations in BEIGIS validation (Long-Term).

3.6 Other Field Studies

We know isoprene ER's for many agricultural plants, we are uncertain that we have methyl butenol, total terpenes, and oxygenated species ER's for all the important agricultural plants (Long-Term). We know fertilizer application and irrigation of the fields occur year around in California, and we are uncertain that we have properly estimated gaseous nitrogen species contributions from these practices (Long-Term). We know that green waste recycling practices are expanding in California and that aromatic and other hydrocarbons with unknown ozone and aerosol formation potential are emitted from these practices. We need to identify emitted species and decide whether we need to develop ER's for green waste recycling (Long-Term).

3.7 Boundary Conditions & Trans Pacific Transport

California's emission control strategy relies on simulations that use "clean" boundary conditions as input parameters off the coast. There are now new data and analysis that suggest emissions from Japan and the Asian mainland can have a significant effect on California boundary conditions. Aside from our efforts to convince emission control concerns from that region to adopt our technology, we should also look at source dynamics to better understand the character of aerosols measured in field studies to be able to distinguish species from long range transport from those of California origin (Long-Term).

3.8 Net Effects

California flora, including agricultural crops, emit hydrocarbons, they also may provide substantial amount of deposition surfaces. California flora reduce the heat island effect, uptake carbon dioxide, and emit nitrogen oxides and hydrocarbons during fires as well. In the interest of fairness and supporting the agricultural community, modeling simulation should begin to incorporate these phenomena as well as emissions (Long-Term). Unlike findings in one California study, soil emissions of nitric oxide have been found to be significant in Eastern United States. Further, contribution of fertilizer addition to soil nitrogen oxides emissions may be significant everywhere (Long-Term). Regional haze analysis would benefit from these understandings coupled with seasonal nature of condensation nuclei that would be better understood with net effects research.

Research into speciated hydrocarbon and nitrogen species inventory, modeling, chemical mechanisms, and reactivity should take into consideration net effects (Short & Long-Term).

There are some concerns about geogenic emissions from seepage of petroleum reserves and other natural processes, we could address these in areas where such processes are important (Long-Term).

3.9 Green Recycling

With the expansion of garden and yard waste recycling in California, there is a concern that we are unaware of any studies on emission profile of recycling besides production of methane from these green waste-recycling sites (Long-Term).

3.10 Improving Inputs

With significant impact of agricultural and ornamental vegetation, we need to deal with spatial dispersion and variety of such plants; patterns of emissions, all important chemical species, for agricultural crops should also be investigated (Short-Term). For vegetation maps and leaf mass in agricultural areas, use of satellite data may be appropriate; for leaf mass in well irrigated urban areas, we may need to have ground level LAI measurements there. Alternatively, to address heterogeneity of leaf mass in urban areas we could use volumetric approach to calculate leaf mass instead of LAI (Short-Term).

There is a need for frequently updated ER databases that would be widely available (e.g., Internet). We would need a steering committee for review of data, facilities to host the site, and volunteer labor necessary to populate the database (Long-Term) [Unified ER Databases Process]. Current ER databases lack steering committees that would deal with scaling problems and different methods used to gather the data. Currently ER data is collected mostly via leaf cuvette method and this fact argues for moving BEIGIS inputs towards a leaf based ER and incorporating a canopy model over time (Long-Term). We would maintain branch level ER data and convert it as BEIGIS evolves (Long-Term). This will particularly assist us when we incorporate methyl butenol and terpenes ER's that will likely exclusively be leaf level data.

There is also a need for widely accepted Leaf Weight and other Leaf Mass databases that would be widely available. We would use the structure and resources of the Unified ER Database Process for the Leaf Weight and Leaf Mass databases [Unified Leaf Mass Process].

In supporting both these databases and designing of future vegetation maps, we will incorporate seasonality as an important parameter of the process (Long-Term). Field studies will reflect this incorporation by extending the measurement programs to over several seasons or years (Short & Long-Term). For detailed vegetation maps, we need to continue to work with utilities, water agencies, urban and wild land foresters (CDF and USFS in particular), and other resource agencies whenever possible (Short & Long-Term).

