DEVELOPMENT AND VALIDATION OF DATABASES FOR MODELING BIOGENIC HYDROCARBON EMISSIONS IN CALIFORNIA'S AIRSHEDS

FINAL REPORT

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ABSTRACT

Quantifying biogenic volatile organic compound (BVOC) emissions is critical in the development of effective ozone and fine particle control strategies in certain of California's airsheds. However, because of the diversity and complexity of California's vegetation (e.g. more than 6000 plant species), as well as the large areal extent of its airsheds, additional field data are needed to produce reliable gridded, speciated BVOC emission inventories from current and future ARB modeling efforts. The principal objectives of this field-based research project were to generate data needed to further develop predictive methods for BVOC emissions and leafmass for the large number of plant species relevant to California, and to further validate the vegetation landcover maps currently in use. To meet these objectives, we surveyed total BVOC emissions for more than 200 plant species not previously measured, using a photoionization detection system to identify emitters vs. non-emitters of BVOC for important California plant species; developed and tested methods for estimating leafmass, leaf area index, and leafmass densities for urban trees; conducted biomass sampling in a blue oak savanna to test leaf mass and leaf area index allometric relationships for this high-emitting species; conducted quantitative field-based analysis of the GAP GIS landcover vegetation database for the San Joaquin Valley; and continued to work collaboratively with ARB staff to further develop a state-of-the-science methodology for the generation of a quantitative statewide BVOC emission inventory for California. Among our principal findings were that plant taxonomy provided a useful framework for categorizing emitting plant species, genera, and families; the volumetric method for estimating leafmasses, and corresponding leaf area indices, gave good agreement with field measurements, including whole-tree harvests for urban trees and oaks; mean leafmass densities for urban trees and a natural stand of blue oak trees were higher and lower, respectively, than values for eastern deciduous forests; and the GAP GIS database for the Central Valley, while showing substantial agreement with species found in the field, exhibited enough discrepancies between GAP listings and our field surveys to imply the need for a careful review of the utility of GAP for BVOC inventory development in California. The detailed data and predictive methods resulting from this field program will be directly useful in testing and improving current BVOC emissions models being developed by ARB, including the statewide BEIGIS model.

1.0 EXECUTIVE SUMMARY

It is now well known that volatile organic compounds (VOC) are emitted from vegetation, including urban landscapes, agricultural crops, and natural plant communities in unirrigated areas. The overall magnitudes of biogenic volatile organic compound (BVOC) emissions of an individual plant are affected by its leafmass and by its intrinsic BVOC emission rates, as well as by environmental factors such as temperature and light intensity. An accurate estimate of the magnitude of BVOC emissions relative to anthropogenic VOC emissions in California's airsheds is critical for formulating effective strategies to reduce concentrations of fine particles, ozone, and other secondary air pollutants which affect human health and reduce yields of agricultural crops.

Although considerable attention has been given to determining BVOC emission rates in past research, leafmass quantification and plant species composition and dominance may be the weaker links in the development of BVOC emissions estimates both for plants in urban settings and for emission inventories at a regional level. Of particular interest in this regard are California native oaks, because of their high emission rates, large aereal extent, and large foliar masses. For California airsheds, the development of the GAP landcover database in principle offers plant species-specific data useful for BVOC emission inventories. However, although GAP is arguably the most recent and comprehensive landcover database available, it has been developed for other purposes, especially for identifying habitats of threatened plant or animal species, and thus may lack the degree of quantification needed for biogenic emissions inventory development. Moreover, the translation of landcover data such as GAP to emissions models is problematic because a value for leaf mass must be added to the existing data or a relationship must be derived between data from remote sensing and foliar mass.

The present study addressed these issues through an integrated field study employing a "ground-truth" approach, generating experimental data with which to test existing empirical relationships and remote-sensing data. Results of this project will be useful in improving biogenic VOC emission inventories, and informing airshed modeling approaches for development of future ozone and fine particle control strategies by the Air Resources Board. The study was divided into four major subprojects: measurement of BVOC emissions from plant species found in California; investigation of methods for estimating leaf mass of urban trees; leaf mass measurements for native blue oaks; and evaluating the accuracy of the GAP landcover database. The study was conducted primarily in the southern San Joaquin Valley and surrounding mountain ranges.

To measure BVOC emissions, replicate samples of live foliage of more than 250 plant species were placed in plastic bags in both light and darkened conditions, and the emissions measured with a calibrated portable analyzer, and categorized as low, medium or high. Urban trees were photographed with a digital camera and their dimensions were measured in the field, followed by whole tree harvest and separation and weighing of leaves. Measured weight of leaves was compared for each tree to estimates from published equations, estimates derived from calculations of crown volumes, and estimates derived from digital analysis of the photographs. For native oak trees, methods and data analyses were similar to those for urban trees but also included measurements of leaf area made with an electronic plant canopy analyzer. The GAP database was evaluated through field surveys at specific locations in which foliage dimensions of all plants along randomly selected transects were measured and

species identities noted. These field data were then compared with species identities and crown closure information listed in the GAP database.

To validate the portable analyzer unit (PAU) approach we compared PAU-measured BVOC emissions for approximately 60 plant species with published values and found them to be wellcorrelated. For approximately 200 plant species not previously measured, the PAU data indicated that plant taxonomy served as a useful method for characterizing the magnitude and nature of emissions (either light or dark, or both), where appropriate comparisons could be made. Specifically, willows, poplars, eucalyptus, and many oak species had high emissions in the light, whereas plants in the rose and olive families had low emissions in the light. Eucalyptus trees and Chinese pistache had medium emissions from darkened foliage. Sub-family classification of legumes was helpful in characterizing emission behavior, as was sub-genus classification of oaks.

For estimating leafmass, the volumetric method worked well for urban trees, with tree crowns modeled with a paraboloid shape yielding estimates closer to the experimentally measured whole-tree harvest values than for any other geometric solid. For oak trees, leaf mass and leaf area per area of ground surface area gave values lower than those reported for eastern U.S. forests, but in reasonable agreement with a database used recently by Air Resources Board modelers. Accuracy of the GAP database was found to vary between locations surveyed, but BVOC emission calculations based on field data rather than the GAP database would give lower results for a majority of locations we surveyed.

This project has provided data vital for quantifying BVOC emissions in California's airsheds. The results provide further evidence that plant taxonomy can serve as a useful guide for estimating BVOC emission rates for unmeasured species, and that it is possible to generalize the emissions behavior of many, but not all, plant families and genera. Native blue oak trees at the measurement site studied contained less leaf mass and leaf area than would be expected based on data from eastern oaks, but were in reasonable agreement with leaf area data from a database used recently by Air Resource Board modelers. Moreover, the volumetric method for estimating leaf mass of individual urban trees worked well for the species we studied. These results strengthen and validate the methodology currently used by ARB in developing the statewide BEIGIS model. However, landcover data for plant species composition and distribution remain problematic based on our assessment of the GAP database for the southern San Joaquin Valley and southern Sierra Nevada mountains. Also still unresolved is the issue of scaling emission rates measured at leaf- or branch-level to whole-tree or landscape-scale flux measurements, and an inter-comparison of results at these different scales would be important in validating current ARB BVOC emission inventory methodology. Other future research needs include further validation of landcover databases, and measurement of BVOC aerosol-precursor emission rates and plant species-specific gaseous and particulate pollutant deposition rates to vegetation, in order to characterize "net-effects" of plants on air quality.

2.0 INTRODUCTION AND BACKGROUND

2.1 Introduction

As the result of several decades of cost-effective air pollution control programs by the California Air Resources Board, and a succession of regional air quality agencies, air pollution in the California South Coast Air Basin (SoCAB) reached a fifty year low in 2000. The reduction in ozone first stage alerts in the SoCAB, for example, from a high of 121 in 1978 to none in 1999 and 2000 (SCAQMD 2000). This is a profound achievement given the enormous growth in population and emission sources in the SoCAB over the period of these control programs. Unfortunately, the degrees of improvement in other airsheds of California, including the Central Valley, have not been nearly as dramatic (ARB 1997).

One possible contributing factor to the disparity in progress in various California airsheds is the role of volatile organic compounds (VOC) from vegetation, or biogenic VOC (BVOC). Modeling studies by the ARB suggest that development of specific emission control strategies for reducing ambient ozone in certain areas of California is dependent upon estimated emissions of BVOC. These studies, using the Urban Airshed Model (UAM), showed that emissions of hydrocarbons from vegetation can make the difference between NO_x vs. VOC emission controls being the most effective in reducing ozone concentrations (Jackson 1997).

A study published from our laboratory (Benjamin et. al. 1997) estimated isoprene and monoterpene emissions in the SoCAB to be no more than 10% of anthropogenic VOC, and therefore BVOC are not expected to limit the effectiveness of VOC controls in the SoCAB (until anthropogenic VOC emissions are reduced far below current levels). Our assessment of the lack of a significant role for BVOC in the SoCAB is supported by a modeling study of Kuklin and Seinfeld (1996). In contrast, however, in heavily vegetated airsheds in California, BVOC emissions may limit the effectiveness of VOC control, setting a floor under the reduction in ozone that can be achieved by reducing anthropogenic VOC [although at present there remains too much uncertainty in current BVOC estimates for airsheds other than the SoCAB to draw definitive modeling conclusions (Jackson 1997)].

Concern about the possible critical role of BVOC emissions is reinforced by (a) the fact that on average many BVOC are as reactive, or more reactive, in the atmosphere than

emissions from mobile or stationary anthropogenic sources (Carter 1994, Benjamin and Winer 1998); and (b) a growing body of research from studies throughout the world suggesting that BVOC can constitute a significant and even dominant contribution to the overall VOC inventory in both regional airsheds and the global atmosphere [Workshop on Biogenic Hydrocarbons (WBH) 1997, Gordon Conference 2000].

Given the key role played by BVOC in the atmosphere, and the enormous costs associated with further reducing VOC and NO_x in California to meet state and federal air quality standards (AQS), it is critical to quantify the essential databases needed to assemble reliable BVOC emission inventories; to expand and refine predictive methods for emission rates and leafmass constants; and to further develop and validate key components of ARB BVOC models such as BEIGIS. Indeed, placing the air quality role of biogenic hydrocarbons on a more quantitative basis must be ranked as a priority of state and federal air quality regulators.

2.2 Background

The emission of reactive hydrocarbons such as isoprene and monoterpenes by vegetation has been known for several decades (Went 1960, Rasmussen 1972) and as discussed below, the ARB (with characteristic foresight) funded one of the earliest experimental investigations of the emissions and role of such compounds in air pollution in California (Winer et. al. 1983). Only in the last decade, however, has interest in the fundamental and applied aspects of BVOC in the atmosphere expanded dramatically, both in the scientific and regulatory communities.

Evidence of the widespread attention to the role of BVOC in photochemical smog and other atmospheric processes was provided at the international Workshop on Biogenic Hydrocarbons in the Atmospheric Boundary Layer held in August 1997 at the University of Virginia, the first truly international conference devoted exclusively to BVOC. Nearly one hundred papers from the United States, many countries in Europe, Japan, Russia, Canada, India, and China were presented on the emissions, atmospheric chemistry, ambient concentrations, and impacts on ozone and particulate formation of isoprene, monoterpenes and other BVOC. Three years later, the first Gordon Research Conference on Biogenic

Hydrocarbons was held, a clear indication of the growing scientific importance of this area of research. The Gordon Conference also was attended by a large number of international scientists, as well as key investigators from the U.S. It was clear from these two international conferences that regulatory agencies throughout the world, including the U.S. Environmental Protection Agency and the California Air Resources Board, are now concerned with better characterizing the importance of VOC, relative to anthropogenic VOC, in key air pollution processes. Research presented at these meetings (WBH 1997, Gordon Research Conference 2000), as well as recent advances in understanding the atmospheric chemistry of BVOC (Atkinson and Arey 1997), also reinforce the need to generate reliable emission rate and biomass data unique to each region, illustrating that data generated for the other parts of the United States may have limited utility for California, for reasons elaborated below.

In the sections which follow, we provide a brief overview of research from this laboratory, and other researchers, relevant to California's airsheds; summarize the BVOC research needs facing the ARB in California at the time the present research project was initiated; present the overall and specific objectives of our proposed research; describe our approach to generating the required data; and discuss the expected benefits to ARB's development of sound future control programs. We emphasize that the overarching goal of the proposed research was to continue, as we have in the past projects, to provide direct, collaborative support to ARB's on-going effort to develop a state-of-science methodology for development of BVOC emissions inventories and models unique to California's airsheds.

2.3 Previous BVOC Studies in California

2.3.1 Principal Investigator and Collaborators

2.3.1.1 South Coast Air Basin

The first survey to determine the magnitude of hydrocarbon emissions from vegetation in a California airshed was completed with ARB support by Winer and co-workers in 1983 for the urbanized region of the SoCAB (Winer et al. 1983). This study employed a combination of aerial photography (Brown and Winer 1986) and ground surveys (Miller and Winer 1984) with a stratified random sampling approach to determine vegetation biomass. Of the more than 180 plant species identified in the study area, hydrocarbon emission rates

were determined experimentally for more than 60 of the dominant species. In addition, leaf mass constants (g per cubic meter) were developed for 55 genera of plant species found in the Basin, permitting conversion of crown volume to dry mass of leaves.

Winer and co-workers used these leaf biomass constants, along with the experimentally determined isoprene and monoterpene emission rates, to estimate the biogenic hydrocarbon emission inventory corresponding to about one-third the area of the SoCAB (specifically the western and middle portions of the Basin containing most of the anthropogenic emissions of VOC and NOx at that time). For this area these workers found a likely range of total isoprene and monoterpene emissions of 20 to 80 TPD (Winer et al. 1983).

In a later study, sponsored by the California Institute for Energy Efficiency (CIEE), Winer and co-workers extended and refined the previous studies for the SoCAB by addressing four areas of uncertainty (Winer et al. 1995, Benjamin et al. 1997). First, land use distribution for the SoCAB was digitized on a geographical information system (GIS) at a 300 m resolution for the urban portions of Los Angeles and Orange Counties, as compared to 5000 m resolution of previous studies (Horie et al. 1990, Causley and Wilson 1991). Second, the existing database of emissions measurements was enhanced by the use of additional experimental measurements for emission rates reported in the literature. Third, as discussed in more detail below, for the more than 200 species without measured emission rates, emission values were assigned based on taxonomic relationships (Benjamin et al. 1996) rather than on the structural class of the vegetation. Finally, a recent correction algorithm for environmental factors such as temperature and light intensity developed by Guenther et al. (1993) was used in place of the Tingey et al. (1979) algorithm.

This study found total leaf biomass for the SoCAB of approximately 6.5 million metric tons both in the winter and summer (neglecting vegetation leaf loss for the natural species), with biomass concentrated in the forested mountains on the northern and eastern boundaries of the Basin. Isoprene and monoterpene total emissions were estimated to be in the range 125-141 TPD in the summer and 40 TPD in the winter, with total emissions as high as 200 TPD for ozone episode days (Benjamin and Winer 1997).

2.3.1.2 Central Valley

In support of an ARB Program to develop a biogenics emission inventory for California's Central Valley, including the Sacramento and San Joaquin Valley Air Basins, Winer and co-workers (Winer et al. 1989, 1992; Arey et al. 1991a,b) measured the rates of emission of speciated hydrocarbons from more than thirty of the most important (based on acreage) agricultural and natural plant types relevant to California's Central Valley. Four dozen individual compounds were identified as emissions from agricultural and natural plant species studied.

Data obtained in this study demonstrated again there can be large variations in emission rates from a single specimen of a given plant species, as well as from multiple specimens of a cultivar. Mean emission rates for total monoterpenes ranged from none detected in the case of beans, grapes, rice and wheat to as high as 12-30 μg per hour for pistachio and tomato (normalized to dry leaf and total biomass, respectively). Agricultural species were found to be overwhelmingly monoterpene emitters and not isoprene emitters (Winer et al. 1992).

In a subsequent ARB-supported project, much of the experimental work was conducted at the University of California's Shafter Research and Extension Center, near Bakersfield. In this project we measured the emission rates of isoprene from nearly seventy plant species, the great majority of which had no previous experimental emission rate data (Karlik and Winer 2001b). These measurements extended over two summer seasons, in many cases involving repeated measurements during the season. This study substantially expanded the emission rate database for key California plant species. These new experimental data were used to test the efficacy of the predictive taxonomic method published earlier from our group (Benjamin et al. 1996).

A second major phase of this study was conducted at Shafter for plant species of relevance to both the Central Valley and other areas of California and involved experimental comparison of calculated vs. measured leaf mass for urban trees. As noted above, one of the most serious deficiencies in current efforts to assemble BVOC emission inventories for urban areas is an absence of reliable leaf mass constants for key plant species. Although destructive whole tree sampling has been used to derive leafmasses of forest trees, few such studies have

been conducted for trees or shrubs in urban settings. Through a variety of strategies, we were able to identify nearly two dozen mature trees of appropriate species at several locations for total leafmass determinations. Plant height and radius were measured, and a geometric solid which best fit the form of each plant in the field identified. From these data the crown volume could be calculated. Next a series of cube samples were taken at random positions within the tree crown and the leaves within the cubes removed, dried and weighed. Finally, the complete trees were then harvested and all leaves removed, dried and weighed. From the resulting data we were able to compare the actual experimentally measured whole-tree leafmasses to leafmasses calculated by a several different approaches, or from the literature, and in comparison with the cube samples. This research was reported at the international Biogenic Hydrocarbon Workshop (WBH 1997) and was subsequently published (Winer et al. 1998, Karlik and Winer 1999).

2.3.1.3 SCOS 97 Study Region

At the request of the ARB, we undertook a field study of the validity of the GAP GIS database for San Diego County, which at that time had the least well characterized BVOC inventory of any of the counties in the SCOS97 study domain. A field protocol for sampling vegetation composition and dominance using line transects was developed and peer-reviewed by appropriate UCLA faculty, and by David Stoms, Principal Investigator for the GAP database in the San Diego County area. Using a statistically randomized selection of transect sites within polygons chosen for their likely high BVOC emissions, we collected data needed to test the validity of the GAP assignment of plant species assemblages in the natural areas of San Diego County. Further details of this study have been published (Chung and Winer 1999).

2.3.2 Other Researchers

2.3.2.1 South Coast Air Basin

Horie and co-workers (Horie et al. 1990) conducted a study supported by the SCAQMD designed to provide a gridded inventory of plant biomass in order to develop an improved hydrocarbon emissions inventory for use in the UAM. High- and low-altitude

photography, in combination with ground surveys, was used to identify vegetation in the SoCAB. More than 470 plant species were identified with total leaf mass of approximately 8 million metric tons. Horie et al. (1990) also compiled an emissions rate database from the literature and suggested values for isoprene and monoterpene emissions rates for the plant species identified in the biomass survey. For those species without measured emissions rates values were assigned based on the average emission rate for the structural class (i.e. conifers, broadleaf deciduous, broadleaf evergreen, shrubs and palms) of that plant. Correction factors were also supplied to account for the effects of seasonal and diurnal changes in light intensity and temperature on vegetative emissions, and for changes in biomass associated with seasonal changes (e.g. deciduous tree leaf fall).

The resulting data were used by the SCAQMD to develop spatially-resolved biogenic emissions estimates for each day of three meteorological episodes (SCQAMP 1991). These emissions ranged between 150 and 250 metric tons per day (TPD), with the majority produced in the heavily vegetated mountain areas downwind of the SoCAB.

Using the same biomass and emissions data compiled by Horie et al. (1990), Systems Applications International (SAI) developed a temporally-resolved gridded inventory of vegetative hydrocarbons for the SoCAB (Causley and Wilson 1991). The computer program "VEGGIES" provided an hourly estimate of vegetative hydrocarbon emissions for each grid square (5 km by 5 km) in the SoCAB during an entire year utilizing temperature and light intensity correction factors and a canopy adjustment factor (EPA 1990) to model the effects of decreased light levels with the leaf crown volume of trees. The results from the SAI survey indicated there were approximately 100 TPD of hydrocarbons emitted from vegetation during the summer compared to approximately 30 TPD emitted in the winter (Causley and Wilson 1990).

2.3.2.2 Central Valley

The Desert Research Institute (DRI) developed a biogenics emission inventory for the SJVAQS/AUSPEX region, based on a combination of satellite imagery used to identify vegetation classes and Radian's Emissions Model System (Tanner et al. 1992). Of 39 identified vegetation classes one was agricultural, two were urban, three consisted of sand,

water or snow-covered areas with negligible biogenic hydrocarbon emissions and the remaining 33 classes were natural vegetation communities with varying degrees of specificity in plant species distribution.

For each species known to be present in each natural community, community-specific biomass factors were assigned, as were either measured emissions rate factors or an emission factor (EF) based on a surrogate species from the same genus or family.

Agricultural emissions were spatially defined only on a county basis, using a species mix of 10 crops identified as significant emitters by Winer et al. (1989, 1992). Agricultural acreages for 1990 were used along with biomass estimates provided by Sidawi and Horie (1992) based on summaries of literature data. Based on county-wide data, Tanner et al. (1992) obtained a preliminary estimate that about 15% of the total biogenic hydrocarbon emissions by mass in the AUSPEX region, approximately 480 TPD of a total 3360 TPD, were produced by agricultural crops.

2.3.2.3 Sacramento Valley

Causley et al. (1991) reported a study to estimate biogenic emissions for the Sacramento modeling domain in which a software system was developed to produce gridded hourly estimates of biogenics in this area. Utilizing California specific emission factors for individual plant species, they generated emission estimates for the isoprene and several monoterpenes. Emissions were spatially allocated using USGS GIS data for various land use categories, and the effects of environmental factors were accounted for using Tingey algorithms and canopy shading adjustment factors.

Three 24 hour gridded biogenic inventories were generated for an August 7-9, 1990 episode, with total emissions of approximately 200 TPD. Isoprene constituted 37% of the inventory and alpha- and beta-pinene and myrcene accounted for 95% of the monoterpene emissions. As in the other studies of this kind, the authors noted the need to determine the sensitivity of the generated inventory to factors with large uncertainties, including biomass spatial allocation and measurements, assignments of known plant emission factors to species with unknown factors, and adjusting for canopy effects (Causley et al. 1991).

2.4 Statement of the Problem

As discussed above, quantifying BVOC emissions and understanding the atmospheric reactivity of isoprene, monoterpenes and other BVOC are critical elements in the development of effective ozone attainment strategies. ARB-funded research has produced a wealth of data related to biogenic hydrocarbon emissions in California and substantial progress has been made in characterizing the atmospheric chemistry of BVOC. However, even allowing for the fact not all plant species emit significant quantities of BVOC, because of the enormous diversity and complexity of California's vegetation (i.e. 6000 species), as well as the large areal extent of its airsheds, substantial gaps remain in the data needed to produce a gridded, speciated, day-specific BVOC inventory for the entire state.

For example, to date less than 5% of all California plant species have undergone even qualitative measurements of BVOC emissions. Although a taxonomic predictive method recently proposed from this research group (Benjamin et. al 1996) shows promise, additional validation is needed to place such a system on a robust statistical foundation. Similarly, to date less than 1% of California species have had experimental leafmass-to-volume ratio determinations. Although additional data, some from the first systematic whole tree measurements ever conducted for urban species, were obtained from our previous ARB project (Karlik and Winer 1999), these data have not yet been tested on the basis of taxonomy or structural class to permit more accurate extrapolation to the more than 95% of California plant species for which no data are available. The lack of such species-specific leafmass measurements has forced the use of structural class averages for recently generated BVOC inventory estimates for Ventura and Santa Barbara Counties, an unsatisfactory approach. Of particular concern for natural plant communities are oaks which are high isoprene emitters and, given their populations and biomass, are a dominant genus of trees in California in producing BVOC fluxes. Whole tree leafmass is not well characterized among oaks, especially for oaks in rangeland settings.

Assignment of spatial allocation of vegetation and species identity (i.e. characterization of composition and dominance) may be the weakest link in the entire BVOC inventory development process at this time. Newly available GIS-based landcover databases such as GAP may be a valuable source of plant species identity and distribution. However,

apart from the prototype study conducted in San Diego County in our previous ARB study (Chung and Winer 1999), we are aware of only one other attempt (unpublished) to validate the GAP database for California, and this was not done for the purpose of assembling BVOC emission inventories. Moreover, plant communities in California are unlike those of eastern temperate forests, differing both quantitatively and qualitatively, requiring caution in applying data for the East and Northwest to California.

It must be emphasized that only with the development and validation of the databases described above, can reliable spatially- and temporally-resolved BVOC emissions models be developed for the rest of California, comparable to the inventory we have developed, with partial ARB support, for the South Coast Air Basin (Benjamin et al. 1997).

2.5 Objectives

2.5.1 Overall Objectives

This present study was designed to provide critical data in four key areas, including qualitative measurements of total BVOC emissions from a large number of California species not previously measured for BVOC emissions, using a portable analyzer instrument; leafmass-to-volume relationships for key California species, including oaks in rangeland communities; ground-based validation of the GAP GIS vegetation database for selected areas of the California Central Valley; and further development of predictive methods for species-specific emissions and biomass. As part of this project, the investigators also continued to work closely with ARB staff to further develop and refine the methodology for development of a statewide BVOC emission inventory.

2.5.2 Specific Objectives

The specific objectives of this research project were:

o Experimentally survey the total BVOC emissions for several hundred key California plant species not previously measured, using a portable analysis unit (PAU) to identify emitters vs. non-emitters of BVOC. Use of a PAU allowed rapid surveying of a much larger number of species than has been possible with either a gas chromatograph-based

Teflon enclosure or leaf cuvette approach. Emphasis was on suspected "high" emitters of either isoprene or monoterpenes/sesquiterpenes, and on plant species which can provide further tests and validation of our taxonomic approach to predicting BVOC emission rates. The data generated in this study will be directly useful for emission inventory building, particularly since it readily identified "non-emitting" plant species.

o Develop and test methodologies for estimating leaf mass, including evaluation of precision and accuracy of the resulting predictive methods. This study extended our recent research on quantitatively evaluating various methods for estimating foliar biomass by experimentally measuring leafmass, including for whole trees, and comparing experimental data for representative tree species to estimates obtained from literature algorithms and volumetric methods.

o Conduct biomass sampling, including whole tree sampling, among high-emitting oak species in rangeland environments to develop statistically robust data on leaf mass per volume and leaf mass per area of crown projection ratios. This research focused specifically on one of the most important genera for natural landscapes in California, the high isoprene emitting oak species, which can dominate isoprene inventories in certain airsheds. Lack of reliable biomass constants for oaks has been a weakness in past BVOC inventories in California.

o Conduct a quantitative, field-based analysis of the GAP GIS landcover vegetation database for the San Joaquin Valley. This task extended to the Central Valley our research on the validity of the GAP database for portions of the SCOS97 domain. In our present project we have applied a field-based protocol for experimentally evaluating the reliability of GAP, and for obtaining field data needed to convert the "flat" GAP landcover map to a three dimensional map permitting estimation of biomass through a volumetric approach, to representative areas of the Central Valley, since this is a critical airshed for BVOC inventory development.

o Continue to work collaboratively with ARB staff to further develop a state of science methodology for the generation of a quantitative statewide BVOC emission inventory for California. This work continued our assistance to ARB staff in the refinement and implementation of the methodology developed, during our earlier projects, for a BVOC emission inventory for the SCOS study domain.

In the following chapters we describe in detail how each of these objectives were carried out, the results obtained, and their implications and significance.

3.0 TOTAL BVOC MEASUREMENTS OF SELECTED PLANT SPECIES

3.1 Introduction

It is now well known that reactive organic gases are emitted from vegetation, including urban landscapes, agricultural crops, and natural plant communities in unirrigated areas. The global budget of volatile organic compounds is dominated by biogenic emissions (Guenther et al. 1995) and BVOC emissions play important roles in tropospheric ozone formation, production of organic acids important in acidic deposition in rural areas, global tropospheric chemistry, and balancing the global carbon cycle (Fesenfeld et al. 1992). More than 70 different BVOC compounds are known to be emitted by plants (Isidorov et al. 1985, Winer et al. 1992, WBH 1997) but only a few are emitted in relatively large quantities. Vegetative emissions are as reactive or more reactive than the VOC emissions from automobiles, and can have higher ozone-forming potential (Carter 1994, Benjamin and Winer 1998).

In general, broadleaved plants, such as oaks and eucalyptus, have as their largest BVOC emission the five-carbon compound isoprene, whereas pines and other conifers have as their largest BVOC emission the family of ten-carbon compounds, the monoterpenes. The magnitudes of BVOC emissions of an individual plant are affected by its leafmass and by its rates of emission of isoprene, monoterpenes and other VOC, as well as by environmental factors such as temperature and light intensity.

Isoprene is the BVOC emitted in greatest quantity by the plant kingdom worldwide (Guenther et al. 1995) and is the dominant BVOC emitted by deciduous forests (Geron et al. 1995) typically accounting for 2% of the carbon fixed during photosynthesis (Monson and Fall 1989, Loreto and Sharkey 1990). Among the plant species measured, emission rates of isoprene differ by more than three orders of magnitude (Benjamin et al. 1996) and the resulting ozone-forming potential (OFP) of individual trees and shrubs ranges over nearly four orders of magnitude (Benjamin and Winer 1998).

Seminal studies of BVOC emissions in California were carried out in the South Coast Air Basin (SoCAB) (Winer et al. 1983, 1989) and green plants are expected to be contributors to VOC emissions in all California airsheds (Arey et al. 1995, Winer et al. 1995, Chinkin et al. 1996b, Benjamin et al. 1997). Recent modeling studies by the California Air Resources Board (ARB) have indicated that development of specific emissions control

strategies for reducing ambient ozone concentrations in some areas of California are dependent upon estimated fluxes of biogenic hydrocarbons (Jackson, 1997). These studies, using the Urban Airshed Model with Carbon Bond IV chemistry, showed that emissions of hydrocarbons from vegetation can determine whether NOx emission controls or VOC emission controls are most effective in reducing ozone concentrations. Similar conclusions concerning the potential importance of biogenic hydrocarbon emissions in determining the efficacy of control programs for anthropogenic emissions have been reached for other airsheds and regions (Chameides et al. 1988); specifically, an accurate estimate of the magnitude of biogenic contributions is important in formulating strategies to reduce peak ozone concentrations, because an effective strategy will take into account the relative strength of NOx and VOC emissions.

For California airsheds such as the San Joaquin Valley Air Basin (SJVAB), vegetative emissions likely comprise a large proportion of total VOC emissions. The SJVAB has been declared a severe non-attainment area for ozone, and ozone concentrations have not been reduced in parallel with those of the South Coast Air Basin (SoCAB) where substantial progress has been made. Despite rapid population growth, the San Joaquin Valley remains largely rural and extensive natural plant communities, including large expanses of oak woodlands, exist below the atmospheric boundary layer on the south and east sides of the Valley. Although agricultural crops, in general, have low to moderate rates of BVOC emissions (Winer et al. 1992), certain tree and shrub species found in urban landscapes and in natural plant communities of California have medium to high BVOC emissions rates (Benjamin et al. 1996) and ozone-forming potential (OFP) (Benjamin and Winer 1998). Plants with both high emissions rates and high leafmass per plant, including several of the oak species, may contribute substantial BVOC emissions (Benjamin and Winer 1998) to the SJVAB and other airsheds.

3.2 Background and Statement of the Problem

3.2.1 Factors Influencing BVOC Emissions from Vegetation

BVOC emissions are affected by many factors, including plant genetics, light, temperature, CO_2 concentration, humidity, plant health, transpiration rate, stomatal conductance, leaf development, time of day, season and environmental stresses (Guenther et

al. 1995). These factors seem to be relatively well understood for biogenic isoprene emission, and less so for other BVOC. The environmental factors of light and temperature have major effects on the measured isoprene emission rate of individual plant species while other environmental factors, such as CO_2 concentration, relative humidity, and nitrogen status, have less influence under normal field conditions. Developmental factors related to leaf age also affect isoprene emission rate, and there are also inter-relationships between light and temperature and developmental factors.

In recent years, the processes leading to isoprene and monoterpene synthesis and emission have become better understood at the physiological level (Sharkey et al. 1991a, Kuzma and Fall 1993, LaFever and Croteau 1993, Monson et al. 1994, Sharkey 1997). Substantial progress has been made in understanding the mechanisms governing BVOC emissions and the dependence of BVOC emission rates upon environmental factors, including quantitative descriptions of the magnitude of emissions under varying conditions of light and temperature. The algorithms proposed by Guenther and co-workers (1993) have stood well against other proposed empirical equations, and appear to offer adequate quantitative description of the effects of light and temperature upon isoprene and monoterpene emission rates. Temperature and the intensity of photosynthetically active radiation (PAR) are the environmental factors which most affect isoprene emission rate and are the only environmental factors included in the widely accepted algorithm of Guenther et al. (1993). The algorithm for isoprene was developed from emission rate data collected over a range of temperatures and light intensities and accounted for about 90% of the diurnal variability in isoprene emission rate. For monoterpenes, temperature is the only environmental factor included in the algorithm for those compounds (Guenther et al. 1993).

Developmental factors would be important when considering isoprene emissions of deciduous plants in the very early spring as leaves unfold and in autumn as leaves senesce, with calendar times of approximately early April for leaf development and November-December for leaf senescence in the southern San Joaquin Valley or Southern California. For BVOC emissions inventories in California, seasonal effects should be minor because the principal smog season extends from about June 1 to September 15. Leaves should be fully expanded and mature throughout this time period.

3.2.2 Rationale and Approach for the Present Investigation

Much of work pertaining to BVOC emissions has been carried out in the temperate continental regions of North America, which has plant species composition and distribution unlike the Mediterranean climate of California. The study of Winer and co-workers (1998) produced isoprene emission rate data for more than sixty plant species important in California and these data provided a test of a proposed taxonomic method for predicting isoprene and monoterpene emission rates (Benjamin et al. 1996). The Biogenic Emission in the Mediterranean Area (BEMA) project has recently been completed, and provides valuable additional BVOC data for a Mediterranean climate region of the world (BEMA 1997, Sharkey et al. 1997), including data for BVOC emissions from plant enclosure studies (Owen and Hewitt 1997, Owen et al. 1997)

In California, 173 families, 1222 genera, 5862 plant species and 1169 subspecies found in natural plant communities have been described (*The Jepson Manual* 1993). Additional exotic species are found in landscapes within urban areas. Clearly it is not possible to quantitatively determine the isoprene emission rates of even a small fraction of the plant species found in California and other regions, although qualitative appraisals of emission rate behavior for substantial numbers of previously unreported species have been published based on detection of BVOC with portable analysis units (Guenther et al. 1996, Lerdau and Keller 1997, Klinger et al. 1998). Because a vast number of species remain to be evaluated, generalizations of BVOC emissions rates based on plant taxonomy have been made (Guenther et al. 1994, Rasmussen and Khalil 1997, Klinger et al. 1998) and used in developing BVOC emissions inventories for urban areas (Geron et al. 1995). An explicit link between isoprene and monoterpene emissions rates and plant taxonomic relationships was proposed for species found in southern California (Benjamin et al. 1996) and was subsequently used (Benjamin et al. 1997) to compile a detailed BVOC emissions inventory for the California South Coast Air Basin (SoCAB) and to estimate the ozone-forming potential of urban trees and shrubs found in the SoCAB (Benjamin and Winer 1998). However, an important exception to the BVOC emissions suggested by taxonomic relationships has been reported for *Quercus ilex* (Staudt and Seufert 1995, Kesselmeier et al. 1996, Loreto et al. 1996) and additional experimental measurements of isoprene and monoterpene emissions for carefully selected plant species are required to expand and further

test the taxonomic predictive method. Therefore, a goal of the present study was to extend the taxonomic method for estimating biogenic emission rates of plants by screening key California species for which no previous emission rate data are available. The resulting measurements of BVOC emissions can then be used with the taxonomic method to categorize BVOC emissions for unmeasured species on the basis of plants measured within the same genus or family (Benjamin et al. 1996).

