BIOGENIC HYDROCARBON INVENTORIES FOR CALIFORNIA: GENERATION OF ESSENTIAL DATABASES

Final Report

Contract No. 95-309

STATE OF CALIFORNIA AIR RESOURCES BOARD

Principal Investigator

Arthur M. Winer

Environmental Science and Engineering Program
Department of Environmental Health Sciences
School of Public Health
University of California
Los Angeles, CA 90095

Co-Investigators

John Karlik
Cooperative Extension
University of California, Bakersfield

Janet Arey
Air Pollution Research Center
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Contributing Researchers

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ABSTRACT

Given growing evidence of the key role played by biogenic hydrocarbons (BHC) in the atmosphere, it is critical to obtain the measurement data needed to assemble reliable BHC emission inventories in California's airsheds; to test and refine predictive methods for BHC emission rates, and for leafmass constants; and to validate spatially resolved, species-specific vegetation databases through field surveys.

In the present study, mean isoprene emission rates were measured by the branch enclosure method for 63 species within 29 families and 49 genera. All species sampled within 18 of the families had isoprene emissions below the detectable limit (BDL), consistent with the literature cited in Benjamin et al. (1996) for ten of these families. These results are important because the Rosaceae and Compositae families are large and well-represented in agriculture, native plant communities and urban landscapes. Genera which, as expected, included two or more moderate-to-high isoprene emitting species included *Eucalyptus* (eucalyptus) and *Populus* (poplar and aspen). Isoprene emission rates were consistent within most genera studied, with the exception of *Quercus* (oak) as noted by others. For 15 of 19 "predictions" found in Benjamin et al. (1996), isoprene emission rates measured in the present study were within $\pm$50% of the predicted rate. If oaks are not considered, since *Quercus* is so variable, agreement with taxonomic prediction increased to 14 of 16 species. All nine species predicted to have no isoprene emissions were BDL. Thus, with a few important exceptions like *Quercus*, the taxonomic method provides a useful general framework for organizing and characterizing isoprene emission rates.

Accurate leafmass determination is critical in estimating biogenic hydrocarbon emissions. The present study evaluated the precision and accuracy of a volumetric approach, and expanded the limited database of experimentally measured leafmass constants. A further goal was to develop leafmass-leaf area relationships. Twenty-one urban trees were felled and all leaves removed for drying and weighing. Given the high labor requirements for leaf removal, it is not surprising very few similar datasets have been generated for urban trees. Using height and radius data for each tree crown, volumes for five geometric solids approximating tree shapes were calculated and corresponding whole-tree leafmasses obtained by multiplying the respective volumes by a leafmass constant found in the literature. Two of the solids (sphere and vertical ellipsoid) and the solid identified as "preferred" in the field gave estimates of total leafmass for all trees within 20% of the measured value. For many individual trees, the preferred solid resulted in a leafmass estimate within $\pm$30% of the measured whole-tree value but for several individual trees leafmass estimates varied greatly depending on the solid selected, and tended to overestimate measured leafmass.

Whole-tree leafmass constants based on the entire tree leafmass and volume were calculated and compared to experimentally-determined literature values where available. These literature values appear to be reasonably accurate for the species tested. Mean leafmasses per unit projected crown area for the urban deciduous and broadleaf evergreen trees studied were 1.7 and 5.0 times greater, respectively, than leafmass per unit ground area data reported for eastern deciduous forests. This suggests trees in urban landscapes have higher leafmass per surface area than natural forest trees, presumably due to irrigation and fertilization in urban landscapes.

The composition and dominance of natural vegetation in San Diego County was investigated in field surveys, with an emphasis on evaluating the GAP GIS database for this region. The GAP database is plant species-specific and has a high spatial resolution, however assessment of the agreement of GAP with field observations is a prerequisite to its use in developing species-based BHC emissions inventories for California. Eight GAP polygons in San Diego County were selected for the present study: four consisting of woodland/forest vegetation and four of chaparral/scrub vegetation. Data were gathered on plant species identity, crown height, and areal coverage in field surveys from September, 1997 to April, 1998. Within surveyed polygons, the ten most abundant species observed in the field accounted for over 90% of the relative cover of each polygon, and co-dominants (the plant species predicted by the GAP database for individual polygons) accounted for 64-85% of the relative cover of the polygons. Of the species listed by the GAP database, 60% were observed in the field in sufficient abundance to suggest agreement between field data and GAP.

Total crown closure as predicted by the GAP database generally matched the field observations in the present study. However, the community classification of each sample element within a polygon often differed from the GAP database community classification assigned for the entire polygon, revealing a microscale heterogeneity not captured by the GAP database. It is important to note that biomass as derived from crown volume cannot be determined solely from data contained within the GAP database; average crown height of a plant species, or plant crown volume on an area basis, are required for BHC emissions inventories. These data may come from the literature or from field data such as those collected in the present study.

Anthropogenic hydrocarbons are measured on a routine basis in the South Coast Air Basin, but few ambient measurements of BHC or their atmospheric reaction products have been conducted in the basin. Measurements of isoprene, the BHC emitted in greatest quantity by vegetation, and its principal reaction products, methacrolein (MACR) and methyl vinyl ketone (MVK), were undertaken during the SCOS97 campaign between June 16 and October 15, 1997, at three sites: Azusa, Banning and high elevation sites, Pine Mountain or Mount Baldy. Solid adsorbent tubes were utilized for VOC sample collection and concentration, and were analyzed by gas chromatography with mass selective detection. Results for twelve SCOS97 intensive sampling days are given in this report.

The highest isoprene mixing ratios were found at the two mountain sites in late afternoon/early evening samples: 2.2 ppbv on August 4 at Pine Mtn. and 2.3 ppbv on September 28 at Mt. Baldy. The highest mixing ratios for isoprene at Azusa were in the range 0.5 – 0.8 ppbv vs. 0.2 – 0.3 ppbv at the Banning site. The highest mixing ratios for MACR and MWK were observed at Azusa. At the mountain sites during the day, isoprene generally exceeded MACR and MVK, while during the night isoprene was <0.1 ppbv and combined MACR and MVK levels reached 1.7 ppbv. The ratio of MVK/MACR during the day was relatively constant at the mountain sites, with average ratios from 1.6 to 2.2. A ratio of 1.5 for MVK/MACR would be expected from the OH radical-initiated reaction of isoprene given negligible further reaction of MVK and MACR, while at steady-state this ratio would be expected to increase to 2.4. Thus, the observed daytime MVK/MACR ratio at the mountain sites is consistent with the source of MACR and MVK being photooxidation of isoprene.

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DISCLAIMER

The statement and conclusions in this report are those of the University of California and not necessarily those of the California Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

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GLOSSARY OF TERMS, ABBREVIATIONS, AND SYMBOLS

ARB	Air Resources Board
ARCINFO	Vector-format GIS used to provide DRI Landsat TM-based vegetation classification files for the SARMAP/BIOME model
AVHRR	Advanced Very High Resolution Radiometer
BEIS	Biogenic Emission Inventory System (U.S. EPA)
BHC	biogenic hydrocarbon
BVOC	biogenic volatile organic compounds
CALVEG	California Vegetation database developed by the California Division of Forestry
CARB	California Air Resources Board
CDF	California Department of Forestry
CIR	color infrared
CO2	carbon dioxide
DBH	diameter at breast height
EPA	Environmental Protection Agency
GAP	Gap Analysis Project
GC-FID	gas chromatography-flame ionization detection
GC-MS	gas chromatography-mass spectroscopy
GIS	geographical information system
IR	infrared
LA	Los Angeles
LAI	leaf area index
NDVI	normalized difference vegetation index
NMOC	non-methane organic compound
NO_x	oxides of nitrogen ($NO + NO_2$)
NO	nitrogen monoxide
NO_2	nitrogen dioxide
N_2O	nitrous oxide
OVOC	other volatile organic compounds

GLOSSARY OF TERMS, ABBREVIATIONS, AND SYMBOLS (con't)

PAR	photosynthetically active radiation
ppbC	parts per billion carbon
ppmC	parts per million carbon
RH	relative humidity
ROG	reactive organic gases
ROM	Regional Oxidant Model
SCAQMD	South Coast Air Quality Management District
SCAQMP	South Coast Air Quality Management Plan
SJV	San Joaquin Valley
SJVAB	San Joaquin Valley Air Basin
SJVAQS	San Joaquin Valley Air Quality Study
SLA	specific leaf area
SoCAB	South Coast Air Basin
SO_x	oxides of sulfur ($SO_2 + SO_3$)
TM	Thematic Mapper (NASA Landsat satellite instrument)
TPD	tons per day
UAM	Urban Airshed Model
UCCE	University of California Cooperative Extension
UCR	University of California, Riverside
USFS	United States Forest Service
USGS	United States Geological Survey
UTZ	urban terrain zone
VOC	volatile organic compound

1.0 EXECUTIVE SUMMARY

1.1 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 1997. The reduction in ozone first stage alerts in the SoCAB, for example, from approximately 120 annually in the mid-1970's to only one in 1997, is a profound achievement given the enormous growth in population and emission sources in the SoCAB over the period of these control programs. Unfortunately, however, the degree 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 from vegetation (BVOC). Recent 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.

A study recently published from our laboratory (Benjamin et. al. 1997) estimates 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 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 (1995). 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 is too much uncertainty in current BVOC estimates for airsheds other than the SoCAB to draw definitive modeling conclusions (Jackson 1997) at this time.

Concern about the possible critical role of BVOC 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].

Given the growing evidence of 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 relevant ARB models.

The essential steps in assembling a biogenic hydrocarbon emission inventory consist of assessing plant species distribution and abundance, determining green leaf biomass for all of the important plant species, measuring or otherwise estimating the quantitative rate of emission of individual organics from each of hundreds of plant species, and modeling the overall diurnal emission inventory as a function of several key environmental factors, including temperature and light intensity.

A testimony to the difficulty of systematically determining experimental leaf biomass constants and hydrocarbon emission rates is that at the present time, notwithstanding the growing attention paid to VOC of biogenic origin over the past decade, experimental measurements of such essential properties as leaf area indices, crown volumes and emission rates have been conducted only for a distinct minority of the hundreds of plant species typically identified in large California airsheds such as the SoCAB or the SJVAB. Moreover, absent a massive and unrealistic expenditure of funds and personnel, there is no meaningful possibility that comprehensive experimental determination of these properties will be conducted, even on the time scale of decades, let alone the few years available to utilize such data in demonstrating ozone and PM-10 attainment.

Clearly, these constraints and complexities dictate a different approach. In particular, what is needed are cost-effective and focused efforts to generate the experimental data for key plant species which will in turn permit validation of models and methods able to generalize these results to the much larger number of plant species found in California. There was also a unique opportunity during this project to provide

experimental ambient air measurements of isoprene and monoterpenes (and their photooxidation products) during the 1997 Southern California Air Quality Study, supplementing the many other kinds of measurements which were made during this comprehensive monitoring program.

1.2 Project Objectives

The specific objectives of this project were to:

- Experimentally measure isoprene emission rates for a carefully selected set of plant species under realistic field conditions.
- Expand and refine the UCLA taxonomic methodology for "predicting" isoprene emission rates for plant species for which no experimental measurements are available.
- Under field conditions, experimentally measure dry leaf mass per volume, including whole tree leaf mass of plant species which represent the most critical gaps in biomass estimation for key airsheds such as the SJVAB.
- Based on field surveys, determine uncertainties and limitations in the GAP database, and develop recommendations for utilizing this current geographical information system (GIS) database for vegetation in California for development of biogenic hydrocarbon emission inventories.
- Conduct experimental measurements of ambient concentrations of isoprene and monoterpenes, and their photooxidation products, during the 1997 Southern California Air Quality Study in conjunction with the extensive monitoring program for anthropogenic hydrocarbon species.