3.11 Policy Development at ARB and EPA

At ARB, there is a long tradition of interaction with academicians on policy development. With impetus for carbon dioxide uptake, and with cooperation of academia, we have offered advice on what non-emitting trees for urban forests. Because current United States' climate change compliance method relies on trees planting, it is critical to have a voice in what trees are planted. ARB and EPA need to interact with other resource agencies in this area (Short & Long-Term).

3.12 Funding Sources

To complete this substantial menu of required work, we need to enlist a larger and more diverse sponsor pool. In the first place, it is critical to find a sponsor/s for the Unified ER and Leaf Mass Processes. We need to contact utilities, water companies, and volunteer groups (e.g., Tree People) need to be contacted (Short & Long-Term).

4.0 GIS Modeling (Vegetation Maps & Leaf Area)

To build any kind of modern emission inventories, GIS maps are essential building blocks. GIS vegetation maps are the primary layer and leaf area databases are overlaid on top of them.

4.1 Vegetation Maps – GAP & Cal VEG

There are two key vegetation map systems available in California; GAP developed for preservation of biological diversity in United States and Cal VEG developed for fire prevention, management, and prediction, as well as, monitoring land use and a myriad of other California and federal ecological purposes. Cal VEG is a product of California Department of Forestry closely working with United States Forest Service. GAP is a product of the California GAP group spear headed by University of California Santa Barbara Department of Geography. GAP is currently the primary GIS vegetation database for BEIGIS, although vegetation maps from water resources agencies, agricultural concerns, and cities and counties substantially supplement GAP (San Joaquin Valley & other agricultural area vegetation maps).

Applications of Cal VEG in southern California have expanded outside forests although there are some gaps in the San Luis Obispo County. Urban vegetation characteristics are however limited in Cal VEG. Cal VEG builders did not try to model in urban areas although urban foresters are very interested in urban forest vegetation maps. Cal VEG provides information on life form of vegetation such as whether the observed plant is a conifer, hardwood, or a shrub. CDF products like Cal VEG are primarily designed to provide statewide coverage of wild lands. Urban vegetation mapping on a large scale is not likely on the horizon. There is not a lot of data on urban vegetation otherwise and it is outside CDF jurisdiction.

Methods used in wild lands also do not work well in urban settings due to introduced species and ornamentals. Perhaps we can ignore non-native vegetation and not identify them. There is some interest from non-profit organizations (SMUD, Tree People, and Tree Foundation) in this approach. Past efforts in Sacramento & southern California have used ground surveys from other cities by land use type and recorded tree species mass (e.g., top 20 trees) and leaf mass per square meter. These surveys have captured street and yard trees. Other approaches that have used landscape type analysis have relied on urban planning ideas evolving in cities like Phoenix, Ventura, and Bakersfield that lend themselves easily to GIS mapping. We need to find means to combine all these

efforts and to encourage them in producing urban GIS vegetation maps (Short-Term).

In eastern United States, tree density is high and native forests extend to urban areas. Given these circumstances an approach that used low altitude photography allowing taxonomists to identify tree species has proven effective. California is unlike the east, mostly semi-arid areas where ornamentals are planted; but some of the same techniques may succeed here as well.

GAP and Cal VEG have their own strengths and disadvantages. GAP may not be properly geo-located. Its development from point-sampling field work means that it is imperfect because its components are imperfect. GAP is probably right to one significant figure on species and does an even better job on crown closure. CDF has linked GAP to forest inventories using ground based observations of species grouped into strata and applied to GAP data. CDF has concluded that GAP predictions are good in timberlands. We still need species components in all our vegetation maps. We need more specificity than GAP provides.