The approach within the present study was to use a PAU [defined in Section 2.5.2] to measure total BVOC from sampled plants to rapidly expand the number of plant families, genera and species which have been at least qualitatively measured, while using previous quantitative emissions rate data as benchmarks upon which to relate new PAU-based estimates of BVOC emissions. Also, plants without reported emission rates, but critical on the basis of areal coverage or biomass, were surveyed. The data acquired were then used to place sampled plant species into high, medium, or low emission categories.

3.2.3 Availability and Location of Plant Specimens

Most urban tree and shrub species sampled in this study were found in irrigated landscapes on the San Joaquin Valley floor (elevation ca. 500 ft), including species within the plant collection surrounding the University of California Cooperative Extension office in Bakersfield, in city parks and in residential landscapes within the Bakersfield metropolitan area, and on the campus of California State University, Bakersfield. Plant genera more frequent in cooler climates, such as *Cornus* and *Viburnum*, were sampled within the Mourning Cloak Botanic Garden, located in the Tehachapi mountains 30 miles east of Bakersfield at ca. 4000 ft, an irrigated location. Native species were found primarily in various unirrigated mountain locations, but were also found at Rancho Santa Ana Botanic Garden in Claremont, and at the UC Riverside Botanic Garden. Other plants were sampled in mother blocks in commercial nurseries found in Fresno and Tulare Counties.

3.2.4 Criteria for the Selection of Plant Species Studied

Because the study was necessarily limited, candidate plant species were carefully selected to allow expansion of plant species surveyed, and evaluation of the taxonomic predictive method. An additional criterion was availability, which was based on previous

knowledge of species occurrence in the southern San Joaquin Valley and surrounding mountains.

In this report, the plant nomenclature follows Mabberley (1997) and we use the family names Compositae, Leguminosae and Palmae rather than Asteraceae, Fabaceae and Arecaceae, their respective equivalents in some taxonomic schemes. We attempt to give equivalent identities where alternative names exist.

For intrafamily comparison of emission rate data, plants were chosen because of their placement within certain families to evaluate whether corresponding genera within families had similar emission rates. For intrageneric comparisons, certain species were chosen where others within the genus had been reported in Benjamin et al. (1996), allowing comparison of species to others within the genus with previously published isoprene emission rates.

3.3 Experimental Methods

3.3.1 Introduction

During the spring, summer and fall of 1999 and 2000, 250 plant species were surveyed for emissions of BVOC using a static bag enclosure system and a portable VOC analysis instrument. In the 1999 study, the PAU employed was a Model 580B (Thermo Environmental Instruments, Franklin, MA) which measured the concentration of BVOC from a continuous sampling stream of air through irradiation by an ultraviolet (UV) light source. The resulting ionization was measured by a photoionization detector (PID) which provided an index of VOC concentration in the sample relative to the response factor of a given calibration gas. In the study conducted during 2000, a ppbRAE instrument (Model PGM-7240, RAE Systems, Sunnyvale, CA) was used to measure the concentration of BVOC based on the same approach but with greater sensitivity.

3.3.2 Total BVOC Measurements Using a PAU

3.3.2.1 Previous Studies Using a PAU

The study described here is patterned after the methods Lerdau and Keller (1997) used for a survey of isoprene emissions from 30 tree species in a dry subtropical forest, and the Hand-held Emissions Screening system employed by Guenther et al. (1996a) in a survey of VOC emissions from southern African savanna trees. Each of these methods employed a

polyethylene bag enclosure to collect the VOC emitted from leaves which were then measured using a PAU fitted with a PID. In a variation of this method, Klinger et al. (1998) measured VOC emissions from the green leaves of plants in the field using a modified cuvette containing approximately 20 cm^2 of leaf, coupled to a PAU of the same model and manufacturer as employed in our 1999 study.

3.3.3 Overview of BVOC Sampling Using a Portable Analyzer - 1999

3.3.3.1 Instrument Model and Characteristics

The portable analyzer operates by drawing a stream of sample air into a chamber and past a UV light source using a pump located downstream of the lamp. The pump runs continuously resulting in a steady flow of sampled air past the light source. The UV light causes ionization of molecules within the air stream, and their concentration is measured by changes in electrical potential. The ionization potential of the molecules differs according to their electronic configuration, with alkenes and aromatic compounds being more easily ionized than alkanes. To quantify the relative response of the Model 580B analyzer to various common BVOC compounds a laboratory study was also conducted, the results of which are detailed in Section 3.3.3.7.1.

According to the manufacturer, the Model 580B portable analyzer has a detection range of 0-2000 parts per million (ppm) VOC with a lower detection limit (LDL) of 0.1 ppm for most organic vapors. However, the sensitivity of the instrument is reduced if water vapor condenses on the detector lamp or if the lamp glass becomes coated by deposition of aerosol. To prevent water condensation or aerosol deposition, a desiccant column containing magnesium perchlorate was constructed (Section 3.3.3.2) and fitted ahead of the input port. A similar column was used in the study of Klinger et al. (1998).

3.3.3.2 Desiccant Column Construction

To prevent signal loss due to condensation of water on the UV lamp, a desiccant column was fitted to the input port of the PAU which removed water vapor contained in the sample air before the sample air passed over the UV lamp. The column was constructed from the chamber of a 20 ml disposable tuberculin syringe that was attached to the PAU by a 9 cm length of flexible PVC vacuum tube (6.4 mm ID, 9.5 mm OD) using Teflon connectors

and a Teflon-stainless steel fitting at the PAU inflow port. The PVC tubing provided flexibility for sampling foliage with limited accessibility. Before calibrating the PAU each day, a fresh desiccant column was loosely packed using a small mat (1.0 cm^2) of glass wool at each end of the chamber.

3.3.3.3 Choosing the Desiccant

Prior to beginning summer sampling, three desiccants were tested for their effectiveness for removing water from the sample-air inflow stream without reducing flow rate. The anhydrous compounds were calcium chloride ($CaCl_2$), cobalt chloride ($CoCl_2$), and magnesium perchlorate [$Mg(ClO_4)_2$]. The desiccant chosen for this study was anhydrous, crystalline $Mg(ClO_4)_2$ (Fisher Scientific, Pittsburgh, PA), which showed airflow properties similar to $CaCl_2$ pebbles and considerably better than $CoCl_2$ crystals. $Mg(ClO_4)_2$ also absorbed water more effectively than the other desiccants without becoming sticky. This preferred desiccant provided sufficient water absorption to prevent condensation on the UV lamp while allowing adequate airflow to purge BVOC between samples. The same desiccant was employed by NCAR (Klinger et al. 1998) in a similar study due to its very high water absorption properties. The substance is listed second only to diphosphorus pentoxide (P_2O_5) in water absorption efficiency of desiccants (Lide 1991). Approximately 8 grams of $Mg(ClO_4)_2$ provided sufficient desiccation and adequate airflow, resulting in a rapid purging of sample gases and return to background VOC levels between sample runs.

3.3.3.4 Effect of Dust Accumulation on PID Sensitivity

It was discovered the transmissivity of the UV lamp was impaired by the accumulation of dust and dirt. Data in Table 3.1 indicate the sensitivity of the PAU to 1.0 ppm α-pinene and 1.0 ppm isoprene became lower on successive test dates. These results illustrated the importance of regularly cleaning the lamp since this had not been done between successive test dates. Over a period of prolonged sampling of transpiring vegetation, signal loss could occur due to condensation of water on the UV lamp (Klinger et al. 1998). Therefore, daily maintenance procedures such as cleaning the UV lamp, replacing the desiccant in the desiccant column, and recalibration of the PAU were developed to minimize loss of instrument sensitivity, and were employed throughout the field study.

3.3.3.5 Assessment of the Instrument Lower Detection Limit and Sensitivity to BVOC Compounds

On April 1, 5, 22 and June 18, 1999, a series of tests were conducted that compared the relative sensitivity and lower detection limit (LDL) of the portable analyzer to both isoprene and α-pinene under laboratory conditions. For the tests conducted on April 1 and 5 the PAU was connected to the power source, and for the tests conducted on April 22 and June 18, the PAU was operated using battery power. For all tests the instrument was calibrated using a procedure similar to that described in Section 3.3.3.3; however, instead of using 1.0 ppm α-pinene or isoprene as the upper reference concentration, isobutylene was used at 250 ppm with calibration set to read 250 ppm. For the sensitivity tests, α-pinene or isoprene were introduced directly from their respective cylinders into the instrument through Nalgene 890 Teflon tubing (4.8 mm ID, 6.4 mm OD) fitted with a T-junction coupler to serve as a release for excessive pressure. The desiccant column was not attached. The ambient air value was recorded prior to introducing each reference standard and test gas values were recorded after reference samples had been introduced for at least 30 seconds. Results of the sensitivity tests are summarized in Table 3.1 below.

Table 3.1 Sensitivity of the PAU to 1.0 ppm isoprene and 1.0 ppm α-pinene. The instrument had been calibrated to read 250 PAU units with 250 ppm isobutylene as the calibration gas, a 1:1 calibration ratio as shown.

Test Gas	Test Date	PAU Calibration	Ambient Air Value (PAU units)	Test Gas (PAU units)
α-pinene	4/01/99	1:1	0.0 – 0.1	6.9 – 7.0
α-pinene	4/05/99	1:1	0.0 – 0.3	5.8 – 5.9
α-pinene	4/22/99	1:1	0.0	4.7
isoprene	4/05/99	1:1	0.0 – 0.3	4.8 – 4.9
isoprene	4/22/99	1:1	0.0	2.5 – 2.6
isoprene	6/18/99	1:1	0.0	1.2 – 1.3

Data indicate the sensitivity of the PAU to α-pinene and isoprene relative to the calibration gas, isobutylene, ranged from 1.2 to 4.9 and 4.7 to 7.0 times greater, respectively. Thus the PAU was more sensitive to α-pinene than to isoprene and the instrument was more sensitive to both BVOC compounds than to isobutylene.

3.3.3.5.1 Assessment of the LDL of the Portable Analyzer

The LDL of the PAU was measured on April 5, 22 and June 18. Dilutions were made by injecting a known volume of 1.0 ppm standard isoprene or α-pinene into a 4.7 L (30cm x 30cm) Chemware Teflon FEP Gas Sampling Bag (Fisher Scientific, Pittsburgh, PA) using a 100 ml glass gas sampling syringe (Popper and Sons Inc., New Hyde Park, N.Y.), and then injecting a balance of air to obtain dilutions of 5/10, 2/10 or 1/10, corresponding to mixing ratios of 500 ppb, 200 ppb, and 100 ppb, respectively. The sample bags containing diluted volumes of isoprene or α-pinene were sampled by attaching the Teflon sampling tube directly to the sample bag on/off valve and then to the PAU sampling port. The desiccant column was not attached. The reference gas was 250 ppm isobutylene, and the instrument was set to read 250 PAU ppm in this 1:1 calibration. The instrument was not cleaned or calibrated between successive test dates. Results of the LDL study are shown in Table 3.2.

Table 3.2 Measurements to determine the LDL of the PAU to isoprene and α-pinene.

Test Gas	Dilution Concentration	Test Date	Ambient Air Value (PAU units)	PAU Value (PAU units)
α-pinene	100 ppb	4/05/99	0.0 – 0.3	0.2 – 0.3
α-pinene	100 ppb	4 /22/99	0.0	0.0
α-pinene	200 ppb	4/22/99	0.0	0.1
α-pinene	500 ppb	4/22/99	0.0	0.8 – 0.9
α-pinene	100 ppb	6/18/99	0.0	0.0
α-pinene	200 ppb	6/18/99	0.0	0.0
α-pinene	500 ppb	6/18/99	0.0	0.1 – 0.2
isoprene	100 ppb	4/05/99	0.0 – 0.3	0.2 – 0.3
isoprene	100 ppb	4/22/99	0.0	0.0
isoprene	200 ppb	4/22/99	0.0	0.0
isoprene	500 ppb	4/22/99	0.0	0.4 – 0.5
isoprene	100 ppb	6/18/99	0.0	0.0
isoprene	200 ppb	6/18/99	0.0	0.0
isoprene	500 ppb	6/18/99	0.0	0.0

The results in Table 3.2 show that on April 5, 100 ppb of both isoprene and α-pinene were detected, but did not result in a steady PAU reading. Subsequent measurements of these compounds made on April 22 and June 18 showed that 100 ppb concentrations were

not detected. These results indicated the LDL of 100 ppb specified by the manufacturer was not consistently observed during our lower concentration threshold studies using isoprene or α-pinene. Results also showed the effect that accumulation of aerosols on the glass lens of the UV lamp had on the LDL. A value of 200 – 300 ppb appeared to be a more realistic LDL under field sampling conditions where aerosol contamination was more likely.

3.3.3.5.2 Relative Sensitivity of the Portable Analyzer to Selected BVOC

The relative sensitivity of the Model 580B portable analyzer to eleven BVOC compounds of known concentrations was tested under controlled conditions on February 14 and 15, 2000, at the Air Pollution Research Center (APRC) at the Riverside campus of the University of California. The compounds were introduced into large Teflon chambers bag with a total volume of either 7500 L or 8500 L, at amounts calculated to give concentrations of approximately 500 ppb in a balance of air. A measured amount of each compound was taken from pure stock solutions using a 50 µl glass sampling syringe (Hamilton Series 700 standard microliter syringe) and injected into a 1.0 L glass bulb for transfer into the gas mixing bag. The bulb was connected to the Teflon chambers bags through a Teflon tube and O-ring assembly. To evacuate the compound into the chamber, the glass bulb was heated from beneath using a hand-held forced-air heating gun (Master Appliance Corp., Model HG-751B). The chamber was filled with a balance of air. Each compound was sampled with the portable VOC analyzer using field calibration procedures (Section 3.3.3.3 and 3.3.3.9). In most cases the $Mg(ClO_4)_2$ desiccant column was attached. Following sampling with the portable analyzer, the concentration of each compound was measured using GC-FID analysis (Hewlett Packard model HP5710A). The procedure for sampling the air from the Teflon chambers for GC analysis involved drawing 100 ml gas samples through Tenax packed sampling cartridges using a Perfektum 100 ml gas-sampling syringe. The samples were cryogenically loaded into the GC for analysis. After sampling each compound the chamber was purged prior to the introduction of the next compound. Results are summarized in Table 3.3.

3.3.3.5.3 Relative sensitivity to the selected BVOC compounds

Relative sensitivities of the compounds tested at the APRC were compared to the sensitivity of the PAU for isoprene, and were expressed as a relative sensitivity index (RSI). For this comparison, a 1000 ppb isoprene standard was used and the PAU calibrated to read 100 (for explanation of the scale adjustment refer to section 3.3.3.7).

$$\frac{\text{Compound (PAU units)}}{\text{Compound (ppb)}} \times \frac{\text{Isoprene (ppb)}}{\text{Isoprene (PAU units)}} = \text{RSI} \qquad \text{(Eq. 3.1)}$$

As seen in Table 3.3, the relative sensitivity of the PAU to the eleven compounds as compared to the sensitivity for isoprene ranged from 3 % for cineole, an alkane, to 72 % for Δ^3-carene, an alkene, respectively.

The oxygenated BVOC, 2-methyl-3-butene-2-ol, was not detectable with the desiccant assembly attached. After removing the desiccant column, methylbutenol was detected with a 27 % relative sensitivity, indicating the compound was adsorbed by the desiccant column. Adsorption by the $Mg(ClO_4)_2$ desiccant may have occurred for each BVOC compound to varying degrees; however, since in this laboratory study the calibration span gas (1.0 ppm isoprene) was introduced with the desiccant column assembly attached, the relative sensitivity index value accounted for both differing sensitivity of the PAU sensor to these BVOC compounds and differing adsorption of each compound by the desiccant column relative to the sensitivity and adsorption of isoprene.

3.3.3.6 General Calibration Procedures for the PAU

Calibration involved providing two points of reference: a lower zero air value and an upper value of a known concentration of a given VOC. We used two gases for calibrating and standardizing the instrument, isoprene (2-methyl-1,3-butadiene) and α-pinene. Both gases were certified as 1.0 ppm accurate to ± 5 %, in a balance of nitrogen gas, traceable to a Scott Reference Standard (Scott Specialty Gases Inc., San Bernardino, CA). The calibration standard used for most fieldwork was 1.0 ppm isoprene in N_2.

Table 3.3 Summary of data indicating the relative sensitivity of BVOC measured with the Model 580B portable VOC analyzer. The Relative Sensitivity Index (RSI) refers to the concentration of each compound measured with the portable analyzer, relative to the calibration standard gas of 1.0 ppm isoprene.

Compound Name	GC value (ppb)	Compound Sample (PAU units)	Mean Compound (PAU units)	Ambient Air (PAU units)	Mean Ambient Air (PAU units)	Increment Size [3] (PAU units)	RSI[2]
Camphene	500	20.6 – 23.8	22	1.5 – 4.7	3.1	3.2	0.38
Δ^3-Carene	490	38.0	38	1.4 – 4.2	2.8	2.8	0.72
Cineole	500	0.0 – 3.3	1.6	0.0	0.0	3.3	0.03
p-Cymene	503	4.8 – 8.0	6.4	1 – 1.6	1.3	3.2	0.10
Limonene	566	22.2 – 25.0	24	2.7 – 5.5	4.1	2.7	0.35
Methyl–butenol[1]	473	12.0 – 15.5	14	0 – 1.7	0.9	3.5	0.27
Myrcene	430	16.6 – 19.6	18	1.5 – 4.5	3.0	3.0	0.35
α-pinene	493	24.5 – 28.0	26	3.5	3.5	3.5	0.46
β-pinene	544	14.4 – 17.6	16	1.6	1.6	3.3	0.26
Sabinene	577	21.1 – 23.9	22	1.4 – 4.2	2.8	2.8	0.33
Terpineole	279	10.4 – 13.9	12	0 – 3.4	1.7	3.5	0.37

1) Methylbutenol (2-methyl-3-buten-2-ol) was measured without the desiccant column attached as the compound was adsorbed by magnesium perchlorate.

2) RSI (Relative Sensitivity Index) calculated using Equation 3.1.

3) Increment size refers to the number of PAU units as displayed on the instrument readout per step, between successive changes in concentration measured by the portable analyzer (refer to Section 3.3.3.8 for explanation).

3.3.3.6.1 Setting the Zero Calibration

Zero air was introduced by attaching to the inflow port the charcoal filter that was provided as part of the support kit of the PAU instrument. The $Mg(ClO_4)_2$ desiccant column was removed for zeroing. Under battery power the PAU was set aside to equilibrate for five to ten minutes. After the zero airflow reached a steady state, the instrument was zeroed according to the procedures detailed in the instruction manual.

3.3.3.6.2 Setting the Span Calibration

Prior to introducing the span or calibration gas, in this case isoprene, the $Mg(ClO_4)_2$ desiccant column assembly was attached and allowed to equilibrate for five to seven minutes. The calibration standard was then introduced through the column via Teflon tubing with a T-junction attachment to allow for pressure stabilization. The 1.0 ppm isoprene standard was introduced into the tubing assembly and given approximately two minutes to fill the column

and reach a steady-state concentration before the upper VOC concentration parameter was set according to the procedures detailed in the instruction manual.

3.3.3.7 Scaling the Calibration to Improve Readability of the Portable Analyzer

To improve the readability of values from the PAU the calibration scale was altered by introducing 1.0 ppm isoprene as the upper parameter span gas but the instrument was programmed to read 100 ppm. This provided a calibration scale of 100:1. Alternative calibration scales of 50:1, 10:1 or 1:1 were used for species that had high (e.g. *Salix* sp.) or very high (e.g. *Liquidambar styraciflua*) measured emissions.

Altering the calibration scale of the instrument had the effect of changing the PAU value for incremental steps between VOC samples of different concentrations. For example, as the sample tube was placed in a bag containing vegetation, the display panel of the PAU may have initially read a background VOC value of 7.0 PAU units. As the VOC concentrations detected by the PID increased, the display showed increases in value to 10.5 PAU units, then 14.0 PAU units, before reaching a maximum of 17.5 PAU units. Thus, in this example, the value of the increment between detectable concentration shifts was 3.5 PAU units. The PAU unit value per increment varied from day to day but usually fell within the range of 2.4 - 4.5 PAU units. The concentration change required to elicit one increment change indicated the precision of the portable analyzer. Each step or increment change represented an isoprene equivalent concentration of between 30 and 40 ppb. This range can be calculated given that at calibration, 0 ppb of isoprene reads 0 PAU units and 1000 ppb isoprene reads 100 PAU units. If the value per increment is 3.5 PAU units, there were (100/3.5) = 28.6 increments per 1000 ppb isoprene, or 35 ppb per increment. It may be possible to standardize all the PAU values according to the number of increments triggered per sample.

The value of the increment was also affected by the optical quality of the UV lens. A dirty lens impaired the transmission of UV light responsible for ionizing molecules in the sample stream, causing signal loss and decreasing the sensitivity of the instrument. A greater increment value between sample concentration shifts occurred if the lens was not thoroughly cleaned. Once calibrated however the value of the increment did not change until the PAU was recalibrated.

Due to the fact that the PAU detected a variety of VOC species, an RSI was not obtained for all potential BVOC species. Also the VOC speciation emitted by a particular vegetation sample was unknown and for this reason the PAU values were considered to be semi-quantitative. Rather, the normalized PAU units represent an index of BVOC emissions from a particular sample. For example, for a calibration of 100:1 using 1 ppm isoprene as the calibration standard, a PAU unit value of 100 represented a concentration of BVOC with a response factor equivalent to 1 ppm isoprene in the sample stream. The response of the PAU to different VOC species was specific as demonstrated by Table 3.3, and was based primarily on the ionization potential of the compound in question. Thus, the relative sensitivity index represented the sensitivity of the PAU to any given VOC relative to the calibration gas and scale. Because isoprene was the calibration standard for field sampling and also for the sensitivity study, the sensitivity index value of isoprene was 1.

For data interpretation purposes, the PAU unit value obtained for each sample was normalized by adjusting for the span calibration. For example, given a PAU reading of 100 using a calibration scale of 100:1 and a 1 ppm isoprene standard, adjusting the PAU value to a normalized PAU unit that accounted for calibration was done using equation 2:

$$\text{PAU reading} \times \frac{\text{ppm calibration gas}}{\text{PAU setting}} \times \frac{1000\ \text{ppb}}{\text{ppm}} = \text{normalized PAU units} \qquad \text{(Eq. 3.2)}$$

For example, with a calibration of 100:1 and a measured value of 12.6 PAU units,

$$12.6\ \text{PAU reading} \times \frac{1\ \text{ppm}}{100\ \text{ppm}} \times \frac{1000\ \text{ppb}}{\text{ppm}} = 126\ \text{normalized PAU units} \qquad \text{(Eq. 3.3)}$$

3.3.3.8 Characterizing Emissions From the Polyethylene Sample Bags

Although previous investigations using polyethylene bags (Lerdau and Keller 1997, Guenther et al. 1996a) indicated no release of VOC, it remained possible the polyethylene bags contributed a low level of volatile emissions that were detectable by the PAU. These emissions could contribute to the values measured for enclosed vegetation giving elevated readings. Therefore, experiments were conducted to assess VOC emissions from polyethylene bags themselves. The experiments were conducted under field conditions on

September 7 and 14 and October 20 and 25, and in the laboratory on November 17, 1999. For the field experiments, PAR was recorded and ranged between 350 - 1780 μmol m^{-2} s^{-1}. PAR in the laboratory was 11.4 μmol m^{-2} s^{-1}. In the field, fresh bags were filled with ambient air and held for five minutes at the ambient temperature. As a result of routine field assessment of control (air filled) bags, an apparent relationship between high temperature and the release of background emissions from empty bags was observed. For this reason, in the laboratory experiments, fresh bags were filled with surrounding air and the temperature of the bag was increased by moving the bags progressively closer to an electric fan heater (Patton Electric Company Inc., New Haven, Ind.). The temperature of the bag was recorded from the mean of three readings from thermocouples, (Omega T-type thermocouples, Omega Engineering Inc., Stamford, CT) taped to the outer surface of each bag. The atmosphere within the bag was continually monitored for VOC, and emissions were recorded as the bag temperature increased at intervals of 5 °C. For both field and lab experiments, the atmosphere within the bag was measured using the PAU and desiccant assembly. Results of the experiments are summarized in Figure 3.1.

Background emissions of VOC from polyethylene bags were again tested using GC-FID on February 15, 2000, at the APRC, at UC Riverside. A sample bag was filled with laboratory air and tied at one end with tape. A digital thermometer was pushed into the bag to obtain temperature measurements. The air inside the bag was heated to 40 °C using a hand-held heat gun (Master Appliance Corp., Model HG-751B). The air inside the bag was sampled using the portable VOC analyzer. In this case, however, background emissions from the plastic bag remained below detectable levels. Coincident with sampling using the portable analyzer, an air sample was also drawn through sampling cartridges packed with Tenax using a Perfektum 100 ml gas syringe for analysis using GC-FID (Hewlett Packard model HP5710A). GC-FID revealed no identifiable peaks.

Data displayed in Figure 3.1 show that emissions from polyethylene sampling bags increased, as measured using the portable analyzer, as temperature increased. The effect of temperature appeared to be linear between 15 °C and 50 °C before emissions leveled off above 50 °C. Background emissions from the bags were consistent under both laboratory and field conditions indicating PAR had little or no effect.

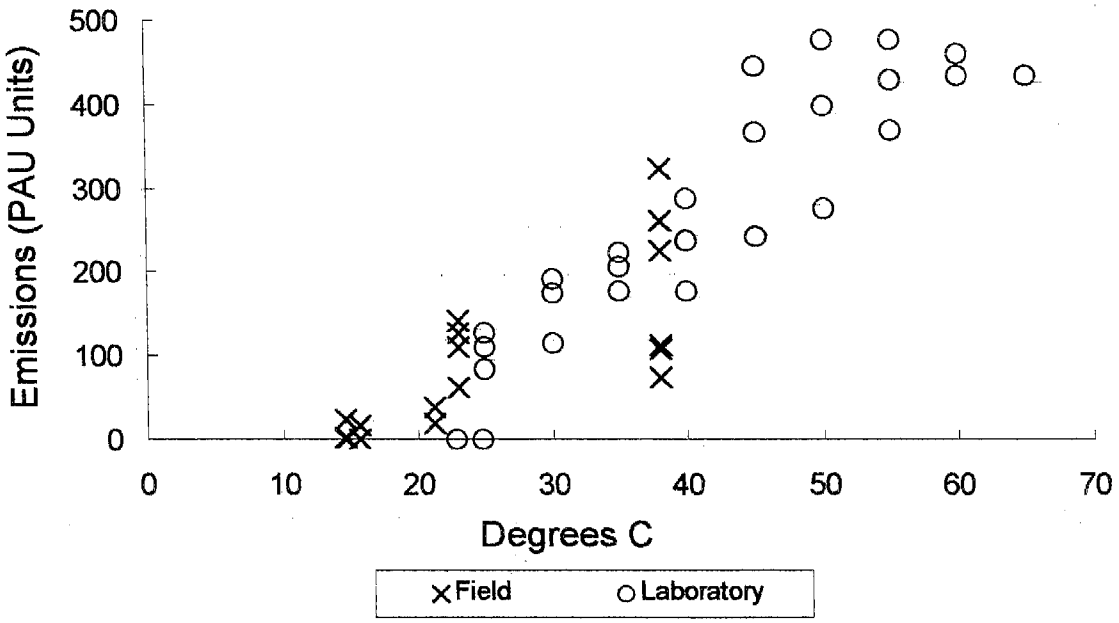

Figure 3.1 Release of volatile emissions from polyethylene bags as a function of temperature. Emissions values represent the maximum PAU value obtained minus the ambient value. For all values the PAU had been calibrated to a scale of 100:1.

3.3.3.9 BVOC Field Sampling Procedures for Year 1999

3.3.3.9.1 Selecting Field Locations for Sampling in 1999

Sampling locations were selected based on access and the number of target tree and shrub species available. During the 1999 summer sampling season, permission was granted for access to a variety of San Joaquin Valley locations including Bakersfield City Parks, the campus of California State University Bakersfield, and Bakersfield College, all of which were irrigated and at elevation ca. 150 m (500 ft). A number of naturalized and exotic *Quercus* species were sampled at the Los Angeles Arboretum, 301 N. Baldwin Avenue, Arcadia CA.

Plants from a variety of naturalized and exotic genera were sampled within the Mourning Cloak Botanic Garden, located in the Tehachapi Mountains 30 miles east of Bakersfield at elevation ca. 1,200 m (4000 ft), an irrigated location. A few plants were sampled in other unirrigated locations, such as the Mojave Desert 60 miles east of Bakersfield at elevation ca. 700 m (2300 ft), or Hart Flat 15 miles east of Bakersfield at elevation ca. 600 m (2000 ft).

3.3.3.9.2 Daily Maintenance for Sampling with the Model 580B Portable Analyzer

The lamp was removed and cleaned on a daily basis prior to sampling. Removal was done according to the procedures detailed in the instruction manual. To clean the lamp, aluminum oxide powder provided with the instrument was applied to the lens in a circular motion using a Kim wipe. Excess powder was then blown off the lens and the lens was rinsed with ethyl alcohol, set to dry, and replaced.

3.3.3.9.3 Calibration Procedures for the Model 580B

Prior to measuring foliage each day, the instrument was calibrated. An additional calibration was sometimes performed if the instrument seemed unresponsive. Calibration involved providing two points of reference: a lower zero value and an arbitrary upper value of a known concentration of a given volatile compound. As discussed earlier, due to the relatively low concentration of VOC emitted from vegetation, programming the PAU to read 100 PAU units while introducing only 1 ppm isoprene resulted in a 100:1 calibration scale which, in effect, expanded the intervals between readings on the digital display of the instrument. The following is a summary of calibration procedures.

3.3.3.9.3.1 Setting the Zero Calibration

A zero air value was introduced by attaching the charcoal filter that was provided as part of the support kit of the instrument to the inflow port. The PAU was turned on under battery power and set aside to equilibrate for five to ten minutes. After the zero airflow reached a steady-state the instrument was zeroed according to the procedures detailed in the instruction manual.

3.3.3.9.3.2 Setting the Span Calibration

Prior to introducing the 1.0 ppm isoprene span gas, the $Mg(ClO_4)_2$ desiccant column assembly was attached and allowed to equilibrate for five to seven minutes. The calibration standard gas was then introduced through the column via Teflon tubing with a T-junction attachment to allow for pressure stabilization. The 1.0 ppm isoprene standard was introduced into the tubing assembly and given approximately two minutes to fill the column and reach a steady-state concentration before the upper parameter was reset.

3.3.3.9.4 Temperature and Light Measurement

It is well established that several environmental factors influence emissions of BVOC from vegetation and among them light and temperature are most important (Guenther et al. 1993). For this reason ambient air temperature and photosynthetically active radiation (PAR) were recorded before sampling each plant. Temperature was measured in degrees Celsius (°C) using a Fisher Scientific Digital Thermometer with calibration traceable to NIST. Light intensity was measured as a thirty-second average PAR value ($\mu mol\ m^{-2}\ s^{-1}$) using a quantum sensor (LiCor 190 SA) and a digital meter (LiCor LI-250). Due to the light dependency of the isoprene metabolic pathway, sampling was usually carried out at a light intensity greater than 1000 $\mu mol\ m^{-2}\ s^{-1}$.

3.3.3.9.5 Procedures for Measurement of BVOC Emissions from Attached Foliage

Prior to sampling, for each series of bags, an ambient air VOC value was noted representing the background concentration. The time of day, air temperature in the shade and the full-sun light intensity (PAR) were also recorded. The general procedures for sampling the VOC emissions from a given tree, shrub, or herbaceous plant involved carefully placing a polyethylene bag over a clump of foliage and sampling the atmosphere within the bag with the PAU after 5 minutes. For each plant sampled, five bags were placed in a canopy position in full sunlight (PAR > 1000 $\mu mol\ m^{-2}\ s^{-1}$). Five bags were also placed over foliage and then darkened using black plastic sleeves. Air from within at least two of the fully lighted bags was again measured after leaves were manually crushed. The difference between BVOC values from the light minus those from the dark may be considered to represent isoprene or other light dependent emissions. The readings from sampled foliage that had been crushed may be considered to represent the release of pooled BVOC.

For each measurement, a clear polyethylene bag 15 x 8.9 x 38 cm (6 x 3.5 x 15 in) with a 5.0 L volume (measured by water displacement) was placed over a well-lighted branch or spur enclosing the leaves. Care was taken when placing a bag over the foliage so that values from the light or dark did not represent VOC released due to "rough handling." The open end of each bag was closed snugly with a rubber band at the base. A small sampling hole was made in the bag at the seam end using a sharp pencil.

A Timex timer was employed to record a time-in value at the point each bag was secured on a branch. Time values were measured in minutes and seconds. After five minutes, the BVOC concentration in the bag was measured by inserting the end of the Teflon sampling tube into the sampling hole of the bag. The sampling tube was kept in the bag for at least 8 seconds (to ensure one complete gas exchange through the PAU), or until the PAU value had reached a maximum. The time for one complete gas exchange was calculated as 7.8 seconds, based on a measured flow rate from the PAU exit port of 688 ml min^{-1} and a total volume of the sampling tube and desiccation chamber assembly of 90 ml. When the maximum PAU value for each bag was reached, the value was recorded on the data sheet and a time out value was noted. After VOC emissions values were recorded for all five replicate bags, the sample leaves were removed sequentially from the plant and placed into a paper bag labeled for each replicate and placed in a drying oven at 65 °C (150 °F). Dry weights were used for normalization of BVOC emissions to leafmass.

3.3.3.10 Calculated Branch Level Emission of BVOC Using Polyethylene Enclosure Method

For a branch with 5 g of leaf mass (a typical amount) and a branch-level isoprene emission rate of 25 μg g^{-1} hr^{-1}, the isoprene emission after 5 minutes would be 10.4 μg. If the isoprene were fully contained and the bag fully expanded to its measured volume of 5.0 L, the concentration of isoprene would be 750 ppb at the time of sampling. For monoterpenes with a branch-level emission rate of 1 μg g^{-1} hr^{-1}, the amount emitted after five minutes would be 0.42 μg and the corresponding concentration in the sampling bag would be 15 ppb. Thus, considering the relative sensitivity of the detector for isoprene compared to monoterpenes, and the generally lower emission rates for monoterpenes as compared to isoprene, the dominant emissions measured by this method were isoprene.