1.3 Isoprene Emission Rate Measurements

More than 70 different BHC 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. Isoprene is the BHC emitted in greatest quantity by the plant kingdom (Guenther et al. 1995) and is the dominant BHC 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). Isoprene emission probably increases thermotolerance of plants (Sharkey and Singsaas 1995, Singsaas et al.

1997) and may also act as a plant growth regulator, for example, accelerating the onset of flowering (Terry et al. 1995). Among the plant species measured to date, emission rates of isoprene differ by more than three orders of magnitude (Benjamin et al. 1996) and the resulting ozone-forming potential of individual trees and shrubs ranges over nearly four orders of magnitude (Benjamin and Winer 1998). Isoprene emission rates are often expressed in units of micrograms of isoprene per gram of dry leafmass per hour which we will represent throughout this report as ug g^{-1} h^{-1}.

Oxygenated compounds may comprise a significant fraction of biogenic emissions in California airsheds and be as important as isoprene for certain plant species, such as *Pinus subiniana* (digger pine) and *P. coulteri* (Coulter pine) (Guenther 1998). A large number of oxygenates is proposed for inclusion in the BEIS III model. However, oxygenated compounds may also be reaction products rather than biogenic emissions and careful experimental protocols are therefore necessary to measure emissions of oxygenated compounds (Fruckilde et al. 1998). Additional measurements of oxygenates should be made for California plant species, but this was beyond the scope of the present project.

1.3.1 Rationale and Approach for the Present Investigation

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 measure experimentally the isoprene emission rates of even a small fraction of the plant species found in California and other regions, although quantitative emission rate data for additional species have been accumulated during the BEMA project (Owen et al. 1997) and qualitative appraisals of emission rate behavior for previously unreported species have also been published (Guenther et al. 1994, Lerdau and Keller 1997, Klinger et al. 1998). However, a vast number of species remain to be evaluated, hence generalizations of BHC 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 BHC emissions inventories for urban areas (Geron et al. 1995).

An explicit link between isoprene and monoterpene emissions rates and plant taxonomic relationships has been proposed for species found in southern California (Benjamin et al. 1996) and was subsequently used (Benjamin et al. 1997) to compile a detailed BHC 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 BHC 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 emission rates for carefully selected plant species are required to test further the taxonomic predictive method. In response to this need, the present study expanded the measured isoprene emission rate database by more than sixty key California species and provided data for further evaluating isoprene emission rates inferred from taxonomic relationships.

Most urban tree and shrub species sampled in the study were found in irrigated landscapes on the San Joaquin Valley floor (elevation ca. 500 ft). Plant genera more frequent in cooler climates, such as *Cornus* and *Viburnum*, were sampled within the Mourning Cloak Botanic Garden (MCBG), 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 (MTN) such as Caliente, approximately 15 miles east of Bakersfield (elev. ca. 1000 ft), and California Hot Springs, approximately 60 miles northeast of Bakersfield (elev. ca. 2300 ft).

Because the study was necessarily limited, candidate plant species were carefully selected to allow evaluation of the taxonomic predictive method and expansion of the isoprene emission rate database. 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).

The Teflon enclosure method was adopted as the primary method for sampling isoprene emissions in this study, with a design similar to that utilized by Winer and co-

workers (Winer et al. 1983, 1992) and Arey and co-workers (Arey et al. 1995). Complete experimental details are provided in Section 3.0.

1.3.2 Results

Mean isoprene emission rates were measured for 63 species within 29 families and 49 genera and normalized to standard conditions (see below). Sixty-one of the 63 plant species studied represent species not reported in the compilation of Benjamin et al. (1996). A complete description of emission rates and associated environmental parameters measured in the present study may be found in Appendix A. Isoprene emission rates were normalized to PAR and temperature of 1000 umol m^{-2} sec^{-1} and 30°C, respectively, using the algorithm proposed by Guenther et al. (1993) and subsequently modified by Guenther (1997).

We have followed the example of Guenther et al. (1994) in describing isoprene emission rate ranges with slight modifications: our ranges are based on branch-level data, we use the units of ug g^{-1} h^{-1} and we have assigned endpoints so ranges do not overlap. Quantitatively, our branch-level isoprene emission rate ranges correspond very closely to the leaf-level ranges of Guenther et al. (1994). In the following discussion we refer to four branch-level emission rate categories (ug g^{-1} h^{-1}): (1) negligible or below detection limit (BDL), <1; (2) low, 1-10; (3) moderate, 10-25; and (4) high, 25-70.

1.3.2.1 Isoprene Emission Rates Within Families

As seen from Table 1-1, all members sampled in this study within 19 families had isoprene emissions below the detection limit (BDL). These results are consistent with the literature cited in Benjamin et al. (1996) for nine families, including Anacardiaceae (cashew), Bignoniaceae (bignonia), Caprifoliaceae (honeysuckle), Compositae (composite), Cupressaceae (cypress), Juglandaceae (walnut), Lamiaceae (mint), Oleaceae (olive), Rosaceae (rose) and Taxodiaceae (bald cypress), all of which may be regarded as containing mostly if not all negligible-emitters. These results are important because the Rosaceae and Compositae are very large families, well-represented in agriculture, native plant communities and urban landscapes.

Table 1-1. Plant families where all members sampled in the present study had mean adjusted isoprene emission rate measurements (ug g^{-1} h^{-1}) below detection limits (BDL).

Scientific Name	Common Name	Number of Enclosure Runs
Anacardiaceae		
Pistacia chinensis	Chinese Pistache	1
Betulaceae		
Betula nigra	River Birch	3
Betula papyrifera	Paper Birch	1
Bignoniaceae		
Macfadyena unguis-cati	Cat's Claw Vine	3
Caprifoliaceae		
Viburnum trilobum	American Highbush Cranberry	2
Chenopodiaceae		
Atriplex polycarpa	Saltbush	1
Compositae		
Artemisia ludoviciana	Silver Wormwood	2
Baccharis pilularis	Coyote Brush	2
Chrysothamnus nauseosus	Rubber Rabbitbrush	2
Euryops pectinatus	Euryops Daisy	3
Cornaceae		
Cornus stolonifera	Redtwig Dogwood	3
Cupressaceae		
x Cupressocyparis leylandii	Leyland Cypress	2
Euphorbiaceae		
Sapium sebiferum	Chinese Tallow Tree	3
Hippocastanaceae		
Aesculus californica	California Buckeye	2
Juglandaceae		
Carya illinoensis	Pecan	2
Lamiaceae		
Rosemarinus officinalis	Rosemary	2
Salvia greggii	Autumn Sage	2

Table 1-1. (Continued)

Scientific Name	Common Name	Number of Enclosure Runs
Malvaceae		
Gossypium barbadense	Cotton 'Pima'	1
Gossypium hirsutum	Cotton 'Maxxa'	1
Hibiscus rosa-sinensis	Hibiscus	1
Oleaceae		
Fraxinus velutina 'Modesto'	Modesto Ash	1
Syringa vulgaris	Common Lilac	2
Pinaceae		
Abies concolor	White Fir	1
Picea pungens glauca	Colorado Blue Spruce	1
Proteaceae		
Grevillea robusta	Silk Oak	2
Rosaceae		
Rosa hybrida	Rose	2
Steruliaceae		
Brachychiton populneus	Bottle Tree	2
Taxaceae		
Torreya californica	California Nutmeg	1
Taxodiaceae		
Sequoiaodendron giganteum	Giant Sequoia	2
Sequoia sempervirens	Coast Redwood	1
Verbenaceae		
Latana camara	Lantana	1
Vitex agnus-castus	Chaste Tree	1
Zygophyllaceae		
Larrea tridentata	Creosote Bush	2

Additional families not reported in Benjamin et al. (1996) but sampled in this study and found to contain only negligible emitters included Betulaceae (birch), Cornaceae (dogwoods), Hippocastanaceae (buckeye), Malvaceae (mallow), Sterculiaceae (sterculia), Taxaceae (yew), Verbenaceae (verbena), and Zygophyllaceae (caltrop). Deciduous and broadleaf evergreen plants within the Anacardiaceae, Compositae and Oleaceae families sampled in this study had isoprene emission rates which were below detection limits (Table 1-1), including *Pistacia chinensis* (Chinese pistache), *Baccharis pilularis* (coyotebrush), *Chrysothamnus nauseosus* (rubber rabbitbrush), *Euryops pectinatus* (euryops daisy), *Fraxinus velutina 'Modesto'* (Modesto ash), and *Syringa vulgaris* (common lilac). Our results are consistent with the reported isoprene emissions of other plants within these families (Zimmerman 1979, Winer et al. 1983, Winer et al. 1989, Corchnoy et al. 1992, Arey et al. 1995).

The Betulaceae (birch) family contains *Betula* and *Carpinus*, genera with species reported to have negligible emissions of isoprene (Lamb et al. 1985, 1987) and *Betula nigra* (river birch) and *Betula papyrifera* (paper birch) sampled in this study were also found to have negligible isoprene emission rates.

Certain families appear to contain predominately negligible emitters, but with some moderate or high emitters, as seen in Table 1-2. Although most members of Leguminosae (legume) family which have been studied have reported isoprene emission rates BDL, exceptions exist, such as *Robinia pseudoacacia* (black locust) (Lamb et al. 1983, Winer et al. 1983). All of the legumes sampled in the present study had emission rates BDL except *Sophora secundiflora* (Texas mountain laurel) and *Spartium junceum* (Spanish broom), for which we found values of 34 and 21 ug g^{-1} h^{-1}, respectively.

All the legumes of the Caesalpiniodeae subfamily sampled in the present study, *Caesalpinia gillessii*, the *Cassia* species, *Ceratonia siliqua*, and *Cercidium floridum*, did not emit detectable quantities of isoprene.

The Mimosoideae subfamily of the Leguminosae contains the *Acacia* species and *Prosopis alba* 'Colorado' sampled in the present study, which were found to be negligible isoprene emitters.

Table 1-2. Summary of plants from urban and natural environments of California sampled in the present study where at least one species of the family had a mean adjusted isoprene emission rate (ug g^{-1} h^{-1}) above the detection limit.

Scientific Name	Common Name	Isoprene Emission Rate	Number of Enclosure Runs
Fagaceae			
Quercus chrysolepis	Canyon Live Oak	19	3
Quercus douglasii	Blue Oak[1]	27	3
Quercus kelloggii	California Black Oak[1]	54	2
Quercus lobata	Valley Oak[1]	23	3
Quercus palustris	Pin Oak	27	1
Quercus suber	Cork Oak	BDL	1
Hamamelidaceae			
Liquidambar styraciflua	Sweetgum[1]	26	6
Leguminosae			
Acacia aneura	Mulga	BDL	1
Acacia melanoxylon	Blackwood Acacia	BDL	3
Caesalpinia gilliesii	Bird of Paradise Bush	BDL	2
Cassia artemisiodes	Feathery Cassia	BDL	2
Cassia nemophila	Desert Cassia	BDL	2
Ceratonia siliqua	Carob	BDL	1
Cercidium floridum	Blue Palo Verde	BDL	2
Cytisus spachinanus	Broom	BDL	1
Lysiloma thornberi	Feather Bush	BDL	2
Prosopis alba 'Colorado'	Colorado Mesquite	BDL	1
Sophora secundiflora	Texas Mountain Laurel	34	2
Spartium junceum	Spanish Broom	21	2
Moraceae			
Morus alba 'Fruitless'	Fruitless Mulberry	BDL	2
Ficus carica	Edible Fig	18	1
Myrtaceae			
Eucalyptus camaldulensis 'C2'	Red Gum	28	4
Eucalyptus grandis 'GCT'	Rose Gum	21	4
Eucalyptus polyanthemos	Silver Dollar Gum	10	2
Palmae			
Syagrus romanzoffiana	Queen Palm	BDL	2
Washingtonia robusta	Mexican Fan Palm	14	1

Table 1-2. (Continued)

Scientific Name	Common Name	Isoprene Emission Rate	Number of Enclosure Runs
Salicaceae			
Populus alba	White Poplar	25	2
Populus euramerica 'R111'	Hybrid Poplar	31	2
Populus euramerica 'R112'	Hybrid Poplar	28	2
Populus fremontii	Western Cottonwood	43	2
Populus nigra italica	Lombardy Poplar	36	3

[1]The last measurements of the season were excluded from the mean because of senescence of leaves.