Cal VEG Statewide databases may break out individual species in the near future. Cal VEG has somewhat better data than GAP because of the extensive field validation programs and covers half of the state. Within the next 5 years, Cal VEG will have products that cover the entire state excluding the southeast desert. GAP might be adequate in the southeast desert but there is no species breakdown and desert species are potentially high emitters. Should we then use Cal VEG instead of GAP? Best option is to overlay Cal VEG and GAP and use the best detailed map in BEIGIS (Short-Term).

4.2 Leaf Mass Databases (Leaf Density, Leaf Area Index, Leaf Mass Constants)

BEIGIS generally relies on a satellite derived LAI database developed by Dr. Ned Nikolov. LAI data and leaf weight constants for particular species then combine to deliver leaf mass for use in emission rate equations (leaf area (m^2) x grams leaf/ m^2 x grams emissions/grams leaf). For species found in California and Eastern United States, BEIGIS Leaf mass values are substantially lower

than other simulated leaf mass values. These lower leaf mass values are the result of scaling LAI values over a one kilometer grid that includes vegetated and non-vegetated areas. We have struggled to know if the satellite LAI is too low for California and in particular is it reasonable for oaks and pistachios (high emitters). Because of the substantial differences between urban forests and wild lands, we may be able to have a different strategy to deal with urban leaf mass issues; we may be able to use a volumetric approach for urban forests. This is particularly appropriate because urban trees have more leaves due to year around irrigation. Nevertheless, validation of the satellite LAI database for the greater area of California composed of wild lands remains an important area of inquiry.

LAI validation program has relied on whole tree harvests, dried leaf for leaf mass, and measured leaf areas. Mass to leaf area conversions are based on samples and should be within 5% of actual values (e.g., 1.3 m²/m² and 310 to 375 grams/m²). At many field sites, we have seen that areas around trees are often grasslands and this leads to LAI and leaf mass density both to decline rapidly. For comparison, we have used regression allometric relationships for blue oak and ground based estimates for LAI. For further comparison, we have used a photographic instrument to contour pictorial data to leaf overlays, and 2 LAI instruments (CI-110 and LAI-2000) to measure light intensity and leaf orientation (newly acquired LAI 2000). For oaks, we have considered spatial resolution of leaves and distribution of plants within the grid. We have integrated grid data on LAI 2000. Clear areas lead to lower ground level LAI values, and the field data correlate well with the satellite data.

Field data may properly validate our approach because it may suggest that leaf mass is not as dense in California as in the Eastern United States. This is because in California trees are widely dispersed and the semi-permanent drought may allow less foliage as well. Certainty in this conclusion is pivotal for leaf mass determination in BEIGIS. This conclusion may be buttressed by observations of declining LAI values as we move in elevation from high (dense

oak woodlands) to low (oak savannas). We also know that satellite data does account well for leaf distribution.

We have other concerns regarding measurements because they work best in open canopies. There are more problems with dense forests that have more layers of trees (young, mature, and old with respective canopy covers from the forest floor to the highest canopy). In dense forests, there are also more vertical zonation of canopies with leaves and needles at each elevation having particular characteristics suitable to that zone. This is particularly true in conifer zones.

We still need to continue measurements (Short-Term) for other plant species and other ecosystems (e.g., urban forests), gather other data suitable for comparison with our LAI database such as from photographs or other means, and see if we can connect and relate the LAI database to the GAP vegetation maps. Our next immediate steps should be to fully analyze the new ground based LAI data and compare them to citrus and pistachios as a clear test of the satellite LAI database. Ultimately, we have to be able to develop LAI processes that can correct LAI data for species other than oaks, citrus, and pistachios. Our future efforts should concentrate on measurements in highest leaf mass areas to address various complexities that high leaf density generates. Crown data for many plant species may also be widely available and side by side comparisons with data from LAI and other methods would be useful. We would continue with comparing leaf area and LAI as estimated by satellites with ground level measurements. We would also attempt to compare both of these databases with calculations based on specific leaf mass constants.