3.3.3.11 Sampling BVOC Emissions from Foliage in the Light

A "light run" involved systematically placing five replicate bags over well-lighted branches or clumps of vegetation (PAR > 1000 μmol m^{-2} s^{-1}) and carefully closing the base of each bag with a rubber band. The instant that each bag was closed was recorded as time-in on a data sheet (see section 3.3.4.9). After five minutes the accumulated BVOC within the bag were sampled using the portable analyzer, the PAU values were recorded and the time at

which each bag was sampled was also recorded as time-out. The interval between securing each of the five sampling bags in the series was between 45 – 60 seconds to ensure that after the BVOC values were measured the PAU could return to background levels.

3.3.3.12 Sampling BVOC Emissions from Darkened Foliage

The general procedure for measuring BVOC emissions from leaves that were darkened was similar to those described above with the exception that black plastic sleeves were used to cover the five sampling bags of each series. The black plastic sleeves were loosely fastened over each bag at the instant of time-in and sampling the accumulated BVOC was made after approximately five minutes with the sleeve intact.

3.3.3.13 Sampling BVOC Emissions from Crushed Foliage

Of the five replicate sample branches measured in the light, between two and five were manually crushed within their bags and the PAU response noted as an indication of the release of pooled VOC. Some species released a large quantity of BVOC after crushing by hand, sometimes exceeding the operating range of the PAU. In these cases a nominal PAU unit value of 2000+ was recorded. The time-out, at which the crushed bags were sampled, was between seven and ten minutes after the bags were initially fastened and may have been longer on occasions when crushing the leaves led to a significant rise in BVOC emissions, in which case the time required for the instrument to re-equilibrate to background levels increased.

3.3.4 BVOC Field Sampling Procedures for Year 2000

3.3.4.1 Instrument Model and Characteristics

During the summer of 2000, the ppbRAE instrument (Model PGM-7240 RAE Systems, Sunnyvale, CA), was used to measure the concentration of BVOC. Through the irradiation by a UV lamp of a continuous sampling stream of air, the BVOC were ionized and their total concentration was measured by a PID. This provided an index of VOC concentration in the sample relative to the response factor of a given calibration gas, which was isoprene in this study.

The portable analyzer operated by drawing a stream of sample air into a chamber and past a UV lamp using a pump located downstream of the lamp. The pump ran continuously resulting in a steady flow of sampled air with a minimum flow rate of 400 cm^3min^{-1} past the light source. The UV light caused ionization of molecules within the air stream, and their concentration was measured by changes in electrical potential. The ionization potential of the molecules differed according to their electronic configuration, with alkenes and aromatic compounds being more easily ionized than alkanes.

3.3.4.2 Desiccant Column and Water Trap Filter Utilization

A desiccant column was not utilized with the ppbRAE analyzer, although the ppbRAE did require the removal of water vapor upstream of the ionization chamber. Instead of a desiccant column, a water trap filter, provided as part of the support kit, was utilized for the entire duration of sampling. The water trap filter was made of PTFE (Teflon®) membrane with a 10-micron pore size to prevent water vapor from being pulled into the sensor manifold, which would cause reduced sensitivity. It also removed any dust and other particles from entering the measuring instrument and prolonged the operating life of the sensor. The water trap filter was simply inserted into the front of the inlet tube of the ppbRAE unit.

3.3.4.3 Effect of Dust Accumulation and Humidity on PID Sensitivity

Dust and other particles could cause severe damage to the sensor and significantly affect PAU readings under prolonged use. Over a period of prolonged sampling of transpiring vegetation, signal loss could occur due to condensation of water on the UV lamp (Klinger et al. 1998). The manufacturer recommended performing regular cleanings and utilizing the water trap filter to prevent damage and loss of sensitivity.

Water vapor will absorb UV light, thus decreasing intensity of the UV lamp. The ppbRAE design minimizes this effect as much as possible. A dirty sensor could also cause drifting high readings under non-condensing conditions. Non-condensing humidity would have little effect on non-emitting plant species but could potentially skew values of low, moderate, and high emitting plant species. The degree to which non-condensing humidity affects the ppbRAE measuring instrument is not fully understood.

Condensing humidity in a PID will cause false high values by conducting current across the sensor electrodes. This is very common when using a cool instrument in hot, humid air. In order to prevent false high signals readings, the ppbRAE was kept dry. The sensor was also kept at least as warm as the gas being sampled in order to prevent condensation from occurring.

3.3.4.4 Assessment of the Instrument Lower Detection Limit and Linearity for BVOC Compounds

On June 30, 2000, and July 20, 2000, tests were conducted that compared the relative sensitivity of the portable analysis unit to both isoprene and α-pinene dilutions under laboratory conditions. Ten dilutions at 100 ppb increments were used for isoprene and six dilutions beginning at 200 ppb increments were used for α-pinene tests using a Perfektum 100 ml gas sampling syringe and a Tedlar bag. The dilutions ranged from 0 to 1000 ppb. Results of the tests are shown in Figures 3.2 and 3.3.

The ppbRAE VOC measuring instrument was calibrated with 1.0 ppm isoprene according to the general calibration procedures below. Both the isoprene dilution and α-pinene dilution tests indicated a relatively linear relationship between the known compound concentration and the measured instrument reading. The data also indicated that the ppbRAE was about 25% more sensitive to α-pinene than it was to isoprene for measured values below about 700 ppb.

The relative sensitivity of the portable analyzer to eleven BVOC compounds of known concentrations was tested under controlled conditions on July 24 and 25, 2000, at the APRC at UC Riverside using the same procedures described in Section 3.3.3.5.2. Relative sensitivities of the compounds tested at the APRC Laboratory were compared to the sensitivity of the PAU for isoprene, and were expressed as the relative sensitivity index (RSI) defined earlier by Equation 3.1. Results are summarized in Table 3.4.

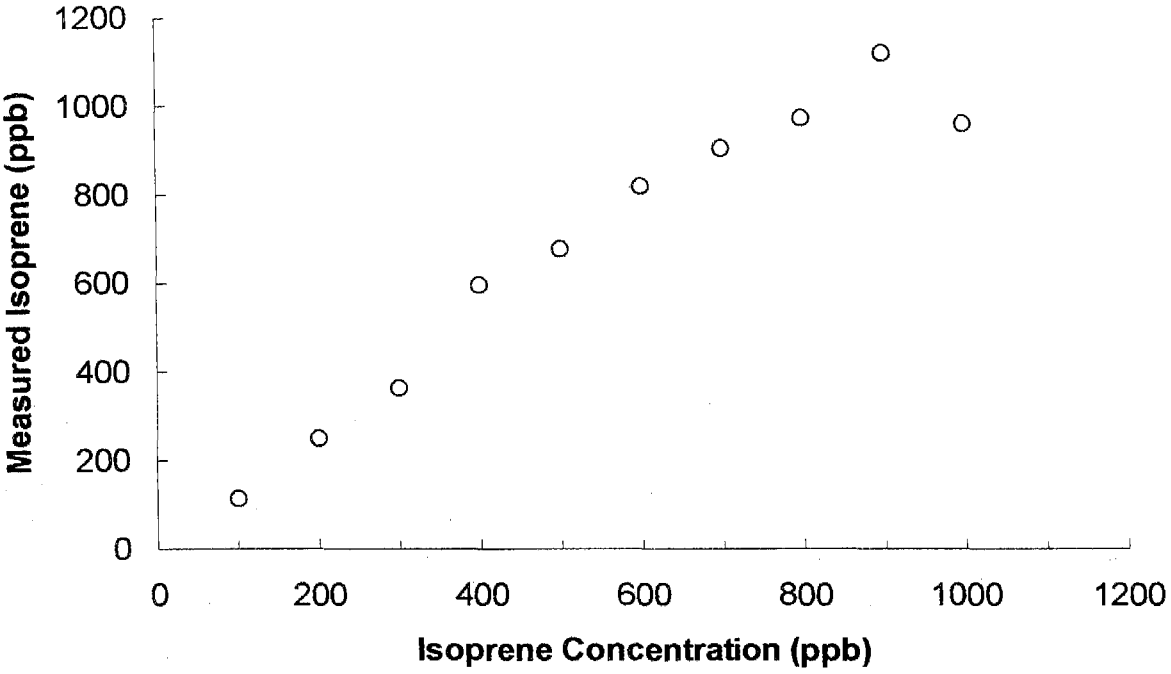

Figure 3.2. Relationship between known isoprene concentration and corresp. measured isoprene reading. Ambient air was used for dilutions. Test conducted 7/20/00, UCCE lab.

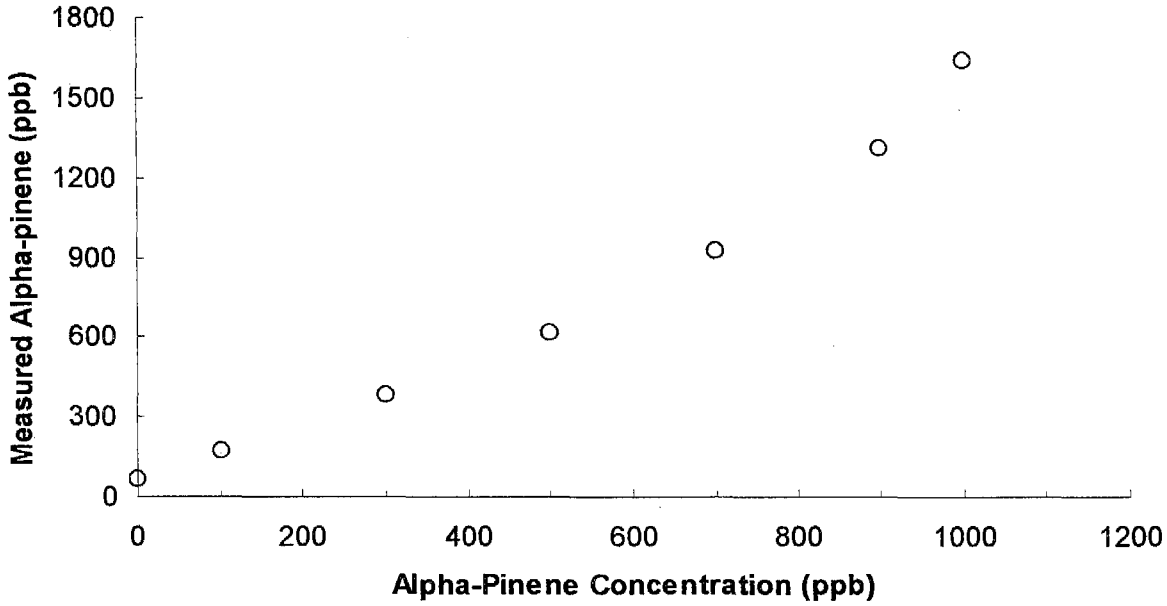

Figure 3.3. Relationship between known α-pinene concentration and corresponding measured α-pinene reading. Ambient air was used for dilutions. Test conducted 6/30/00, UCCE lab.

Table 3.4. Summary of data indicating the relative sensitivity of BVOC measured with the ppbRAE portable VOC analyzer. The Relative Sensitivity Index (RSI) refers to the concentration of each compound measured with the portable analyzer, relative to the concentration measured with the GC. The RSI for isoprene was 1.0 ppm, set at calibration.

Compound Name	GC Value (ppb)	Mean PAU Reading (ppb)	Chamber Air (ppb)	Net PAU Value (ppb)	RSI[1]
Camphene	487	430	122	308	0.63
Δ^3-Carene	383	591	104[2]	487	1.27
Cineole	400	453	104[2]	349	0.87
ρ-Cymene	424	360	99	261	0.62
Limonene	496	534	104[2]	430	0.87
Methyl-butenol	519	261	104[2]	157	0.30
Myrcene	346	403	102	301	0.87
Alpha-pinene	381	505	98	407	1.07
Beta-pinene	611	689	104[2]	585	0.96
Sabinene	444	506	97	409	0.92
Terpinolene	243	294	104[2]	190	0.78

1. Relative sensitivity index calculated using Equation 3.1.
2. Indicates mean chamber air values calculated from five chamber air readings as measured with the PAU.

As seen in Table 3.4, the relative sensitivity of the PAU to the eleven compounds as compared to the sensitivity for isoprene ranged from 30 % for methyl-butenol to 127 % for Δ^3-carene, respectively.

3.3.4.5 General Calibration Procedures

These procedures were the same as described in Section 3.3.3.6.

3.3.4.5.1 Setting the Zero Calibration

Zero air was introduced by attaching the charcoal filter (provided with the support kit) to the inlet port of the water trap filter, which was attached to the inlet port of the ppbRAE instrument. After the zero airflow reached a steady state, the instrument was zeroed according to the procedures detailed in the instruction manual.

3.3.4.5.2 Setting the Span Calibration

Prior to the application of the calibration gas, in this case 1.0 ppm isoprene, the particle filter was attached to the inlet port of the measuring instrument. The 1.0 ppm isoprene standard was first introduced into a Tedlar bag. The ppbRAE was than attached to the Tedlar bag and the instrument was span calibrated according to the procedures detailed in the instruction manual.

3.3.4.6 Routine Maintenance

A regular maintenance routine was developed and applied throughout the field study in order to prolong the life of the ppbRAE measuring instrument and to confidently obtain accurate readings. Daily maintenance procedures included cleaning the UV lamp, checking dust filters, and recalibration of the PAU in attempt to minimize loss of instrument sensitivity. Because a dirty sensor can cause condensation more readily than a clean sensor and give false readings, the sensor was cleaned every three of weeks according to the procedures outlined by the manufacturer.

3.3.4.7 Characterizing Emissions from the Polyethylene Sample Bags

Polyethylene bags were used during the first month of sampling in 2000. Experiments were conducted to assess VOC emissions from polyethylene bags themselves because emissions might contribute to the values measured for enclosed vegetation giving elevated readings. Experiments were conducted under laboratory conditions on June 30, 2000, and under field conditions on July 31, 2000. In the laboratory experiments fresh polyethylene bags were filled with surrounding ambient air. The internal bag temperature was increased by positioning the bags progressively closer to an electric fan heater (Patton Electric Company Inc., New Haven, Ind.) and readings were made with thermocouples (Type-T thermocouples, Omega Engineering Inc., Stamford, CT). The atmosphere within the bags was continually monitored for VOC emissions with the ppbRAE measuring instrument and recordings were made at 5 °C intervals. Three separate trials were conducted under laboratory conditions and results are shown in Figure 3.4.

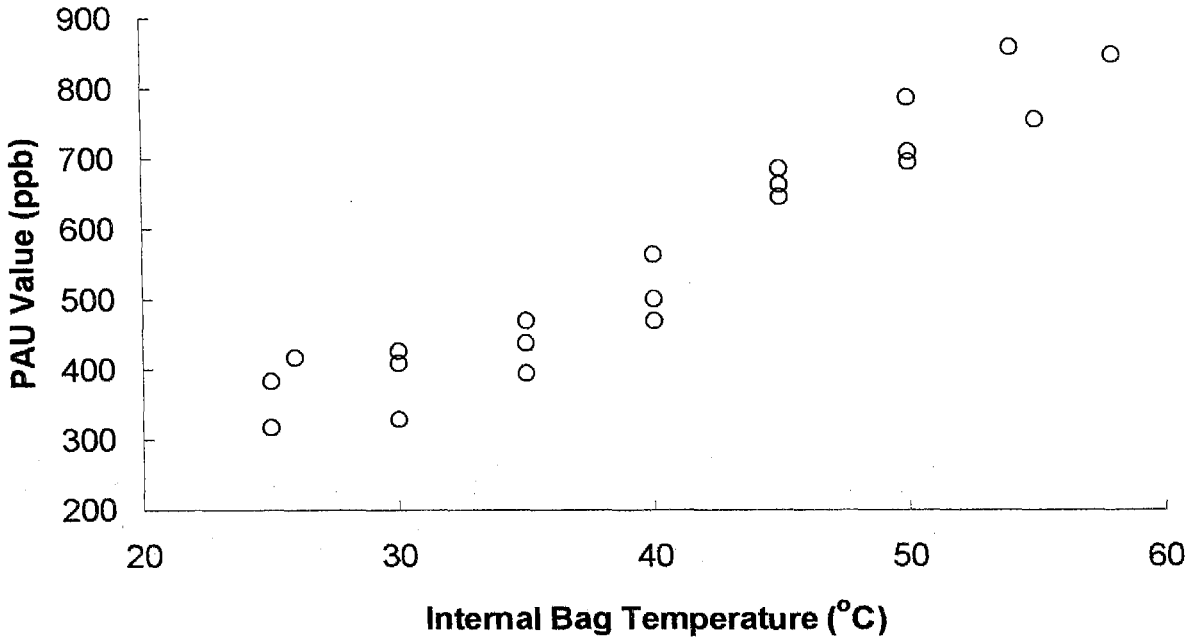

Figure 3.4. Relationship between temperature and polyethylene sampling bag emissions. Test was conducted in a laboratory setting using an electric fan to heat the polyethylene sampling bags on 6/30/00.

The bag emissions experiments under field conditions were conducted according to the established field procedures. Five fresh polyethylene bags were filled with surrounding ambient air and were held for 5 minute intervals in sunlight and dark conditions. Temperature and VOC readings were recorded for each bag trial at the end of the 5 minute time period. The results for the field condition experiment are summarized in Figure 3.5.

Data from the bag emissions for the laboratory experiment indicated a relationship between the internal bag temperature and VOC emissions read by the ppbRAE instrument. This test showed that as temperature increases, VOC emissions increased linearly. However, the test under field conditions showed little relationship between internal bag temperature and VOC emissions in either sunlight or dark conditions.

Background emissions of VOC from polyethylene bags were again tested using GC-FID on July 25, 2000 at the APRC at the University of California, Riverside. A fresh polyethylene bag was filled with laboratory air and tied at one end with tape. A digital thermometer was pushed into the bag to obtain temperature measurements. The air inside the bag was heated to 56.5 ° C using a hand-held heat gun (Master Appliance Corp., Model

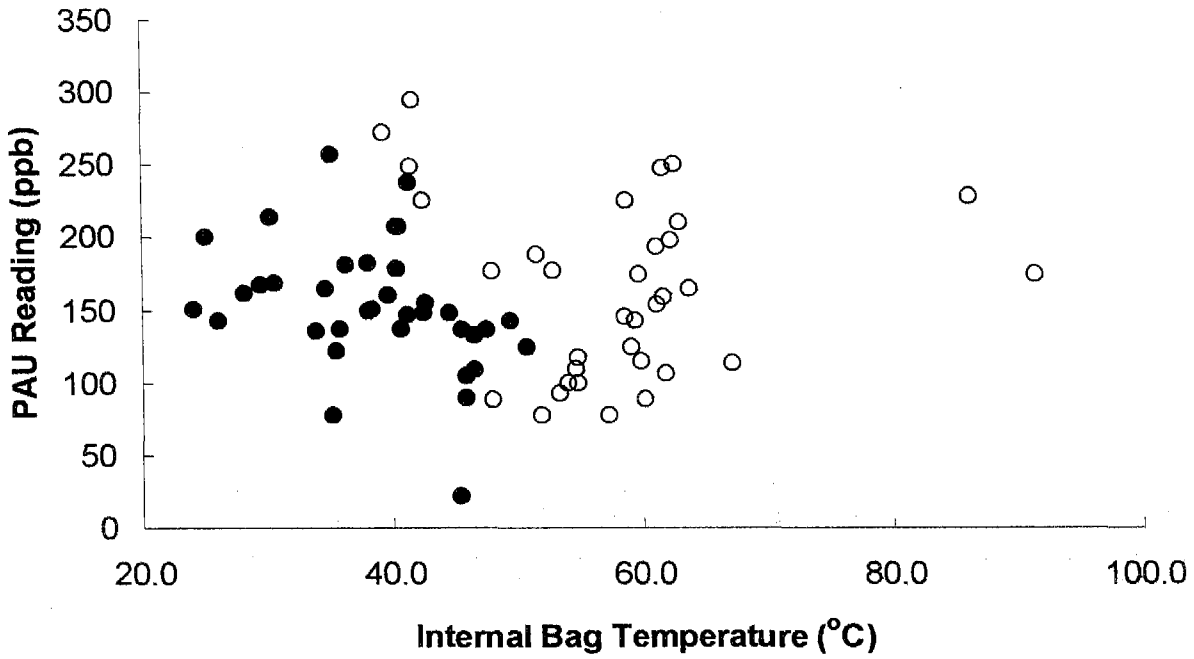

Figure 3.5. Relationship between temperature and polyethylene bag emissions under field conditions (sun = heat source). Data indicate net PAU values (PAU reading – ambient air reading). Test conducted July 31, 2000 at UCCE Office, Bakersfield. Hollow circles = light readings, filled circles = dark readings.

HG-751B) and the corresponding VOC reading was 835 ppb. An air sample was also drawn through sampling cartridges packed with Tenax using a Perfektum 100 ml gas syringe for analysis using GC-FID (Hewlett Packard model HP5710A). GC-FID revealed no identifiable peaks; however, the chromatograph indicated emissions from the bags. Even with the field data and GC-FID data indicating no, or relatively low (a few hundred ppb), VOC emissions it was apparent the ppbRAE instrument gave a measurable signal.

3.3.4.8 Characterizing Emissions From the Teflon Sample Bags

Given the apparent release of compounds from the polyethylene sample bags, it was decided to test and characterize the use of Teflon sampling bags, using the same field tests for VOC emissions as were used for the polyethylene bag test (Section 3.3.4.8). Results from the Teflon sampling bag test are summarized in the Figure 3.6.

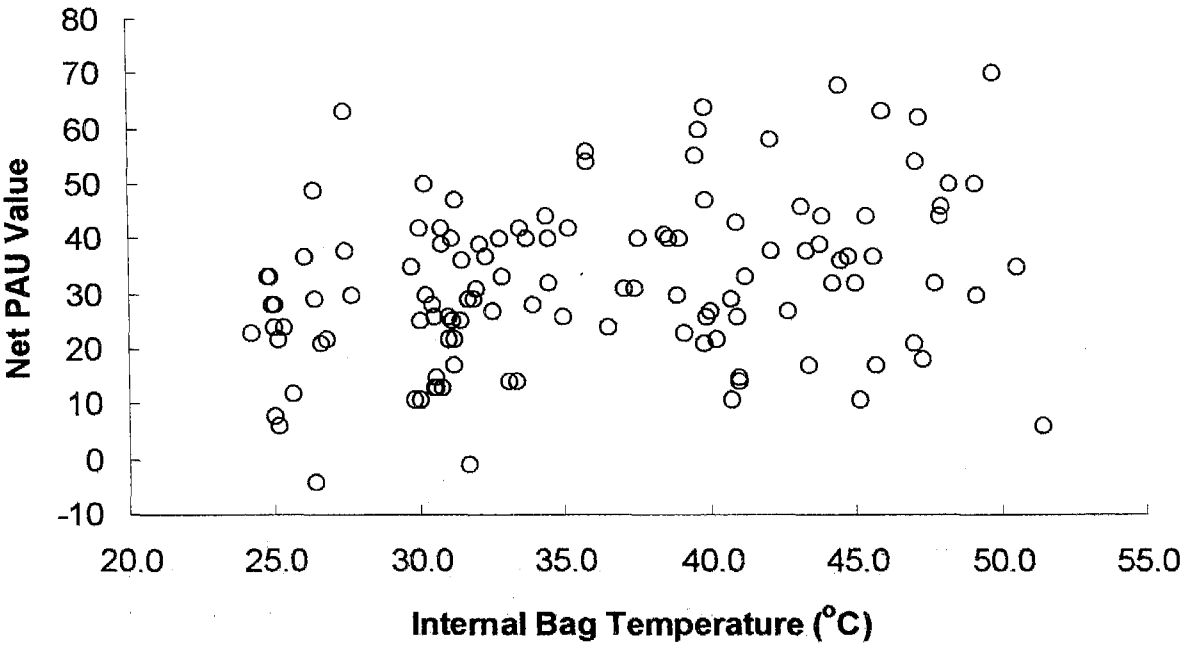

Figure 3.6. Relationship between internal air temperature of Teflon bags and corresponding net PAU value (PAU bag reading – PAU ambient reading). Test conducted at UCCE on 8/17/00 and 8/18/00.

No relationship was found between temperature and bag emissions for the Teflon bags. With a maximum of 70 PAU units of background emissions, the Teflon samplings bags were found to be a more suitable choice than the polyethylene bags, with much lower background VOC readings. Field sampling with the Teflon sampling bags began on August 22, 2000.

3.3.5 BVOC Field Sampling Procedures for Year 2000

3.3.5.1 Selecting Field Locations For Sampling in 2000

Sampling locations for the 2000 sampling season were primarily selected based on access and the number of tree and shrub species available. During the 2000 summer sampling season, permission was granted to sample plants in a number of locations including CSU Bakersfield campus, UCCE Shafter Research and Extension Center, L.E. Cooke Wholesale Nursery in Visalia, Intermountain Nursery in Fresno, UC Riverside Botanical Garden, Rancho Santa Ana Botanical Garden in Claremont, Mourning Cloak Botanical Garden in Tehachapi, and several residential sites in Bakersfield. All of these sites combined provided a variety of plant species from exotic and rare species to California natives.

3.3.5.2 Temperature and Light Measurement

These procedures were the same as described in Section 3.3.3.9.4.

3.3.5.3 Procedures for Measurement of BVOC Emissions from Attached Foliage

These procedures were the same as described in Section 3.3.3.9.5 except that polyethylene bags were used until August 21, 2000, and Teflon bags were used from August 22, 2000 until the end of the season.

3.3.5.4 Sampling BVOC Emissions from Foliage in the Light

A "light run" involved systematically placing five replicate bags over well-lighted branches or clumps of vegetation (PAR > 600 μmol m^{-2} s^{-1}) and carefully closing the base of each bag with a 2-inch binder clip. The instant that each bag was closed the time-in was recorded on a data sheet. After five minutes the accumulated BVOC within the bag were sampled using the portable analyzer, the PAU values were recorded and the time at which each bag was sampled was also recorded as time-out. The interval between securing each of the five sampling bags in the series was between 45 – 60 seconds to ensure that after the BVOC values were measured, the PAU could return to background levels.

3.3.5.5 Sampling BVOC Emissions from Darkened Foliage

The general procedure for measuring BVOC emissions from leaves that were darkened was similar to those described above with the exception that white plastic sleeves were used to cover the five sampling bags of each series. The white plastic sleeves were loosely fastened over each bag at the instant of time-in and sampling the accumulated BVOC was made after approximately five minutes with the sleeve intact. The white plastic sleeves were constructed in a manner as to reflect as much light as possible while preventing light from entering the sampling bags. In order to minimize the leaf disturbance and prevent "rough handling," the plastic dark sleeves were constructed with a drawstring end to close around the branch and the other end was closed with a rubber band.

3.3.5.6 Sampling Crushed Foliage

The foliage within two additional samples were manually crushed using polyethylene bags. The PAU response was noted as an indication of the release of pooled VOC. Some species released a large quantity of BVOC after crushing by hand, sometimes exceeding the operating range of the PAU. In these cases a nominal PAU unit value of 99900 was recorded.

3.4 Results

3.4.1 Data Entry and Analysis

Data recorded for each sample plant included sample date, time, and general location, plant species and common name (if possible), ambient air temperature (° C), and PAR (μmol $m^{-2}s^{-1}$). The calibration ratio was also noted. If the sample plant species could not be determined, a description of the plant's specific location, growth habit, leaves and fruits or flowers was noted and a sample taken for later identification.

Prior to each replicate sample, a PAU value was recorded that represented ambient air. A time-in value was recorded at the time the bag was closed and a time-out value was noted at the time the sample value was recorded. Field data was recorded manually using a datasheet and clipboard. Leaf mass of each sample was recorded after oven drying so that PAU values could be normalized to leafmass.

The data were entered into a Microsoft Excel spreadsheet so that fields could be manipulated to adjust the PAU value adjusted for calibration ratio and leafmass, and the emissions recorded in the light relative to those from the dark.

3.4.1.1 1999 PAU data

As discussed in detail earlier, data were collected in 1999 using the Model 580B PAU analyzer. As seen in Appendix A, the range of values recorded for light readings was 0 to more than 2000, although readings above 500 were uncommon. For dark readings, the highest values were above 500, but values above 200 were uncommon. For readings of crushed foliage, values ranged from 0 to above 10,000. At times it was necessary to allow the instrument to clear by taking in ambient air after exposure to high VOC levels from crushing leaves. An advantage of the PAU instruments was their fast response times, and the

ability to observe in "real time" the effects of "rough handling" as noted in the literature. It was obvious when taking samples of some plants, notably those in the Lamiaceae family, that high-value spikes occurred when bags were placed around the foliage.

3.4.1.2 2000 PAU data

Data were collected in 2000 using the ppbRAE PAU analyzer. As seen in Appendix B, the range of values recorded for light readings (after subtracting ambient values) was 0 to more than 3000, although readings above 1000 were uncommon. For dark readings, the highest values were above 1000, but values above 200 were uncommon. For readings of crushed foliage, values ranged from 0 to above 99900, the limit of the instrument. As in the 1999 study, at times it was necessary to allow the instrument to clear by taking in ambient air after exposure to high VOC levels from crushing leaves.

3.4.2 BVOC Emissions from Foliage in the Light

Isoprene is the dominant BVOC compound emitted from plant species, and the emission rate is dependent upon light and temperature. Other compounds, such as 2-methyl-3-butene-2-ol, monoterpenes from *Quercus ilex*, and perhaps other oxygenated compounds, also show light-dependence for emissions. However, we consider isoprene to likely be the dominant emission detected by the PAU instruments, although GC confirmation was not performed. In Table 3.5 and in subsequent places, we assign high (H), medium (M), and low (L) categories for each sampled plant species to represent the magnitude of emissions found in the light. We are hesitant to assign a zero or non-emitting category, since many plants emit isoprene at very low levels (Rasmussen and Khalil, 1997) and because of the rather high detection limits of the measurement systems employed in this study. The categories were assigned corresponding to ranges within the PAU data. Specifically, for the 580B instrument used in 1999, PAU values for samples taken in the light of <75, 75-200, and >200 were considered to be low, medium, and high, respectively. For the ppbRAE instrument used in 2000, the respective values were <100, 100-500, and >500 for low, medium and high.

Table 3.5 Categorization of PAU measurements for plant species.

Genus and Species	Family	Emission Categorization			Year	No. of Specimens Sampled
		Light	Dark	Crushed		
Acer ginnala	Aceraceae	L	L	L	00	1
Acer macrophyllum	Aceraceae	L	L	L	99	1
Acer negundo	Aceraceae	L	L	L	00	1
Acer rubrum	Aceraceae	L	L	L	99	1
Hesperaloe funifera	Agavaceae	L	L	L	99	1
Agapanthus africanus	Amaryllidaceae	L	L	L	00	1
Cotinus coggygria 'Purpureus'	Anacardiaceae	L	L	H	00	1
Pistacia chinensis	Anacardiaceae	L	M	H	99	3
Pistacia vera	Anacardiaceae	L	M	H	99	3
Rhus glabra	Anacardiaceae	L	L	L	00	2
Rhus lancea	Anacardiaceae	L	L	H	00	2
Rhus ovata	Anacardiaceae	L	M	H	99/00	2
Rhus typhina	Anacardiaceae	L	L	L	99	1
Schinus molle	Anacardiaceae	L	M	H	99/00	4
Trachelospermum jasminoides	Apocynaceae	L	L	L	00	1
Berberis mentorensis	Berberidaceae	H	L	M	99	2
Berberis thunbergii	Berberidaceae	H	M	M	00	2
Mahonia aquifolium	Berberidaceae	M	L	M	99	1
Mahonia nevinii	Berberidaceae	H	L	M	99	2
Alnus rhombifolia	Betulaceae	L	L	L	00	1
Betula papyrifera	Betulaceae	L	M	M	00	3
Betula pendula	Betulaceae	L	L	L	99	2
Carpinus betulus	Betulaceae	L	L	L	00	1
Corylus cornuta	Betulaceae	L	L	L	00	1
Corylus maxima	Betulaceae	L	M	L	00	2
Chilopsis linearis	Bignoniaceae	L	H	L	99	2
Chilopsis linearis 'Burgundy'	Bignoniaceae	L	H	L	00	1
Chitalpa tashkentensis	Bignoniaceae	L	M	L	99	2
Macfadyena unguis-cati	Bignoniaceae	L	M	L	00	2
Podranea ricasoliana	Bignoniaceae	L	L	L	00	2
Simmondsia chinensis	Buxaceae	M	L	M	00	2
Calycanthus occidentalis	Calycanthaceae	H	M	M	00	2
Isomeris arborea	Caparidaceae	L	L	M	99	1
Lonicera nitida	Caprifoliaceae	L	L	L	99	2
Lonicera tartarica	Caprifoliaceae	L	M	M	00	2
Sambucus mexicana	Caprifoliaceae	L	L	L	00	2
Symphoricarpos albus	Caprifoliaceae	L	L	L	99	2
Casuarina cunninghamiana	Casuarinaceae	H	M	M	99/00	5
Euonymus alata	Celastraceae	L	L	L	00	2
Euonymus japonica	Celastraceae	L	L	L	00	1
Cercidiphyllum japonicum	Cercidiphyllaceae	L	L	L	00	2
Salsola tragus	Chenopodiaceae	L	M	L	00	2
Cistus purpureus	Cistaceae	L	L	M	99	1
Achillea clavennae	Compositae	L	M	H	99	2
Artemisia californica	Compositae	H	L	H	99	1
Artemisia frigida	Compositae	L	H	H	99	1
Artemisia 'Powis Castle'	Compositae	L	L	H	99	1
Artemisia tridentata	Compositae	L	H	H	00	1
Baccharis pilularis	Compositae	L	L	M	99	1
Baccharis salcifolia	Compositae	L	H	H	00	2
Chrysothamnus nauseosus	Compositae	L	M	H	99	2

Table 3.5 continued.