Certain families seem to contain mostly species with high emissions rates, such as the Salicaceae (willows and poplars) (Zimmerman 1979, Winer et al. 1983, Evans 1982). The poplars sampled in the present study, *Populus alba* (white poplar), *P. euramerica* 'R111' and 'R112' (hybrid poplars), *P. fremontii* (western cottonwood), a California native, and *P. nigra italica* (lombardy poplar) were clearly high isoprene emitters with mean emission rates of 25, 31, 28, 43, and 36 ug g^{-1} h^{-1}, respectively.

The Myrtaceae (myrtle) family also contains several genera with high isoprene emission rates, such as *Eucalyptus*, *Callistemon*, and *Myrtus* (Evans et al. 1982, Winer et al., 1983). The Eucalyptus species sampled in this study, *E. polyanthemos* (silver dollar gum), *E. grandis* 'GCT' (rose gum), and *E. camaldulensis* 'C2' (red gum) had moderate to high emission rates of 10, 21, and 28 ug g^{-1} h^{-1}, respectively.

1.3.2.2 Isoprene Emission Rates Within Genera

Genera which included two or more moderate-to-high emitting species sampled in this study included *Eucalyptus* (eucalyptus or gum trees) and *Populus* (poplar and aspen). The three eucalyptus species measured in this study had emission rates ranging from 10-28 ug g^{-1} h^{-1}. The four poplar species were high emitters, ranging from 25-43 ug g^{-1} h^{-1}. These results are consistent with previous reports (Evans et al. 1982, Winer et al. 1983, Guenther et al. 1994)

Isoprene emission rates were consistent within most genera with the chief exception of *Quercus* (oak), a frequently occurring genus in native stands as well as in urban landscapes in California. For example, of the *Quercus* reported here, mean emission rates of isoprene emission ranged from negligible for *Q. suber* (cork oak) to moderate (19 ug g^{-1} h^{-1}) for *Q. chrysolepis* (canyon live oak) and high (27 ug g^{-1} h^{-1}) for *Q. palustris* (pin oak) to very high (54 ug g^{-1} h^{-1}) for *Q. kelloggii* (California black oak). These observations are consistent with the variability observed within the *Quercus* genus by other researchers.

1.3.3 Comparison of Results of the Present Study to Taxonomic Predictions

As shown in Table 1-3, the data obtained in the present study may be compared to specific emission rate predictions for plant species made on the basis of taxonomy in Table 3 of Benjamin et al. (1996). For *Euryops pectinatus* (Compositae family) the predicted isoprene emission rate was 0, assigned on the basis of family, and agreed with results of this study. Based on the literature and results from the present study, the family Compositae appears to contain plants with negligible isoprene emission rates.

For *Ceratonia siliqua* (Leguminosae) the predicted emission rate was 4 ug g^{-1} h^{-1} based on an average of species within the legume family while our measured value was BDL. Within the Leguminosae family a mean of all genera is probably unsatisfactory, although BDL is well within the factor or ten criterion established by Benjamin et al. (1996), because legumes of most genera appear to have negligible isoprene emission rates with exception of certain subfamilies, such as the Papilionoideae (= Faboideae) (Rasmussen and Khalil 1997). The predicted isoprene emission rate for *Sophora japonica* of 4 (Benjamin et al. 1996) should probably be replaced with a predicted rate of about 20, based on a mean of *Robinia pseudoacacia* (Lamb et al., 1983), and *Spartium junceum* and *Sophora secundiflora* measured in this study.

For *Acacia melanoxylon*, *Fraxinus velutina* 'Modesto' and *Morus alba* 'Fruitless', the predicted isoprene emission rates (Benjamin et al. 1996) were 0, assigned on the basis of genus and confirmed by this study. For *Ficus carica* (edible fig), the predicted isoprene emission rate and the rate found in this study were 27 and 18 ug g^{-1} h^{-1}, respectively, in good agreement. For unmeasured *Quercus* species, such as *Q. suber* and

Table 1-3. Mean plant isoprene emission rates (ug g^{-1} h^{-1}) from the present study compared to the specific rates predicted on the basis of plant taxonomic relationships (found in Table 3 of Benjamin et al. (1996)).

Scientific Name	Common Name	Present Study	Predicted Rate	Ratio[1] (Pres. Study/ Predicted)
Anacardiaceae				
Pistachia chinensis	Chinese Pistache	BDL	0.0	1
Compositae				
Baccharis pilularis	Coyote Brush	BDL	0.0	1
Euryops pectinatus	Euryops Daisy	BDL	0.0	1
Fagaceae				
Quercus chrysolepis	Canyon Live Oak	19	24.8	0.8
Quercus kelloggii	California Black Oak	54	24.8	2.2
Quercus suber	Cork Oak	BDL	24.8	N/A
Leguminosae				
Acacia melanoxylon	Blackwood Acacia	BDL	0.0	1
Ceratonia siliqua	Carob	BDL	4.3	N/A
Cercidium floridum	Blue Palo Verde	BDL	4.3	N/A
Moraceae				
Ficus carica	Edible Fig	18	27.0	0.6
Morus alba 'Fruitless'	Fruitless Mulberry	BDL	0.0	1
Myrtaceae				
Eucalyptus camaldulensis	Red Gum	28	32.5	0.9
Eucalyptus polyanthemos	Silver Dollar Gum	10	32.5	0.3
Oleaceae				
Fraxinus velutina 'Modesto'	Modesto Ash	BDL	0.0	1
Rosaceae				
Rosa sp.	Rose	BDL	0.0	1
Palmae				
Washingtonia robusta	Mexican Fan Palm	14	9.9	1.4
Pinaceae				
Abies concolor	White Fir	BDL	1.4	N/A
Taxodiaceae				
Sequoia sempervirens	Coast Redwood	BDL	0.0	1
Sequoiadendron giganteum	Giant Sequoia	BDL	0.0	1

[1] Where emissions were BDL in the present study and a zero was assigned by Benjamin et al., the ratio is given as 1 indicating agreement. N/A = Not Applicable.

Q. chrysolepis, an isoprene emission rate of 25 was proposed by Benjamin et al. (1996), calculated as the mean of reported *Quercus* species. However, for the *Quercus*, a mean of the genus is probably not satisfactory because of the range in reported emission rates for species within that genus. For the *Quercus* species reported here (see Table 1-2), isoprene emission rates ranged from BDL for *Q. suber* (cork oak) to 54 ug g^{-1} h^{-1} for *Q. kelloggii* (California black oak).

In summary, for 13 of 19 "predictions" found in Benjamin et al. (1996) (Table 1-3) isoprene emission rates measured in the present study were within ±50% of the predicted rate. Nine of the nine species expected to have zero isoprene emissions were measured as BDL (and the ratio of the predicted to the measured rate was considered to be one). By considering subfamily taxonomy of the Leguminosae, the predictive accuracy (±50%) rises to 15 of 19. In addition, if oaks are not considered, since *Quercus* is so variable, the proportion rises to 14 of 16. For the remaining two species, *Eucalyptus polyanthemos* and *Abies concolor*, it would be of interest to further test agreement with the genus-based prediction of Benjamin et al. (1996).

No predictions were made in Benjamin et al. (1996) for many other species measured within this study. However, species measured in this study may be compared with mean values for families and genera as seen in Section 3.5.2. The family mean for Fagaceae and the genus mean for *Quercus* (oaks) were each 25 ug g^{-1} h^{-1} based on data from this study compared to 24.8 ug g^{-1} h^{-1} in Benjamin et al. (1996), excellent agreement. For the Hamamelidaceae family and the *Liquidambar* genus, the means were 26 ug g^{-1} h^{-1} based on the present study compared to 18.9 calculated from the data in Benjamin et al. (1996), very good agreement. For the Salicaceae family, the family mean calculated from the data found in Benjamin et al. (1996) was 47.2 and the genus mean for *Populus* (poplar) species contained within this family was almost identical, 44 ug g^{-1} h^{-1}. The mean of *Populus* species measured in this study was 33 ug g^{-1} h^{-1} and individual poplar species were within ±35% of this value.

The taxonomic method is thus seen to provide a useful framework for organizing and understanding isoprene emission rates, especially for families and genera containing few if any anomalous species. The method is seen to work well in many cases but with exceptions (Seufert et al. 1997) and the most troublesome genus for taxonomic

predictions at this time is *Quercus* (oaks) (Geron et al. 1995, Seufert et al. 1997) and further characterization of this genus is recommended. Oaks are very important for BHC emission inventories in California because of their wide distribution in both urban and natural settings, and high leafmass. In this study we have reported isoprene emission rates for one exotic species found in urban settings and four additional native species.

Data from the present study represent a significant expansion of the published isoprene emission rate database, and will be useful for building BHC emissions inventories in California, as well as other regions where these plants are found, including other Mediterranean climate types of the world, and the arid southwestern U.S. where several of the species investigated in this study may be found.

1.4 Leafmass and Leaf Area Relationships Determined from Sampling and Whole-Tree Harvest: Implications for Leafmass Estimation Methods

Accurate leafmass determination is a critical factor in estimating the magnitude of biogenic hydrocarbon emissions from green plants. As discussed earlier, emission rates, expressed as ug BHC 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 BHC 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. Foliar estimates may be obtained through three types of methods (Campbell and Norman 1989): (1) use of allometric equations, (2) remote sensing, including light interception and photography; or (3) direct measurement methods, including the volumetric method.

1.4.1 Evaluation of the Volumetric Method for Leafmass Estimation Through Whole-Tree Harvest

The principal goals of the present study were to evaluate the precision and accuracy of a volumetric approach, using geometric solids to compare estimated

leafmasses to measured whole tree leafmasses; and to compare leafmass constants derived from selective sampling to whole-tree values. A related goal was to expand the very limited database of experimentally measured leafmass constants. Another goal of the study was to develop leafmass-leaf area relationships, which may then be used to bridge between leafmass-based and leaf area-based BHC emission rate and inventory data.

In both years of this study, trees were felled with a chain saw and all leaves removed for drying and weighing. In 1996, painstaking leaf removal was accomplished by research staff, and each tree required as much as one week for leaf removal with a crew of four. In 1997, the inmates from the county correctional facility provided approximately 800 hours of labor for leaf removal. Given the high labor requirements for leaf removal, it is not surprising very few similar datasets have been generated for urban trees.