We are aware that there are other approaches as well; we can work on clumping index or other description of light intensity through the leaves of a plant to support data from the new LAI instruments that may show orientation of the leaves. Although, allometric approaches are probably best suited for the Eastern United States, there are considerable areas in California with closed canopy. We should start to evaluate species composition, leaf mass density, and crown area coverage on the one hand and the amount of open space on the other to balance

analyses of leaf mass determination. Both these approaches tend to describe effective leaf area and leaf mass for purposes of emissions but they do not necessarily show effective area for deposition purposes. Our needs for LAI validation research is short-term and pressing.

5.0 Simulation Validation

National biogenic emissions inventories simulation platform is Biogenic Emissions Inventory System (EPA's BEIS) III that simulates only ozone forming hydrocarbons currently. BEIS III without speciated oxygenated hydrocarbon emissions may be available by end of January 2001. Isoprene, terpenes, and other species will be lumped into appropriate categories. Methyl butenol may be treated separately. BEIS III does not speciate mono terpenes since EPA has not yet connected BEIS III to any SOA model.

5.1 Validation for Ozone Simulations

An understanding of ecosystem's dominant features are a first step in design of field programs and analysis of validation data. In Ponderosa pine plantations, methyl butenol and terpenes emissions are important to ozone and aerosols formation. Yet, we know that different kinds of terpenes have different ozone and aerosol forming potential. We know that with ambient higher temperatures most biogenic hydrocarbon emissions become important; but after rain events, terpene emissions also increase. Isoprene emissions increase through the middle of day and coincide with a peak in ambient ozone concentrations. Temperature, relative humidity, and meteorological events for a particular ecosystem are thus quite important for proper simulation and validation of biogenic emissions and ozone.

An example of the change in context of atmospheric chemistry is at Blodgett Forest, where UC Berkeley Cohen's group found speciation changes in gaseous reactive nitrogen during the day. These changes suggest that compliance with the 8-hour ozone standard would likely require regional as well as landscape assessments. At Blodgett Forest, a distance from isoprene emissions, it is clear that there is more ozone produced from direct emissions that most understandings of isoprene oxidation would allow (as much as 25%

more). It is likely that oxidation of secondary compounds from isoprene oxidation (e.g., methyl vinyl ketone) are a source of this added ozone. Far from areas of isoprene and nitrogen oxides emissions, ozone production continues with perhaps higher ozone forming potential for reactive nitrogen species. Then, once again, BEIGIS validation (landscape and regional) is not possible without validation of the photochemical models (regional). Both validation paths would thus play a significant role in compliance with the 8-hour ozone standard.

BEIS field validation in deciduous forests has relied on leaf branch level measurements to instrumented balloons and airplanes. These field validation programs benefit from homogeneous regions with little change in elevation but have been limited by lack of detailed chemistry information. Due to upwind and down wind slope flows and nocturnal surface level jets common with changes in elevation, meteorological parameters change on the path to Oak forests like Blodgett, while the forest itself alters the chemical content of air parcels. Understanding wind patterns through the mountains has been a long-term concern of meteorological data gathering and modeling at ARB. Field validation of biogenic emission inventory simulations in California may have to be different than the national efforts in the same vein.

Emission inventory models often behave unexpectedly and produce anomalous results. Continuous review of vegetation maps, EF and leaf mass databases, and continuing emphasis on isoprene chemistry for ozone help to understand and explain such results. We still need to develop North-South and East-West transects, choose and develop campaign sites of maximum model sensitivity, and concentrate on type of chemical signatures we should see (for example in Central Valley's agricultural areas). For oaks, we may begin by emission validation as an exercise. Transect analyses and multi-year campaigns may be difficult to sustain for ARB, but for developing a consensus, these programs should benefit from multiple sponsorship at any rate.