Genus and Species	Family	Emission Categorization			Year	No. of Specimens Sampled
		Light	Dark	Crushed		
Ericameria laricifolia	Compositae	L	H	H	99	1
Euryops pectinatus	Compositae	L	L	L	00	1
Santolina chamaecyparissus	Compositae	H	H	H	99	1
Cornus stolonifera	Cornaceae	L	L	L	00	2
Corokia virgata	Cornaceae	M	L	M	99	2
Cupressocyparis leylandii	Cupressaceae	L	L	M	99	3
Cupressus nevadensis	Cupressaceae	M	M	H	99/00	3
Juniperus californica	Cupressaceae	L	L	H	99	2
Thuja occidentalis	Cupressaceae	L	L	H	00	1
Cycas revoluta	Cycadaceae	L	L	L	00	2
Diospyros virginiana	Ebenaceae	L	L	L	00	2
Elaeagnus angustifolia	Elaeagnaceae	L	L	L	99/00	2
Arbutus menzeisii	Ericaceae	L	L	L	99/00	2
Arbutus unedo	Ericaceae	L	L	L	00	1
Arctostaphylos hookeri	Ericaceae	L	L	L	99	1
Arctostaphylos manzanita	Ericaceae	L	L	L	99	1
Arctostaphylos morroensis	Ericaceae	L	L	L	00	1
Euphorbia martinii	Euphorbiaceae	L	L	L	99	1
Sapium sebiferum	Euphorbiaceae	L	L	L	99	3
Quercus berberidifolia	Fagaceae	M	M	L	00	2
Quercus boissieri	Fagaceae	L	H	M	99	2
Quercus brewerii	Fagaceae	L	L	L	00	2
Quercus coccinea	Fagaceae	H	M	M	99	1
Quercus durata 'durata'	Fagaceae	M	L	L	00	2
Quercus emoryi	Fagaceae	H	L	M	99	1
Quercus englemannii	Fagaceae	M	M	M	99	3
Quercus john-tuckeri	Fagaceae	M	L	L	00	1
Quercus lobata	Fagaceae	H	L	M	99/00	6
Quercus macrocarpa	Fagaceae	H	L	M	99	1
Quercus pacifica	Fagaceae	M	L	L	00	2
Quercus palmeri	Fagaceae	M	M	M	00	1
Quercus palustris	Fagaceae	H	M	H	99	1
Quercus peninsularis	Fagaceae	M	L	L	00	2
Quercus tomentella	Fagaceae	M	L	L	00	1
Quercus vacciniifolia	Fagaceae	M	L	L	00	1
Quercus virginiana	Fagaceae	H	L	M	99	4
Quercus suber	Fagaceae, Quer. -- Cer.	L	L	L	99	2
Quercus agrifolia	Fagaceae, Quer. -- Ery.	H	L	M	99	4
Quercus rubra	Fagaceae, Quer. -- Ery.	H	H	M	99	2
Quercus wislizensii	Fagaceae, Quer. -- Ery.	H	M	H	99	2
Quercus douglasii	Fagaceae, Quer. -- Lep.	H	L	M	99/00	6
Quercus robur	Fagaceae, Quer. -- Lep.	H	M	H	99	2
Quercus chrysolepis	Fagaceae, Quer. -- Pro.	M	L	M	00	3
Garrya elliptica	Garryaceae	L	L	L	00	2
Garrya flavescens	Garryaceae	L	L	L	99	2
Gingko biloba	Gingkoaceae	L	L	L	99	2
Cortaderia selloana	Graminae	L	L	L	00	2
Ribes odorata	Grossulariaceae	M	M	M	00	2
Liquidambar styraciflua	Hamamelidaceae	H	H	H	99/00	4
Aesculus californicum	Hippocastanaceae	M	M	M	00	2
Juglans californica	Juglandaceae	L	M	M	00	2

Table 3.5 continued.

Genus and Species	Family	Emission Categorization			Year	No. of Specimens Sampled
		Light	Dark	Crushed		
Juglans regia	Juglandaceae	L	M	M	99/00	5
Hyptis emoryi	Lamiaceae	L	H	H	99	1
Lavandula angustifolia	Lamiaceae	H	H	H	00	1
Marrubium rotundiflora	Lamiaceae	L	L	H	99	1
Phlomis fruticosa	Lamiaceae	L	L	H	99	1
Rosmarius officinalis	Lamiaceae	L	M	H	99	2
Salvia apiana	Lamiaceae	L	L	H	99	1
Salvia 'Bee's Bliss'	Lamiaceae	H	H	H	00	2
Salvia chamedryoides	Lamiaceae	L	H	M	99	1
Salvia clevelandii	Lamiaceae	H	H	H	00	2
Salvia darcyi	Lamiaceae	L	H	H	99	2
Salvia dolomitica	Lamiaceae	H	M	H	00	1
Salvia gregii	Lamiaceae	L	H	H	00	2
Salvia officinalis	Lamiaceae	M	H	H	99	2
Umbellularia californica	Lauraceae	H	H	H	00	1
Caesalpinia gilliesii	Leguminosae -- Cae.	L	M	L	99	2
Cassia artemisiodes	Leguminosae -- Cae.	L	M	H	99	1
Cassia nemophila	Leguminosae -- Cae.	L	L	L	99	1
Ceratonia siliqua	Leguminosae -- Cae.	H	M	M	99/00	3
Cercis canadensis	Leguminosae -- Cae.	L	L	M	00	2
Cercis occidentalis	Leguminosae -- Cae.	H	M	M	99/00	2
Gleditsia triacanthos inermis 'Shademaster'	Leguminosae -- Cae.	L	L	L	00	2
Acacia melanoxylon	Leguminosae -- Mim.	L	L	L	00	2
Albizia julibrissin	Leguminosae -- Mim.	L	L	L	00	2
Calliandra eriophylla	Leguminosae -- Mim.	M	M	M	00	1
Lysiloma thornberii	Leguminosae -- Mim.	L	L	L	00	2
Prosopis alba 'Colorado'	Leguminosae -- Mim.	L	L	L	99	1
Cytisus scoparius	Leguminosae -- Pap.	H	M	M	99	1
Dalbergia sissoo	Leguminosae -- Pap.	M	L	L	00	1
Erythrina caffra	Leguminosae -- Pap.	H	H	M	00	1
Genista racemosa	Leguminosae -- Pap.	H	M	L	00	2
Genista tinctoria	Leguminosae -- Pap.	H	M	M	99	2
Olneya tesota	Leguminosae -- Pap.	H	H	H	00	1
Robinia pseudocacia	Leguminosae -- Pap.	M	L	M	99	2
Sophora secundiflora	Leguminosae -- Pap.	M	M	M	99	3
Buddleia alternifolia	Loganiaceae	L	M	L	99	2
Buddleia davidii	Loganiaceae	L	L	L	99	1
Buddleia marrubbifolia	Loganiaceae	L	H	M	99	2
Magnolia grandiflora	Magnoliaceae	L	L	M	99	2
Magnolia soulangiana	Magnoliaceae	L	L	M	00	2
Magnolia stellata	Magnoliaceae	L	L	L	99/00	4
Althaea 'W.M.R. Smith'	Malvaceae	L	L	L	00	2
Anisodontea x hypomadarum	Malvaceae	M	M	M	00	1
Malacothamnus niveus	Malvaceae	L	M	H	99	1
Ficus carica 'Mission'	Moraceae	M	L	L	00	2
Maclura pomifera	Moraceae	L	L	L	00	2
Eremophila glabra	Myoporaceae	L	L	L	99	2
Callistemon citrinus	Myrtaceae	L	M	M	99	3
Eucalyptus accedens	Myrtaceae	H	M	H	00	1
Eucalyptus camaldulensis 'C2'	Myrtaceae	M	M	M	99	3
Eucalyptus ebbanoensis	Myrtaceae	H	M	H	00	1

Table 3.5 continued.

Genus and Species	Family	Emission Categorization			Year	No. of Specimens Sampled
		Light	Dark	Crushed		
Eucalyptus grandis 'G3'	Myrtaceae	H	M	H	99	3
Eucalyptus grandis 'GCT'	Myrtaceae	H	M	H	99	3
Eucalyptus megacornuta	Myrtaceae	M	M	M	00	1
Eucalyptus polyanthemos	Myrtaceae	H	M	H	99	3
Eucalyptus sideroxylon	Myrtaceae	H	M	H	99	3
Eucalyptus spathulata	Myrtaceae	M	M	H	00	1
Bougainvillea brasiliensis	Nyctaginaceae	M	H	M	99	1
Nyssa sylvatica	Nyssaceae	H	M	M	00	2
Chionanthus retusus	Oleaceae	L	L	L	00	2
Forestiera neomexicana	Oleaceae	L	L	L	99	1
Fraxinus americana 'Junginger'	Oleaceae	L	L	L	00	2
Fraxinus depetela	Oleaceae	L	M	L	00	1
Fraxinus oxycarpa	Oleaceae	L	L	L	00	2
Fraxinus pennsylvanica 'Patmore'	Oleaceae	L	L	L	00	2
FraxInus velutina 'Modesto'	Oleaceae	L	L	L	99	1
Olea europaea	Oleaceae	L	L	L	99	1
Syringa vulgaris 'Clark's Giant'	Oleaceae	L	M	L	99	1
Zauschneria californica	Onagraceae	L	L	L	99	1
Syagrus romanzoffinaum	Palmae	M	L	L	00	2
Dendromecon rigida	Papaveraceae	M	L	M	99	1
Romenya coulteri	Papaveraceae	M	L	M	99/00	3
Caloacedrus decurrens	Pinaceae	M	L	M	00	2
Cedrus lebani	Pinaceae	L	L	M	00	2
Larix kaempferi	Pinaceae	L	L	H	00	2
Picea breweriana	Pinaceae	H	M	H	99	2
Picea pungens-glauca	Pinaceae	M	M	H	00	2
Pinus attenuata	Pinaceae	M	H	H	00	1
Pinus halepensis	Pinaceae	L	M	H	99	2
Pinus monophyla	Pinaceae	L	M	H	00	2
Pinus pinea	Pinaceae	L	L	M	99	2
Pinus ponderosa	Pinaceae	L	L	M	00	2
Pinus sabiniana	Pinaceae	L	M	H	99	3
Pinus strobus 'nana'	Pinaceae	L	M	H	00	1
Pinus sylvestris	Pinaceae	L	L	H	99	1
Platanus racemosa	Platanaceae	M	M	L	99	3
Platanus x acerifolia 'Yarwood'	Platanaceae	H	L	M	00	2
Woodwardia fimbriata	Polypodiaceae	H	M	M	99	2
Grevillea noellii	Proteaceae	M	L	L	00	1
Punica granatum	Punicaceae	L	L	L	00	2
Ceanothus cuneatus	Rhamnaceae	L	M	L	00	1
Ceanothus 'Dark Star'	Rhamnaceae	M	M	L	00	1
Ceanothus thyrsiflorus 'Skylark'	Rhamnaceae	L	L	L	00	1
Rhamnus californica	Rhamnaceae	H	L	M	99	2
Rhamnus cathartica	Rhamnaceae	L	L	L	99	2
Ziziphus jujuba 'Li'	Rhamnaceae	L	L	L	00	2
Amelanchier alnifolia	Rosaceae	L	L	L	00	1
Cercocarpus ledifolius	Rosaceae	L	L	L	99	2
Cerocarpus montanus	Rosaceae	L	L	H	99	2
Chaenomeles 'Toyo Nishiki'	Rosaceae	L	L	L	99	1
Crataegus laevigata	Rosaceae	L	L	L	00	2
Crataegus laevigata 'Washington'	Rosaceae	L	L	L	00	2

Table 3.5 continued.

Genus and Species	Family	Emission Categorization			Year	No. of Specimens Sampled
		Light	Dark	Crushed		
Cydonia oblonga 'Cookes Jumbo'	Rosaceae	L	L	L	00	2
Heteromeles arbutifolia	Rosaceae	L	L	L	99/00	3
Malus domestica 'Yellow Delicious'	Rosaceae	L	L	L	00	2
Malus 'Prairifire'	Rosaceae	L	L	L	00	2
Potentilla fruiticosa	Rosaceae	L	L	L	99	2
Prunus cerasifera	Rosaceae	L	L	L	00	1
Prunus cistena	Rosaceae	L	L	L	00	2
Prunus domestica	Rosaceae	L	L	L	00	2
Prunus ilicifolia	Rosaceae	L	L	L	00	1
Prunus laurocerasus	Rosaceae	L	L	L	99	2
Purshia tridentata	Rosaceae	L	M	L	99	2
Pyracantha 'Mojave'	Rosaceae	L	L	L	99	2
Spiraea vanhouttei	Rosaceae	L	L	M	00	2
Spiraea x bumalda 'Anthony Waterer'	Rosaceae	L	L	L	00	2
Vauquelina californica	Rosaceae	L	L	L	99	1
Cephalanthus occidentalis	Rubiaceae	L	M	L	00	2
Galium odoratum	Rubiaceae	L	L	M	99	1
Correa pulchella	Rutaceae	M	H	M	99	1
Populus alba	Salicaceae	H	L	M	99	3
Populus balsamifera	Salicaceae	H	L	M	00	2
Populus fremontii	Salicaceae	H	L	M	99	3
Populus nigra italica	Salicaceae	H	M	M	99/00	5
Populus tremula erecta	Salicaceae	H	M	M	99	3
Populus tremuloides	Salicaceae	H	M	M	00	2
Salix babylonica	Salicaceae	H	M	M	99	2
Salix caprea	Salicaceae	H	M	L	00	2
Salix laevigata	Salicaceae	H	L	M	99	2
Salix matsudana	Salicaceae	M	L	L	00	2
Salix purpurea	Salicaceae	H	M	M	00	2
Salix x blanda 'Fan-Giant'	Salicaceae	H	H	H	00	2
Koelreuteria paniculata	Sapindaceae	L	H	M	99/00	5
Escallonia rubra	Saxifragaceae	L	L	M	00	2
Leucophyllum frutescens 'White Cloud'	Scrophulariaceae	L	L	L	99	3
Ailanthus altissima	Simaroubaceae	L	L	L	00	1
Datura meteloides	Solanaceae	L	L	L	00	1
Lycium brevipes	Solanaceae	M	H	M	00	1
Nicotiana glauca	Solanaceae	L	L	L	00	2
Fremontodendron californicum	Sterculiaceae	M	M	M	00	2
Tamarix parviflora	Tamaricacae	L	L	L	00	2
Sequoiadendron giganteum	Taxodiaceae	L	L	H	00	1
Daphna caucasica	Thymelaeaceae	M	L	L	00	1
Celtis occidentalis	Ulmaceae	L	L	L	00	2
Ulmus parvifolia	Ulmaceae	L	L	L	99	1
Callicorpa japonica	Verbenaceae	M	M	M	00	2
Lantana montevidensis	Verbenaceae	L	H	M	00	2
Vitex agnus-castus	Verbenaceae	L	H	H	00	2
Vitis vinifera 'Thompson Seedless'	Vitaceae	L	M	L	00	2
Larrea tridentata	Zygophyllaceae	L	L	L	99	2

For the samples taken in the dark with the 580B instrument, the ranges were <20, 20-60, and >60 for low, medium, and high, respectively; for the ppbRAE instrument the respective ranges for low, medium, and high were <40, 40-125, and >125. For crushed readings, the ranges for the 580B instrument were <100, 100-1000, and >1000. For the ppbRAE instrument, the respective values were <200, 200-2000, and >2000 for low, medium and high. These ranges were established based on results of the present field measurements of selected plant species, as compared with isoprene and monoterpene emission rates measured by gas chromatography (GC) and reported for those same species, with the primary literature reference being the compilation of Benjamin et al. (1996). To validate the PAU approach we compared PAU-measured BVOC light emissions for 63 plant species and PAU dark emissions for 33 plant species with reported emission rates of isoprene and monoterpenes, as seen in Table 3.6, and found them to be well-correlated.

For assignment in the light readings for a species to low, medium or high categories, we also considered the relative magnitudes of the PAU values for dark and crushed measurements. If both light and crushed values were high for a plant species, such as those in the Lamiaceae family, we considered the possibility that emissions had occurred from handling foliage during the in-the-light measurements, despite care taken and our awareness of the "rough handling" possibility. Therefore, a species might not be assigned to the high light emission category if the crushed value was high. We also considered the PAU values of the light measurements compared to the dark readings. For a plant to be categorized as having a high light reading, the dark reading had to be some fraction of the light reading. If the light and dark readings were of the same approximate magnitude, we judged we were observing temperature-dependent emissions for both illuminated and darkened foliage. An example, as seen in Appendix A, is that of *Pistacia vera* (pistachio) where the light and dark readings were similar. In such cases we assumed the emissions measured when foliage was illuminated was due to the same level of emissions observed from darkened foliage. Therefore, we placed this species in the low category for light emissions and in the medium category for dark emissions.

Table 3.6 Comparison of PAU emission categorization with reported emission rate measurements for plant species.

Family	Genus Species	Light Present Study	Iso. Emiss. Rate ug $g^{-1}h^{-1}$	Ref.	Dark Present Study	Mono. Emiss. Rate ug $g^{-1}h^{-1}$	Ref.
Aceraceae							
	Acer rubrum	L	BDL	B96	L	3.5	B96
Anacardiaceae							
	Pistacia chinensis	L	BDL	KW01	M	--	--
	Pistacia vera	L	BDL	B96	M	9.0	B96
	Rhus ovata	L	BDL	B96	M	BDL	B96
	Schinus molle	L	BDL	B96	M	3.7, BDL	B96
Betulaceae							
	Betula pendula	L	BDL	H97	L	--	--
Compositae							
	Artemisia californica	H	0.0, BDL	B96	L	9.6, 47	B96
	Baccharis pilularis	L	BDL	KW01	L	--	--
	Euryops pectinatus	L	BDL	KW01	L	--	--
Cornaceae							
	Cornus stolonifera	L	BDL	KW01	L	--	--
Cupressaceae							
	Cupressocyparis leylandii	L	BDL	KW01	L	--	--
Fagaceae -- Quercus -- Subfamily Unknown							
	Quercus coccinea	H	20.1	B96	M	3.2	B96
	Quercus lobata	H	3.4, 23	B96, KW01	L	0.0	B96
	Quercus palustris	H	27	KW01	M	--	--
	Quercus virginiana	H	9.5, 30.9	B96	L	BDL, 0.3	B96

Table 3.6 continued.

Family	Genus Species	Light Present Study	Iso. Emiss. Rate ug $g^{-1}h^{-1}$	Ref.	Dark Present Study	Mono. Emiss. Rate ug $g^{-1}h^{-1}$	Ref.
Fagaceae -- Quercus -- Cerris							
	Quercus suber	L	BDL	KW01	L	--	--
Fagaceae -- Quercus -- Erythobalanus							
	Quercus agrifolia	H	35.3	B96	L	BDL	B96
	Quercus rubra	H	14.8	B96	H	1.8	B96
	Quercus wislizensii	H	12.5, 12.5	B96, CS99	M	0.0, 0.0	B96, CS99
Fagaceae --Quercus -- Lepidobalanus							
	Quercus douglasii	H	8.7, 27	B96, KW01	L	0.0	B96
	Quercus robur	H	76.6	B96	M	--	--
Fagaceae -- Quercus -- Protobalanus							
	Quercus chrysolepsis	M	11.7, 19	CS99, KW01	L	0.1	CS99
Gingkoaceae							
	Gingko biloba	L	BDL	B96	L	3.0	B96
Hamamelidaceae							
	Liquidambar styraciflua	H	35.3, 17.8, 3.5; 2	B96; KW01	H	3.0, 2.9, 51.5	B96
Hippocastanaceae							
	Aesculus californicum	M	BDL	KW01	M	--	--
Juglandaceae							
	Juglans regia	L	BDL	B96	M	1.8	B96
Lamiaceae							
	Salvia gregii	L	BDL	KW01	H	--	--

Table 3.6 continued.

Family	Genus Species	Light Present Study	Iso. Emiss. Rate ug $g^{-1}h^{-1}$	Ref.	Dark Present Study	Mono. Emiss. Rate ug $g^{-1}h^{-1}$	Ref.
Leguminosae -- Caesalpinioideae							
	Caesalpinia gilliesii	L	BDL	KW01	M	--	--
	Cassia artemisiodes	L	BDL	KW01	M	--	--
	Cassia nemophila	L	BDL	KW01	L	--	--
	Ceratonia siliqua	H	BDL	KW01	M	--	--
	Cercis canadensis	L	0.0	B96	L	BDL	B96
Leguminosae -- Mimosoideae							
	Acacia melanoxylon	L	BDL	KW01	L	--	--
	Albizia julibrissin	L	4.3	B96	L	1.4	B96
	Lysiloma thornberi	L	BDL	KW01	L	--	--
	Prosopis alba 'Colorado'	L	BDL	KW01	L	--	--
Leguminosae -- Papilionoideae							
	Robinia pseudoacacia	M	10.1, 13.5	B96	L	0.0, 4.7	B96
	Sophora secundiflora	M	34.0	KW01	M	--	--
Magnoliaceae							
	Magnolia grandiflora	L	BDL	B96	L	5.9	B96
Myrtaceae							
	Callistemon citrinus	L	16.0	B96	M	BDL	B96
	Eucalyptus camaldulensis 'C2'	M	28	KW01	M	--	--
	Eucalyptus grandis	H	12.1, 21	B96, KW01	M	--	--
	Eucalyptus polyanthemos	H	10	KW01	M	--	--
Oleaceae							
	Fraxinus velutina 'Modesto'	L	BDL	B96, KW01	L	BDL	B96, KW00
	Olea europaea	L	BDL	B96	L	0.5, 0.1	B96
	Syringa vulgaris	L	BDL	KW01	M	--	--

Table 3.6 continued.

Family	Genus Species	Light Present Study	Iso. Emiss. Rate ug $g^{-1}h^{-1}$	Ref.	Dark Present Study	Mono. Emiss. Rate ug $g^{-1}h^{-1}$	Ref.
Pinaceae							
	Picea pungens	M	12	K96	M	--	--
	Pinus halepensis	L	BDL	B96	M	0.2, 0.5	B96
	Pinus pinea	L	BDL	B96	L	BDL, 0.4	B96
	Pinus sabiniana	L	BDL	B96	H	0.6	B96
	Pinus sylvestris	L	BDL	B96	L	0.8, 12.1	B96
Platanaceae							
	Platanus racemosa	M	10.9	B96	M	BDL	B96
Rhamnaceae							
	Rhamnus californica	H	29.3	B96	L	BDL	B96
Rosaceae							
	Prunus domestica	L	BDL	B96	L	0.0	B96
Salicaceae							
	Populus alba	H	25	KW01	L	--	--
	Populus fremontii	H	43	KW01	L	--	--
	Populus nigra italica	H	36	KW01	M	--	--
	Populus tremuloides	H	50.2	B96	M	BDL	B96
	Salix babylonica	H	115	B96	M	BDL	B96
Taxodiaceae							
	Sequoiadendron giganteum	L	BDL	KW01	L	--	--
Ulmaceae							
	Ulmus parvifolia	L	BDL	B96	L	BDL	B96
Verbenaceae							
	Vitex agnus-castus	L	BDL	KW01	H	--	--

Table 3.6 continued.

Family	Genus Species	Light Present Study	Iso. Emiss. Rate ug $g^{-1}h^{-1}$	Ref.	Dark Present Study	Mono. Emiss. Rate ug $g^{-1}h^{-1}$	Ref.
Zygophyllaceae							
	Larrea tridentata	L	BDL	KW01	L	--	--

B96 = Benjamin et al., 1996
CS99 = Csiky and Seufert, 1999
H97 = Hakola et al., 1997
K96 = Kempf et al., 1996
KW01 = Karlik and Winer, 2001b

3.4.3 BVOC Emissions from Foliage in the Dark

We consider monoterpenes to likely be the emissions detected in greatest quantity from darkened foliage, while recognizing other compound classes may also be emitted. The PAU instruments were less sensitive to most monoterpenes than to isoprene, as seen in Tables 3.3 and 3.4, and the magnitude of monoterpene emission rates are often generally an order of magnitude lower or less than those isoprene emission rates (Benjamin et al., 1996). Therefore, our ability to detect monoterpenes was limited in this study. It is possible other compounds were present in significant quantities relative to monoterpenes, but no additional identification of such compounds was done during this project.

3.4.4 BVOC Emissions from Crushed Foliage

We consider values for crushed foliage to be indicative of stored volatile compounds within the leaf. However, we make no assumptions about the emission rates from intact foliage of these compounds. It was obvious that some plants emit BVOC upon lightly touching foliage, because when plants were lightly touched we saw a sharp rise in PAU readings to high levels, at times above the upper limit of the instruments. Sensitivity to handling could also result in high standard deviations for light and dark PAU readings if stored BVOC were inadvertently released during sampling. However, relatively few species displayed a sharp rise in PAU emissions when leaves were touched, and handling, short of breaking leaves, did not increase PAU measured emissions for the majority of species.

3.4.5 BVOC Emissions within Plant Families

As noted in Winer et al. (1998), plant families represent a less certain basis for inferring emissions of BVOC for unmeasured plant species than do genera. However, generalizations may be possible for some families, in which genera and their species are uniform in behavior. For other families, generalization may not be possible, and consideration of emission behavior at the genus level will be necessary. In the following discussion, we begin with families which seem to be the most homogeneous in emission measurement results from the present study.

As seen in Table 3.5, some families contain species with similar emission behavior. Families containing plants with low light, dark, and crushed emissions include the Aceraceae

(maple), Betulaceae (birch), Ericaceae (heath), Oleaceae (olive), and Rosaceae (rose) families. These families contain numerous species frequent in California's native and urban landscapes. For example, Aceraceae contains the many species of maples found as shade trees in California. Betulaceae contains the birches and alders, the latter common in riparian areas, with one species used extensively as a shade tree. Ericaceae contains *Arctostaphylos* species, the manzanitas, which are common native shrubs and trees in the Sierra Nevada. The Oleaceae family contains olives, found in both commercial groves for fruit production and as individual specimens in urban landscapes in the southern half of the state, and ash trees, widely used as shade trees throughout California. The Rosaceae family contains both stone and pome fruits found as large-acreage agricultural crops, including almonds, apricots, plums, peaches, nectarines, apples and pears. Roses, the most common plant in landscapes and gardens, are also within this family. California native plants which are members of the Rosaceae include *Heteromeles arbutifolia* (toyon) and *Cercocarpus sp.* (mountain mahoganies).

Characterization of the rose, olive and maple families as containing low-emitters is in agreement with the compilation of Benjamin et al. (1996) and additional GC measurements within the Oleaceae and Rosaceae families (Winer et al., 1998; Karlik and Winer, 2001b). Isoprene emissions were not detected for *Betula pendula* (Hakola et al., 1997) or for *Alnus rhombifolia* (white alder) contained within the Betulaceae (Karlik and Winer, 2001b).

From PAU measurements of willows and poplars, the Salicaceae family may be characterized as containing plants with high light emissions, low-to-medium dark emissions, and medium crushed emissions. Several of the willows and poplars have been measured by GC and found to have high isoprene emission rates (Karlik and Winer, 2001b).

The Myrtaceae seem similar to the Salicaceae in emission profile in that all species except one measured in this study had high light emissions. However, this family contained species with medium dark emissions, suggesting the possible emission of monoterpenes or other temperature-dependent compounds, and most species had high levels of stored BVOC.

For the Pinaceae, light emissions ranged from low to high among species and genera, which is in general agreement for the range of isoprene emission rates reported (Benjamin et al., 1996). Dark emissions ranged from low to high, while emissions from crushed foliage were medium to high. The present PAU measurements and observations are in agreement

with GC measurements of monoterpene emission rates (Benjamin et al., 1996) and the well-known fact that needle evergreens contain stored resin and other compounds (Cronquist, 1971; Stern, 1996).

All four plant species measured within the Berberidaceae (barberry) family had medium to high light emissions, three of four had low dark emissions, and all four had medium crushed emissions. Based on these very limited data, the family may contain mostly plants with light-dependent emissions. However, there are no GC or GC-MS measurements to compare with the present data.

The Compositae (composite, aster) family contains ray-flowered plants and is the largest of all plant families, containing numerous species found in natural plant communities and those used as ornamentals. Examples include sunflowers, asters, black-eyed Susan, rudbeckia, gloriosa daisy, yarrow, and coyotebrush. Plants within this family are mostly herbaceous, but some are semi-woody, such as the California native *Baccharis* (coyotebrush) species measured in this study. As a whole, the family contained plants with low light emissions, dark emissions from low to high, and high emissions from crushed foliage.

The Anacardiaceace family contained plants with low light emissions, low or medium dark emissions, and low or high crushed emissions. The detection of emissions from darkened foliage is consistent with Benjamin et al. (1996), in which two species within that family had monoterpene rates which were medium in one case and high in the other case, 1.3 and 10.4 $\mu g\ g^{-1}\ h^{-1}$, respectively.

For the Bignoniaceae, emissions from illuminated foliage were low, from darkened foliage emissions were low to high, and from crushed foliage emissions were low. Thus, the four species measured in this study were consistent in their light and crushed assignments. In the compilation of Benjamin et al. (1996), both species within the Bignoniaceae, *Jacaranda acutifolia* and *Tecomaria capensis*, had negligible isoprene and monoterpene emission rates. In possible contrast, three of the four plant species measured in the present study had medium or high emissions from dark foliage.

For the Caprifoliaceae (honeysuckle) family, three of the four species measured had low emissions of foliage in the light, low emissions of darkened foliage and low crushed values. The fourth species differed only in medium values for both darkened and crushed foliage. Thus, based on this very limited sample, this family contains low-emitting species.

Three of four plants measured within the Cupressaceae (cypress) family were low light-emitters, low dark-emitters, and had high crushed values, with one plant showing medium light and dark emissions, and another medium rather than high crushed values. These observations are consistent with data for species in this family given in the compilation of Benjamin et al. (1996).

Several families contained species less homogeneous in emission behavior than the families discussed above. The Leguminosae (legume) family was impossible to characterize on a whole-family basis. This family is divided into three sub-families in the scheme of Mabberley (1997), and these sub-families are listed as genera in arrangements used by some investigators (Klinger et al., 1998). With this separation, it can be seen in Table 3.5 that the species with medium or high light emissions were concentrated in the Papilionoideae sub-family, and that none of the species within this sub-family was in the low light emission category. Most plants in this sub-family also had medium or high dark and crushed emissions. In contrast, four of five species within the Mimosoideae sub-family had low light, dark and crushed emissions, suggesting this sub-family may contain low emitters. The Caesalpiniodeae was intermediate as compared with the other two sub-families with respect to emissions from its members.

The Lamiaceae (mint) family contained plants with high crushed values; indeed, some of the field measurements for these species exceeded the range of the instrument. Although some species within this family are listed as having high values for light emissions, and some as having medium or high emissions for dark emissions, we regard these data with caution, since leaves of plants within this family were observed in the field to be sensitive to crushing. Several of these species may have emissions as noted in Table 3.5; however, the results may be confounded by leaf emissions triggered by contact, despite our recognition of this problem and care to avoid it.

For the Malvaceae (mallow) family, only one species in each of three genera were measured and the results were not consistent. The three species were either low or medium light and dark emitters, and crushed values were low, medium and high.

For the Rhamnaceae (buckthorn) family, light emissions ranged from low to high. The high category was found for *Rhamnus californica*, the native California buckthorn. Dark emissions for plants within the family were low or medium, and crushed emissions were

low with the exception of *R. californica*. Thus, this family cannot be readily characterized with respect to BVOC emissions on the basis of the limited data from the present study.

Two of the three genera, and corresponding species, within the Solanaceae (nightshade) family were low in light, dark, and crushed emissions. The third contained a species with medium light and high dark emissions. Tomato (*Lycopersicon esculentum*) is found within this family, and has a measured monoterpene emission rate of greater than 20 μg g^{-1} h^{-1} (Winer et al., 1992). Thus, it would not be surprising to find another species within the family with measurable monoterpene emissions, and the high category for dark emissions for *Lycium brevipes* may indicate an emission behavior similar to tomato.

The medium and high dark emissions for the three genera within the Verbenaceae indicate monoterpene emissions may occur from plants within this family, and moderate isoprene emission may also occur, as seen by the medium category for light measurement for one genus-species.

Within the Fagaceae (beech), Loganiaceae, and Magnoliaceae (magnolia) families, all of the species measured in the present study were within single genera, and their emission characteristics are discussed in section 3.4.6.

For the following families only one or two species per family were measured, and generalization within each family based on data from the present study is not possible. These families were: Agavaceae, Amaryllidaceae, Apocynaceae, Buxaceae, Calycanthaceae, Caparidaceae, Casuarinaceae, Celastraceae, Cercidiphyllaceae, Chenopodiaceae, Cistaceae, Cornaceae, Cycadaceae, Ebenaceae, Eleagnaceae, Euphorbiaceae, Elaeagnaceae, Garryaceae, Ginkgoaceae, Graminae, Grossulariaceae, Hamamelidaceae, Hippocastanaceae, Juglandaceae, Lauraceae, Moraceae, Myoporaceae, Myctaginaceae, Nyssaceae, Onagraceae, Palmae, Papaveraceae, Polypodiaceae, Proteaceae, Punicaceae, Rubiaceae, Rutaceae, Sapindaceae, Saxifragaceae, Scrophulariaceae, Simaroubaceae, Sterculiaceae, Tamaricacae, Taxodiaceae, Thymelaeaceae, Ulmaceae, Vitaceae, and Zygophyllaceae. The present PAU results for individual species within these families could be compared in certain cases isoprene or monoterpene emission rates found in Benjamin et al. (1996) and Karlik and Winer (2001b) for other species within these families, but we have not done so in this study.

3.4.6 BVOC Emissions within Plant Genera

Some plant genera seem to contain species with consistent emission behavior (Benjamin et al, 1996). In this study, genera within certain families were notable for the uniformity of low, medium, or high categorization of species within these genera. For example, *Salix* and *Populus* genera contained species with high light emissions. Eucalyptus contained species with medium or high light emissions, medium dark emissions, and medium or high crushed values. These genera have been noted previously as containing species with high BVOC emissions (Winer et al., 1998; Karlik and Winer, 2001b).

Genera with low BVOC emissions, both light and dark, include *Acer* (maples), *Fraxinus* (ash), *Prunus* (edible and ornamental plums), and *Ulmus* (elms). These observations are in agreement with the compilation of Benjamin et al. (1996).

Other genera also appear to contain species with consistent emission behavior. *Pistacia* had low light emission, but medium dark emissions, and high crushed values. Consistent with the, *Pistacia vera* had reported a monoterpene emission rate of 9.0 $\mu g\ g^{-1}\ h^{-1}$ (Benjamin et al., 1996).

Four *Rhus* (sumac) species were measured in this study (Table 3.5). All four had low light emissions, low dark emissions (with one exception), and either low or high crushed emissions. Thus, based on these limited data we conclude *Rhus* is composed of low-emitting species.

The four *Artemisia* (sagebrush) species had low light emissions and high crushed values, while dark emissions either low or high. The very high crushed values for *A. frigida* and *A. tridentata* (Appendices A and B) indicate dark readings may have been elevated by emissions triggered by leaf contact (i.e. by "handling").

Both barberry species, *Berberis mentorensis* and *B. thunbergii*, the latter found in urban landscapes, had high light emissions and either low or medium dark emissions.

The *Betula* (birch) species measured in this study had low light emissions, low or medium dark emissions, and low or medium crushed emissions. As noted in Section 3.4.5, *Betula* species are low or negligible isoprene emitters and our data are in agreement insofar as no moderate or high light emissions were noted for Betula.

Both honeysuckle (*Lonicera*) species measured had low light emissions, and were low or medium from darkened foliage, and low to medium for crushed values.

Both *Euonymus* species were low in all three categories, and this genus may be composed of low emitters, based on this limited sample.

Within the Cupressaceae family, three of the four species had low light and dark emissions. *Cupressus nevadensis* had medium light and dark emissions, however, and is an emitter in both light and dark based on these data. The crushed values within this family were medium or high.

Within the Leguminosae, the related *Cytisus* and *Genista* species had high light emissions, medium dark emissions, and low or medium crushed emissions. A *Cytisus* sp. and *Genista scorpius* were found to be moderate isoprene emitters in a previous study (Owen et al., 1997, 1998).

Perhaps the most troublesome genus for BVOC inventories in terms of range and variability of emission rates is *Quercus*. With the exception of *Q. boissieri* and *Q. brewerei*, all the oak species measured in this study had medium or high light emissions. All except *Q. rubra* had low or medium dark emissions, and with the exception of *Q. robur* all had low or medium crushed emissions. Thus, the oak species sampled in this study were uniform in displaying light emissions, but we cannot discriminate between oak species with medium or high emissions.