Using height and radius data for each tree crown, volumes for five geometric solids approximating tree shapes (McPherson and Rowntree 1988) were calculated. Calculated whole-tree leafmasses were obtained by multiplying the respective volumes by a leafmass constant found in the literature. An experimentally determined leafmass constant was used if available (Miller and Winer 1984, Nowak 1991,1997); otherwise, a value for structural class, e.g. broadleaf deciduous, was used. Leafmasses were also calculated using the allometric equations of developed by Nowak (1996).

Total measured leafmass for trees in this study (367 kg) may be compared to estimates of total leafmass derived from the geometric solids, which ranged from 167 kg (cone) to 501 kg (cylinder). For the preferred solid (selected in the field), the total leafmass estimate of 436 kg was a factor of 1.18 greater than the measured. Thus, two of the solids (sphere and vertical ellipsoid) and the preferred solid combination gave estimates of total leafmass for all trees within 20% of the measured value.

For individual trees, leafmasses calculated by the above approaches were compared to the experimentally measured whole tree leafmasses. For trees harvested in 1996, field observation leading to selection of a preferred solid to model the crown resulted in a leafmass estimate within $\pm$30% of the measured value for six of the nine trees. For several trees, leafmass estimates varied greatly depending on the solid selected,

and tended to overestimate leafmass. The overestimation of leafmass has implications for field studies where dimensions of large trees are measured and volumes calculated.

For trees harvested in 1997, the paraboloid solid gave the leafmass estimate closest to the experimentally measured leafmass for two of the 12 trees and was second-best for four others. The cone solid gave the closest estimate for five of the 12 trees and the cylinder solid was closest for four of the 12, including four of the five largest shade trees in the study. For these trees, the field choice for the preferred solid led to estimated leafmasses within ±45% of the measured leafmass for four of the five trees.

The allometric equations employed from the literature underestimated leafmasses for most of the trees in this study. These equations were developed using medium-sized trees of six deciduous species found in northern temperate climates, which may have had thinner leaves of relatively less mass per unit area than several species harvested in this study (Nowak 1997).

1.4.2 Experimental Determination of Leafmass Constants

For the nine trees harvested in 1996, whole-plant leafmass constants (g m^{-3}) based on the entire tree leafmass and volume were calculated. In similar fashion, leafmass constants were calculated for trees harvested in 1997 and compared to experimentally-determined literature values where available.

Based upon the present work, literature values for experimentally-determined leafmass constants appear to be reasonably accurate for the species tested. However, a larger dataset including additional tree species is clearly needed to more accurately quantify leafmasses of urban trees and to better understand structural class values.

1.4.3 Implications for BHC Emission Inventories

In urban areas with subtropical climates, including many cities of California, deciduous tree species are mingled with broadleaf evergreen species. For the urban trees in this study, mean leafmasses per unit projected crown area for deciduous and broadleaf evergreen trees were 1.7 and 5.0 times greater, respectively, than leafmass per unit ground area of eastern deciduous forests, presumably due to irrigation and fertilization of urban trees.

Biogenic emission inventories for urban areas require leafmass estimation for plantings of large variability, including a wide range of ages and species of widely varying forms. A volumetric approach using previously established leafmass 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. A volumetric approach may not precisely account for clumping of tree foliage and the change in leafmass 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. Finally, a further advantage of a volumetric method is its applicability to shrubs.

Leaf area and leaf area index provide tools for describing crowns of trees and especially for describing plant canopies. Leaf area index is more likely to be measurable by remote sensing methods than are leafmasses. Indirect measurement methods using remote sensing technologies may be especially useful for the natural areas of California if problems associated with heterogeneity can be understood and overcome. Leaf area to leafmass conversions provide a method for deriving leafmasses where leaf areas are known, and for linking data generated with the volumetric approach, which has been extensively used in urban areas of California, to the corpus of literature describing forests of other regions in terms of leaf area, leaf area index, specific leaf area and specific leaf weight.

1.5 Field-Survey Assessment of the GAP GIS Database in Natural Vegetation Areas of San Diego County

Developing reliable biogenic emission inventories depends in part on quantifying the spatial distribution and species composition of vegetation. Although several BHC emissions inventories varying in comprehensiveness have been reported for the SoCAB and the San Joaquin Valley Air Basin, a validated spatial distribution and species composition inventory of vegetation has not been established for urban and natural areas of the San Diego County airshed, which was also an important part of the SCOS97

domain. At the request of ARB staff, a portion of the present project was redirected to an investigation of the composition and dominance of natural vegetation in San Diego County, with an emphasis on obtaining data to evaluate vegetation databases in this region.

A potential source of information concerning vegetation in the natural areas of San Diego County is the Gap Analysis Program (GAP) database, a geographical information system coordinated by the National Biological Service to identify the distribution and management status of plant species. 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). Compared to other area-based vegetation databases, the advantages of the GAP database include providing a species-based description of vegetation in terms of relative percent cover, covering a large geographic extent encompassing all of California, and existing in a standard, vector GIS format (ARC/INFO), which allows for easy manipulation and analysis on a microcomputer through the use of GIS software, spreadsheets, and database programs.

Assessment of the agreement of the GAP database with field survey observations is a prerequisite to its use in developing species-based BHC emissions inventories for California. The assessment protocol developed in the present study was designed to assess the accuracy of the GAP database in predicting the distribution and identity of plant species in a given location, particularly BHC-emitting species, and in providing a quantitative description of plant species assemblages. The present research focused on obtaining "ground-truth" data through field vegetation surveys at selected sites.

1.5.1 Assessment Methodology

The initial protocol for the present study was based on the recommendations of Stoms et al. (1994), with further revisions after trial surveys, to produce a polygon-based survey protocol.

Several considerations were used in selecting polygons for potential inclusion in the present study, including use of an index estimating isoprene or monoterpene

emissions on a relative basis, representativeness (polygons were selected to provide roughly equal numbers with woodland/forest vegetation and scrub/chaparral vegetation), and feasibility. Based on these criteria and the time and resources available for this research, eight polygons were selected for the present study (see Figure 1-1). Four polygons consisted primarily of woodland/forest vegetation, and four polygons consisted primarily of chaparral/scrub vegetation.

Sample elements within four polygons were randomly selected while the other four polygons, where large areas were physically or legally inaccessible, sample elements were chosen from within the few accessible areas. The survey protocol was executed within each sample element. Data were gathered on plant species identity, crown height, and areal coverage in field surveys conducted from September, 1997 to April, 1998. Collected data were then compared to the data provided by the GAP database.

1.5.2 Results

The GAP polygon attributes investigated were species composition and abundance, crown closure, and plant community classification within the polygons. Within surveyed polygons, the ten most abundant species accounted for over 90% of the relative cover of each polygon and co-dominants (the plant species predicted by the GAP database for individual polygons) accounted for 64-85% of the relative cover of the polygons. The observed relative cover of the co-dominants often substantially exceeded the predicted values, resulting in an uneven representation among GAP-predicted species. Of the species listed by the GAP database in the surveyed polygons, 59% of these co-dominants were observed in the field surveys in sufficient abundance to suggest agreement between field data and the GAP database. For the woodland/forest polygons and the chaparral/scrub polygons, there was 61% and 57% agreement between the field surveys and the GAP database, respectively. There were several instances where co-dominants for a polygon were not observed in our field observations, although in some cases, a taxonomically similar species was found instead. Conversely, there were numerous species within the polygons observed in high enough abundance to warrant possible co-dominant designation. Often these species were co-dominants in adjacent polygons. Total crown closure as predicted by the GAP database generally matched the

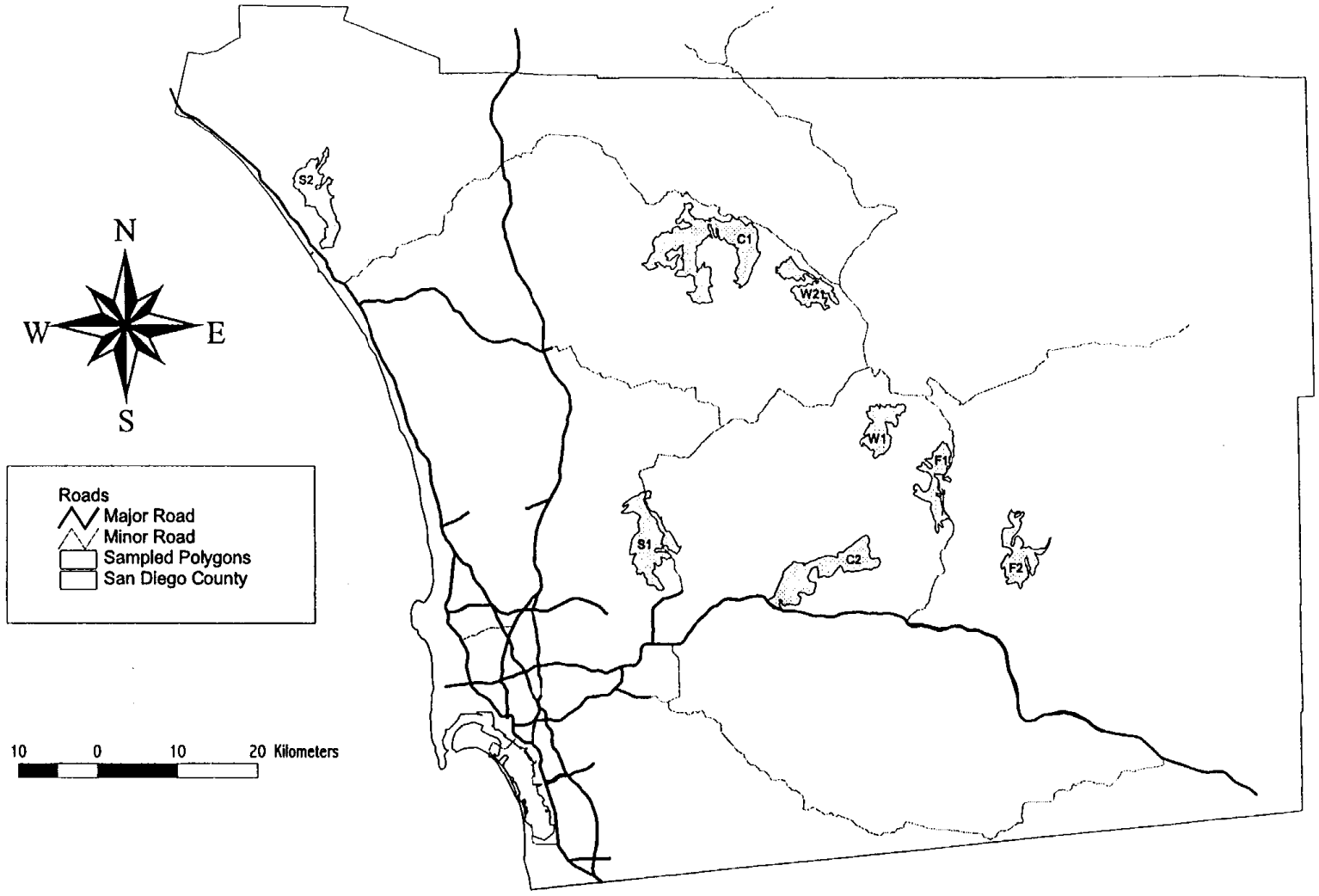

Figure 1-1. GAP polygons surveyed in San Diego County for plant species composition and dominance.

field observations in the present study. This correspondence between predictions and observations can be attributed to the relative ease of accurately estimating crown closure from aerial photographs or remote sensing. The community classification of each sample element within a polygon often differed from the GAP database community classification assigned for the entire polygon, revealing a microscale heterogeneity not captured by the GAP database.