California state-of-the-art monitoring assets include 3 PM_{2.5} super sites, 26 total reactive nitrogen species (NO_y) instruments, and many new organic nitrate and nitric acid instruments. These monitoring assets were designed for

compliance assessment; some have been directed to address scientific questions through the photochemical assessment monitoring stations (PAMS) process. A more mature monitoring system in southern California competes for resources with northern and central California's evolving network; policy makers have responded to scientific demands of the complex natural ecology, agricultural, and rapid urbanization in northern and central California.

Control policies have reduced the bulk of hydrocarbon emissions in southern California; biogenic emissions are less important (10% by volume) but grow more important as anthropogenic emissions decrease even further. With less impact from biogenic emissions and a mature measurement network, model validation in southern California may have to augment the existing monitoring sites. In contrast, appropriate programs have and continue to build new sites, non-ARB and non-urban sites as well, in northern and central California. Land development in San Joaquin Valley urbanizes at an alarming rate; path of compliance with ambient air quality standards for ozone will be even more difficult than for southern California. Programs such as the Nitrogen Species Working Group and PAMS Technical Advisory Committees continue to improve assets in already existing sites in southern California (counter balance to agricultural community's wise and benevolent support for air quality in northern and central California).

We should remember that resource allocation follows over all public health goals and on that issue, the National Research Council's emphasis on PM_{2.5} management is our guide. Nevertheless, as new sites are built, scientific community has assisted and (should assist) the policy makers (e.g., San Joaquin Valley Technical Advisory Committee). Although we understand that one site model validation does not represent proper validation throughout the state and photochemical modeling sensitivity analyses are absolutely required, we should heed the requirements for ozone SIP first and foremost (Short-Term).

5.2 Aerosols Formation Validation

Comparing speciated terpenes with total terpenes and comparing both with ecosystem fluxes of terpenes are among ideas that do not require a full

validation of a biogenic aerosol simulation. Terpene reactions may be quite fast, leading to short lifetimes (5 to 30 minutes) for some primary emitted terpenes. Simultaneous observations of VOC emissions with newly formed small aerosols and deposition of large aerosols may be one way to avoid this problem. Another approach may be to observe “young” terpenes path to aerosols (scanning electron microscope application). Other approaches (UC Davis) have relied on separating time-resolved filters that collect aerosols and full analysis of the filter media to determine the parent hydrocarbons. These approaches are best combined with ways to resolve concentration and flux comparisons; canopy measurements at night are also recommended (Short-Term).

As with ozone formation, terpene formation is dependent on regional and ecological parameters; hot dry days suppress terpene emissions and there is no reason to conduct any measurement programs in those times (Campaigns in the fall and spring are more likely to succeed). Aerosol measurement programs continue to evolve; Peter McMurry has seen no nucleation during summer measurements in Michigan. Researchers in Finland observe nucleation in April, with VOCs perhaps coming from soils and not from plants. Are amines important to nucleation? What is the complete set of parameters that allows spring to provide for better nucleation? What markers are best for SOA in field measurements (di-acids)? Is proton mass spectrometry the right tool to detect some of these markers as well as terpenes? Determining regional and ecological parameters should either be achieved by multi-season campaigns or by extremely careful and fortuitous study design.

PM_{2.5} emission inventories are driven by ammonia and NO₃⁻ ion and both are important reasons for continued emphasis on control of NO_x emissions. Yet, the control assessment would be incomplete unless we address PM_{2.5} of anthropogenic origin (control fraction) and what fraction is biogenic. Formation of biogenic organic aerosols may be the easier to attack as a scientific problem. It is then important to understand regional parameters for ozone and aerosol formation as combine processes and to evaluate east-west transects of regional air pollution as well as north-south transects. For the critical San Joaquin and

Central Coast areas; we should begin from clean ocean air, through outflow of San Francisco Bay, and continue through agricultural inputs such as Davis, and end in the Sierra mountains for an east-west transect regional analysis (Short & Long-Term). Mobile monitoring may be useful in this type of analysis.