The three species within the Loganiaceae were all within the *Buddleia* genus, and were consistent in low values for light emissions, but two species were medium and one was low for darkened foliage, and two species were low with one high for emissions from crushed foliage.

The three species within the Magnoliaceae were all within the *Magnolia* genus, and were low in light- and dark- emissions, but low or medium in crushed.

Among the *Salvia* (sages), the consistent feature of their emission profiles was high crushed values. With one exception, the dark emissions were medium or high. This genus contains plants with stored pools of VOC, but the undisturbed emission rates, for example of monoterpenes, are not known for most species.

For *Liquidambar styraciflua*, all three categories of emissions were high. This finding matches our understanding of this species, in that it has it is a high emitter of both isoprene and monoterpenes (Benjamin et al., 1996; Karlik and Winer, 2001b).

The two *Picea* (spruce) species measured in this study were both high or medium in light emissions, and medium in dark emissions, and high in crushed value. *Picea* has been reported previously as an isoprene emitter (Kempf et al., 1996; Street et al., 1996).

Among *Pinus* (pine) species, all except one had low light emissions. Dark emissions ranged from low to high, and crushed values were medium or high. These patterns follow the understanding of pines gleaned from Benjamin et al. (1996), i.e. that pines tend to be negligible isoprene emitters, but may be moderate or high isoprene emitters.

3.4.7 BVOC Emissions from Common Native or Naturalized Plants Found in California

The *Arctostaphylos* (manzanita) species within the Ericaceae were low in all three categories, suggesting these species, widely occurring in native California landscapes, are low-emitters. *Chrysothamnus nauseosus* (rabbitbrush), found in rangeland settings above 3000 feet in southern California, was found to be low in light emissions, medium in dark emissions, and high in crushed emissions. The *Cercocarpus* species, which are native to the Sierra Nevada, were low in both light and dark emissions. Thus, it is likely these can be considered negligible emitters among plants found in native stands. However, *Fremontodendron californicum* (Fremontia), a signature California native, was medium in all three categories, and thus would be considered a non-negligible BVOC emitter. *Baccharis* (coyotebrush) species are native to California and *B. pilularis* is also used as a groundcover in urban settings and in freeway landscapes. Both *Baccharis* species had low light emissions, medium or high dark emissions, and high crushed values. Thus, these species may be monoterpene emitters.

Tamarix (Tamarisk) is an introduced genus containing several species which has naturalized in the desert and in intermittent streambeds. The species measured from this genus was low in light, dark, and crushed categories. Also found in the middle-elevation and low desert is *Larrea tridentata*, creosote bush, which was found to be low in all three measurement categories.

Although giant sequoia (*Sequoiadendron gigantea*) was previously measured for isoprene emission and found to be a negligible emitter (Karlik and Winer, 2001b), no data were available for dark emissions. The species was found to be low in dark emissions, but to

contain pooled BVOC, as seen by its high crushed value. The native tree species *Umbellularia californica* had high light, dark, and crushed emissions.

3.4.8 BVOC Emissions from Herbaceous Plants

Most of the reported literature values for BVOC emission rates are for woody species. In this study several herbaceous plants were measured for light, dark, and crushed emissions. *Agapanthus africanus* (agapanthus, lily-of-the-Nile) is used for accent in urban landscapes, and thrives in summer heat. It was found to have low values in all three emission categories. *Trachelospermum jasminoides* (star jasmine) used as a fragrant groundcover in urban landscapes was also found to be low in all three categories. *Achillea clavennae* (yarrow) was low in light emission, but medium in dark and high in crushed. Indeed, this plant emits a spicy aroma if crushed with the fingers (although fragance is not synonymous with BVOC emission).

Cycas revoluta is semi-woody, and although called sago palm is not found within the Palmae, but rather in the Cycadaceae, an ancient family within the Gymnosperms well represented in the fossil record, but with few living members. *C. revoluta* is found frequently in urban landscapes in the southern San Joaquin Valley, and was found to be low in all three emission categories. *Zauschneria californica* is a herbaceous plant and also a California native. It was low in all three categories of emissions.

The two poppies studied, members of the Papaveraceae (poppy) family were found to be medium in light emissions, low in dark emissions, and medium in the crushed category. These plants may be isoprene emitters, and *Romneya coulteri* (matilija poppy) is noted for its adaptation to drought-tolerant landscapes. *Cortaderia selloana* (pampas grass) is an escaped exotic forming clumps, and is widely naturalized in California, particularly in cooler, wet locations such as the Bay Area. Found in the Graminae (grass family), this species was low in all three emission categories. The fern *Woodwardia fimbriata* is a member of one of the simplest vascular plant families (the ferns), and was high in light emissions, and medium in the dark and crushed categories. Thus, for the herbaceous plants sampled, only the poppies and the fern species had medium or high light emissions, and the yarrow had medium dark emissions. The other species including herbaceous groundcovers, the sago palm, and the grass species *C. selloana* were low in BVOC emissions.

3.5 Implications for the Taxonomic Method

3.5.1 General Observations

The results of this study yielded few surprises when considered against the published literature. The present results for PAU measurements of emissions in the light were found to correspond to the observations made in previous studies (Benjamin et al. 1996, Winer et al. 1998, Karlik and Winer 2001) for measured isoprene emission rates in relation to family and genus affiliation. For example, in the present study light emissions from most *Quercus* species were medium or high, and for species in the Salicaceae family high emissions were also noted. In contrast, light emissions from plants within the Rosaceae and Oleaceae families were low. These observations were all consistent with our earlier findings for these families (Benjamin et al. 1996, Winer et al. 1998, Karlik and Winer 2001b) and Table 3.6 shows comparison of PAU measurements vs. measured isoprene and monterpene emission rates for plant species sampled in the present study.

3.5.2. Comparison of Results to SpecificTaxonomic Predictions of Benjamin et al. (1996)

As seen in Table 3.7, the emission categorizations based on PAU results for 46 plant species sampled in this study were compared with quantitative assignments of emission rates based on taxonomic predictions as found in Table 3 of Benjamin et al. (1996).

For light emissions, the PAU results for species within the Aceraceae, Anacardiaceae, Bignoniaceae, Caprifoliaceae, Compositae, Cupressaceae, Cycadaceae, Ericaceae, Juglandaceae, Magnoliaceae, Oleaceae, Rhamnaceae, Rosaceae, Sapindaceae, and Taxodiaceae families were categorized as low, in agreement for all of the 25 species within these families of assignments of 0.0 for isoprene emission rates made by Benjamin et al .(1996) based on either family or genus affiliation. Similarly, for *Pinus monophylla* and *Pinus ponderosa* within the Pinaceae, the PAU light emissions were low and the emissions assignment by Benjamin et al. (1996) was 0.0. Thus, for 27 species, the PAU results corresponded to a negligible isoprene emission rate assigned earlier on the basis of taxonomy (Benjamin et al. 1996).

All the species sampled in the present study within the Myrtaceae family were *Eucalyptus* species, which had light emission categorized as medium or high, and which had been assigned a mean emission rates of 32 by Benjamin et al. (1996). The PAU result for

Table 3.7 PAU emission categorization for plant species compared to assigned isoprene and monoterpene emission rates taken from Table 3 of Benjamin et al. (1996). Assigned rates were based on taxonomic relationships.

Family	Genus Species	Light Present Study	Predicted Iso. Emiss. Rate ug $g^{-1}h^{-1}$	Dark Present Study	Predicted Mono. Emiss. Rate ug $g^{-1}h^{-1}$	Basis for Predictions, Family (F) or Genus (G)
Aceraceae						
	Acer macrophyllum	L	0.0	L	2.8	G
	Acer negundo	L	0.0	L	2.8	G
Anacardiaceae						
	Pistacia chinensis	L	0.0	M	9.0	G
	Rhus glabra	L	0.0	L	0.0	G
	Rhus lancea	L	0.0	L	0.0	G
Bignoniaceae						
	Chilopsis linearis	L	0.0	H	5.9	F
Caprifoliaceae						
	Sambucus mexicana	L	0.0	L	0.0	G
Compositae						
	Baccharis pilularis	L	0.0	L	28.3	F
	Euryops pectinatus	L	0.0	L	28.3	F
Cupressaceae						
	Cupressocyparis leylandii	L	0.0	L	0.8	F
	Juniperus californica	L	0.0	L	0.6	G
Cycadaceae						
	Cycas revoluta	L	0.0	L	0.8	F

Table 3.7 continued.

Family	Genus Species	Light Present Study	Predicted Iso. Emiss. Rate ug $g^{-1}h^{-1}$	Dark Present Study	Predicted Mono. Emiss. Rate ug $g^{-1}h^{-1}$	Basis for Predictions, Family (F) or Genus (G)
Ericaceae						
	Arbutus menzeisii	L	0.0	L	0.0	F
	Arbutus unedo	L	0.0	L	0.0	F
Fagaceae -- Quercus -- Subfamily Unknown						
	Quercus englemannii	M	24.8	M	0.6	G
	Quercus durata	M	24.8	L	0.6	G
Fagaceae – Quercus -- Cerris						
	Quercus suber	L	24.8	L	0.6	G
Fagaceae -- Quercus -- Protobalanus						
	Quercus chrysolepis	M	24.8	L	0.6	G
Juglandaceae						
	Juglans californica	L	0.0	M	1.8	G
Lauraceae						
	Umbellularia californica	H	4.3	H	1.4	F
Leguminosae -- Caesalpinioideae						
	Cercis occidentalis	H	0.0	M	0.0	G
	Ceratonia siliqua	H	4.3	M	1.4	F
Leguminosae -- Mimosoideae						
	Acacia melanoxylon	L	0.0	L	4.7	G
	Albizia julibrissin	L	4.3	L	1.4	F

Table 3.7 continued.

Family	Genus Species	Light Present Study	Predicted Iso. Emiss. Rate ug $g^{-1}h^{-1}$	Dark Present Study	Predicted Mono. Emiss. Rate ug $g^{-1}h^{-1}$	Basis for Predictions, Family (F) or Genus (G)
Leguminosae -- Papilionoideae						
	Erythrina caffra	H	4.3	H	1.4	F
	Olneya tesota	H	4.3	H	1.4	F
Magnoliaceae						
	Magnolia soulangiana	L	0.0	L	5.9	G
Myrtaceae						
	Eucalyptus camaldulensis	M	32.5	M	4.6	G
	Eucalyptus polyanthemos	H	32.5	M	4.6	G
	Eucalyptus sideroxylon	H	32.5	M	4.6	G
Oleaceae						
	Fraxinus dipetala	L	0.0	L	0.0	G
	Fraxinus pennsylvanica	L	0.0	L	0.0	G
Pinaceae						
	Caloacedrus decurrens	M	0.0	L	0.8	F
	Picea breweriana	H	10.1	M	1.9	G
	Pinus attenuata	M	0.0	H	3.5	G
	Pinus monophylla	L	0.0	M	3.5	G
	Pinus ponderosa	L	0.0	L	3.5	G
Platanaceae						
	Platanus acerifolia	H	19.2	L	0.0	G
Rhamnaceae						
	Ceanothus thyrsiflorus	L	0.0	L	2.4	G

Table 3.7 continued.

Family	Genus Species	Light Present Study	Predicted Iso. Emiss. Rate ug $g^{-1}h^{-1}$	Dark Present Study	Predicted Mono. Emiss. Rate ug $g^{-1}h^{-1}$	Basis for Predictions, Family (F) or Genus (G)
Rosaceae						
	Cercocarpus ledifolius	L	0.0	L	0.1	G
	Heteromeles arbutifolia	L	0.0	L	0.1	F
	Prunus cerasifera	L	0.0	L	0.1	G
	Prunus ilicifolia	L	0.0	L	0.1	G
Salicaceae						
	Populus fremontii	H	43.6	L	0.0	G
Sapindaceae						
	Koelreuteria paniculata	L	50.9	H	0.0	F
Taxodiaceae						
	Sequoiadendron giganteum	L	0.0	L	8.5	F

light emissions for *Platanus acerifolia* (Platanaceae family) and *Populus fremontii* (Salicaceae family) were high, and the assignments of Benjamin et al. (1996) for these species were 19 and 44, respectively. Thus, the results for these six species were also in general agreement with earlier taxonomic assignments. Thus, for the 33 species within the families and genera noted above, the PAU measurements corresponded well to earlier taxonomic assignments.

For the Leguminosae family, the approach taken in Benjamin et al. (1996) was to assign a family-wide isoprene emission rate of 4 $\mu g\ g^{-1}\ h^{-1}$ for unmeasured legume species (if a genus-based rate was not available). As noted in a previous study (Winer et al. 1998, Karlik and Winer 2000), the isoprene emission rates for species within the Leguminosae family were difficult to characterize based on family association alone, and subfamily affiliations for legume species were thought to provide possible guidance for characterizing isoprene emission rates, with emitting species more likely found in the Papilionoideae subfamily. In the present study, both species within that subfamily had PAU light emissions characterized as high, while both species within the Mimosoideae subfamily had light emissions characterized as low. However, the two species in the Caesalpinoideae subfamily had high PAU light emissions, suggesting a subfamily affiliation may not provide certainty for isoprene emission rate assignments. The results of a PAU study in Africa (Klinger et al. 1998) showed that subfamily placement of legumes aided in characterizing isoprene emissions, but anomalies within subfamilies were found.

The isoprene emissions of species within the *Quercus* genus are perhaps the most troublesome to characterize because a range of two orders of magnitude exists in measured isoprene emission rates for species within that genus (Benjamin et al. 1996, Winer et al. 1998, Karlik and Winer 2001b). A taxonomic assignment of 25 $\mu g\ g^{-1}\ h^{-1}$ was made by Benjamin et al. (1996) for unmeasured oak species, which works well for many North American species and those native to California. However, the study of Csiky and Seufert (2000) employed a subgenus classification of oak species which, for example, was useful for grouping species native to Europe, such *Q. suber* (cork oak), which have negligible isoprene emission rates, in contrast to native North American species such as *Q. agrifolia* (coast live oak), which have high isoprene emission rates. In the present study, the species *Q. englemannii*, *Q. durata*,

and *Q. chrysolepis*, for which specific isoprene emission rate assignments of 25 μg g^{-1} h^{-1} were made by Benjamin et al. (1996), had PAU light measurements categorized as medium. The PAU light emission measurement of *Q. suber* was low, in contrast to its value in Benjamin et al. (1996) but in harmony with the subgenus categorization (Csiky and Seufert 1999) and GC measurements of its isoprene emission rate (Winer et al. 1998, Csiky and Seufert 1999, Karlik and Winer 2001b).

There were six species outside of the legume family or oak genus for which the PAU light results were in contrast to the taxonomic assignments of Benjamin et al. (1996) for isoprene emission rate. They included *Umbellularia californica*, which had a PAU category of high and an assigned isoprene emission rate of 4 μg g^{-1} h^{-1}. *Pinus attenuata* and *Calaocedrus decurrens* had PAU light results of medium contrasted with an assigned isoprene emission rate of zero μg g^{-1} h^{-1}. For *Eucalyptus camaldulensis*, the PAU-light result of medium contrasted with an assigned isoprene emission rate of 32 μg g^{-1} h^{-1}. For *Platanus acerifolia*, and *Picea breweri*, the PAU light results of high contrasted with assigned isoprene emission rates of 19.2 and 10.1, respectively (Benjamin et. al. 1996) Differences in measured categorization vs. assigned taxonomic values for the latter three species do not seem significant, given the uncertainties in the magnitudes of reported isoprene emission rates and the semi-quantitative nature of the present PAU measurements.

As noted above in Section 3.3.3.10, the detection limit of the PAU system employed in the present study could preclude resolution of BVOC emission rates below about 10 μg g^{-1} h^{-1}, which would include most of those reported for monoterpenes (Benjamin et al. 1996). Accordingly, the PAU results from this study are more likely to identify high monoterpene emitters rather separating negligible, low, or medium emitters from one another.

The PAU results for dark emissions for species within Table 3.7 within the Aceraceae, Caprifoliaceae, Cupressaceae, Cycadaceae, Ericaceae, Oleaceae, Platanaceae, Rhamnaceae, Rosaceae, and Salicaceae were low, and the taxonomically assigned monoterpene emission rates (Benjamin et al. 1996) were less than 3.0 μg g^{-1} h^{-1}. Similarly, PAU results were low for darkened foliage for *Rhus* species, *Acacia melanoxylon*, *Albizia julibrissin*, *Quercus suber*, *Quercus chrysolepis*, *Caloacedrus decurrens*, and *Pinus ponderosa*, all of which had assigned monoterpene rates less than 4 μg g^{-1} h^{-1} (Benjamin et. al. 1996).

PAU measured emissions from darkened foliage were categorized as medium for *Pistacia chinensis* which had an assigned monoterpene emission rate of 9 μg g^{-1} h^{-1}. The *Eucalyptus* species also had dark emissions characterized as medium, with taxonomically assigned monoterpene emission rates of 5 μg g^{-1} h^{-1}. For *Pinus monophylla*, the dark PAU result of medium compares with an assigned monoterpene emission rate of 4 μg g^{-1} h^{-1}. Thus, for these species also there is general correspondence between PAU results and monoterpene assignments based on taxonomy, and these species likely contribute temperature-dependent BVOC emissions to California airsheds.

Species for which the PAU dark results and taxonomic assignments for monoterpene emission rates are in less harmony, but are still plausible given the uncertainties involved, include *Chilopsis linearis* (PAU dark emissions category of high; 6 μg g^{-1} h^{-1} monoterpene emission rate assignment), *Cercis occidentalis* (PAU dark category of medium; zero μg g^{-1} h^{-1} monoterpene emission rate assignment), *Ceratonia siliqua* (PAU dark category of medium; 1 μg g^{-1} h^{-1} monoterpene emission rate assignment), *Quercus engelmanii* (PAU dark category of medium; 0.6 μg g^{-1} h^{-1} monoterpene emission rate assignment), and *Juglans californica* (PAU dark category of medium; 2 μg g^{-1} h^{-1} monoterpene emission rate assignment).

For several species, the PAU dark results appear to be in contrast with monoterpene emission rates assigned from Benjamin et al. (1996). Specifically, the low dark PAU results for *Baccharis pilularis* and *Euryops pectinatus* do not correspond to their 28.3 μg g^{-1} h^{-1} monoterpene emission rate assignment. This assignment was based on a family-level association, with reported results for *Artemisia californica* the basis of the mean for the family. As noted above, the Compositae family is the largest of plant families, and variability would be likely among its genera and species; thus, the low PAU results for darkened foliage for *B. pilularis* and *E. pectinatus* suggest species with low temperature dependent emissions within the Compositae. The low PAU result for darkened foliage for *Sequoiadendron giganteum* may indicate a species with low or moderate temperature dependent emissions, although the taxonomic emission rate assignment of 8 μg g^{-1} h^{-1} is still possible given the detection limit of the PAU system employed in the present study.

Both *Erythrina caffra* and *Olnea tesota* are within the Papilionoideae subfamily of the Leguminosae, and the high dark PAU results may indicate these species have high temperature dependent emissions. The high PAU result for the California native *Umbellularia californica* and the urban ornamental *Koelreuteria paniculata* also suggest species having high emissions from darkened foliage, in possible contrast to their taxonomically assigned monoterpene emission rates of 1 and zero $\mu g\ g^{-1}\ h^{-1}$.

In summary, for most species, PAU results for darkened foliage correspond relatively well to taxonomic assignments of monoterpene emission rates, and provide a broader base upon which to make assignments for unmeasured species. Survey results also indicate the likelihood of heretofore unrecognized species with high monoterpene emission rates.

3.5.3 Summary and Future Direction for Emission Rate Measurements

With the conclusion of this study, most of the frequently occurring woody plant families in California have now been at least surveyed qualitatively for BVOC emissions under light and dark conditions. Less is known of the families with mostly herbaceous members. These families tend to be found within both monocot and dicot groups among the angiosperms. However, many herbaceous plants are relatively small compared to woody shrubs and trees and have correspondingly less biomass, and therefore may not be contributors as significant to BVOC emission inventories as are larger woody species.

Within the present and previous studies, many species significant in California's agriculture, urban landscapes, and native vegetation have been measured at least with a portable analyzer. The relative consistency of the findings of this study compared with taxonomic predictions gives increased confidence for applying the taxonomic method to estimate BVOC emissions for unmeasured species within California landscapes. Assessment by ARB modeling staff of any remaining data deficiencies in light of the results of this study may inform future work. The PAU instrument, due to its short response time, may be able to capture stochastic processes in the landscape, such as drying of foliage, cutting of leaves, or herbivory, which could lead to spikes in BVOC emissions, and this should be explored in future research.

4.0 LEAF MASS AND LEAF AREA RELATIONSHIPS FOR URBAN TREES: IMPLICATIONS FOR LEAF MASS ESTIMATION METHODS

4.1 Introduction and Background

The overall biogenic VOC emissions of an individual plant are affected by its green-leaf biomass and by its intrinsic rates of emission of isoprene, monoterpenes and other BVOC, as well as by environmental factors such as temperature and light intensity. Emissions rates, expressed as μg BVOC per gram dry leaf mass per hour, vary by more than three orders of magnitude among plant species (Benjamin et al. 1996, Benjamin and Winer 1998), and trees with both high biomass and high emissions rates (e.g. eucalyptus and oaks), may be dominant BVOC emitters in urban settings. Unlike forest canopies, where foliar mass may be estimated through land cover databases and satellite imagery (Guenther 1997, Kinnee et al. 1997), vegetation within urban areas is often discontinuous and extremely varied in both size and species composition, requiring estimation methods flexible enough to accommodate this heterogeneity.

Within a plant, the mass of individual leaves varies according to leaf size, and is related to leaf density and thickness (Witkowski and Lamont 1991). Various methods have been explored for relating foliar mass to easily-measured dimensions of trees and much of the work has been done in relatively uniform stands, such as timber plantations. The pioneering work of Kittredge (1944) led to an equation relating foliar mass (W) to trunk diameter (D), $\log W = b \log D - a$, with empirical, species-specific coefficients. The relationship of leaf mass to stem diameter was given a theoretical foundation with development of the pipe model (Shinozaki et al. 1964) which proposed that a certain cross-sectional area of sapwood is necessary to support transpiration in a given leaf mass above. This model, or a variation, may give the most accurate results for tree species. For example, Nygren and coworkers (1993) developed relationships between leaf mass and branch cross sectional area with $r^2 > 0.85$ for four clones of each of two tropical broadleaved tree species. A variation of the pipe model was used to estimate the fresh weight of leaves of eight trees of six forest species (Valentine et al. 1984). Branch samples of each of the eight trees were taken based on the pipe model and importance sampling, a Monte Carlo technique. Estimates were within -8 to

+14% of the actual leaf mass of the respective trees.

Other studies have been conducted with trees uniform in size and age, presumably leading to similarity in morphology. For example, in a study of 42 eucalyptus trees found in even-aged monocultured stands, West and Wells (1990) found the 95% confidence interval for measured leaf mass was bounded by values of -60 to +76% of the estimate. Studies with even-aged or single species such as these suggest the limits of accuracy likely to be attainable in estimating leaf masses of urban trees with allometric or volumetric methods.

Attempts to increase the precision and accuracy of leaf mass estimates have included additional variables and led to multivariate statistical analyses accompanied by sophisticated regression equations. For example, in a study by Kershaw and Maguire (1995), a large sample size was accompanied by extensive measurements to determine the empirical coefficients for resulting equations. Branch diameter was the best predictor of branch foliage mass; however, improvements occurred when structural or positional variables were included. Unfortunately, the requirement of a large sample size for each plant species would often be limiting in urban situations.

However, although the pipe model or a variant (Valentine et. al 1984, West and Wells 1990) apparently offers a fairly accurate approach for estimating foliar mass, such a model may not be a practical method for field surveys for developing BVOC emission inventories. A pipe model estimate for an individual tree requires branch removal followed by cutting of branch disks at selected intervals for weighing. The time needed for selecting the branch path and performing the sampling operation may preclude multiple samples. Also, in many survey situations it is not permissible to remove trunks, branches or leaves, and the pipe method cannot be used for shrubs.

A volumetric approach has been developed in past studies because of its relatively simple non-destructive data requirements in field surveys, its potential applicability to the plethora of species found in urban landscapes, and its flexibility in modeling both tree and shrub morphology (Winer et al. 1983, Miller and Winer 1984, Winer et al. 1998, Karlik and Winer 1999) and has been specifically utilized for generating BVOC emission estimates from plant surveys (Winer et al. 1983, Miller and Winer 1984, Horie et al. 1990, Chinkin et al. 1996 a,b, Benjamin et al. 1997, Karlik and Winer 2001a). BVOC emission inventories

for sampled areas have been constructed by estimating foliar volume for each plant species in the study area, multiplying by the appropriate mass-to-volume ratio (the leaf mass constant) from the literature to obtain leaf mass, and then multiplying by the isoprene or monoterpene emission rate for that species (Benjamin et al. 1997). In these studies, plant species identities were tabulated for stratified random samples of urban vegetation and crown shapes were approximated with geometric solids. Leaf mass constants have been experimentally determined through replicate sampling within plant crowns in which all foliage was removed within volumes of 0.016 m^3 (in shrubs) and 1.0 m^3 (in tree crowns) (Miller and Winer 1984) or 0.4 m^3 (in tree crowns) (Nowak 1991, 1997).

Both the leaf mass constant and the calculation of crown volume represent sources of uncertainty in estimating leaf mass. Limitations are imposed by the complex structure of tree crowns in which leaves are not distributed in completely random fashion and crown shapes may not conform to simple geometric solids. Estimation of leaf mass through a volumetric approach has been compared to light interception or measurement of trunk diameter in a forest environment, although the actual leaf masses of trees were not determined (Temple and Mutters 1995). Volumetric estimates of leaf masses were compared to leaf masses from whole-tree harvest for 21 shade trees found in California landscapes (Winer et al. 1998, Karlik and Winer 1999).

Other methods for estimating leaf mass have been developed. Allometric equations for leaf mass and leaf area for urban shade trees was developed by Nowak (1996) based on data from open-grown deciduous trees found in Chicago, and tree data from an earlier study. These equations are based on crown height and radii, and trunk diameter at breast height (DBH). An additional equation from Harris (1973), based on DBH, has also been used to calculate leaf mass.

Digital photography followed by image analysis was among the several indirect leaf area estimation methods compared in the study of Peper and McPherson (1998). In that study the digital photographs were treated as analogs of color film images, and processed in a manner to closely follow the work of Lindsay and Bassuk (1992), in which leaf area was calculated from photographs of trees. However, digital photographs can be analyzed on the basis of number of pixels of various colors, which may allow a more direct analysis of

tree images.

The purpose of the present study was to gather additional data to examine the precision and accuracy of leaf mass and leaf area estimates for urban trees derived through several methods, including a volumetric approach and allometric equations. In addition, a digital photographic method for estimating leaf area was explored. Ancillary goals were to include urban shade trees larger than those harvested previously (Winer et al. 1998, Karlik and Winer 1999), include specimens to represent the broadleaf evergreen structural class, and to compare whole-tree values for leaf mass constants with literature values.

4.2 Experimental Methods

In 1999 and 2000, residents of Bakersfield, CA, were notified through the local paper of an opportunity to participate in the study by allowing a tree on their property to be harvested. From the responses received, 13 trees were selected for harvest, chosen to represent a common urban species of the Central Valley, with emphasis on broadleaf evergreen species and specimens larger than were measured in a previous study (Winer et al. 1998, Karlik and Winer 1999). Trees heights were measured with a telescoping measuring pole to the nearest 0.1 m. The crown radius was approximated by the average dripline, measured in the four cardinal directions with a steel tape to a precision of 0.1 m, and the mean was calculated (Table 4.1). The geometric solid visually approximating the crown shape for each tree was noted in the field and was subsequently referred to as the "preferred" solid. Leaf samples were taken and measured for leaf area with a leaf area meter (Li-Cor model 3100) and subsequently oven-dried. From these data specific leaf area (SLA) ($m^2\ g^{-1}$) was calculated for each tree, and was used for calculation of total leaf area for each tree.

Trees were felled with a chain saw and all leaves removed for drying and weighing. Leaves were placed in large paper bags and dried for at least two weeks. For tree numbers (nos.) 1-10, a vacant greenhouse with daily maximum temperatures of about 65°C and relative humidity less than 20% was utilized. Bags of leaves were weighed to the nearest even gram on a digital scale and masses summed for each tree (Table 4.1). Sample bags were

Table 4.1 Urban trees selected in 1999-2000 for leaf removal and measurement of total leaf mass.

Tree (no.)	Genus, species	Common Name	Tree Height (m)	Ground-Crown Distance (m)	Mean Crown Radius (m)	Trunk Circum. Breast Ht. (cm)	Leaf Mass (kg)
1	*Brachychiton populneus*	Bottle Tree	8.3	1.8	2.3	96	12.2
2	*Brachychiton populneus*	Bottle Tree	8.7	2.4	2.3	96	12.1
3	*Brachychiton populneus*	Bottle Tree	10.2	2.4	2.3	119	18.1
4	*Brachychiton populneus*	Bottle Tree	9.6	1.8	3.2	118	24.6
5	*Populus fremontii*	Cottonwood	11.9	2.1	5.1	145	100
6	*Salix babylonica*	Willow	14.3	2.4	6.8	240	119
7	*Liquidambar styraciflua*	Sweetgum	13.9	1.7	2.4	84	38.5
8	*Cinnamomum camphora*	Camphor	8.2	1.7	2.8	66	15.9
9	*Magnolia grandiflora*	Magnolia	8.9	2.2	5.1	106	78.2
10	*Fraxinus uhdei*	Shamel Ash	15.3	1.8	6.6	247	141
11	*Liquidambar styraciflua*	Sweetgum	14.0	1.4	2.4	116	36.0
12	*Liquidambar styraciflua*	Sweetgum	15.5	1.7	2.4	96	40.6
13	*Liquidambar styraciflua*	Sweetgum	13.4	1.4	3.2	97	44.8

placed in a drying oven and reweighed to both check thoroughness of drying and to provide a conversion factor to calculate oven-dry mass.

For tree nos. 11-13, a drying tunnel measuring 1.5 x 1.5 x 6.1 m (5 x 5 x 20 ft) (height x width x length) was constructed of a 2 x 4 dimension lumber frame covered by plastic sheeting. The tunnel was large enough to hold all the bags from each tree. A 30,000 BTU h^{-1} propane heater with an attached blower was used to warm the air inside the tunnel. The temperature within the tunnel was measured seven times, at three locations each time, during a five-day period with the heater in operation. Mean temperature within the tunnel was 46.9 °C with a range of 38.7 to 55.2 °C. All bags of leaves from each tree were dried together. Bags were placed on raised pallets in the tunnel, and bags were moved within the tunnel three times to allow a more even exposure to temperature gradients. Following 16 h in the tunnel, all bags were weighed. Three sample bags were selected at random, placed in a drying oven, and reweighed after one week to provide a conversion factor to calculate oven-dry equivalent leaf mass from tunnel-dried equivalent values. Therefore, the data presented for all trees for leaf mass represent oven-dry values.

4.3 Leaf Mass and Leaf Area Estimates and Comparisons to the Measured Values for Urban Trees

4.3.1 Whole-Tree Harvest

Tree dimensions and values for dry leaf mass are presented in Table 4.1. Trees harvested for this study were in general larger than those harvested in the ARB-funded study of Winer et al. (1998), and several specimens were large enough for each to require three days for harvest. Trees in this study ranged in height from 8.3 to 15.5 m, and had crown radii ranging from 2.3 to 6.8 m. A *Cinnamomum camphora* (camphor) tree had a circumference at breast height of 66 cm, the smallest of trees harvested in this study, while the largest circumference of 247 cm was that of a *Fraxinus uhdei*, shamel ash. Dry whole-tree leaf masses ranged from 12.1 to 141 kg. Six of the 13 trees were broadleaf evergreens. All trees were apparently healthy, unstressed, and in full leaf when harvested.

Calculated values for these trees are presented in Table 4.2. Trunk DBH ranged from 21-79 cm. Leaf mass densities ranged from 730-2200 g m^{-2}, with a mean of 1500 g m^{-2} for the deciduous species (nos. 5-7, 10-13) and a mean of 820 g m^{-2} for the broadleaf evergreens (nos. 1-4, 8, 9). Leaf areas were calculated from leaf masses by applying Equation 4.1, in which leaf area (LA) was obtained from dry leaf mass (LM) by multiplying the latter by SLA obtained from samples from the harvested trees:

$$LA\ (m^2) = LM\ (g) \times SLA\ (m^2\ g^{-1}) \qquad \text{(Eq. 4.1)}$$

Leaf areas for these trees ranged from 97-1400 m^2. This approach for calculating leaf area for leaf mass has been used by other investigators (Gazarini et al. 1990), and was explored for use in our research in a previous study (Winer et al. 1998) by comparing leaf areas obtained from whole-plant harvest with those obtained from measurements of all leaves made with a leaf area meter. The value calculated via Eq. 4.1 was found to be 94% and 96% of that measured by the leaf area meter for the two plants investigated in that previous study (Winer et al. 1998).

Leaf area index (LAI) (Table 4.2) was obtained from the ratio of LA to the area of crown projection, obtained as πr^2, where r was the mean of crown radii. LAI values ranged

Table 4.2 Calculated values for tree parameters based on crown measurements, whole-tree harvest, and measurement of leaf mass and specific leaf area.

Tree (no.)	Crown Height (m)	Crown Projection (m^2)	DBH (cm)	LMD ($g\ m^{-2}$)	Leaf Area (m^2)	LAI ($m^2 m^{-2}$)
1	6.5	17	31	730	98	5.9
2	6.3	17	31	730	97	5.8
3	7.8	17	38	1100	160	9.5
4	7.8	32	37	760	200	6.2
5	9.8	82	46	1200	1100	13
6	11.9	140	76	820	1400	9.8
7	12.2	18	27	2100	300	16
8	6.5	25	21	640	120	5.0
9	6.7	80	34	980	430	5.4
10	13.5	140	79	1000	1100	8.2
11	12.6	18	37	1900	280	15
12	13.9	19	31	2200	320	17
13	12.0	32	31	1400	450	14

from 5.0-17 $m^2\ m^{-2}$, and of species harvested in this study, the tall columnar *Liquidambar styraciflua* (sweetgum) trees had the highest LAI values of 14-17 $m^2\ m^{-2}$.