In addition to the evaluation of the GAP attributes, species crown volumes within the surveyed polygons were also determined. For all the polygons, the ten most abundant species observed in the field survey were responsible for virtually the entire crown volume. In the woodland/forest polygons, GAP co-dominants accounted for 64-96% of the crown volume. In the chaparral/scrub polygons, GAP co-dominants accounted for 55-75% of the crown volume.

1.5.3 Utility of the GAP Database in Developing BHC Inventories

The GAP database provides potentially valuable information for developing BHC emissions inventories. Compared to previous databases, the GAP database is species-specific and has a higher spatial resolution. As noted earlier, the four classes of information predicted by the GAP database useful for the development of a BHC emissions inventory are crown closure of an assemblage, assemblage cover, species composition within an assemblage, and abundance of species within an assemblage.

Crown closure information predicted by the GAP database was consistent with our field observations. Although the crown closure data were generally accurate, the classes describing crown closure were broad: 25-39%, 40-59%, and 60-100%, respectively. For the three crown closure classes cited above, using mean values of 32%, 50%, and 80% would result in maximum errors of ± 22%, ± 20%, and ± 25%, respectively.

Because the GAP database does not delineate the boundaries of primary versus secondary assemblages within a polygon, the assemblage cover could not be validated from this study. Like crown closure, percent assemblage cover was determined in the GAP database from aerial photographs and satellite imagery and might be expected to have the same degree of accuracy as the crown closure data. For the nine assemblage

cover classes (10-20%, 20-30%, 30-40%, 40-50%, 50-60%, 60-70%, 70-80%, 80-90%, and 90-100%), using the mean values for each class would result in a range of errors from ± 33% for the 10-20% assemblage cover class to ± 5% for the 90-100% cover class.

The species abundance predicted by the GAP database accounted for a large portion of the plant material in terms of both relative cover. However, the observed abundance of individual GAP co-dominants within a polygon was not evenly distributed among the listed species in the GAP database, because one or two co-dominants occupied the majority of the assemblage and the polygon. The GAP database provides information allowing the determination of a possible lower limit to the abundance for a co-dominant, but not a possible upper limit. Consequently, a precise characterization of each assemblage by relative cover cannot be performed without additional data from field observations or the literature. Because co-dominants in the polygons surveyed for the present study accounted for only 60-75% of the relative cover, the remaining 25-40% of the relative cover was attributable to species whose identity cannot be determined from the GAP database.

Biomass as measured by crown volume cannot be determined solely from data contained within the GAP database. Auxiliary data providing average crown height of a plant species, or plant crown volume on an area basis, are required for the GAP database to be useful in determining biomass for development of BHC emissions inventories. Auxiliary data may come from the literature or from field data as collected in the present study.

1.6 Measurements of Isoprene and its Atmospheric Reaction Products Methacrolein and Methyl Vinyl Ketone in Ambient Air

Anthropogenic hydrocarbons are measured on a routine basis in the SoCAB, but few ambient measurements of biogenic hydrocarbons or their atmospheric reaction products have been conducted in the basin. Biogenic hydrocarbons are generally highly reactive in the atmosphere (Carter 1994; Atkinson 1997) and thus can play an important role in tropospheric chemistry (Trainer et al. 1987, Chamedies et al. 1988). Because of their rapid atmospheric reactions, however, the ambient concentrations of BHC are generally low and additional measurements of their atmospheric reaction products are

necessary to understand the full impact of BHC on photochemical processes such as ambient ozone formation (Montzka et al. 1993, 1995). For this reason, measurements of isoprene, the BHC emitted in greatest quantity by vegetation (Guenther et al. 1995), and its principal reaction products, methacrolein (MACR) and methyl vinyl ketone (MVK), were undertaken during the SCOS97 campaign.

The SCOS97 campaign took place during June 16 – October 15, 1997, with six intensive sampling periods and a total of 13 days of intensive sampling. Sampling for biogenic VOC was generally conducted simultaneously at three sites chosen as a mid-basin receptor site for anthropogenic VOC (Azusa), a down-wind receptor site (Banning) and a high elevation site impacted by biogenic VOC (Pine Mountain or Mount Baldy). Solid adsorbent tubes with mass flow controllers were utilized for VOC sample collection and concentration. After sample collection, the adsorbent tubes were cooled and transported to the laboratory where they were analyzed by gas chromatography with mass selective detection (GC-MSD) using a GC-MSD equipped with an Entech thermal desorption/ preconcentrator unit.

Results for ambient diurnal profiles of isoprene and its atmospheric reaction products, methacrolein and methyl vinyl ketone, for the twelve SCOS97 intensive sampling days between August 4 and October 4 are given in this report.

1.6.1 Sampling Sites and Sampling Times

The six intensive sampling periods and sampling sites are presented in Table 1-4.

Table 1-4. Intensive sampling periods and sampling sites.

Sampling Period	Sampling Site
July 14	Azusa, Banning
August 4 - 6	Azusa, Banning, Pine Mtn.
August 22 - 23	Azusa, Banning, LA North Main
September 4 - 6,7	Azusa, Banning, Pine Mtn.
September 28 - 29	Azusa, Mt. Baldy
October 3 - 4	Azusa, Banning, Mt. Baldy

The sampling intervals were 3 hours during daytime and 7-9 hours during nighttime. Typically the sampling periods at Azusa, Pine Mtn., and Mt. Baldy were 0300-0600, 0600-0900, 0900-1200, 1300-1600, 1600-2000, 2000-0300. VOCs were measured at Azusa during the four daytime sampling periods by other investigators participating in SCOS97. At Banning the sampling periods were 0300-0600, 0600-0900, 0900-1200, 1200-1500, 1500-1800, 1800-0300, chosen to coincide with the schedule of the Photochemical Assessment Monitoring Station (PAMS) VOC sampling conducted by the South Coast Air Quality Management District (SCAQMD) at this site. During August 22 - 23 all sites followed the Banning sampling protocol. During September 4 - 7 nighttime sampling was performed more frequently at Azusa and Pine Mtn. with 3 - 4 hour sampling periods (1700-2000, 2000-2400, 0000-0300, 0300-0600).

On August 1, 1997 isoprene sampling was conducted at UC Riverside, Air Pollution Research Center (APRC) between 1430-1815 to allow an intercomparison between the APRC adsorbent tube sampling and canister sampling. Carbotrap tubes were used to collect 5 simultaneous samples for analysis and quantification of isoprene at APRC, as detailed above. Two canister samples (using pre-cleaned canisters supplied by Desert Research Institute and Biospheric Research Corp.) were co-located with the APRC adsorbent samplers. The canisters were mailed to Desert Research Institute and Biospheric Research Corp. for analysis. A 6.3% relative standard deviation in the measured isoprene concentration was obtained for these samples.

1.6.2 Results and Discussion

Examples of isoprene concentrations at 3 sites, during Intensive 4 (Sept. 4-7, 1997), are shown in Figure 1-2. The highest isoprene mixing ratios were found in samples from the two mountain sites, Pine Mtn. and Mt. Baldy. Both were late afternoon/early evening samples. The highest values observed at Pine Mtn. And Mt. Baldy were 2.2 ppbv (August 4) and 2.3 ppbv (September 28) respectively. At Azusa the highest mixing ratios for isoprene were generally in the range 0.5 – 0.8 ppbv. Thus, the highest values at the mountain sites were three to four times higher than the maximum mixing ratios observed at the urban valley site. The maximum isoprene values at the Banning site in the eastern portion of the air basin were 0.2 – 0.3 ppbv, consistently lower than at the other sites.

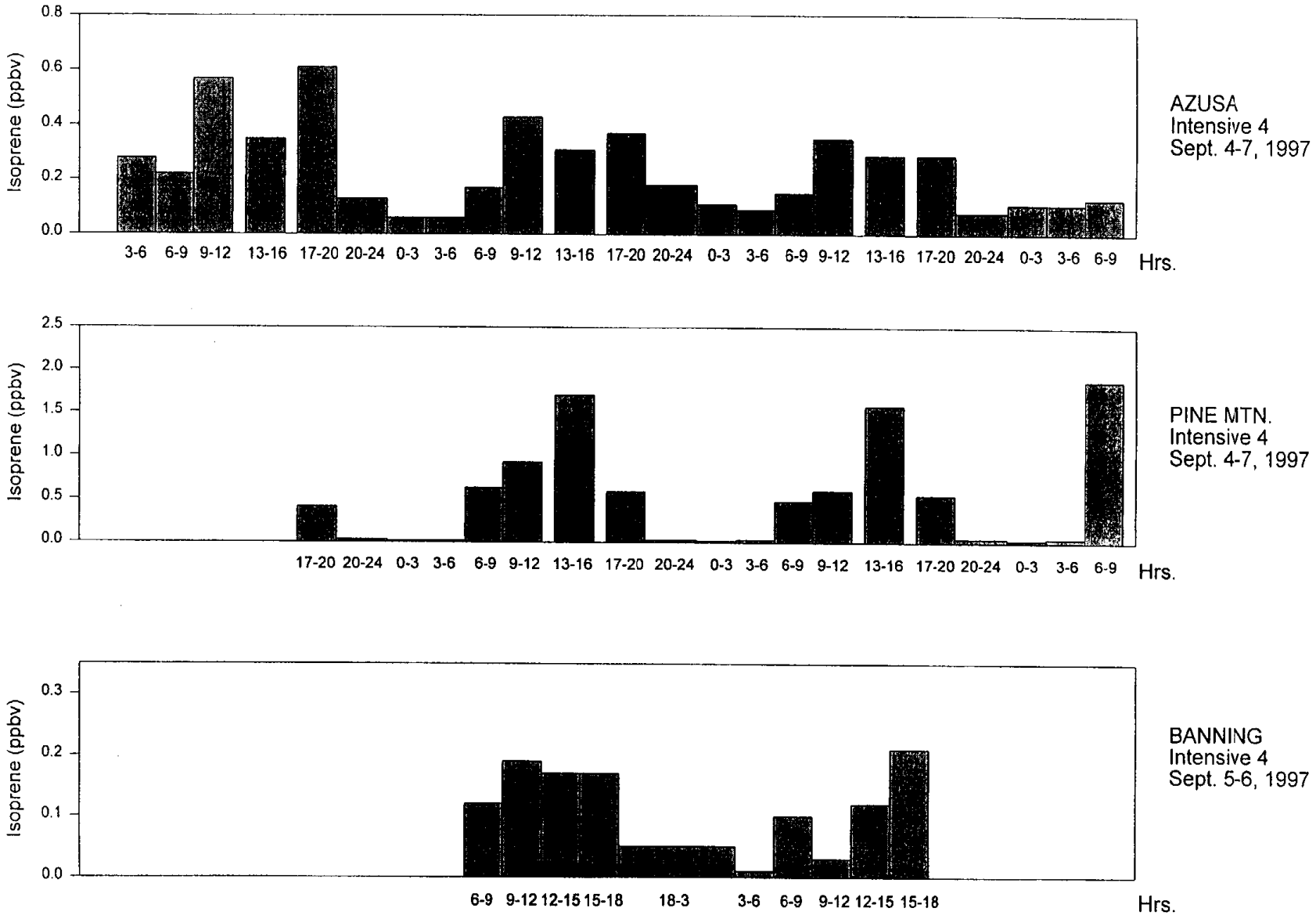

Figure 1-2. Isoprene values during Intensive 4, Sept. 4-7, 1997.