Much of this monitoring effort would focus on low vapor pressure (low volatility) hydrocarbons that are the essence of aerosol formation. Yet chemical standards for many of these hydrocarbon species are not available; use of plants as sources would be messy and inadvisable. These low volatility compounds are necessary to explain the atmospheric growth of nanometer size particles up to cloud condensation nuclei (~60 nm). There is some evidence for their appearance in environmental chamber studies, but mostly higher volatility compounds are found. Based on gas-particle partitioning calculations, many of these higher volatility compounds would not be expected to be in the condensed phase. It is difficult to identify and to measure vapor pressures of low volatility compounds (added complexity). For now, we are highly dependent on environmental chamber studies for characterization. These data are also useful in identifying origins of aerosols. We know that di-carboxylic acids are one of the important compound classes of interest; we also know that some of the unidentified low volatility compounds of interest may be the very compounds that properly explain observed atmospheric nucleation and growth rates. Organic peroxides and nitrates may be important, but it is difficult to measure such compounds by traditional methods. From environmental chamber data, we do not know the contribution of biogenic emissions to SOA formation. Estimates from modeling may not reflect actual atmospheric conditions either. While we do know that biogenic and anthropogenic hydrocarbons form similar types of aerosol compounds, health effects of either are not satisfactorily known. We should sponsor and support environmental chamber research in this area (Short & Long-Term).

6.0 Biogenic Aerosols

We must develop gridded biogenic PM_{2.5} emission inventories through application of BEIGIS outputs as inputs to a SOA model for the SIP in 2006. This

objective translates into developing terpene & other aerosol forming biogenic emissions inventory inputs for BEIGIS, building a SOA or other simulation platform, and validation the combined models.

6.1 Terpenes to Aerosols

Although alpha pinene has been studied in detail, it is agreed that understanding hydrocarbon aerosol kinetics of other terpenes is more difficult. Mechanisms possible from alpha pinene to low volatility species have been identified, other species are more difficult, pinic acid has been identified, and measurement techniques such as thermal desorption in vacuum have been suggested. All low volatility compounds are suspected as important to particle growth processes. Key need to determine terpene concentrations should be met recognizing that standard methods like Flame Ionization Detection have difficulties of conversion to methane equivalence and methods like proton mass spectrometry have substantial gain advantages useful for these low concentrations with short lifetimes.

6.2 SOA Model Building

As a preliminary matter, BWG must appoint a task force for selecting one or two appropriate Secondary Organic Aerosol (SOA) module(s) that would derive BEIGIS aerosol development decisions (Short-Term). Classes of compounds that should be modeled need shorter-term resolution and involve decisions on what classes of hydrocarbon compounds to look at and what hydrocarbon species to lump into a particular class of compounds. We may need to keep the chosen model simple. Where as a necessary choice, a particular area of science is inadequately treated; we should admit the model's limitations. We should evaluate BEIGIS to see if outputs are sensitive to variance in input databases such as leaf area and conduct other sensitivity analyses; we should investigate the probability of wrong predictions such as artificial hot spots. For sensitivity analyses, we should use either an off-the-shelf module or build a simple module ourselves. Finally, we should investigate if biogenic SOA simulations can be generated without a full suite of terpenes data.

We know of Seinfeld and Kamens groups as the only significant SOA model development efforts currently underway (Short-Term). For these modeling paths, partitioning coefficients provide better data on yields and temperature effects, rather than on detailed hydrocarbon to aerosol composition. Seinfeld and Kamens probably include a similar number of terpenes as their inputs. We would still need to better understand atmospheric chemistry of secondarily formed organic aerosols (Long-Term). In particular, we need to understand tracer compounds such as di-acids & other tracers that mass in chamber experiments show are critical in aerosol formation from biogenic hydrocarbons. Our current yield SOA without the detailed speciation would become a more speciated model relying on chemical kinetics (Long-Term).

BEIGIS aerosol development should flexibly incorporate other modules such as hydrocarbon emissions from fires as inputs to the SOA model, deposition of aerosols assessment, and grass cutting emissions (Long-Term). The current development of ammonium and ammonium nitrate emission inventories should be incorporated into SOA model and would account for natural ammonia sources and sinks (Long-Term).