4.3.2 Calculation of Leaf Mass Densities

Leaf mass density (LMD) ($g\ m^{-2}$), the leaf mass per unit area of crown projection, was calculated for each tree based on measured dry leaf mass and mean crown radius (Table 4.2). The mean LMD for deciduous trees measured in this study was 1500 $g\ m^{-2}$, in contrast to the 480 $g\ m^{-2}$ for deciduous trees measured in a previous study (Winer et al. 1998, Karlik and Winer 1999). For the broadleaf evergreen species in the study, the mean value was 820 $g\ m^{-2}$, less than half of the mean value of 1900 $g\ m^{-2}$ for trees of the same structural class measured in a previous study (Winer et al. 1998, Karlik and Winer 1999). These results indicate overall values for LMD for structural classes of urban trees may be difficult to assign without more statistically robust samples. The sample sizes in both our earlier study and the present study were quite modest. Of the trees studied in the 1998 investigation (Winer et al. 1998, Karlik and Winer 1999), only four were broadleaf evergreens and two of these were

very large with dense foliage and a colmnar shape, properties which tend to yield higher LMD values. In contrast, in the present study there were only six broadleaf evergreens and all of them tended to be smaller than the two large trees in the 1998 study. Similarly in the earlier study (Karlik and Winer 1999), of the 17 deciduous trees studied, 8 were quite small purple leaf plums and 3 were small golden rain trees. In the present study the 7 deciduous trees harvested were generally much larger. For example, the largest DBH in the 1998 study was 39 cm. In the present study there were trees with DBH of 37 (two), 38, 46, 76 and 79 cm (see Table 4.2). We believe LMD values scale with tree size up to some point. Thus, these relatively small sample sizes coupled with substantial differences in tree sizes and shapes between the two studies can explain the significant differences observed in mean LMD values. However, additional measurements are needed to confirm this conclusion. Finally, LMD values from the present study may be compared to literature values of LMD ($g\ m^{-2}$) for forests (Geron et al. 1994), which were given as 1500 for needle evergreens in the *Picea, Abies, Tsuga and Pseudotsuga* genera, 700 for other coniferous genera including *Pinus*, and 375 $g\ m^{-2}$ for a broadleaf deciduous forest.

Data from the present study indicate the potential for urban trees to contain more leaf mass per unit ground area than trees found in a continuous canopy environment of a forest. Lack of nearby competition for light, and the availability of water and nutrients (many urban residents add water and nutrients to landscaped areas), may allow urban trees to contain more leaves with greater corresponding leaf mass than trees in temperate forests. Therefore, BVOC emission inventories may underestimate leaf mass of urban trees if such inventories are constructed from aerial photography (or similar methods which allow measurement of tree crowns in two dimensions) and use reference data from forests to convert planar areas to leaf masses.

4.3.3 The Volumetric Method for Leaf Mass Estimation

Using height and radius data for each tree crown, volumes for five geometric solids approximating tree shapes (McPherson and Rowntree 1988, Karlik and Winer 1999) were calculated from the following geometric formulae: $4/3\pi r^3$ (sphere), $\pi r^2 h$ (cylinder), $2/3\pi r^2 h$

(vertical ellipsoid), $1/2\pi r^2h$ (paraboloid) and $1/3\pi r^2h$ (cone). These solids are related mathematically and the volumes of a vertical ellipsoid, paraboloid, and cone are respectively 2/3, 1/2 and 1/3 of the volume of a cylinder with the same radius and height. Calculated whole-tree leaf masses were obtained by multiplying the respective volumes by a leaf mass constant found in the literature. An experimentally determined leaf mass constant for the species was used if available (Miller and Winer 1984, Nowak 1991, 1997); otherwise, a mean value for the genus or other species within the same structural class was used. (These leaf mass constants are the same as noted in Table 4.6.)

As seen in Table 4.3, total measured leaf mass for the thirteen trees in this study, 681 kg, was compared to estimates of total leaf mass derived from the geometric solids, which ranged from 513 kg (cone) to 1,540 kg (cylinder). For the cylinder, vertical ellipsoid, paraboloid, cone, and sphere, total leaf mass estimates were factors of 2.2, 1.5, 1.1, 0.74, and 1.3 of the measured total, respectively. These fractions may be compared with those found previously (Winer et al. 1998, Karlik and Winer 1999), which were 1.4, 0.91, 0.68, 0.46, and 0.92 for leaf masses calculated from the same volumetric shapes, respectively, compared to the measured total. For the sum of the preferred solid data, the total leaf mass estimate of 1,010 kg was a factor of 1.49 greater than the measured total. This compares with a factor of 1.18 for the total preferred solid data compared to the measured total for leaf mass of 21 urban trees in a previous study (Winer et al. 1998, Karlik and Winer 1999). For the present study, the paraboloid and cone solids gave total leaf mass estimates within 25% of the measured. In a previous study (Winer et al. 1998, Karlik and Winer 1999), the vertical ellipsoid, sphere solid and the preferred solid gave estimates of total leaf mass for all trees within 20% of the measured value. As discussed below, we attribute the difference which solid gave the best agreement with measured values to overall differences in crown volumes between trees harvested in the present study and those harvested in the previous study (Winer et al 1998, Karlik and Winer 1999).

Mean values for volumetric estimates for individual trees were 2.4, 1.6, 1.2, 0.80, and 1.2 of the values measured for the cylinder, vertical ellipsoid, paraboloid, cone, and sphere, respectively. Thus, on average, the paraboloid, cone, and sphere solids gave the estimates of

Table 4.3. Whole-tree calculated leaf masses for trees harvested 1999-2000 using geometric solids to approximate tree volumes, and using crown dimensions in allometric equations, expressed as a fraction of experimentally measured whole-tree leaf mass. The solid which was thought in the field to be the best fit is starred.

	Fraction of Measured Leaf mass				
Tree No.	Cylinder	Vert. Ellipsoid	Paraboloid	Cone	Sphere
1	2.9	2.0	1.5*	0.98	1.4
2	2.9	1.9	1.4*	0.95	1.4
3	2.4	1.6	1.2*	0.79	0.94
4	3.4	2.3	1.7*	1.1	1.9
5	2.0	1.3	1.0	0.66*	1.4
6	1.6	1.1	0.80	0.53	1.2*
7	2.2*	1.4	1.1	0.72	0.57
8	0.76	0.50	0.38	0.25	0.43*
9	2.4	1.6	1.2	0.80	2.4*
10	2.2	1.5	1.1	0.74	1.4*
11	2.5	1.6*	1.2	0.82	0.63
12	2.4	1.6*	1.2	0.81	0.57
13	3.2	2.2*	1.6	1.1	1.1
Mean	2.4	1.6	1.2	0.80	1.2
Total	2.2	1.5	1.1	0.74	1.3

leaf mass closest to the measured for individual trees. The mean of the preferred solid estimates was 1.5 times the measured for individual trees and within a factor of 2.5 for all trees; however, the preferred solid was the not the solid giving the estimate closest to the measured for any of the trees. For individual trees, calculated leaf masses based on a paraboloid solid and leaf mass constants from the literature resulted in leaf mass estimates within 20% for eight of the 13 trees harvested. For the preferred solid, leaf mass estimates were within 50% for six of the 13 trees. These results may be compared to a previous study (Winer et al. 1998, Karlik and Winer 1999), in which the preferred solid gave an estimate with a mean ratio of 1.8 of the measured for individual trees, and was within a factor of 4.5 for all trees.

Summation of leaf mass estimates generated using the paraboloid and cone solids for all 13 trees in this study gave values within 25% of measured total leaf mass. Although use of the sphere solid resulted in a total leaf mass value within 30% of the measured total leaf mass, data for individual trees were more scattered for the sphere than for the paraboloid solid. The paraboloid solid has a volume smaller than a vertical ellipsoid with the same height

and radius, and the paraboloid was judged to be the best solid overall for modeling tree crowns in this study. This result is in agreement with an earlier comment (McPherson 1996), but differs from the result of a previous study (Winer et al. 1998, Karlik and Winer 1999) in which the vertical ellipsoid solid gave a sum of calculated leaf masses closest to the measured. The ratio of leaf mass to volume is expected to decrease as crown dimensions increase, so it is not surprising that the paraboloid solid gave results in closer agreement to the measured in this study than did the vertical ellipsoid, since the trees in the present study were on-average larger than those in the previous study (Winer et al. 1998, Karlik and Winer 1999).

4.3.4 Allometric Equations

4.3.4.1 Allometric Equations for Leafmass

Leaf masses were also calculated using the allometric equations developed by Nowak (1996) for application to open-grown deciduous urban species. Equation 4.2 uses crown dimensions and was of the form:

$$\ln Y = 1.9375 + 0.4184H + 0.6218D + 3.0825S - 0.0133C + \text{error} \qquad \text{(Eq. 4.2)}$$

and Equation 4.3 uses trunk diameter and was of the form:

$$\ln Y = 7.6109 + 0.0643X + \text{error} \qquad \text{(Eq. 4.3)}$$

where Y is dry leaf mass, H is crown height (m), D is average crown diameter (m), S is a shading factor (fraction light intensity intercepted by foliated tree crowns), C is (πD(H + D)/2), based on the outer surface area of the tree crown (Gacka-Grzesikiewicz 1980), and X is DBH (cm). The error terms, which were of the form exp(MSE/2), were added to these equations to correct for logarithmic bias. The coefficients, shading factors and the error terms were taken from tabulated values (Nowak 1996). Where the tree species was not listed in Nowak (1996), a value for the shading factor was taken from a similar species or a mean of species within the genus, if available. For the broadleaf evergreen species no values for the species or corresponding genera were available. Where neither the genus nor species was listed, a value of 0.8 was used for the shading factor, as in the previous study (Winer et al. 1998, Karlik and Winer 1999).

These allometric equations are appropriate for deciduous trees with crown heights of 1-12 m, crown widths of 1-14 m, crown height to crown width ratios between 0.5 and 2.0, and DBH between 11 and 53 cm (Nowak 1996). Several of the harvested trees had dimensions outside of these ranges. Specifically, the crown heights of tree no. 10 (shamel ash), and tree nos. 11 and 12 (sweetgum) were greater than 12 m. The DBH of tree no. 6 (weeping willow) and no. 10 (shamel ash) were greater than 53 cm, and the crown height-width ratio of nos. 7, 11, and 12 (sweetgum) were greater than 2.0. We refer to these trees in subsequent discussion of Eq. 4.2 and Eq. 4.3 as outliers. Although the outliers had dimensions nominally outside of the ranges for Eq. 4.2 and Eq. 4.3, the trees represented specimens not atypical for urban landscapes in Central California. Therefore, leaf mass and leaf area were also calculated for these trees to test the applicability of Eq. 4.2 and Eq. 4.3. Tree nos. 1-4 (bottle tree), 8 (camphor) and 9 (magnolia) were broadleaf evergreens, but the equations were used for these also, again to test applicability.

As seen in Table 4.4, leaf mass was calculated with Eq. 4.2 and compared to measured leaf mass for each tree. Eq. 4.2, which was based on crown dimensions, gave calculated values for leaf masses ranging from factors of 0.57-2.7 of the measured for all trees in this study, with a mean factor of 1.0. When leaf masses calculated with this equation were summed and compared to the total for all trees, Eq. 4.2 gave a value of 0.86 of the measured. If outlier trees were removed from calculations, the mean of factors for individual trees dropped to 0.80, and the quotient of the calculated/measured sums of leaf masses was 0.86. For the outliers themselves, the mean of factors for individual trees was 1.4 with the factor for calculated/measured sums of leafmasses for these trees equal to 0.97. The outliers, which were tall columnar sweetgums (nos. 7, 11-13), were the trees for which this equation produced the greatest overestimation of leaf masses, ranging from factors of 1.6-2.7 for each sweetgum tree. No obvious differences were seen in results for deciduous vs. broadleaf evergreen species.

For Eq. 4.3, which was based on DBH, values for calculated leaf mass ranged from factors of 0.32-3.3 of the measured for individual trees, with a mean factor of 1.2. Leaf masses calculated with Eq. 4.3 were summed and the total for all trees was a factor of 1.7 of the measured. If outlier trees with dimensions out of the range were removed, the

Table 4.4 Comparison of calculated leaf mass for urban shade trees based on three allometric equations with measured leaf mass.

Tree No.	Leaf Mass (kg)			Fraction of the Measured		
	Eq. 4.2	Eq. 4.3	Eq. 4.4	Eq. 4.2	Eq. 4.3	Eq. 4.4
1	9.1	21	10	0.75	1.7	0.82
2	8.5	21	10	0.70	1.7	0.82
3	14	33	14	0.78	1.8	0.79
4	21	31	14	0.86	1.3	0.56
5	57	56	20	0.57	0.56	0.20
6	49*	390*	47	0.41*	3.3*	0.40
7	63*	16*	7.9	1.6*	0.42*	0.21
8	12	11	5.2	0.76	0.70	0.33
9	26	25	12	0.33	0.32	0.15
10	69*	450*	49	0.49*	3.2*	0.35
11	73*	31*	14	2.0*	0.87*	0.38
12	109*	21*	10	2.7*	0.51*	0.24
13	74	21	10	1.7	0.47	0.22
Mean of Fractions:				1.0	1.2	0.34
Mean of Fractions without Outliers:				0.80	1.1	N/A
Mean of Fractions of Outliers only:				1.4	1.7	N/A
Calculated/Measured for Sums of All Leaf Masses:				0.86	1.7	0.31
Calc./Meas. Sums of Leaf Masses, without Outliers				0.72	0.72	N/A
Calc./Meas. Sums of Leaf Masses, Outliers Only:				0.97	2.4	N/A

*Trees with dimensions outside the specified range for Eq. 4.2 and Eq. 4.3 of Nowak (1996), and referred to as outliers in the text.
N/A = not applicable

mean factor for individual trees was 1.1, but the factor for the sum of leafmasses, calculated/measured, was 1.2. For the outliers only, Eq. 4.3 gave high estimates for the willow (no. 6) and the ash (no. 10), the trees with largest DBH in this study, and these high estimates skewed the averages for individual outlier trees and the sum of leaf masses for the outliers. No obvious differences were seen in results for deciduous vs. broadleaf evergreen species.

An additional equation (Eq. 4.4) was used to calculate leaf mass (Harris et al. 1973), which gave a leaf mass estimate based on trunk diameter and was of the form:

$$\ln Y = -3.498 + 1.695 \ln DBH \qquad \text{(Eq. 4.4)}$$

As seen in Table 4.4, this equation underestimated leaf masses for all trees, and the total leaf mass for these trees calculated with Eq. 4.4 was 0.31 of the measured.

4.3.4.2 Allometric Equations for Leaf Area

Leaf areas were calculated using the allometric equations developed by Nowak (1996) for application to open-grown deciduous urban species. Equation 4.5 uses crown dimensions and is of the form:

$$\ln Y = -4.3309 + 0.2942H + 0.7312D + 5.7217S - 0.0148C + \text{error} \quad \text{(Eq. 4.5)}$$

and Equation 4.6 uses trunk diameter and is of the form:

$$\ln Y = 0.2102 + 0.0586X + 4.0202S + \text{error} \quad \text{(Eq. 4.6)}$$

where Y is leaf area, H is crown height (m), D is average crown diameter (m), S is a shading factor (fraction light intensity intercepted by foliated tree crowns), C is ($\pi D(H + D)/2$), based on the outer surface area of the tree crown (Gacka-Grzesikiewicz 1980), and X is DBH (cm). The error terms, which were of the form exp(MSE/2), were added to these equations to correct for logarithmic bias. The coefficients, shading factors and the error terms were taken from tabulated values (Nowak 1996). As noted for the leaf mass equations in Section 4.3.4.1, where the tree species was not listed, a value of 0.8 was used for the shading factor. As for Eq. 4.2 and 4.3, these equations for leaf area are appropriate for trees with crown heights of 1-12 m, crown widths of 1-14 m, crown height to crown width ratios between 0.5 and 2.0, and DBH between 11 and 53 cm (Nowak 1996). For outlier trees and broadleaf evergreens, leaf areas were also calculated using Eq. 4.5 and 4.6 to test their applicability.

Leaf areas and corresponding LAI for the trees based on Eq. 4.5 and 4.6 were compared to values calculated with Eq. 4.1, as shown in Table 4.5. Leaf areas calculated with Eq. 4.5 were on average 0.89 of the measured for individual trees, and the sum of calculated values for all 13 trees was a factor of 0.64 of the value calculated with Eq. 4.1. If outliers were removed from calculations, there was little change in mean of factors for individual trees, but the quotient of the sum of leaf areas from Eq. 4.5 compared to Eq. 4.1 had a value of 0.76. For outlier trees, the mean of factors was 0.87, but individual trees showed both under- and over-estimation. The sum of leaf areas was 0.54 of that calculated

Table 4.5 Comparison of leaf area and corresponding LAI for urban shade trees based on two allometric equations, with experimentally determined leaf area based on leaf mass to leaf area conversion via Eq. 4.1.

	Leaf Area (m^2)		LAI (m^2 m^{-2})		Fraction of Measured	
Tree No.	Eq. 4.5	Eq. 4.6	Eq. 4.5	Eq. 4.6	Eq. 4.5	Eq. 4.6
1	96	260	5.8	16	0.98	2.6
2	92	260	5.5	16	0.95	2.7 3
	120	400	7.4	24	0.78	2.5
4	210	380	6.5	12	1.0	1.9
5	580	790	7.1	9.6	0.53	0.72
6	350*	3800*	2.4*	26*	0.25*	2.7*
7	320*	220*	18*	12*	1.1*	0.75*
8	136	150	5.5	6.0	1.1	1.2
9	360	310	4.5	3.9	0.83	0.72
10	390*	4500*	2.8*	33*	0.35*	4.0*
11	360*	410*	19*	22*	1.3*	1.4*
12	450*	280*	24*	15*	1.4*	0.88*
13	430	280	14	8.9	0.95	0.63
Mean of Fractions:					0.89	1.8
Mean of Fractions without Outliers:					0.89	1.6
Mean of Fractions of Outliers only:					0.87	2.0
Calculated/Measured for Sums of All Leaf Areas:					0.64	2.0
Calc./Meas. Sums of Leaf Areas, without Outliers:					0.76	1.1
Calc./Meas. Sums of Leaf Areas, Outliers Only:					0.54	2.7

*Trees with dimensions outside the specified range for Eq. 4.2 and Eq. 4.3 of Nowak (1996), and referred to as outliers in the text.
N/A = not applicable

with Eq. 4.1. Eq. 4.5 underestimated leaf areas for the largest trees, nos. 6 and 10, which skewed the results for the sum of the outliers.

For Eq. 4.6, calculated leaf areas were on average a factor of 1.8 of the measured for individual trees, while the sum of calculated leaf areas for all 13 trees was 2.0 of the measured. If outlier trees were removed, the mean ratio dropped to 1.6 and the ratio for the sum of leaf areas of Eq. 4.5/Eq. 4.1 was 1.1, a close agreement. For the outliers themselves, the mean ratio was 2.0, with the sum 2.7 of the measured sum. Eq. 4.6 gave the largest relative overestimates for the two largest trees in the study, nos. 6 and 10, which had trunk DBH outside of the range assigned for this equation. Thus, in general, Eq. 4.5

underestimated leaf areas whereas Eq. 4.6 overestimated leaf areas for the trees in this study. No obvious differences in results were noted between deciduous and broadleaf evergreen species for either Eq. 4.5 or Eq. 4.6.

4.3.5 Calculation of Leaf Mass Constants

For 21 trees harvested in 1996-97, whole-plant leaf mass constants (g m^{-3}) based on the entire tree leaf mass and volume were calculated and compared to literature values (Winer et al. 1998, Karlik and Winer 1999). To obtain the leaf mass constant for each tree, the measured whole-tree leaf mass was used and each tree crown was modeled as a paraboloid and as the preferred solid, with the preferred solid previously assigned in the field when dimensions of the trees were being measured. Whole-tree leaf mass constants for the paraboloid differed from experimentally determined constants of *Prunus cerasifera* 'Krauter Vesuvius' and two *Eucalyptus* species by less than a factor of two and for the preferred solids for these species the whole tree values ranged from a factor of 0.3 to 1.5 (mean of 0.83) of the literature values. These results agreed reasonably well with the literature values for leaf mass constants for these *Prunus* and *Eucalyptus* species, and suggested the previous selective sampling protocols used to determine these values (Miller and Winer 1984, Nowak 1991, 1997) to be reasonable methods of determining species-specific leaf mass constants. For the larger shade trees in that study (*Morus*, *Fraxinus*, *Liquidambar* and *Acacia* species), the leaf mass constants calculated on the basis of the preferred solid ranged from 0.74-1.6 (mean of 1.1) times the literature values.

In the present study, the preferred solid coupled with literature values for leaf mass constants did not give the best estimate for whole-tree leaf mass for any of the trees, but the paraboloid solid gave estimates close to the measured, and in previous work the vertical ellipsoid solid was within 10% of the measured (Winer et al. 1998, Karlik and Winer 1999). Therefore, leaf mass constants based on whole-tree values were calculated only for the vertical ellipsoid and paraboloid solids, as seen in Table 4.6.

Table 4.6 Comparison between leaf mass constants derived from literature values and those obtained from whole-tree measurements for trees harvested in 1999-2000.

Tree		Leaf mass Constant (g m^{-3})		
			Whole Tree	
No.	Genus, species	Literature Value	(vert. ellipsoid)	(paraboloid)
1	*Brachychiton populneus*	333[1]	170	230
2	*Brachychiton populneus*	333	180	230
3	*Brachychiton populneus*	333	210	280
4	*Brachychiton populneus*	333	150	200
5	*Populus fremontii*	250[2]	190	250
6	*Salix babylonica*	110[3]	100	140
7	*Liquidambar styraciflua*	380[4]	260	350
8	*Cinnamomum camphora*	75[3]	150	200
9	*Magnolia grandiflora*	350[3]	220	290
10	*Fraxinus uhdei*	170[3]	110	150
11	*Liquidambar styraciflua*	380	230	310
12	*Liquidambar styraciflua*	380	240	310
13	*Liquidambar styraciflua*	380	180	240

1. Mean of values for *Cinnamomum camphora*, three Eucalyptus species, and *Podocarpus gracilior* (Miller and Winer 1984, Nowak 1991).
2. Mean of values for the paraboloid solid for two *Populus euramerica* 'R112' (Karlik and Winer 1998).
3. Miller and Winer (1984).
4. Nowak (1991).

Whole-tree values for the four bottle trees (nos. 1-4) ranged from 150-210 g m^{-3} for the vertical ellipsoid, and from 200-280 g m^{-3} for the paraboloid solid. No literature value was available for this species, but a mean of literature values (Miller and Winer 1984, Nowak 1991) for the broadleaf evergreen genera *Cinnamomum* (camphor), *Eucalyptus* , and *Podocarpus* (fern pine) was 333 g m^{-3}, higher than the whole-tree values of this study. The broadleaf structural class value of Horie et al. (1990) was 394 g m^{-3}, also higher than the whole-tree values found in this study.

For the four sweetgum in the present study (nos. 7, 11-13), the leaf mass constant for the vertical ellipsoid ranged from 180-260 g m^{-3}, and for the paraboloid from 310-350 g m^{-3}. The literature value shown in Table 4.6 is 380 g m^{-3} from Nowak (1991). In previous study, whole-tree values of 180 g m^{-3} and 280 g m^{-3} were found for the paraboloid and preferred

solids, respectively, from harvest of a single specimen (Winer et al. 1998, Karlik and Winer 1999). Thus, whole-tree values for sweetgum obtained from harvest of five specimens in two studies were lower than the literature value of 380 g m^{-3}.

For weeping willow (no. 6), the whole-tree values of 100 g m^{-3} and 140 g m^{-3} from this study for the vertical ellipsoid and paraboloid solids bracketed the literature value of 110 g m^{-3} (Winer et al. 1983, Miller and Winer 1984). Similarly, the values of 190 g m^{-3} and 250 g m^{-3} for the poplar (no. 5) were in good agreement with the literature value of 250 g m^{-3} (Winer et al. 1983, Miller and Winer 1984).

For the camphor (no. 8), the whole-tree values calculated in this study were 150 g m^{-3} and 200 g m^{-3} for the vertical ellipsoid and paraboloid solids, respectively, which were at least twice that of the literature value of 75 g m^{-3} (Winer et al. 1983, Miller and Winer 1984). For the magnolia (no. 9), the whole tree values of 220 g m^{-3} and 290 g m^{-3} for the vertical ellipsoid and paraboloid solids were lower but within 60% and 20%, respectively, of the literature value of 350 g m^{-3} (Winer et al. 1983, Miller and Winer 1984). For the ash (no. 10), the literature value of 170 g m^{-3} was greater than those for either the vertical ellipsoid or paraboloid derived from whole-tree harvest.

4.3.6 Leaf Area Estimation with Digital Photography

The leaf area for all 13 harvested trees was estimated using digital photography in a method modified from that of Peper and McPherson (1998). We used a digital camera (Olympus D500L) to photograph the unobstructed crown of each tree from at least two orthogonal directions. Photographs were taken about 10 m from the tree trunk. The distance was measured and noted, but did not enter into the analysis. A white posterboard with dimensions 0.278 x 0.280 m (11 x 11 in), 0.0778 m^2 in area, was held near the trunk to provide a reference for surface area.

The digital photographs for each tree were downloaded into a personal computer for analysis, which required the use of two software packages for each image. Adobe PhotoDeluxe Business Editor v. 1.0 (Adobe Systems, Inc.) was used to cut the portion of each image that represented tree crown from the remainder of the image background. The

polygon trace feature found in the advanced tool bar was used to selectively cut out the crown, and that image-area was then pasted to a new file. The posterboard reference image was also cut and pasted to a new file.

The two-dimensional size of each tree crown relative to the posterboard was obtained by counting the number of pixels represented by each object in the image. An arbitrary range of 0-220 was used to select the pixel color intensity that represented a majority of tree leaves in both sun and shade. A range of around 200 to the maximum value of 255 was used to select the pixels that represented the white posterboard. Pixels were then counted selectively based on their intensity threshold using SigmaScan Pro v. 5.0 (SPSS, Inc.).

Once measured by counting, the values for the number of pixels in a tree crown relative to the value for the number of pixels in a posterboard were used to calculate the apparent one-sided leaf surface area of the crown, which was 0.0778 m^2 times the quotient of pixels for leaves to pixels for poster board. Our method differed from that of Peper and McPherson (1998) in that we did not attempt to treat the digital image as an analog color film image through calculating frame area, silhouette area, frame dimensions, and scaling from a pseudo-negative to a print. Rather, we calculated apparent area of leaf surface directly by comparing pixel numbers for leaves with pixel numbers for the reference poster board.

Results may be seen in Table 4.7. The digital method as employed in this study gave leaf area results consistently lower than the measured, with a mean fraction of 0.13 of those calculated with Eq. 4.1, with a standard deviation of 0.038, and a coefficient of variation of 29% for individual trees. For the sum of leaf areas, the digital method gave a value of 0.11 of the measured. For an additional comparison, the leaf areas were multiplied by a factor of 10, also presented in Table 4.7, which yielded estimates much closer to the measured. We assigned this value of 10 empirically, and have no theoretical basis at this time upon which to base such a conversion factor. However, some adjustment factor for calculating actual leaf area seems necessary, since the surface area of leaves "seen" by the camera will be affected by leaf angle, and only vertically oriented leaves will be "seen" as having 100% of their actual leaf area. Other leaves will be "seen" as having apparent leaf area = actual leaf area x sin(leaf angle) where 0° is a horizontal leaf. Thus, our digital photographic method would be expected to underestimate leaf area because of leaf angle distribution, and also because of

Table 4.7. Calculated values for leaf area based on digital photography, and compared to values from whole-tree harvest obtained through Eq. 4.1.

Tree (no.)	LA from digital photos (m^2)	LA mean (m^2)	LA from Eq. 4.1 (m^2)	Fraction of the measured	Digital LA x 10 (m^2)	Fraction of Eq. 4.1
1	18.1	16.3	98	0.17	160	1.7
	14.5					
2	15.3	15.4	97	0.16	150	1.6
	15.5					
3	15.5	20.8	160	0.13	210	1.3
	26.0					
4	23.5	24.7	200	0.12	250	1.2
	25.9					
5	110	116	1100	0.11	1200	1.1
	121					
6	129	120	1400	0.08	1200	0.84
	111					
7	27.9	27.5	300	0.09	280	0.92
	27.1					
8	23.3	24.5	120	0.20	240	2.0
	26.4					
	23.5					
	24.7					
9	56.7	51.3	430	0.12	510	1.2
	43.4					
	53.7					
10	107	85.9	1100	0.08	860	0.77
	70.2					
	80.2					
11	51.4	43.9	280	0.15	440	1.6
	36.4					
12	60.8	57.9	320	0.18	580	1.8
	55.1					
13	48.1	52.1	450	0.12	520	1.2
	56.1					
Mean of Fractions				0.13		1.3
Sum of Calculated LA/Sum of Eq. 4.1 LA				0.11		1.1

obstruction of leaves in the background by leaves in the foreground.

4.4 Implications for BVOC Emission Inventories

Accurate leaf mass determination is a critical factor in estimating the magnitude of BVOC emissions from green plants. Vegetation within urban areas is often discontinuous and extremely varied in both size and species composition, requiring estimation methods

flexible enough to accommodate this heterogeneity.

In several past studies which developed BVOC emissions estimates for urban areas, a volumetric approach was used to estimate leaf masses of urban trees. A purpose of the present study was to examine the precision and accuracy of a volumetric approach, using geometric solids to compare estimated leaf masses to measured whole-tree leaf masses; and to compare leaf mass constants derived from selective sampling within crowns to whole-tree values. Accordingly, total leaf masses obtained through tree harvest and leaf removal of 13 urban trees were compared to leaf masses calculated using geometric solids to model the shapes of tree crowns and leaf mass constants found in the literature. Results from this study suggest leaf mass estimates developed for individual trees through a volumetric approach may be well within approximately 50% of actual values. For the 13 trees in this study, sums of leaf mass estimates were within 10% of the sum of the measured leaf masses when the paraboloid solid was used, and the paraboloid was judged to be the best solid overall for modeling tree crowns. This result is in agreement with an earlier comment (McPherson 1996), but differs from the result of a previous study (Winer et al. 1998, Karlik and Winer 1999) in which the vertical ellipsoid solid gave a sum of calculated leaf masses closest to the measured sum. However, the ratio of leaf mass to volume is expected to decrease as crown dimensions increase, so it is not surprising that the paraboloid solid gave results in closer agreement to the measured than did the vertical ellipsoid, since the trees in the present study were on-average larger than those in the previous study (Winer et al. 1998, Karlik and Winer 1999). It appears assignment of either a paraboloid solid or a vertical ellipsoid solid, or perhaps taking a mean of leaf mass estimates from both solids, may be more reliable than attempting to assign a "preferred" solid in the field to individual specimens.

Using the experimentally measured total leaf mass and dimensions of each tree, whole-tree leaf mass constants were also calculated. Literature values for experimentally-determined leaf mass constants appeared to be reasonably accurate for the species tested, and were within a factor of two compared to those derived from whole tree harvest, with the exception of the value for the camphor. The literature value of 75 g m^{-3} seems too low for this species. A still larger dataset including additional tree species is clearly desirable to more

accurately quantify leaf masses of urban trees and to better understand structural class values.

Biogenic emission inventories for urban areas require leaf mass estimation for highly heterogenous plantings, including a wide range of ages and species of widely varying forms. A volumetric approach using previously established leaf mass constants has utility because of its relatively simple non-destructive data requirements in field surveys, its potential applicability to the wide range of species found in urban landscapes, and its flexibility in modeling both tree and shrub morphology. However, a volumetric approach may not precisely account for clumping of tree foliage and the change in leaf mass density as tree crowns expand and mature, especially for larger species.

Despite these limitations, a volumetric approach may have particular utility in California because of the enormous number of both native and introduced tree species and the moderate size of many trees as compared to the mature urban forests found in the eastern United States. The volumetric approach with the paraboloid solid worked well for estimating total leaf masses for the 13 trees of this study, as did Eq. 4.2.

Leaf masses per unit area of crown projection for these urban trees were greater than the values of leaf mass per ground surface area reported for eastern deciduous forests. The mean LMD for deciduous trees measured in this study was 1500 g m^{-2}, in contrast to the 480 g m^{-2} for deciduous trees measured in a previous study (Winer et al. 1998, Karlik and Winer 1999). For the broadleaf evergreen species in the study, the mean value was 820 g m^{-2}, less than half of the mean value of 1900 g m^{-2} for trees of the same structural class measured in a previous study (Winer et al. 1998, Karlik and Winer 1999). As discussed above, we believe these differences in mean LMD values for the two vegetation classes between the previous and present studies can be explained in part by the relatively small sample sizes and the significant differences in sizes and shapes of the trees harvested in the two studies. However, additional measurements for larger samples of trees in each class would be needed to confirm this conclusion.

Leaf masses were also calculated from recently published allometric equations. Eq. 4.2 of Nowak (1996), based on crown dimensions, gave estimates closer to the measured than did Eq. 4.3, based on trunk diameter. The leaf mass estimates from Eq. 4.2 were on

5.0 IMPLICATIONS FOR LEAFMASS AND LEAF AREA ESTIMATION METHODS FOR CALIFORNIA OAK SAVANNAS FROM WHOLE-TREE HARVEST OF BLUE OAKS

5.1 Rationale for the Present Study

The BVOC emissions of an individual plant are affected by its green-leaf biomass and by its rates of emission of isoprene, monoterpenes and other VOC, as well as by environmental factors such as temperature and light intensity. Emissions rates, expressed as μg BVOC per gram dry leafmass per hour, vary by more than three orders of magnitude among plant species (Benjamin et al. 1996, Benjamin and Winer 1998), and trees with both high biomass and high emissions rates, such as oaks, may be dominant BVOC emitters in California's natural landscapes. A volumetric approach to estimates of leaf mass has been used in past studies (Miller and Winer 1984, Karlik and Winer 1999) because of its relatively simple non-destructive data requirements in field surveys, its potential applicability to the plethora of species found in natural landscapes, and its flexibility in modeling both tree and shrub morphology. The principal goal of the present study was to develop leafmass and leaf area data for native oaks, which may then be used to estimate leafmasses of oaks found in California oak savannas, and to compare the resulting calculated leaf area index (LAI) values to those derived from remote-sensing data.

5.2 Experimental Methods for Blue Oaks

In July 2000, a grove containing 14 blue oak trees (*Quercus douglasii*) which could be harvested was selected on private land in the Sierra Nevada foothills near California Hot Springs, approximately 50 miles northeast of Bakersfield. This group of trees appeared to be representative of the scattered groves of blue oaks found on other parts of the ranch, to which access had been given, and in rangeland in the foothill areas of the eastern San Joaquin Valley. These trees had received no cultural attention such as pruning, irrigation, or fertilizer, and had become established from natural acorn dispersion.