Consistent with light-dependent biogenic sources, the lowest values for isoprene were usually measured during nighttime. The diurnal variation of isoprene at the different sites generally followed a similar pattern: higher mixing ratios during the daylight hours, lower during nighttime. However, the difference between day and night was most apparent at the mountain sites, where the daytime values ranged between 0.4 – 2.3 ppbv and the nighttime values did not exceed 0.1 ppbv. At Azusa and Banning the day-night variation was much less pronounced and sampling at the Los Angeles North Main site gave low isoprene concentrations with little decrease during the single night sampled.

For methacrolein and methyl vinyl ketone the highest mixing ratios were observed at Azusa. On August 22–23 for the 1800–0300 sampling interval the methacrolein mixing ratio was 3.3 ppbv, and on September 28 between 0300–0600 the methyl vinyl ketone mixing ratio was 2.3 ppbv. At Banning on August 22–23 at 1800–0300 mixing ratios for both MACR and MVK were high, being 2.4 ppbv and 2.9 ppbv, respectively. At Pine Mtn. and Mt. Baldy the highest values for MACR were measured in the afternoon/early evening reaching 1.1 ppbv and 0.5 ppbv, respectively, and the highest values for MVK were 1.6 ppbv and 1.0 ppbv, respectively.

At the mountain sites during the daytime, the isoprene values generally exceeded the MACR and MVK concentrations, while during the nighttime the isoprene values were <0.1 ppbv and the combined MACR and MVK levels reached 1.7 ppbv. The isoprene, MACR and MVK concentrations at Pine Mtn. for the Sept. 4-7 intensive are shown in Figure 1-3. Note that the isoprene begins to increase early in the morning (0600-0900) with increases in MACR and MVK lagging behind temporally. The highest MACR and MVK levels observed at the mountain sites occurred at Pine Mtn. during Intensives 2 and 4 when the MVK + MACR reached 2.5 ppbv. The ratio of MVK/MACR during the daytime was relatively constant at the mountain sites, with average values for this ratio ranging from 1.6 to 2.2. A ratio of 1.5 for MVK/MACR would be expected from the OH radical-initiated reaction of isoprene if negligible further reaction of MVK and MACR occurred, while at steady-state this ratio would be expected to increase to 2.4 (Atkinson, 1997). Thus the daytime MVK/MACR ratio at the mountain sites is consistent with the source of MACR and MVK being photooxidation of isoprene (Montzka et al. 1993, 1995).

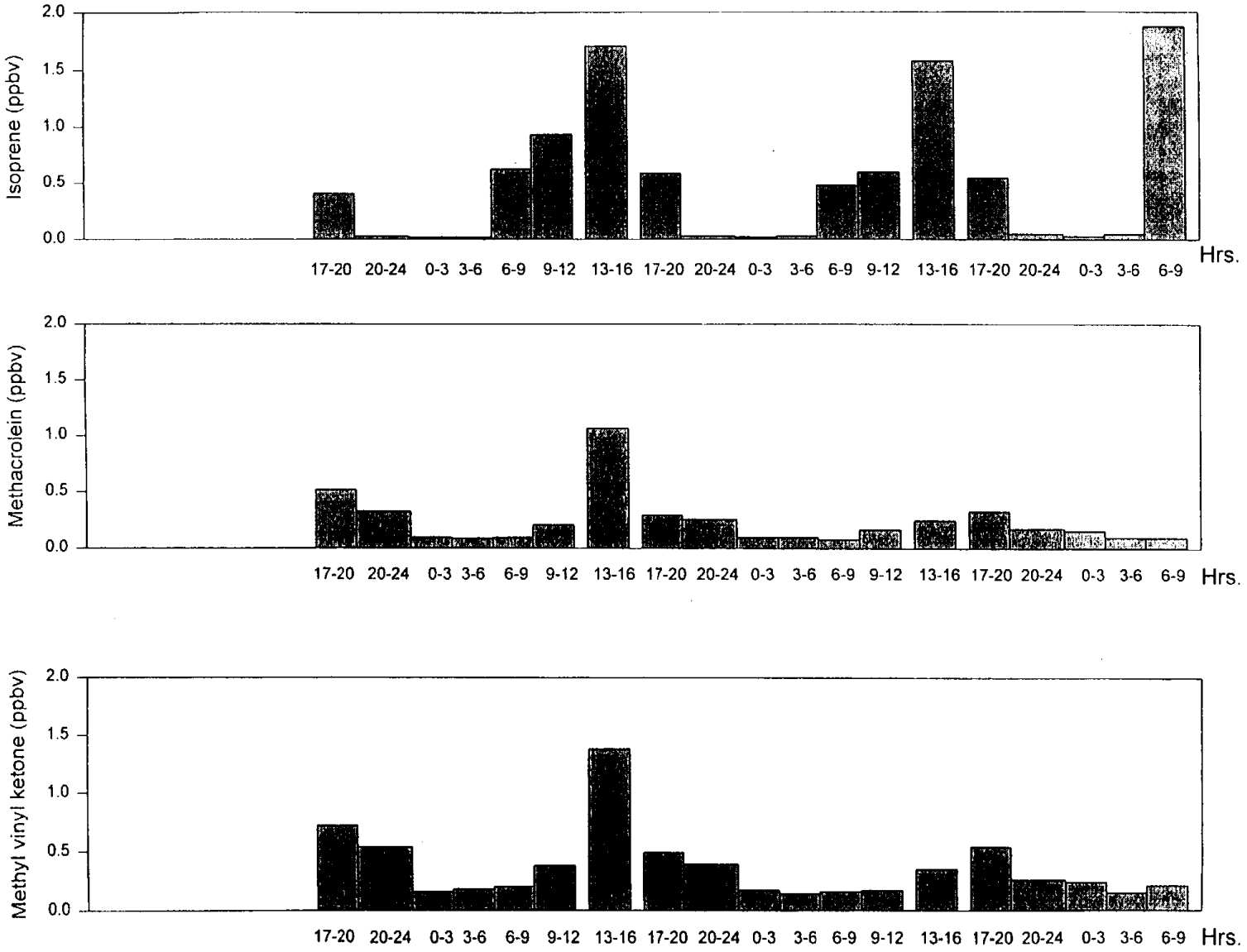

Figure 1-3. Isoprene, methacrolein and methyl vinyl ketone values at Pine Mtn. during Intensive 4, Sept. 4-7, 1997.

In contrast to the mountain sites, at Azusa, Banning, and LA North Main the MACR and MVK levels generally exceeded those of isoprene. The ratios of MVK/MACR were generally similar at Azusa during Intensives 2 and 4, but unusual ratios occurred during Intensives 3, 5 and 6. For example, high MVK values at Azusa producing high MVK/MACR ratios were observed on Sept. 28 and Oct. 4 both for the 0300-0600 sampling period. These data suggest that a source other than the photooxidation of isoprene may exist for some of the MVK observed at Azusa, at least during certain sampling periods. Further interpretation of these data may be possible when the anthropogenic VOC data for Azusa and Banning become available.

1.7 Summary and Conclusions

1.7.1 Isoprene Emission Rate Measurements: Taxonomic Method

Data from the present study for more than 60 plant species represent a significant expansion of the published isoprene emission rate database, and will be useful for building BHC emissions inventories in California, as well as other regions where these plants are found. Based on the present measurements, the taxonomic method proposed by Benjamin et al. (1996) is seen to work well for isoprene in most cases investigated, particularly at the genus level. However, there are important exceptions and the most troublesome genus for taxonomic predictions at this time (from both the present study and published literature) is *Quercus* (oaks). Further characterization of this genus is recommended. Oaks are important for BHC emission inventories in California because of their wide distribution in both urban and natural settings, and their high leafmass. In this study we have reported isoprene emission rates for four additional native oak species.

Given the enormous number of plant species in California and worldwide, a reference framework for understanding and categorizing emissions rates, and for assigning rates to unmeasured species, will be necessary. Within an order of magnitude uncertainty for families (Benjamin et al. 1996) and for many genera within factors of two to five, or even $\pm$50% as shown in the present study (see below), plant taxonomy appears to be a reasonable framework for organizing isoprene emission rate information, and taxonomy seems to be increasingly useful when descending to the lower levels of hierarchical classification (i.e. to subfamilies and genera). As Benjamin et al. (1996)

emphasized, the taxonomic relationship they proposed to meet this need is possible because there is a range of almost four orders of magnitude in emission rates of isoprene from the lowest to the highest emitting plant species. With the important exceptions noted, the data developed in the present study support the taxonomic predictive methodology for isoprene, especially if previous measurements within specific families, sub-families, genera and species are considered and compared (see below), and the results of such assignment treated with proper caveats.

1.7.1.1 Emission Rates: Family and Genus-Level Results

All plant species sampled within 19 of the families investigated in this study had isoprene emissions below detection limit. These results are consistent with the literature cited in Benjamin et al. (1996) for ten families, including Anacardiaceae (cashew), Betulaceae (birch), Bignoniaceae (bignonia), Caprifoliaceae (honeysuckle), Compositae (composite), Cupressaceae (cypress), Juglandaceae (walnut), Lamiaceae (mint), Oleaceae (olive), Rosaceae (rose) and Taxodiaceae (bald cypress), all of which may be regarded as containing mostly, if not all, negligible-emitters. These results are important because the Rosaceae and Compositae in particular are very large families, well-represented in agriculture, native plant communities and urban landscapes.

Certain families appear to contain predominately negligible emitters, but with several moderate or high emitters, while other families seem to be dominated by plants emitting isoprene at moderate-to-high rates, such as the Palmae family (palms), or high emissions rates, such as the Salicaceae family (willows and poplars.)

For 13 of 19 "predictions" found in Benjamin et al. (1996) isoprene emission rates measured in the present study were within ±50% of the predicted rate. Nine of the nine species expected to have zero isoprene emissions were measured as BDL. By considering subfamily taxonomy of the Leguminosae, the predictive accuracy (±50%) rises to 15 of 19 species. If oaks are not considered, since *Quercus* is so variable, the proportion rises to 14 of 16. Thus the taxonomic approach is seen to work particularly well at the genus level, with a few important exceptions.

1.7.1.2 Species Selection for Large-Scale Planting Programs

Among the oaks, preference for planting species with low isoprene emissions rates and low OFP may offer horticultural benefits in addition to reduction of BHC emissions. For example, many of the eastern North American deciduous oak species, such as *Q. borealis* (northern red oak), *Q. coccinea* (scarlet oak), *Q. palustris* (pin oak) and *Q. rubra* (red oak) display chlorotic foliage and lack vigor, typical symptoms of iron deficiency. However, other oak species, such as *Q. suber* (cork oak), have negligible isoprene emission rates and possess desirable horticultural characteristics, including tolerance to alkaline soils. Therefore the latter are better choices for many California landscapes than are oak species native to the eastern United States.

In any large-scale tree planting program, it is important to include the ozone-forming potential of specific plant species (Benjamin and Winer 1998) along with other criteria for plant species selection, such as adaptability, pest resistance, irrigation requirement, aesthetic qualities and other horticultural and landscape factors.

1.7.2 Leafmass and Leaf Area Relationships Determined from Sampling and Whole-Tree Harvest: Implications for Leafmass Estimation Methods

Results from this study suggest leafmass estimates developed for individual trees through a volumetric approach may generally be within approximately 50% of actual values. Summation of leafmass estimates generated using the preferred solid, vertical ellipsoid and sphere solid for all 21 trees in this study gave values within 20% of the measured total leafmass. Although use of the sphere solid resulted in a total leafmass value within 10% of the measured total leafmass, data for individual trees using a sphere solid were more scattered than those for the vertical ellipsoid, which was judged to be the best solid overall for modeling tree crowns in this study.