Finally, interaction of PM2.5 and ozone in simulations is a key issue; can we separate PM2.5 and ozone simulations? A complete set of chemically speciated hydrocarbon and aerosol data would help us. Where air quality models are sensitive to ozone, simulation results of eliminating biogenic emissions would inform us. Both would define where the model is most sensitive and where to develop monitoring assets. Similar analyses should be done for urban forests. These are issues for SOA modelers to entertain (Short and Long-Term).

6.3 Inputs to Aerosol BEIGIS

Having determined the SOA model, we have to define inputs to that model and the character and parameters required for the inputs to fit the particularities of the SOA model. We will need a reliable terpenes emission inventory, gridded and speciated, to input into SOA to estimate contribution of biogenic aerosols to

ambient PM_{2.5} (Short & Long-Term). We ought to determine how much we know about particular biogenic emissions that form biogenic aerosols. We ought to prioritize terpenes and other biogenic emissions on basis of reactivity (aerosol forming potential), and we should focus on obtaining or developing better emission rate information on abundantly emitted terpenes that have substantial aerosol reactivity.

A speciated terpene emissions database is incomplete without accounting for total terpenes emissions (including sesqui-terpenes). Such total and speciated terpenes and other emission rates are best obtained in pine plantations like Blodgett Forest. Remembering that agricultural and urban vegetation may play a key role in ozone formation, we should include contribution of agricultural emissions to aerosol formation into the emissions rate database. With these priorities in mind, we should populate the terpenes emission rates database. We would need continuous monitoring programs covering seasonal and annual variation and at multiple locations where ozone and PM would be most important such as San Joaquin Valley, Kingswood, etc. As noted before and aside from emission rates, critical input databases to properly determine plant species distribution and leaf mass are proper vegetation maps.

6.4 Model Validation through Field Work

Primarily, we need to understand the nature of PM_{2.5} problem in each part of California. Analogous to ozone modeling, we need to validate two models – Aerosol BEIGIS and the SOA (with BEIGIS simulations as input)(Short & Long-Term). To this end, we need ambient PM_{2.5} and terpenes emission inventory data. To design appropriate measurements programs, we need to figure out where emissions hot spots are (e.g., Blodgett Forest). At these measurement sites, we may initially need to create global estimate of emissions and apply crude models to check on kinetics, yields, and other biogenic aerosol formation parameters. As noted in SOA selection and aerosol formation, we may have to develop new monitoring techniques in particular to measure tracer compounds or a list of important tracer compounds. We should measure aerosols within the larger context of the effects of other pollutants, landscape changes, seasonality,

and other programs in effect. In particular, Ameri-Flux program sites should be considered.

For SOA validation, we have to provide aerosol composition information and not just mass. We may require more than one site for both these developments; 3 or 4 stations for speciated terpenes and aerosols would be best (Long-Term). We may have to resort to a mobile monitoring unit an annual monitoring program at each site.

Coordination with California's Regional Particulate Air Quality Study (CRPAQS) is a critical issue; we should work with the Central Valley programs, Fresno super site in particular, in our validation project. Our cooperation with CRPAQS in winter time and fall measurement programs for ozone & spring and summer for PM_{2.5} should include terpene monitoring from a tower for spatial resolution (biogenic aerosol assessment measurements). To properly monitor agricultural contribution, we should measure outside the city to minimize urban inputs and look for di-acids and other markers (Short & Long-Term).

We should use particle concentrators developed for health studies to help us strengthen the aerosol and terpenes signal. We should also use direct measurements of organic aerosols to understand proper dispersion and deposition of biogenic aerosols (Short & Long-Term).

7.0 Conclusion

Cooperation, communication, and interaction between scientists and policy makers at this and similar planning efforts builds consensus necessary to sustain air quality control programs. We hope the workshop made a substantial contribution in this area.