A rectangular grid was established in the field by placing 50 m measuring tapes at right angles so as to encompass the driplines of all of the trees. The trees were numbered, and the position of each tree was noted (Figure 5.1). The UTM coordinates, measured with

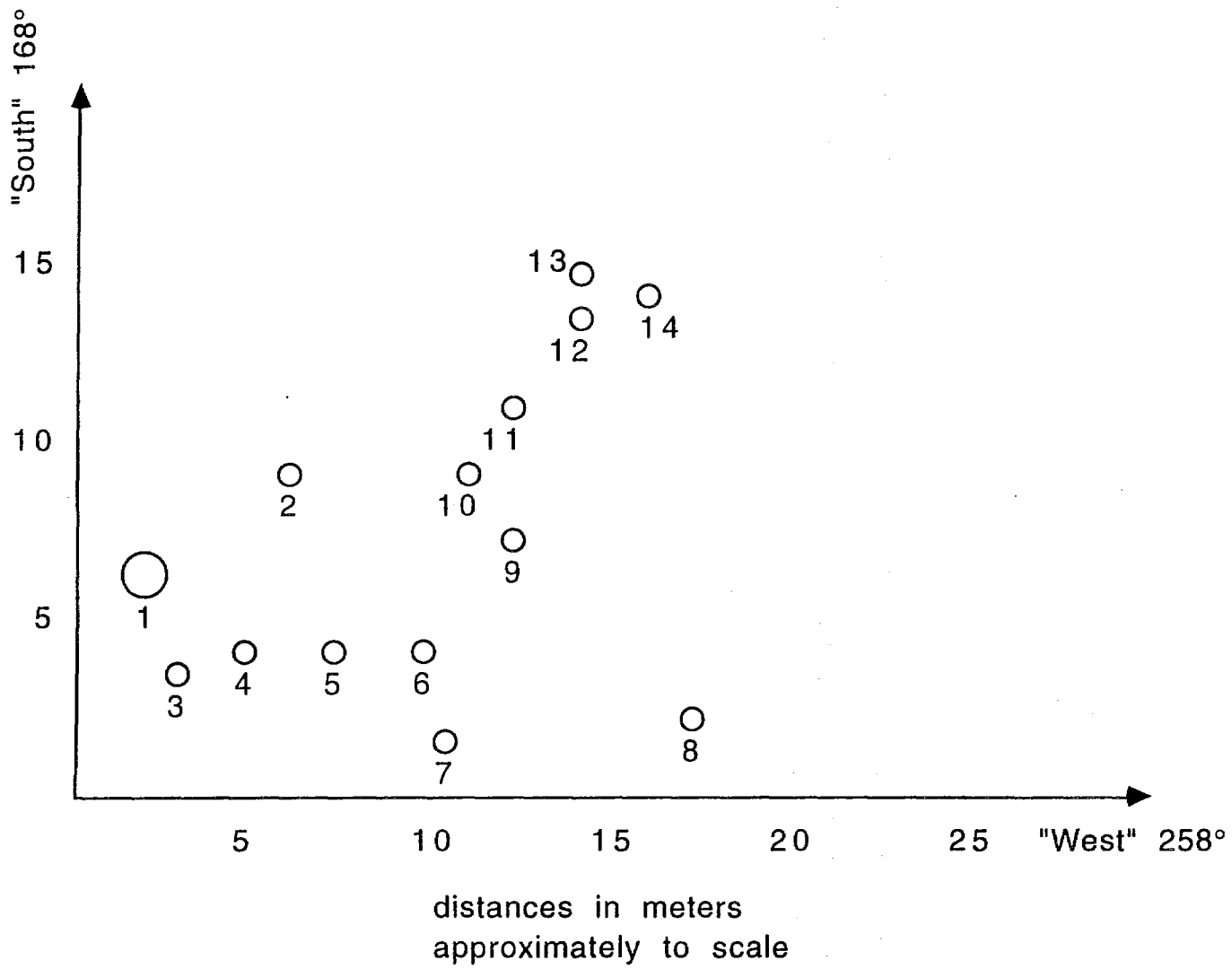

Figure 5.1 Planar view of oak tree placements at the experimental site, with trunk sizes shown approximately to scale.

a Garmin GPS receiver (Model 12XL) and checked against a Magellan GPS receiver (Model 2000), for the corner of the grid were 11S 0345696E and 3970295N, and the corresponding latitude-longitude coordinates were 35° 51' 53" N and 118° 42' 33", respectively. The quadrant marked with the measuring tapes opened to the southwest; the compass headings for the baselines were 168° and 258°. Elevation was 975 m (3,210 ft) measured with a portable altimeter (Model Altiplus A2, Pretel Inc.). Tree heights were measured with a telescoping pole to a precision of 0.1 meter, and the distance from the ground to the base of the crown was measured with a steel tape. From these measurements crown height was calculated. Crown radii of trees were measured by noting the average dripline, measured in the four cardinal directions with a steel tape to a precision of 0.1 meter, and the mean was calculated (Table 5.1). Trunk circumference at breast height was also measured.

Trees were felled with a chain saw approximately 5 cm above the soil surface, the stump diameter was measured in two directions, and the number of sapwood rings was counted. Each tree was separated in the field into twigs with leaves, branches, and trunk sections. Branches, defined as stems with diameters between two and 10 cm, and trunk sections with diameters greater than 10 cm, were weighed in the field to the nearest gram. The twigs with leaves were transported to the laboratory and all leaves were removed for drying and weighing, and the twigs were weighed. Leaves were placed in large paper bags and dried for approximately two weeks in a vacant greenhouse with daily maximum temperatures of about 65°C and relative humidity less than 20%. Bags of leaves were weighed to the nearest even gram on a digital scale and masses summed for each tree (Table 5.1). Bags were spot checked to verify complete drying and no decomposition was noticed. Leaf area of a subsample of fresh leaves was measured with a LiCor 3100 leaf area meter and weighed after drying under the same conditions as the rest of the oak leaves. This sample was also weighed after 48 hr in a drying oven. Samples of trunks, branches, and twigs were dried under greenhouse conditions to obtain fresh-weight to dry-weight ratios. These ratios were used to calculate dry weight of wood.

Table 5.1. Native blue oak trees selected for leaf removal and measurement of total leafmass.

Tree (no.)	Tree Height (m)	Ground-to Crown Distance (m)	Mean Crown Radius (m)	Trunk Circum. at Breast Ht. (cm)	Stump Diameter (cm)	Sapwood Rings (no.)	Leafmass (g)
1	7.4	3.0	1.1	202	85	N/A	3750
2	6.7	2.6	2.0	77	30	112	9750
3	4.7	1.5	1.1	45	29	89	2210
4	7.8	1.5	1.4	57	22	97	5230
5	7.5	3.0	1.8	75	30	130	6790
6	5.9	1.4	1.2	37	14	70	1950
7	7.2	1.6	1.1	57	22	113	4420
8	6.7	1.7	1.5	60	23	103	5380
9	9.9	2.4	3.6	132	49	172	29300
10	4.2	1.4	1.1	38	25	86	1830
11	6.8	2.3	1.5	59	22	76	5230
12	6.3	1.7	1.2	42	17	72	2200
13	7.5	2.0	1.8	68	29	95	9040
14	4.4	2.4	2.1	53	21	86	5930

5.3.1 Results from Whole-Tree Harvest for Leafmass, LMD, and LAI

Blue oak dimensions and leafmasses are given in Table 5.1. Total dry leafmass for the 14 trees was 92.9 kg. Tree no. 1 had extensive dieback and decay resulting in a hollow center; it was excluded from data analysis where trunk diameter was included in allometric equations, but its leafmass and crown dimensions were included in calculations. Calculated values for crown height, crown projection and DBH are seen in Table 5.2.

Calculated per-tree values for leaf mass density (LMD) are seen in Table 5.2, which ranged from 410 to 1300 with a mean of 730 g m^{-2} for these blue oak trees. LMD calculated on the basis of total leafmass divided by the sum of areas of crown projection was 720 g m^{-2}, slightly lower than the mean LMD values for the individual trees. The minimum grid dimensions needed to encompass the driplines of all oak crowns were 16.7 x 18.1 m, encompassing an area of 302 m^2, and the LMD calculated for the site based on total leafmass divided by area of the grid was 310 g m^{-2}. This latter value is thought to be the site LMD value. This value may be compared to literature values for oak woodlands of various locales, including 375 g m^{-2} for Atlanta, GA (Geron et al. 1995); 375 g m^{-2} for the contiguous

Table 5.2. Calculated values for tree parameters for native blue oak trees based on crown measurements, whole-tree harvest, and measurement of leafmass and SLA of a 100-leaf sample.

Tree (no.)	Crown Height (m)	Crown Projection (m^2)	DBH (cm)	LMD ($g\ m^{-2}$)	Leaf Area (m^2)	LAI ($m^2 m^{-2}$)
1	4.4	3.6	64	980	15	4.2
2	4.1	13	25	780	42	3.3
3	3.2	3.6	14	610	9.4	2.6
4	6.3	5.7	18	910	22	3.9
5	4.5	10	24	650	29	2.8
6	4.5	4.7	12	410	8.3	1.8
7	5.6	3.5	18	1300	19	5.4
8	5.0	6.8	19	790	23	3.4
9	7.5	40	42	740	120	3.2
10	2.8	4.0	12	460	7.8	2.0
11	4.5	7.3	19	720	22	3.0
12	4.6	4.5	13	490	9.4	2.1
13	5.5	9.6	22	940	38	4.0
14	2.0	14	17	440	25	1.9

United States (Lamb et al. 1987, 1993); 338-600 g m^{-2} for Castelporziano, Italy (Seufert et al. 1997); and a global value of 100-500 g m^{-2} (Box 1981). However, the oak grove harvested and measured was surrounded by open grassland, and therefore the measured LMD value of 310 g m^{-2} represents a maximum for that landcover. If the oak leafmass was considered on the basis of the area of the grove and the open grassland surrounding, the value would have been approximately half. No quantitative data for oak coverage were available in the vicinity of the grove studied, but a gradation from scattered trees at lower elevations to apparent crown closure on slopes at higher elevations was observed in surrounding mountains.

Leaf areas of harvested trees were also calculated (Table 5.2) by Equation 5.1:

$$Y = LM * SLA \qquad \text{(Eq. 5.1)}$$

where Y is leaf area (m^2), LM is whole-tree leafmass (g) and SLA is specific leaf area ($m^2\ g^{-1}$) obtained from a 100 leaf sample of blue oak leaves, with a value of 42.6 cm^2 per dry gram.

Total leaf area calculated with Eq. 5.1 was 396 m^2. The mean value for the fourteen trees for leaf area was 28.3 m^2.

The sum of areas of crown projection was 130 m^{-2}, although overlap of foliage occurred. The mean value for LAI for the 14 trees was 3.1 m^2 m^{-2}. LAI calculated on the basis of total leaf area divided by the sum of areas of crown projection was also 3.1 m^2 m^{-2}, with crown projection taken as a circle with mean radius as noted in Table 5.1. (LAI was also calculated using crown radii and the equation for the area of an ellipse to find the area of crown projection, but the resulting values for LAI differed by only 1% on average.) LAI calculated on the basis of total leaf area divided by grid area was 1.3 m^2 m^{-2}. This latter value was thought to be the LAI which would be seen by an overhead observer. This value was appropriate for the grove only; consideration of surrounding area devoid of trees would result in an overall LAI value of less than 1.3 m^2 m^{-2}.

5.3.2 The Volumetric Method for Leafmass Estimation

Using height and radius data for each tree crown, volumes for five geometric solids approximating tree shapes (McPherson and Rowntree 1988, Karlik and Winer 1999) were calculated from the following geometric formulae: $4/3\pi r^3$ (sphere), $\pi r^2 h$ (cylinder), $2/3\pi r^2 h$ (vertical ellipsoid), $1/2\pi r^2 h$ (paraboloid) and $1/3\pi r^2 h$ (cone). These solids are related mathematically and the volumes of a vertical ellipsoid, paraboloid, and cone are respectively 2/3, 1/2 and 1/3 of the volume of a cylinder with the same radius and height. Calculated whole-tree leafmasses were obtained by multiplying the respective volumes by a leafmass constant found in the literature. An experimentally determined leafmass constant of 280 g m^{-3} was used, the mean to two significant figures for *Quercus agrifolia* (Miller and Winer 1984) and *Q. wislizenii* (Horie et al. 1990).

Total measured leafmass for trees in this study (92.9 kg) may be compared to estimates of total leafmass derived from the geometric solids, which ranged from 63.4 kg (cone) to 190 kg (cylinder). For the paraboloid, vertical ellipsoid and sphere, total leafmass estimates were factors of 1.02, 1.36 and 1.15 of the measured, respectively. Therefore, two

of the solids gave estimates of total leafmass for all trees within 15% of the measured, and the third within approximately 35%.

In the present oak study, mean per-tree calculated values for leafmass were within 20% of the measured when the vertical ellipsoid, paraboloid, or sphere solids were used to model crown shapes (Table 5.3). Thus, the leafmass constant of 280 g m^{-3} coupled with the paraboloid solid seemed to best represent the crown shapes of the native blue oak trees of this study. For comparison, for 21 urban trees in the 1999 study of Karlik and Winer (1998), sums of leafmass estimates were within 0.91, 0.68, or 0.92 of the total measured leafmass when the vertical ellipsoid, paraboloid, or sphere solids were used, respectively.

We can compare data from the present study to results from studies using other methods which also may have used trees more uniform in size and age, presumably leading to similarity in morphology. For example, in a study of 42 eucalyptus trees found in even-aged monocultured stands, West and Wells (1990) found the 95% confidence interval for measured leafmass was bounded by values of -60 to +76% of the estimate. In another study, a variation of the pipe model was used to estimate the fresh weight of leaves of eight trees of six forest species (Valentine et al., 1984). Branch samples of each of the eight trees were taken based on the pipe model and importance sampling, a Monte Carlo technique. Estimates were within -8 to +14% of the actual leafmass of the respective trees. Studies such as these set limits on accuracies likely to be attainable in estimating leafmasses of urban trees with a volumetric method.

5.3.3 Allometric Equations for Leafmass Estimation Based on Crown and Trunk Dimensions

Leafmasses were also calculated using the allometric equations developed by Nowak (1996). Equation 5.2 was developed for urban tree species and uses crown dimensions, and was of the form:

$$\ln Y = 1.9375 + 0.4184H + 0.6218D + 3.0825S - 0.0133C + \text{error} \qquad \text{(Eq. 5.2)}$$

Equation 5.3 uses trunk diameter and is of the form:

$$\ln Y = 7.6109 + 0.0643X + \text{error} \qquad \text{(Eq. 5.3)}$$

Table 5.3. Whole-tree calculated leafmasses for blue oak trees harvested using geometric solids to approximate tree volumes, and using crown dimensions and DBH in allometric equations, expressed as a fraction of experimentally measured whole-tree leafmass. The mean fraction for each estimation method is given, as is a total for each solid or equation obtained by summing the estimated leafmasses and dividing by the total measured leafmass for all trees.

	Fraction of Measured Leafmass							
Tree	Cyl.	Vert. Ellips.	Parab.	Cone	Sphere	Eq. 5.2	Eq. 5.3	Eq.5.4
1	1.2	0.84	0.63	0.42	0.41	0.43	N/A	N/A
2	1.5	0.99	0.74	0.49	0.96	0.30	1.2	0.70
3	1.5	0.98	0.74	0.49	0.66	0.44	2.8	1.3
4	1.9	1.3	0.97	0.64	0.55	0.74	1.5	0.79
5	1.9	1.3	0.97	0.65	1.0	0.43	1.6	0.96
6	3.0	2.0	1.5	1.0	1.1	0.92	2.6	1.0
7	1.2	0.82	0.61	0.41	0.31	0.53	1.8	0.93
8	1.8	1.2	0.89	0.59	0.70	0.49	1.5	0.83
9	2.8	1.9	1.4	0.94	1.8	0.64	1.2	0.58
10	1.7	1.1	0.85	0.57	0.91	0.48	2.9	1.1
11	1.8	1.2	0.88	0.59	0.80	0.44	1.6	0.83
12	2.6	1.8	1.3	0.88	0.92	0.83	2.6	1.11
13	1.6	1.1	0.82	0.55	0.70	0.43	1.1	0.61
14	1.3	0.85	0.64	0.43	1.8	0.26	1.2	0.61
Mean	1.9	1.2	0.93	0.62	0.90	0.53	1.8	0.87
Total	2.05	1.36	1.02	0.68	1.15	0.52	1.5	1.13

where Y is dry leafmass, H is crown height (m), D is average crown diameter (m), S is a shading factor (fraction light intensity intercepted by foliated tree crowns), C is ($\pi D(H + D)/2$), based on the outer surface area of the tree crown (Gacka-Grzesikiewicz, 1980), and X is DBH (cm). The error terms, which were of the form exp(MSE/2), were added to these equations to correct for logarithmic bias. The coefficients, shading factors and the error terms were taken from tabulated values (Nowak 1996). A shading factor of 0.78 was used, the mean of four *Quercus* species, in lieu of a shading factor for the species *Q. douglasii*. The equations are appropriate for trees with crown height-to-crown width ratios between 0.5 and 2.0, and DBH between 11 and 53 cm (Nowak 1996). Several of the harvested trees had ratios outside of this height-width ratio range, however, leafmass was calculated for those trees using these equations to test their applicability. Eq. 5.2 was not applied to tree no.1 which had a broken and hollow trunk. We recognize the equations of Nowak were not

developed for application to native oak stands; however, we chose to use them to see the results for oaks and whether the equations might be useful for this species in natural stands.

Another leafmass estimation equation (Harris et al., 1973) was also applied to the fourteen trees, and was of the form:

$$\ln Y = -3.498+1.695*\ln X \qquad \text{(Eq. 5.4)}$$

For Eq. 5.4, calculated total leafmass was a factor of 1.13 of the measured for trees 2-14; tree no. 1 was excluded because of its broken and hollow trunk.

Allometric relationships for leafmass estimation were also obtained by plotting leafmass against crown and trunk dimensions, and also by plotting leafmass against calculated values such as area of crown projection. Figure 5.1 shows the relationship of leafmass vs. circumference at breast height, with a coefficient of determination (r^2) of 0.96. Circumference at breast height is perhaps the easiest tree dimension to measure, so the high value for r^2 is encouraging, and suggests oak circumference may be used with the allometric equation derived from these data to estimate leafmasses for blue oaks. A second-order polynomial regression was chosen rather than a linear regression, because the leaf-carrying capacity of a plant is dependent upon vascular transport of water, and the area of the vascular system increases as the cross-sectional area of the stem, which is proportional to the square of the circumference or diameter. Therefore, as seen in Figure 5.3, the shape of the second-order regression line for leafmass vs. trunk DBH is identical to Figure 5.2, with the same value for r^2.

For leafmass vs. mean crown radius, a second-order polynomial was also chosen because the leafmass should increase as a function of the radius squared, and for this regression an r^2 of 0.96 was obtained, as seen in Figure 5.4. Leafmass vs. area of crown projection modeled with a linear relationship, as seen in Figure 5.5, resulted in an r^2 of 0.95. Therefore, leafmass and either trunk or crown radius measurements appeared to be well-correlated for the trees studied.

A correlation of leafmass vs. stump diameter (Figure 5.6) resulted in an r^2 of 0.92, and the relationship of leafmass vs. rings of sapwood (Figure 5.7) gave an r^2 of 0.74. Either stump diameter or ring counts might be available in sites where trees have been cut, although

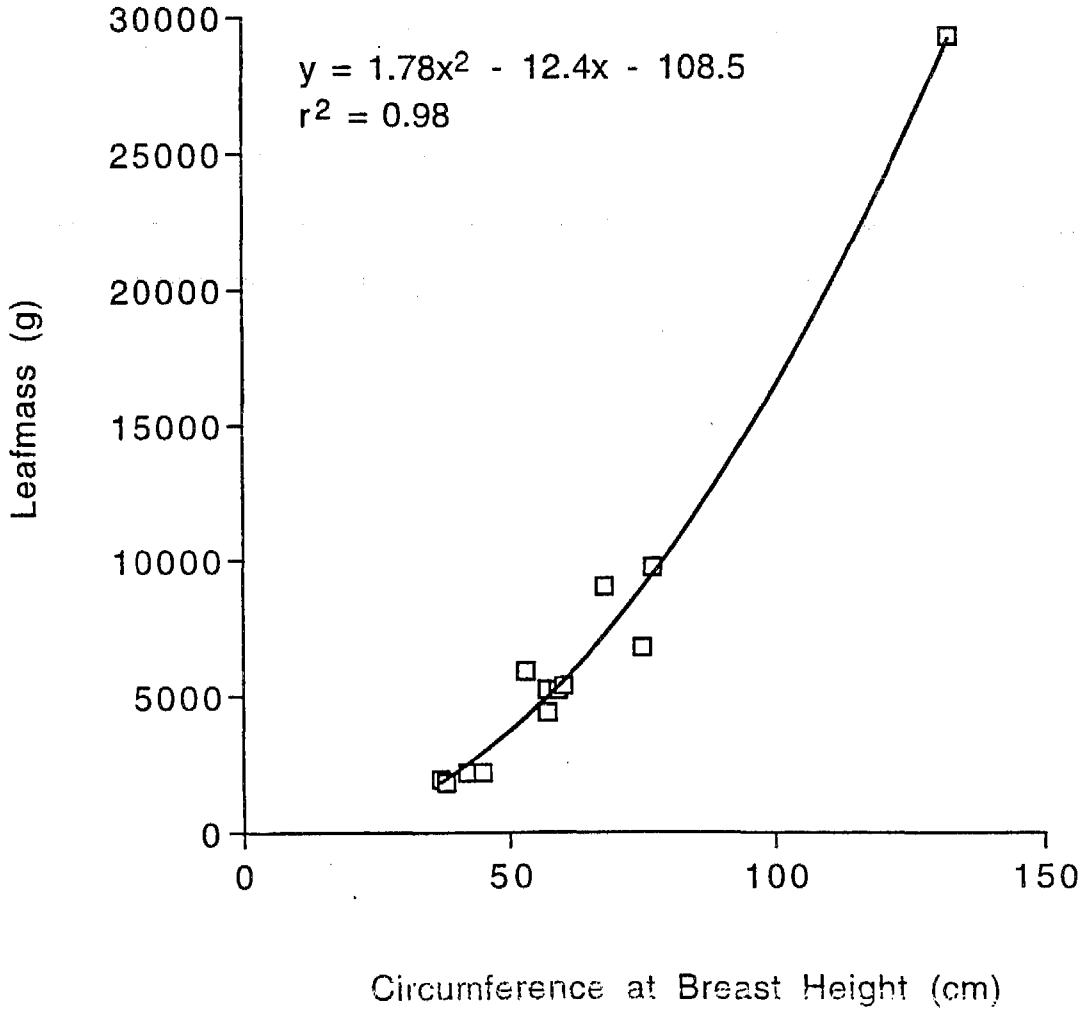

Figure 5.2 Allometric relationship between measured leafmass and circumference at breast height for *Quercus douglasii* trees harvested in a natural stand in the Sierra foothills.

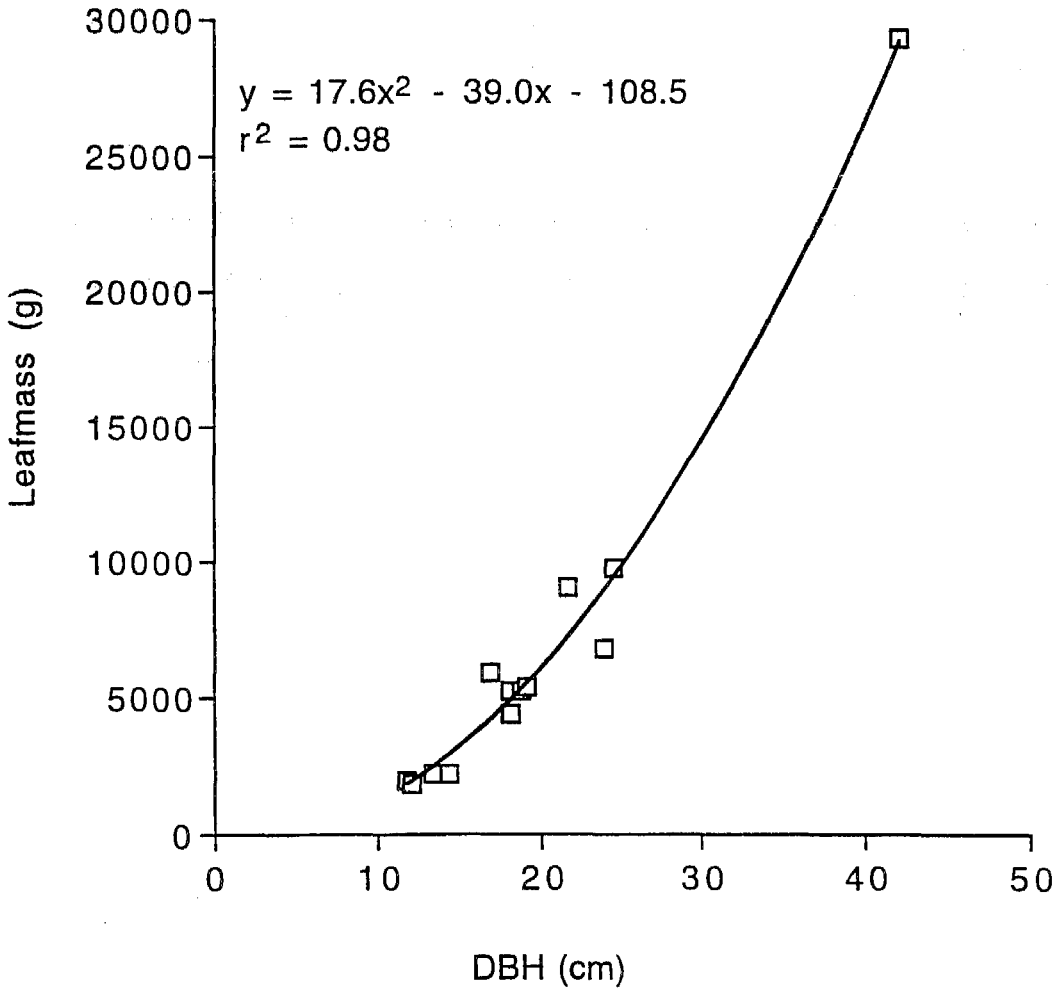

Figure 5.3 Allometric relationship between measured leafmass and diameter at breast height for *Quercus douglasii* trees harvested in a natural stand in the Sierra foothills.

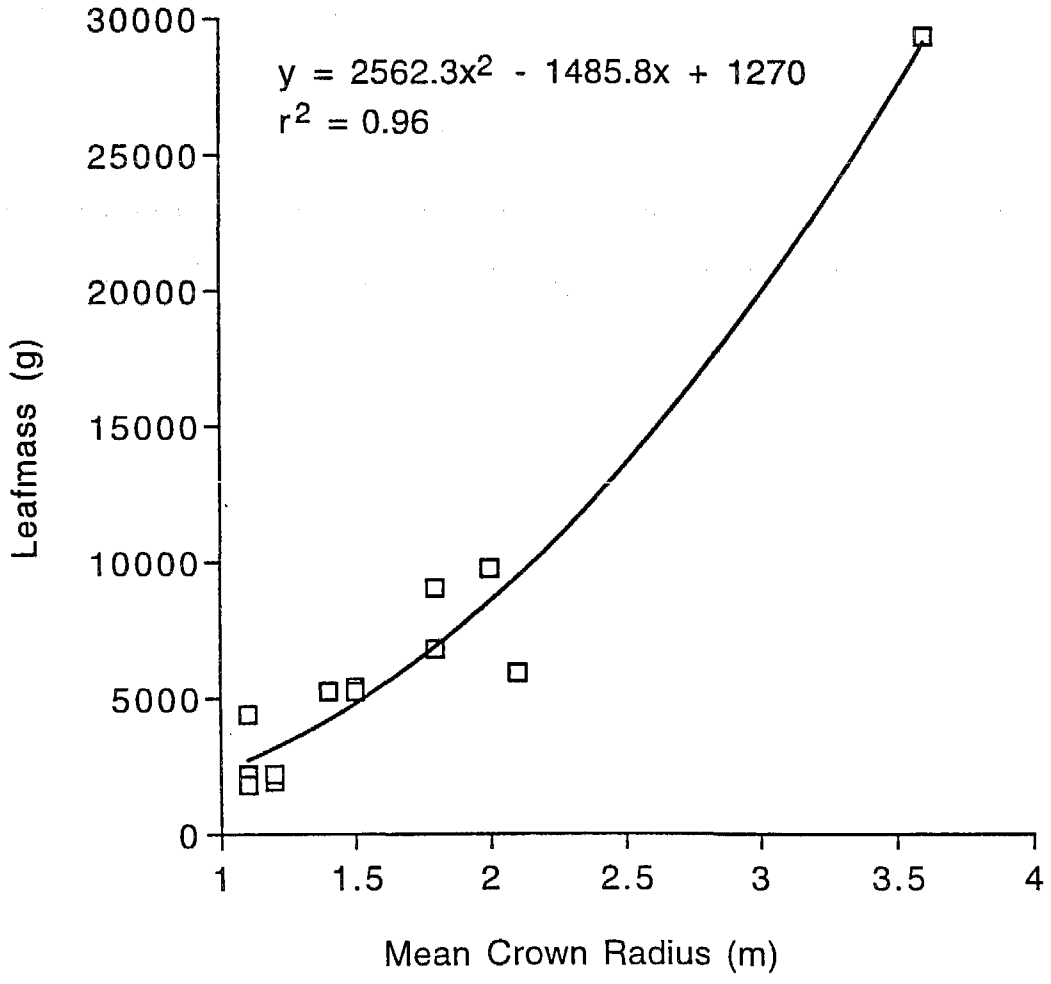

Figure 5.4 Allometric relationship between measured leafmass and mean crown radius for *Quercus douglasii* trees harvested in a natural stand in the Sierra foothills.

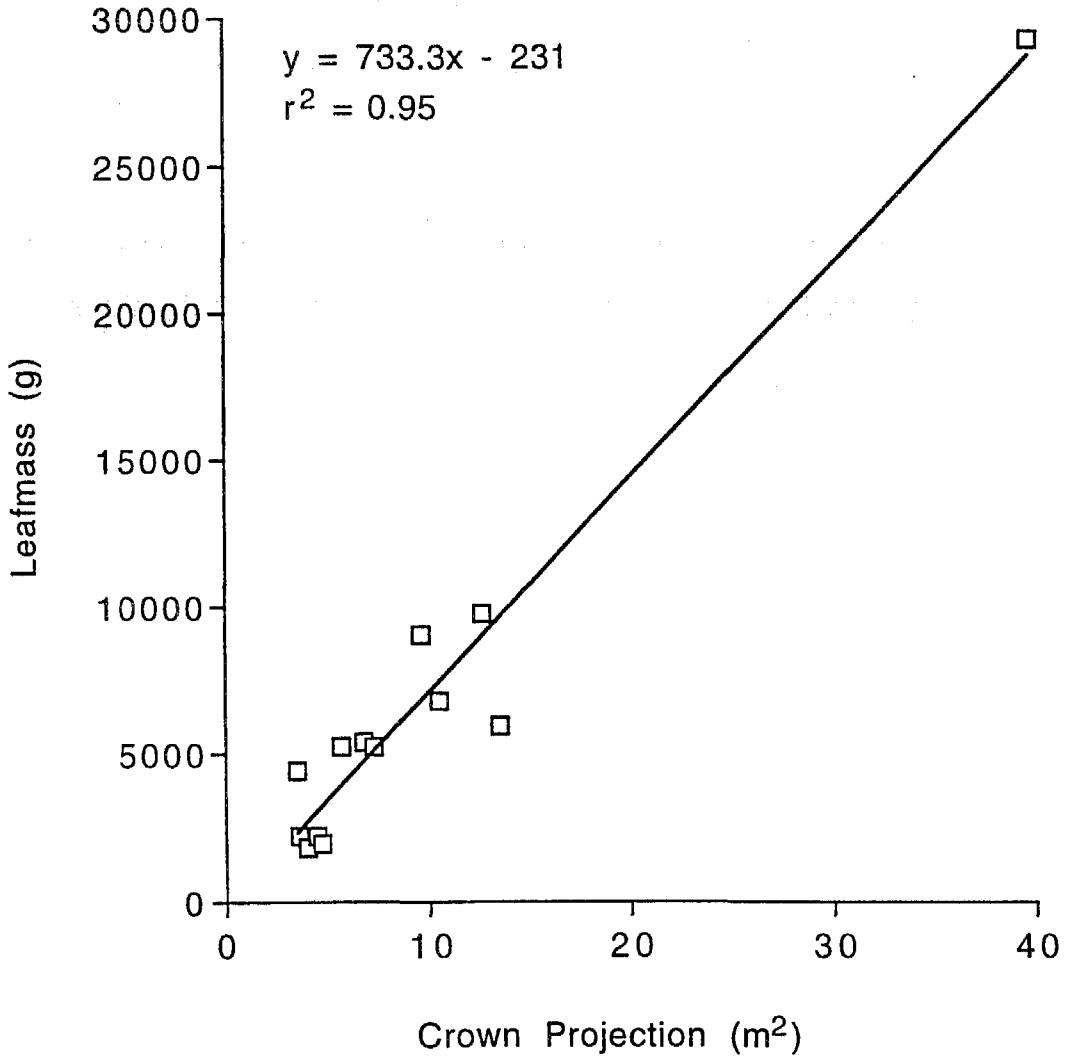

Figure 5.5 Allometric relationship between measured leafmass and crown projection for *Quercus douglasii* trees harvested in a natural stand in the Sierra foothills.

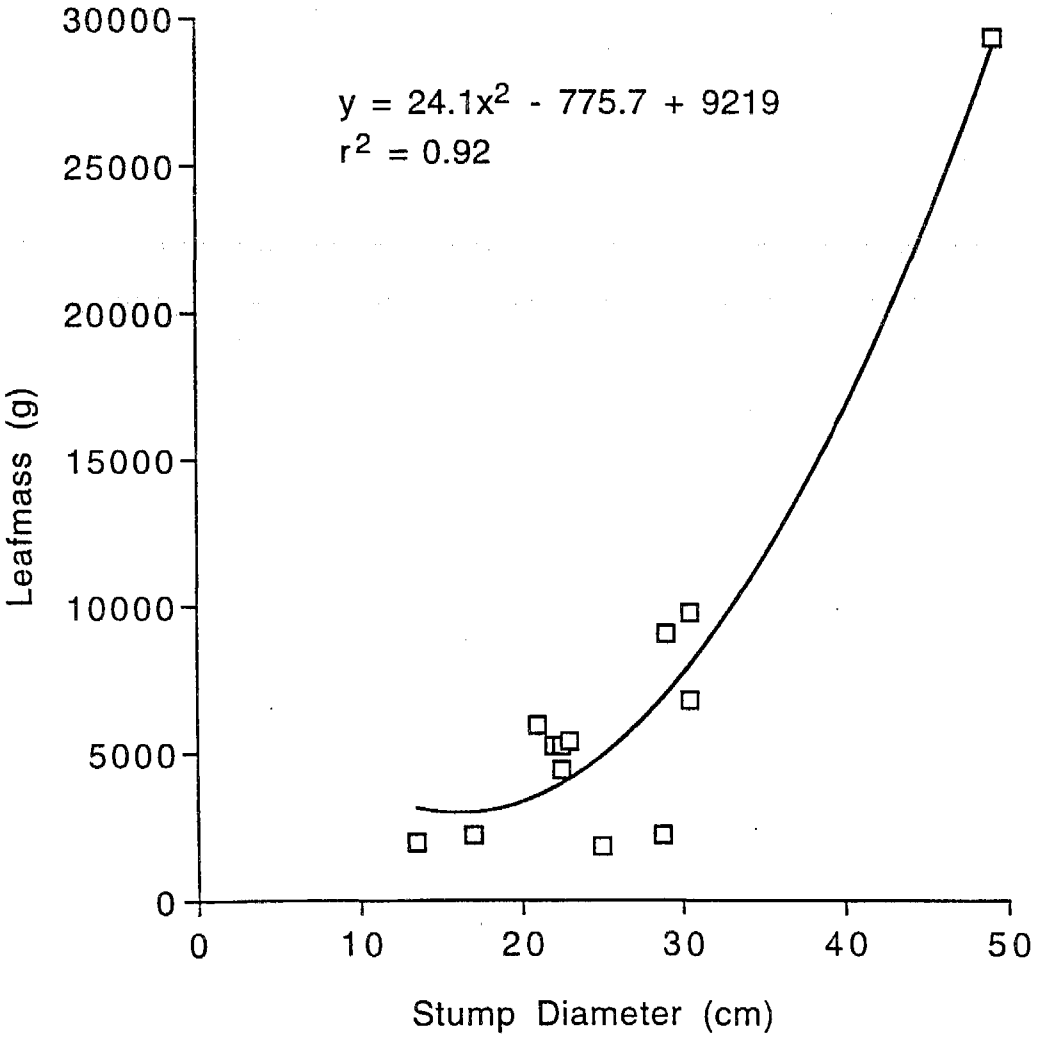

Figure 5.6 Allometric relationship between measured leafmass and stump diameter for *Quercus douglasii* trees harvested in a natural stand in the Sierra foothills.