A volumetric approach may not precisely account for clumping of tree foliage and the change in leafmass density as tree crowns expand and mature, especially for larger species. Despite these limitations, a volumetric approach to estimating leafmass 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. Also, a further advantage of a volumetric method is its applicability to shrubs.

Based on results from the present study, literature values for experimentally-determined leafmass constants appear to be reasonably accurate for the species tested. However, a larger dataset including additional tree species is needed to more accurately quantify leafmasses of urban trees and to better understand structural class values.

In urban areas with subtropical climates, including many cities of California, deciduous tree species are mingled with broadleaf evergreen species. Mean values of leafmass per unit area of crown projection for such species in the present study were factors of 2 to 5 higher than leafmass per unit ground area data cited in the literature for eastern deciduous forests. Thus, leafmasses may be underestimated for trees in many of California's urban areas if calculations based on areal coverage and literature data do not take into account this difference. In summary, despite more limited areal coverage than natural forests, urban areas may contain a disproportionate amount of leafmass when compared to natural vegetation due to irrigation and fertilization in urban landscapes.

1.7.3 Field-Survey Assessment of the GAP GIS Database in Natural Vegetation Areas of San Diego County

The four classes of information predicted by the GAP database useful for the development of a BHC emissions inventory are crown closure within a polygon, cover of species assemblages within a polygon, species composition within an assemblage, and abundance of species within an assemblage. Crown closure within a polygon as predicted by the GAP database was generally consistent with our field observations. The accuracy of areal cover of GAP species assemblages within a polygon could not be assessed in this study, because the GAP database does not delineate the boundaries of primary versus secondary assemblages within a polygon. However, the species assemblages data in GAP might be expected to have the same degree of accuracy as the crown closure data.

About 60% of the co-dominants listed in the GAP database for the polygons studied were observed in our field survey in large enough proportions to justify their co-dominant designation. Field observation agreement with GAP was more common in

polygons dominated by forests and woodlands than in polygons dominated by chaparral and sage scrub.

GAP co-dominants provided 60-85% of the observed relative cover. However, the observed abundance of individual GAP co-dominants within a polygon was not evenly distributed among the listed species in the GAP database. Often, one or two co-dominants occupied the majority of the assemblage and the polygon.

It is important to note that biomass as derived from crown volume cannot be determined solely from data contained within the GAP database. Auxiliary data, either from field studies or from the literature, are needed to account for the 15-40% of the relative cover attributable to species whose identity cannot be determined from the GAP database, as well as to estimate crown volume and biomass using GAP.

1.7.4 Ambient Measurements of Isoprene and Its Atmospheric Reaction

The highest isoprene mixing ratios during SCOS 97 were found in samples from the two mountain sites, Pine Mtn. (2.2 ppbv on August 4) and Mt. Baldy (2.3 ppbv on September 28) in late afternoon/early evening samples. At Azusa the highest mixing ratios for isoprene were generally in the range 0.5 – 0.8 ppbv. Thus, the highest values at the mountain sites were three to four times higher than the maximum mixing ratios observed at the urban valley site. The maximum isoprene values at the Banning site in the eastern portion of the air basin were 0.2 – 0.3 ppbv, consistently lower than at the other sites.

Consistent with light-dependent biogenic sources, the lowest values for isoprene were usually measured during nighttime. However, the difference between day and night was most apparent at the mountain sites, where the daytime values ranged between 0.4 – 2.3 ppbv and the nighttime values did not exceed 0.1 ppbv. At Azusa and Banning the day-night variation was much less pronounced.

The highest mixing ratios for methacrolein and methyl vinyl ketone observed at Azusa were up to 3.3 ppbv and 2.3 ppbv, respectively, and at Banning highest values were 2.4 ppbv and 2.9 ppbv, respectively. At Pine Mtn. and Mt. Baldy the highest values for MACR were measured in the afternoon/early evening reaching 1.1 ppbv and 0.5 ppbv, respectively, and the highest values for MVK were 1.6 ppbv and 1.0 ppbv, respectively.

At the mountain sites during the daytime, the isoprene values generally exceeded the MACR and MVK concentrations, while during the nighttime the isoprene values were <0.1 ppbv and the combined MACR and MVK levels reached 1.7 ppbv. The daytime MVK/MACR ratios at the mountain sites were consistent with the source of MACR and MVK being photooxidation of isoprene.

In contrast to the mountain sites, at Azusa, Banning, and LA North Main the MACR and MVK levels generally exceeded those of isoprene. A source other than the photooxidation of isoprene may exist for some of the MVK observed at Azusa, at least during certain sampling periods.

2.0 INTRODUCTION AND PROJECT GOALS

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 1997. The reduction in ozone first stage alerts in the SoCAB, for example, from approximately 120 annually in the mid-1970's to only one in 1997, is a profound achievement given the enormous growth in population and emission sources in the SoCAB over the period of these control programs. Unfortunately, however, the degree 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 from vegetation (BVOC). Recent 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 recently published from our laboratory (Benjamin et. al. 1997) estimates 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 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 (1995). 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 is too much uncertainty in current BVOC estimates for airsheds other than the SoCAB to draw definitive modeling conclusions (Jackson 1997) at this time.

Concern about the possible critical role of BVOC 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].

Given the growing evidence of 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 relevant ARB models.

2.2 Background

The emission by vegetation reactive hydrocarbons such as isoprene and monoterpenes (which we will generally refer to throughout this report as biogenic hydrocarbons or BHC) 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 BHC in the atmosphere expanded dramatically, both in the scientific and regulatory communities (Lamb et al. 1985, Lamb et al. 1986, Chamedies et al. 1988, Arey et al. 1991a-c, Grinspoon et al. 1991, NRC 1991, Sharkey 1991, Corchnoy et al 1992, Winer et al. 1992, Kuzma and Fall 1993, Lamb et al. 1993 Konig et al. 1995 Geron et al 1995, Guenther et al. 1995, Sharkey and Singsaas 1995, Harley et al. 1996, Guenther et al. 1996a-c, Winer et al. 1996, 1997, 1998).

Additional evidence of the widespread attention to the role of BHC 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 BHC. 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. It was clear from this international conference, that regulatory agencies throughout the world, including the U.S. Environmental Protection Agency, are now concerned with better characterizing the importance of BVOC, relative to anthropogenic VOC, in key air pollution processes. Research presented at this meeting (WBH 1997), as well as recent advances in understanding the atmospheric chemistry of BHC (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.

2.3 Previous BHC Studies in California

2.3.1 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 areal 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, biomass constants (g per cubic meter) were developed for 55 genera of plant species found in the Basin, permitting conversion of crown volume to green leaf biomass. Interestingly, these biomass constants and those obtained in our present study under ARB funding (Karlik and Winer 1997), remain the only such data generated to date for plant species of interest in California.

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 for an extra corresponding to about one-third the area of the SoCAB (specifically the western and middle portions of the Basin containing a majority of the anthropogenic emissions of VOC and NO_x 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 subsequent 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 a taxonomic relationships (Benjamin et al. 1996) rather than on the structural class of the vegetation. Finally, the most 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 green 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 125-140 TPD in the summer and 40 TPD in the winter, with total emissions as high as 200 TPD for ozone episode days (Benjamin et al. 1997).

Horie and co-workers (Horie et al. 1990) conducted a study supported by the South Coast Air Quality Management District (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 biomass 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 vegetation 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 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 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 1991).

2.3.2 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-c) 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. Approximately four dozen individual compounds were identified as emissions from the 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).

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 rates or an emission rate based on a surrogate species from the same genus or family. Although a large portion of the species leaf biomass in the AUSPEX area was accounted for by plant species in the AUSPEX area due to limitations in the experimental database.

Agricultural emissions were spatially defined only on a county basis, using a species mix of 10 crops identified as significantly emitted by Winer et al. (1989, 1992). Agricultural acreage's 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 MTBD of a total 3360 MTBD, were produced by agricultural crops.

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 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 abundance, assignments of known plant emission rates to species with unknown rates, and adjusting for canopy effects (Causley et al. 1991).

2.4 Statement of the Problem

Although, as noted above, a significant body of data has accumulated over the past twenty years related to the generation of emission inventories for biogenic hydrocarbons in California, for various reasons present databases and models may still not be adequate for regulatory purposes, especially considering the importance of decision-making concerning NO_x vs. VOC control (Winer et. al. 1995). Among the most important reasons for this situation is the enormous complexity and variation inherent in a biological system consisting of the vegetation in a particular airshed.

The essential steps in assembling a biogenic hydrocarbon emission inventory consist of assessing plant species distribution and abundance, determining green leaf biomass for all of the important plant species, measuring or otherwise estimating the quantitative rate of emission of individual organics from each of hundreds of plant species, and modeling the overall diurnal emission inventory as a function of several key environmental factors, including temperature and light intensity.

A testimony to the difficulty of systematically determining experimental leaf biomass constants and hydrocarbon emission rates is that at the present time, notwithstanding the growing attention paid to VOC of biogenic origin over the past decade, experimental measurements of such essential properties as leaf area indices, crown volumes and emission rates have been conducted only for a distinct minority of the hundreds of plant species typically identified in large California airsheds such as the

SoCAB or the SJVAB. Moreover, absent a massive and unrealistic expenditure of funds and personnel, there is no meaningful possibility that comprehensive experimental determination of these properties will be conducted, even on the time scale of decades, let alone the few years available to utilize such data in demonstrating ozone and PM-10 attainment.

Clearly, these constraints and complexities dictate a different approach. In particular, what is needed are cost-effective and focused efforts to generate the experimental data for key plant species which will in turn permit validation of models and methods able to generalize these results to the much larger number of plant species found in California. There was also a unique opportunity during this project to provide experimental ambient air measurements of isoprene and monoterpenes (and their photooxidation products) during the 1997 Southern California Air Quality Study, supplementing the many other kinds of measurements which were made during this comprehensive monitoring program.

2.5 Objectives

2.5.1 Overall Objective

The overall objective of this integrated program of focused experimental and taxonomic studies was to furnish the ARB with information essential to the development of sound and cost-effective control strategies in those California airsheds where biogenic hydrocarbon emissions are critical.

An important element of this approach is the taxonomic methodology, for grouping and "predicting" emission rates, developed over the last several years by UCLA researchers (Benjamin et al. 1996). As discussed in more detail in Section 3.0, this methodology offers a powerful tool for directing leaf biomass and emission rate measurements (including those conducted in the present study) in a focused and highly cost-effective manner.

2.5.2 Specific Objectives

The specific objectives of this project were to:

- Experimentally measure isoprene emission rates for a carefully selected set of plant species under realistic field conditions.
- Expand and refine the UCLA taxonomic methodology for "predicting" isoprene emission rates for plant species for which no experimental measurements are available.
- Under field conditions, experimentally measure dry leaf mass per volume, including whole tree leaf mass of plant species which represent the most critical gaps in biomass estimation for key airsheds such as the SJVAB.
- Based on field surveys, determine uncertainties and limitations in the GAP database and develop recommendations for utilizing this current geographical information system database for vegetation in California, for development of biogenic hydrocarbon emission inventories.
- Conduct experimental measurements of ambient concentrations of isoprene and monoterpenes, and their photooxidation products, during the 1997 Southern California Air Quality Study in conjunction with the extensive monitoring program for anthropogenic hydrocarbon species.