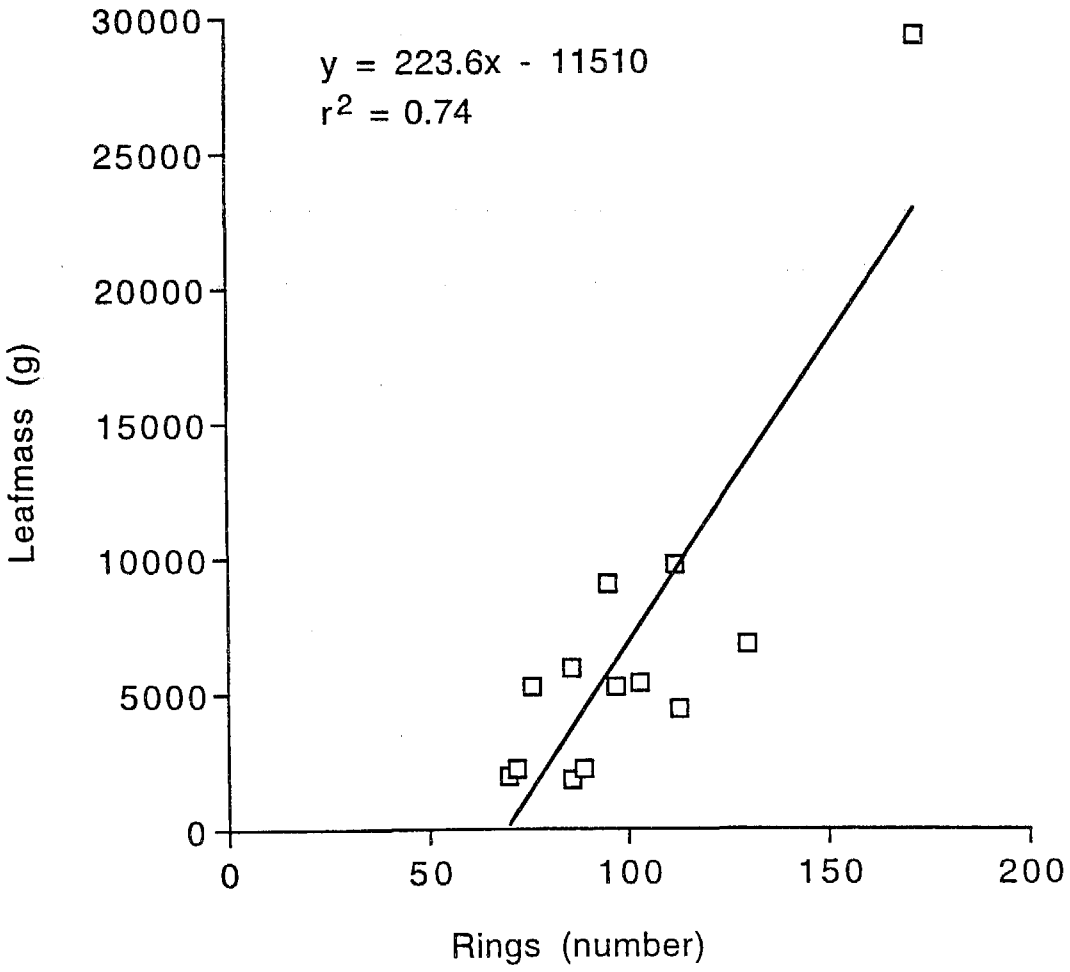

Figure 5.7 Allometric relationship between measured leafmass and sapwood rings for *Quercus douglasii* trees harvested in a natural stand in the Sierra foothills.

the harvest of mature blue oaks in California is uncommon.

Neither crown height nor tree height were well-correlated with leafmass, as seen in Figures 5.8 and 5.9. Figure 5.10 is presented to show how DBH changed with tree age. Where the growing season is well-defined resulting in vigorous spring growth diminishing as summer proceeds into autumn, a single observable ring of sapwood is likely to be formed per year, and so the number of rings counted approximately equals tree age. However, the number of rings may not represent single years in all parts of California, and so we show the ordinate simply as rings rather than years. The blue oak trees harvested were likely between 50 and 200 years old, and their rate of growth was much less than would be expected for a stand of urban trees.

5.3.4 Allometric Equations for Calculation of Leaf Area and LAI

Leaf area may be used to describe the amount and distribution of leaf surfaces. Leaves of deciduous and broadleaf evergreen trees may be modeled by a general ellipsoid (Lang 1991) and the leaf areas measured unambiguously with a planimeter or analogous instrument. For a single tree, the ratio of the sum of leaf areas (one-sided) to the area of crown projection (which is the ground area outlined by a vertical projection of the crown perimeter) is the LAI. As tree crowns expand, the LAI remains relatively constant, because light is intercepted by upper leaves and each successive layer of leaves intercepts more light, with sufficient light for only a certain number of layers. The number of layers will be strongly affected by the light compensation point (species-specific) of the leaves, which is the level of light needed to balance photosynthesis and respiration. Shade tolerance is a qualitative term used to provide an approximate description of the light compensation point of respective species, and trees with low shade tolerance have relatively high light compensation points, and may not survive beneath the canopies of larger trees, or may display open centers at a young age as growth of outer foliage causes death of inner foliage, such as in *Juniperus* species. Although LAI will remain relatively constant as a tree grows, the ratio of leafmass-to-volume will tend to decrease, because the outer surface of the crown moves up and out as branches grow, and crown volume increases as the cube of the distance from the center

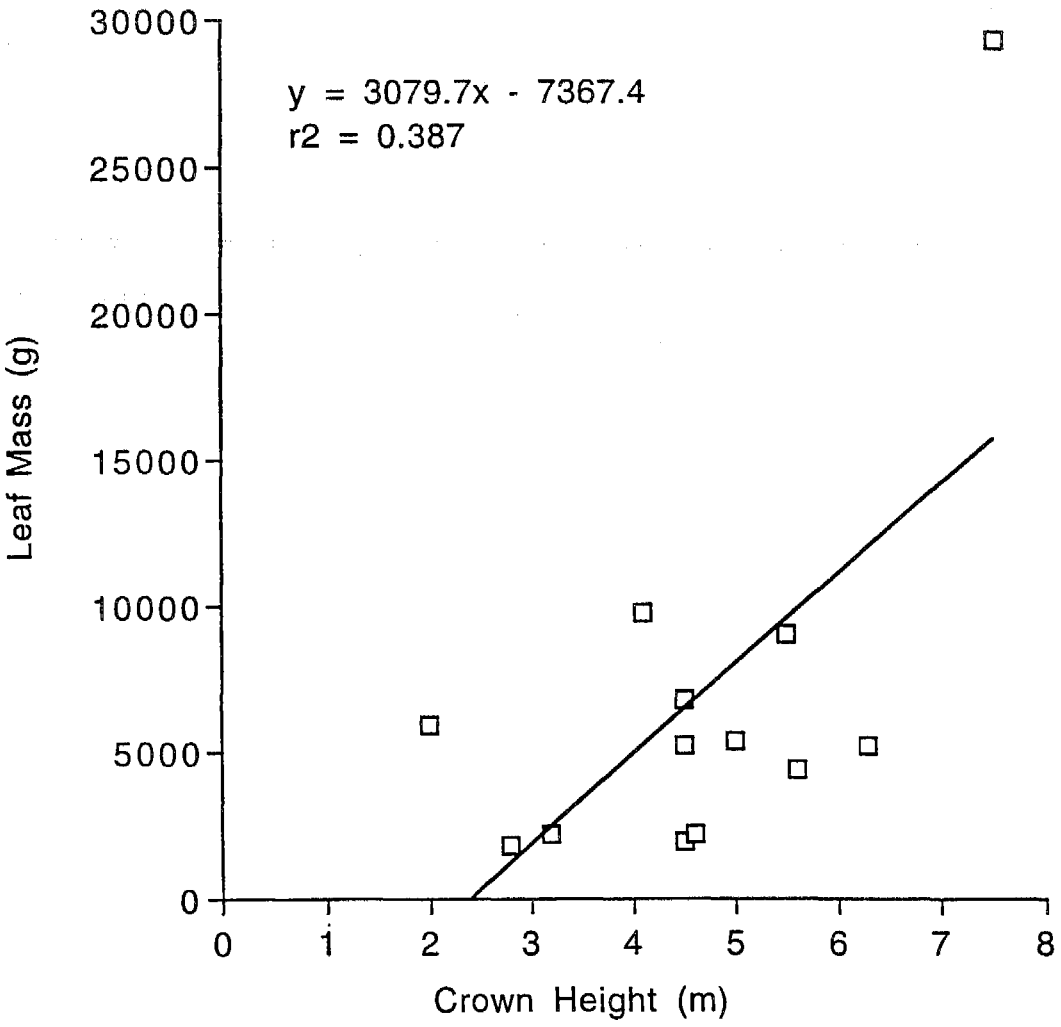

Figure 5.8 Allometric relationship between measured leafmass and crown height for *Quercus douglasii* trees harvested in a natural stand in the Sierra foothills.

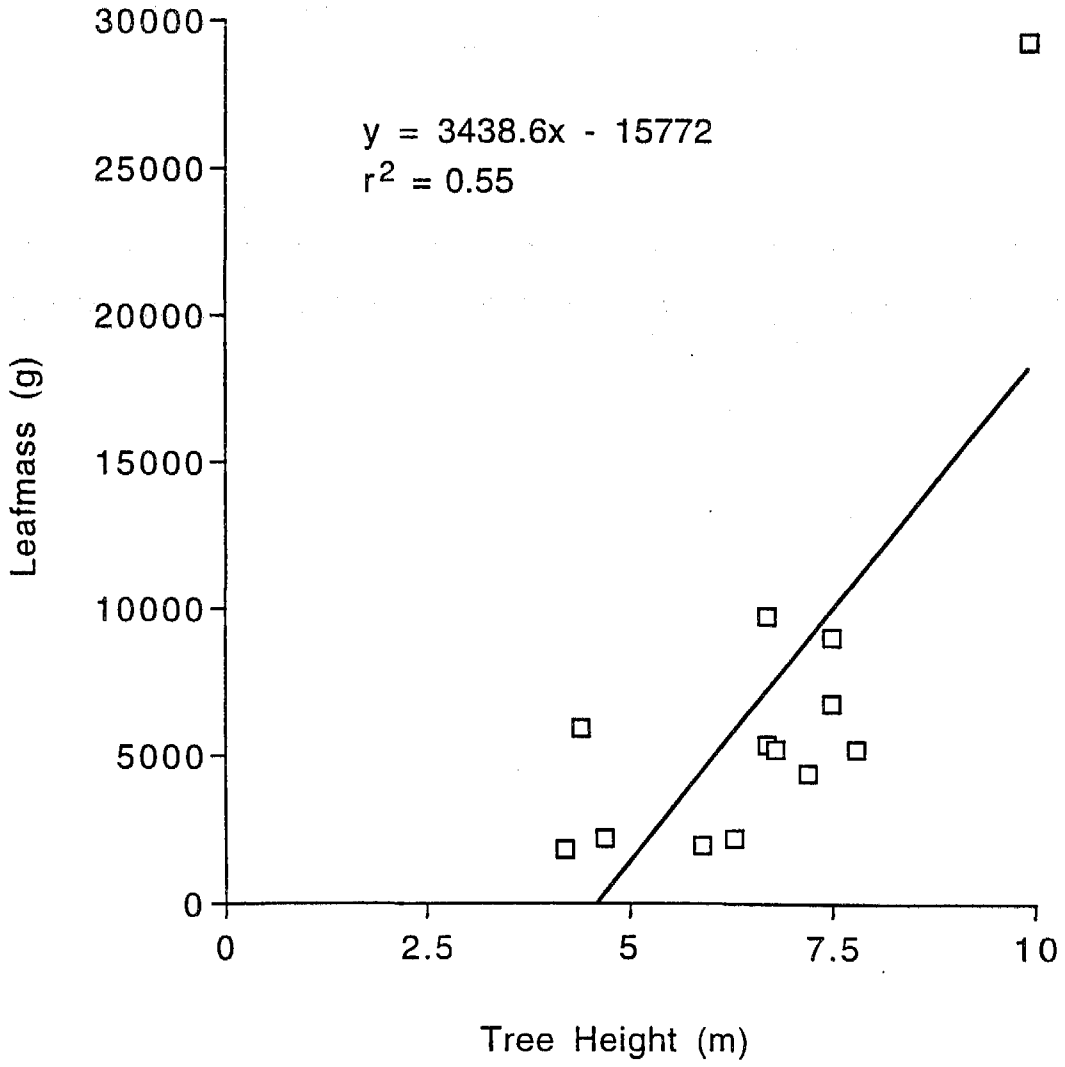

Figure 5.9 Allometric relationship between measured leafmass and tree height for *Quercus douglasii* trees harvested in a natural stand in the Sierra foothills.

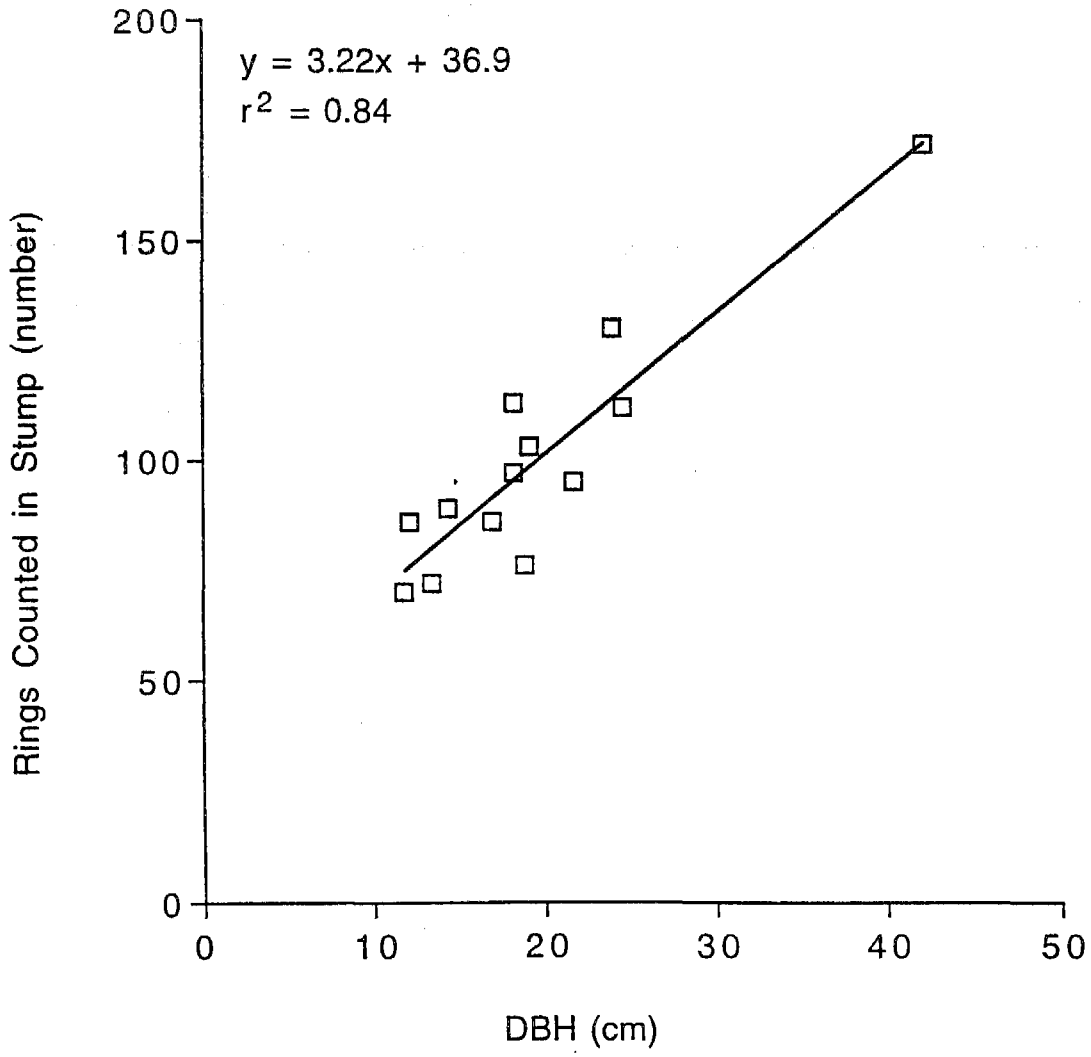

Figure 5.10 Allometric relationship between rings counted in stumps and diameter at breast height for *Quercus douglasii* trees harvested in a natural stand in the Sierra foothills.

of the tree to the outer leaves. Therefore, for large trees, LAI probably provides a more uniform description of foliar density, and by extension, foliar mass, than does a description derived from leafmass per volume ratios of small-to-medium sized trees. If leafmass per volume remained constant for trees of all sizes, large (> 20 m tall) trees should have a crown with leaves present uniformly from top to bottom and inside to outside, clearly not the case even to the casual observer.

Leaf area may be calculated using allometric equations, or by using leafmass to leaf area conversions. As seen in Table 5.4, leaf areas of harvested trees were calculated using the equations of Nowak (1996). Equation 5.4 is based upon crown dimensions and is of the form:

$$\ln Y = -4.3309 + 0.2942H + 0.7312D + 5.7217S - 0.0148C + \text{error} \qquad \text{(Eq. 5.5)}$$

and Equation 5.5 (Eq. 5.5) is based upon trunk diameter and is of the form:

$$\ln Y = 0.2102 + 0.0586X + 4.0202S + \text{error} \qquad \text{(Eq. 5.6)}$$

where Y is leaf area (m^2). Consistent with the allometric equations for leafmass (Section 5.3.3), H is crown height (m), D is average crown diameter (m), S is a shading factor (fraction light intensity intercepted by foliated tree crowns), C is $(\pi D(H + D)/2)$, based on the outer surface area of the tree crown (Gacka-Grzesikiewicz, 1980), and X is dbh (cm). The error terms, which were of the form exp(MSE/2), were added to these equations to correct for logarithmic bias. The coefficients, shading factors and the error terms were taken from tabulated values (Nowak, 1996). Where the tree species was not listed, a value of 0.8 was used for the shading factor. The equations should be used for trees with crown height to crown width ratios between 0.5 and 2.0 and DBH between 11 and 53 cm (Nowak, 1996). Several of the harvested trees had ratios outside of this height-width ratio range (nos. 4, 7, 14); however, leaf area was calculated using these equations to test their applicability. As seen in Table 5.4, Eq. 5.5 gave values closer to leaf areas calculated with Eq. 5.1 for the oak trees than did Eq. 5.6, but both overestimated leafmass. This is not surprising, since these equations were developed for urban trees which are given supplemental water and nutrients, and would be expected to have greater leaf area for given crown radii and trunk diameters than would oaks in the dry natural landscapes of California.

Table 5.4. Calculated values for LA and LAI for native blue oak trees from allometric equations based on crown dimensions (Eq. 5.5), DBH (Eq. 5.6), and leafmass-to-leaf area calculation with experimentally determined SLA (Eq. 5.1).

	Leaf Area (m^2)			Leaf Area Index (m^2 m^{-2})			Fraction of Eq. 5.1	
Tree No.	Eq. 5.5	Eq. 5.6	Eq. 5.1	Eq. 5.5	Eq. 5.6	Eq. 5.1	Eq. 5.5	Eq. 5.6
1	16	N/A	15	4.5	N/A	4.2	1.1	N/A
2	38	140	42	3.0	11	3.3	0.90	3.4
3	12	78	9.4	3.3	21	2.6	1.3	8.3
4	33	97	22	3.9	17	3.9	1.5	4.4
5	35	140	29	3.3	13	2.8	1.2	4.7
6	19	67	8.3	4.1	14	1.8	2.3	8.0
7	21	97	19	6.1	28	5.4	1.1	5.2
8	28	100	23	4.1	15	3.4	1.2	4.5
9	190	390	120	4.7	10	3.2	1.5	3.1
10	12	68	7.8	2.9	17	2.0	1.5	8.7
11	26	100	22	3.6	14	3.0	1.2	4.5
12	19	74	9.4	4.3	16	2.1	2.1	7.8
13	40	120	38	4.2	12	4.0	1.0	3.1
14	27	90	25	2.0	6.7	1.9	1.0	3.6

5.3.5 Summary and Conclusions from Whole-Tree Harvest of Native Oaks

The LMD for the oak site we studied was calculated as the total leafmass divided by area of the grid needed to encompass the tree crowns. This value of 310 g m^{-2} is designated as the site LMD value, and may be compared to literature values for oak woodlands of various locales, including 375 g m^{-2} for Atlanta, GA (Geron et al. 1995); 375 g m^{-2} for the contiguous United States (Lamb et al. 1987, 1993); 338-600 g m^{-2} for Castelporziano, Italy (Seufert et al. 1997), and a global value of 100-500 g m^{-2} (Box, 1981). However, the oak grove we harvested and measured was surrounded by open grassland, and therefore the measured LMD value of 310 g m^{-2} represents a maximum for that landcover. If the oak LMD was calculated on the basis of the area of the grove plus the open grassland surrounding it, the value would have been half or less. The resulting value of approximately 150 g m^{-2} or less is less than 50% of the value for eastern deciduous forests, and suggests California's oak savannas to contain less leaf mass than their eastern counterparts by a factor of two or more.

The mean value for LAI for the 14 individual trees in this oak site was 3.1 m^2 m^{-2}. LAI calculated on the basis of total leaf area divided by the sum of areas of crown projection was also 3.1 m^2 m^{-2}. LAI calculated on the basis of total leaf area divided by grid area was 1.3 m^2 m^{-2}. This latter value was thought to be the LAI which would be seen by an overhead observer. This value was appropriate for the grove only; consideration of the surrounding area which was devoid of trees would result in an overall LAI value of less than 1.3 m^2 m^{-2}. Reference LAI values for eastern forests were not available at the time of the writing of this report, but 1.3 m^2 m^{-2} is low compared to eastern deciduous forests.

The volumetric method worked well for estimating the leaf mass of the oak trees. The total leaf mass for trees in this study estimated by the paraboloid solid was within 2% of the measured total, and for the sphere solid the result was within 15% of the measured value. Thus, the leafmass constant of 280 g m^{-3} coupled with the paraboloid solid seemed to best represent the crown shapes of the native blue oak trees investigated in this study.

Allometric relationships for leafmass estimation were also obtained by plotting leafmass against crown and trunk dimensions, and from resulting calculated values such as area of crown projection. The relationship between leafmass and circumference at breast height had a coefficient of determination (r^2) of 0.96. Circumference at breast height is perhaps the easiest tree dimension to measure, so the high value for r^2 is encouraging, and suggests oak circumference may be used with the allometric equation derived from these data to estimate leafmasses for blue oaks. Mean crown radius and crown projection were also well-correlated with leaf mass, and therefore either measurements of trunk circumference or crown dimensions could be used to estimate leaf mass for this species. In contrast, measurements of tree or crown height were not well-correlated with leafmass, and therefore leaf mass estimates for blue oaks should not be based on them.

6.0 FIELD ASSESSMENT OF THE CALIFORNIA GAP GIS DATABASE IN NATURAL VEGETATION AREAS OF THE SOUTHERN SAN JOAQUIN VALLEY

6.1 Introduction and Background

Plant species distributions, BVOC emission rates, and leaf mass constants have been developed for a substantial number of species relevant to certain areas of California (Winer et al. 1983, 1992, Miller and Winer 1984, Horie et al. 1991, Karlik and Winer 2000). With the proposal of a taxonomic methodology for assigning isoprene and monoterpene emission rates to unmeasured plant species (Benjamin et al. 1996), emission rates can in principle be estimated for many of the 6,000 plant species in California without direct experimental measurements. Of the Southern California airsheds, the vegetation spatial distribution and composition has been established for urban and natural areas within Orange County and the non-desert portions of Los Angeles, Riverside, and San Bernardino Counties (Winer et al. 1983, Miller and Winer 1984, Horie et al. 1990, Benjamin et al. 1997), and a limited BVOC emission study for Santa Barbara and Ventura Counties has also been reported (Chinkin et al. 1996b). However, a validated inventory of vegetation species composition and spatial distribution, specifically to develop a BVOC emissions inventory, has not been established for the San Joaquin Valley air basin.

A potential source of information concerning vegetation in the natural areas of the Central Valley and the Sierra Nevada is the Gap Analysis Program (GAP) database, which is coordinated by the United States Geological Service–Biological Resources Division (formerly the National Biological Service) to identify the distribution and management status of plant communities, especially to identify gaps in habitats for plant or animal species needing protection. GAP compiled a geographic information system (GIS) database (based primarily on remote-sensing data) describing vegetation type and dominance in terms of areal coverage (Davis et al. 1995). Unlike other vegetation maps which describe geographic areas using only plant communities, the California GAP database describes vegetation in given geographic areas using dominant plant species.

Because BVOC emissions inventories rely on species-specific measurements of both leaf mass and BVOC emission rates (Benjamin et al. 1997), GAP offers the advantage of

providing species-specific vegetation distribution data. Moreover, the GAP GIS database is recent for California (Davis et al. 1995) and therefore more up-to-date than older vegetation databases employed in California, such as the vegetation type map (VTM) surveys conducted in the 1930s and CALVEG generated in the 1970s (Sawyer and Keeler-Wolf 1995). However, although large-area small-scale GIS databases based on remote-sensing data, such as GAP, offer a potentially inexpensive and simple approach to characterizing the distribution and species identities of natural vegetation within an airshed, use of such GIS databases for BVOC emissions inventory development requires evaluation of their accuracy and reliability through ground-based observations.

We report here the results of a ground-based assessment of the GAP GIS database within the Central Valley and Sierra Nevada ecological regions using vegetation surveys of representative GIS polygons. The surveys employed a modified stratified random sampling approach and a survey protocol based in part on the recommendations of the developers of the GAP database (Stoms et al. 1994), and refinements from a preceding study of GAP in San Diego County (Winer et al. 1998, Chung and Winer 1999). Data gathered from field surveys conducted during the 1999 and 2000 summers in the Central Valley and Sierra Nevada were used to assess the utility of the GAP GIS database for describing the distribution and species identities of vegetation, and for providing quantitative information of plant species coverages for BVOC emission inventories.

6.2 GAP Validation in San Diego County

The current GAP validation project was modeled after a previous study conducted in San Diego County (Winer et al. 1998, Chung and Winer 1999). That assessment of the GAP database, through ground-based vegetation surveys, was conducted prior to using the database to develop a BVOC emission inventory for Southern California. Quantitative vegetation surveys were conducted along belt transects in four polygons dominated by trees, and along line transects in four polygons dominated by shrubs, in order to determine percent cover of major plant species. The species listed by GAP accounted for two-thirds to three-quarters of the relative cover in these selected polygons. About 60% of the species listed by GAP were found in high enough proportions in the field surveys to justify their listing.

Although isoprene and monoterpene emission indices summed over all eight polygons based on GAP data were in good agreement with the sum of corresponding emission indices generated with data from field surveys, individual polygon emission indices based on GAP data were more than 50% different from the corresponding indices calculated from field data for half the polygons. However, on balance, the GAP database was judged to be a useful source of species composition and dominance information for the purpose of assembling BVOC emission inventories, for the San Diego County area (Chung and Winer 1999).

6.3 Assessment Methodology

6.3.1 Acquisition and Preparation of the GAP Database

As noted earlier, GAP's purpose was to identify the distribution and management status of selected components of biodiversity. The central tool of this program was an ARC/INFO GIS database with plant species and vegetation class attributes associated with polygons within a defined geographic region. This database was generated from summer 1990 Landsat Thematic Mapper satellite imagery, 1990 high altitude color infrared photography, VTM surveys based on field surveys conducted between 1928 and 1940, and miscellaneous vegetation maps and ground surveys (Davis et al. 1995). Polygons were delimited based on climate, physiography, substrate, and disturbance regime. Landscape boundaries were subjectively determined through photointerpretation by expert personnel so that between-polygon variation was greater than within-polygon variation. The final result was a vegetation map with a 100-hectare minimum mapping unit and a 1:100,000 mapping scale (Davis et al. 1995).

For each polygon in the database, one primary, one secondary and, for some polygons, a tertiary vegetation assemblage was listed. Each assemblage consisted of up to three co-dominant overstory species, each covering a minimum of 20% of the relative cover of that assemblage. Overstory plants were those plants viewable directly from above. The primary assemblage was defined as the assemblage covering the majority of the polygon, and the secondary and tertiary assemblages as covering relatively smaller areas of the polygon. Relative cover of a given plant species within an assemblage was the fraction of total assemblage vegetation cover occupied by the given species. In addition, GAP listed the

percent crown cover of each assemblage in the polygon in four classes, which were 0-24, 25-39, 40-59, and 60-100 percent.

The GAP database for the southern portion of the Sierra Nevada and Great Valley ecological regions which included land in the counties of Kern, Tulare, Kings, Fresno, and Madera was obtained at the beginning of the project. There were 742 polygons in the Great Valley and 1420 polygons in the Sierra Nevada ecological regions of the GAP database found within these five counties.

6.3.2 Polygon Selection

GAP data for each polygon were used to obtain an isoprene and monoterpene index for the polygon (Winer et al. 1998). The compilation of Benjamin et al. (1996) was the primary reference for plant species emission rates, and a taxonomic approach was applied to assign emission rate values to unmeasured species. Of the 742 polygons in the study area within the Great Valley portion of the GAP database, 88 were found to have a non-zero sum for isoprene values for plant species present in the polygons, and 40 were found to have non-zero values for monoterpenes. For the polygons in the study area within the Sierra Nevada portion of the GAP database, 1130 were found to have non-zero sums for isoprene values for plant species contained in assemblages, and 1048 had non-zero values for monoterpenes. The total number of such polygons was 2306, and each was assigned a unique number from 1-2306 for the initial process of polygon selection for field validation.

After lengthy discussions, and after review of comments on the previous study design for GAP (Winer et al., 1998; Chung and Winer, 2000), it was decided to use a completely random selection process within polygons containing emitting species as the starting point for polygon selection for field validation in this study. In other words, the goal of the field surveys was to be primarily GAP validation, without a focus on highest-emitting polygons. Accordingly, a random number table with whole-number values from 1-2306 was generated. (One polygon with an both iso and mono emission indices of zero was also included in the study in 1999 to test GAP assignments for a non-emitting polygon. A second non-emitting polygon was chosen in conjunction with a test of GAP registration, as noted below. With

those exceptions all the polygons were thought to have non-zero emission indices for either isoprene or monoterpenes or both.)

Polygon selection began by identifying polygons corresponding to the entries in the random number table. Beginning with the left-hand column of numbers, each polygon listed was checked for inclusion in the field survey by further examining its characteristics in view of additional criteria. To remain a candidate for field validation, the polygon had to be below the atmospheric boundary layer, taken as 1800 m (6000 ft) elevation, and within the San Joaquin Valley air basin. Further selection from the remaining polygons involved an iterative process accounting for representativeness and feasibility. In considering feasibility, physical access and permission to survey vegetation on private or military property were important. A road map was overlaid on the area to see if there was access by roadways, and if so a universal transmercator (UTM) grid would then be generated. Polygons with a large public land component (e.g. California State Parks, United States National Forest, Bureau of Land Management, and local parks) were favored due to the relative ease of gaining permission to conduct surveys on such properties compared to privately owned properties.

For identification, polygons were rank-ordered on the basis of their isoprene and monoterpene emission indices, with 1 assigned to the polygon with the highest isoprene or monoterpene index within each ecological region. For example, the first polygon surveyed was assigned the name SN Iso 58 Mono 373, indicating it was found in the Sierra Nevada ecological region, and had ordinal values of 58 and 373 for isoprene and monoterpene emission indices, respectively. Sierra Nevada polygons with iso- and mono- rankings below 1050 and 1052, respectively, would have non-zero isoprene and monoterpene emissions based on their areas and GAP species listings. Great Valley polygons with iso- and mono- rankings below 88 and 58, respectively, would likewise have non-zero isoprene and monoterpene emissions based on GAP data.

A subsample of polygons was selected as a test for correctness of the geographic location of a specific GAP polygon; in other words, a test of the registration of the GAP database. Three surrounding polygons adjacent to polygon SN Iso 630 Mono 1133 were selected for survey during the summer, 2000, sampling season. The plants found in these surrounding polygons could then be compared with those listed for the center polygon to see

if plant communities listed for the center polygon were found rather in a surrounding polygon. The three surrounding polygons were SN Iso 315 Mono 630 located to the southeast, SN Iso 225 Mono 1194 located on the western end, and SN Iso 1333 Mono 1095 located to the northeast of the center polygon.

Based on these criteria and the time and resources available for this research, eighteen polygons were selected and surveyed for the present study. Four polygons, located in the Central Valley, consisted primarily of shrub/chaparral vegetation, and fourteen polygons, located the Sierra Nevada mountains and foothills, consisted primarily of woodland/forest vegetation, as seen in Tables 6.1 and 6.2. Tables 6.1 and 6.2 also list GAP data for each polygon surveyed in the summers of 1999 and 2000, respectively, including the expected species assemblages, their percentages of cover within the polygon, and percentages of crown closure. Figure 6.1 shows the locations of the polygons.

6.3.3 Selection of Sample Elements

After a polygon was chosen by the process described above, sample elements within the polygon were selected. The minimum square-shaped area needed to encompass a sample element within a polygon was determined to be 25 ha (62 acres) for forests and woodlands, and 9.0 ha (22 acres) for scrub and chaparral. These areas were different because of the differing transect lengths within the sampling protocols employed these landcover types, as described in Section 6.3.4. Knowledge of ownership of the land was needed to obtain permission to survey. Written permission was requested and received from the National Park Service for no-cost access to all polygons within the boundaries of Sequoia and Kings Canyon National Parks. It was decided land under private ownership would first be visited and agreement for access obtained from the landowners before plant surveying could begin. A letter of introduction on UC letterhead was prepared requesting permission to conduct a vegetation survey and stating the goals of the research and was kept on hand in the event the research team was confronted by someone such as a skeptical land owner or park ranger.