3.0 ISOPRENE EMISSION RATE MEASUREMENTS

3.1 Introduction

BHC emissions are a major source of VOC entering the atmosphere, and play important roles in (1) tropospheric ozone formation, (2) production of organic acids important in acidic deposition in rural areas, (3) global tropospheric chemistry, and (4) balancing the global carbon cycle (Fesenfeld et al., 1992). More than 70 different BHC 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. Isoprene is the BHC emitted in greatest quantity by the plant kingdom (Guenther et al. 1995) and is the dominant BHC 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). Isoprene emission probably increases thermotolerance of plants (Sharkey and Singsaas 1995, Singsaas et al. 1997) and may also act as a plant growth regulator, for example, accelerating the onset of flowering (Terry et al. 1995) . Among the plant species measured to date, emission rates of isoprene differ by more than three orders of magnitude (Benjamin et al. 1996) and the resulting ozone-forming potential of individual trees and shrubs ranges over nearly four orders of magnitude (Benjamin and Winer 1998). Isoprene emission rates are often expressed in units of micrograms of isoprene per gram of dry leafmass per hour which we will represent throughout this chapter as ug g^{-1} h^{-1}.

Seminal studies of biogenic emissions were carried out in California in the South Coast Air Basin (SoCAB) (Winer et al. 1983, 1989). However, much of work pertaining to BHC emissions has been carried out in the temperate continental regions of North America, which has plant species distribution unlike the Mediterranean climate of California. The Biogenic Emission in the Mediterranean Area (BEMA) project has recently been completed, and provides valuable additional data for Mediterranean climate regions of the world (BEMA 1997, Sharkey et al. 1997).

3.2 Background and Statement of the Problem

3.2.1 Factors Influencing Isoprene Emissions from Vegetation

BHC 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.

Isoprene is formed in plants via the mevalonic acid pathway (Sharkey et al. 1991). The emission rate is related to the photosynthate pool and, therefore, to photosynthetic rate (Loreto and Sharkey 1993). The final step biochemical step is the conversion of dimethylallyl phosphate to isoprene, catalyzed by isoprene synthase (Silver and Fall 1991). Unlike monoterpenes, the pool of isoprene is small, which was seen experimentally as an immediate decline in isoprene emission rate of leaves of quaking aspen (*P. tremuloides*) when darkness was imposed (Monson et al. 1991). Isoprene emission rate is species-specific and ultimately governed by genotype. The isoprene emission rate will be affected by the isoprene synthase activity of individual leaves, determined in part by genetics (Schnitzler et al. 1997).

As discussed below, 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, although these factors are most important at the very beginning and end of the season, and there are also inter-relationships between light and temperature and developmental factors. Developmental factors would be most 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.

3.2.1.1 Principal Factors Affecting Isoprene Emission Rate of Plants in the Field

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) which was slightly modified (Guenther 1997). The algorithm 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 observed isoprene emission rate. The algorithm can be used to normalize isoprene emission rates measured in the field to standard conditions of photosynthetically active radiation (PAR) and temperature of 1000 umol m^{-2} sec^{-1} and 30 °C, respectively. The formulae and use of the algorithm are discussed in detail below in section 3.4.1.

Both temperature and light intensity will vary within a tree crown or plant canopy. Leaf temperature will be affected by shading and by evaporative cooling. For single trees and branches in enclosures, leaf temperature may be within 2 °C of air temperature (section 3.3.2.3). Light intensity is attenuated by leaves and decreases rapidly below the level of canopy closure. An approximation of light intensity at varying canopy depths may be obtained from the Beer-Lambert law but there is substantial spatial variability (Parker 1995). Light also affects leaf size and specific leaf area (section 3.2.1.5). Modeling of temperature and light environment within the crown or canopy was beyond the scope of this project.

3.2.1.2 CO_2 Level and Isoprene Production

In laboratory studies (Guenther et al. 1991), isoprene emission rates were constant for eucalyptus leaves for CO_2 concentrations between 50 and 600 ppm, boundaries well outside the range of CO_2 of about 350-370 ppm expected in outdoor air one meter or more above the soil surface. A dramatic drop in CO_2 partial pressure surrounding leaves can limit isoprene production but the effect of reduced CO_2 is not immediately apparent. For example, isoprene emissions from a single leaf decreased after CO_2 was reduced from 330 ppm to 0 ppm (Guenther et al. 1991) but the response time for an initial drop in isoprene emission was more than 10 minutes. In these experiments (Guenther et al. 1991), a slight decrease (5-10%) in isoprene emission rate occurred during the first 15

minutes of CO_2 reduction followed by a gradual decrease over the next 30 min. Even at 45 minutes the emission rate was about 50% of its initial value. A drop in CO_2 does not immediately affect isoprene emission rate because isoprene synthesis is tied to phosphoglyceric acid pools (Loreto and Sharkey 1993) or other metabolites (Monson et al. 1991). CO_2 concentration was included in an earlier algorithm for normalizing isoprene emission rate (Guenther et al. 1991) but eliminated in a subsequent version (Guenther et al. 1993).

3.2.1.3 Plant Water Relationships and Isoprene Emission

Plant water stress may occur because of a lack of water available to the root system or because of a high rate of evapotranspiration resulting in a temporary deficit, such as may occur on a warm, sunny afternoon in the Central Valley. More specifically, a combination of soil water depletion, low relative humidity, wind, high solar radiation and high ambient temperature may result in water stress. To preserve water within a plant, stomata close during periods of water stress and therefore stomatal conductance, i.e. stomatal opening, provides a means of evaluating plant water status.

In a Mediterranean climate, such as found in most of California, the available water in the soil profile is replenished during winter rains, and little if any precipitation occurs during summer while native plants, such as oaks and sages, continue to deplete the soil reservoir. Drought stress is expected, especially later in the summer, and could occur earlier and be more pronounced if winter rains are marginal and do not bring the soil profile to field capacity throughout the rooting depth.

Because isoprene emission is dependent upon photosynthesis, severe water stress will curtail isoprene emissions as photosynthesis and plant metabolism in general come to a halt. However, although isoprene emission occurs through stomata, the rate of emission is controlled by isoprene synthesis rather than by stomatal opening (Fall and Monson 1992) and isoprene emission rate appeared to remain fairly constant in oaks which are drought-stressed as measured by a large (93%) reduction in stomatal conductance (Fall 1991). When stomata closed, the intercellular concentration of isoprene increased, resulting in an undiminished emission rate (Fall and Monson 1992). Under conditions of moderate water stress, the percentage of carbon converted to isoprene may increase

slightly, but the total isoprene emission remains about the same (Fall 1991). A decrease in stomatal conductance also results in a decrease in transpiration rate, which leads to an increase in leaf temperature, and thus has an indirect effect on isoprene emission rate (Guenther et al. 1995).

Relative humidity was included in an earlier algorithm developed by Guenther et al. (1991). However, a relative humidity increase from 40 to 50% resulted in only a 2.4% increase in emission rate. The relative humidity term was eliminated in a later version of the algorithm (Guenther et al., 1993). Oaks and other species in natural stands of vegetation in the SoCAB and surrounding the San Joaquin Valley of California would be expected to be limited in growth rate by lack of water and would likely experience a degree of stomatal closure due to drought stress, but without affecting isoprene emission rate.

3.2.1.4 Nitrogen Shortage and Isoprene Emission

Nitrogen is often limiting in field soils but, except for the late season period of leaf senescence, nitrogen fertility appears to only slightly affect isoprene emission rate during the growing season. A study with velvet bean leaves (*Mucuna* sp.) compared isoprene emission under different levels of nitrogen fertilization (Harley et al. 1994). The rate of emission decreased with decreasing nitrogen level, but comprised a greater fraction of carbon, which was attributed to the plant shunting carbon into the isoprene molecule, which does not contain nitrogen. In a study of *Populus tremuloides* (quaking aspen) (Harley et al. 1994), the late season isoprene emission rate was determined by leaf nitrogen concentration. Nitrogen is expected to be at low (1 -2 ppm) levels in unamended soils of California, which typically have less than 1% organic matter and therefore low reserves of this element. However, the effect of soil fertility on BHC emissions would be indirect, reflected in growth rate of trees and shrubs and resulting foliar mass rather than in isoprene emission rate.

3.2.1.5 Effect of Light Intensity During Leaf Development on Isoprene Emission

In addition to conditions of light intensity at the time of measurement, leaves developing in the sun have higher capacity for emitting isoprene than leaves developing

in the shade; for example, a difference of three- to five-fold, expressed on an emission per leaf area basis, was found in a study of *Quercus alba* (Sharkey et al. 1996). Differences between sun- and shade-leaves should be less pronounced when expressed on an emission-per-leafmass basis rather than emission-per-area basis (Harley, 1995) because leafmass per area will be higher in sun leaves than shade leaves. Isoprene emissions expressed on a leafmass basis for sun- and shade-leaves did not differ significantly ($p = 0.05$) in a study of *Quercus alba* leaves (Harley et al. 1997) but did differ significantly ($p = 0.01$) for leaves of *Liquidambar styraciflua* (Harley et al. 1996). The mass-area ratios of sun- and shade-leaves are discussed further in Chapter 4.

3.2.1.6 Changes in Isoprene Emission Rate Related to Leaf Age

Plant leaves go through a life cycle of growth, maturation, senescence, and death, and the phenology of leaf development affects isoprene emission rate as a result of biochemical changes within leaves. The quantity of isoprene emitted by a plant will also change as leaves increase in size and number. Seasonal emission of isoprene has been investigated in several studies as briefly discussed below, and, for emitting species, generally follows a pattern of low spring emissions followed by a rise to a summer plateau and then decline in autumn as leaves senesce.

In the early stages of leaf unfolding and expansion, the isoprene emission rate is more closely correlated with isoprene synthase activity rather than with photosynthetic rate. For example, the photosynthetic capability of velvet bean (*Mucuna* sp.) leaves increased 3-5 days before emission rate increase occurred, and was followed by an increase in emission rate of as much as 125-fold as leaves developed (Grinspoon et al. 1991). In related experiments, both leaf emission and isoprene synthase activity increased more than 100-fold from 0-14 days (Kuzma and Fall 1993) but the rate of isoprene emission was more strongly correlated with isoprene synthase activity rather than photosynthesis from 0-23 days. In another study with velvet bean, Harley et al. (1994) demonstrated that during the early stages of leaf development isoprene emission and photosynthesis were decoupled and, apparently, induction of isoprene synthase was required because isoprene emission rate lagged behind the rate of photosynthesis as leaves emerged. However, in later stages of leaf development a correlation between

isoprene synthesis and photosynthesis was apparent because the rate of emission was correlated with photosynthetic activity during the middle age of the leaf, and declined in parallel with photosynthesis as the leaf died.

Temperature appears to be an important factor in early induction of isoprene synthase (Monson et al. 1994). Aspen trees, *P. tremuloides*, more quickly exhibited isoprene emission if exposed to high ambient temperatures. Leaves emerging during cool weather had not emitted isoprene, but could be induced to emit isoprene by exposure to temperature of 32°C for two hours. From comparison of aspen at three sites, induction occurred when leaves had accumulated 400 degree-days from a 0°C base. Emission rate rose to a plateau during the summer, then fell with the onset of senescence.

Seasonal isoprene emission patterns of individual trees in the field has been investigated during the growing season. For example, a red oak (*Quercus rubra*) was measured by Flyckt (1979) on a monthly basis from spring to autumn. Emission was low in the spring, reached a maximum in early summer, and decreased from that time to near zero in autumn. Another oak, *Q. serrata* (Asian live oak) was measured by Ohta (1986) at hourly intervals on six days during the period June to November. The highest emission rate occurred in September, although the highest light intensity was, of course, in midsummer.

In study of the deciduous species *Quercus alba* (white oak) in Alabama, leaf unfolding occurred about mid April (Pier and McDuffie 1997). Normalized isoprene emissions increased from mid-May, were relatively constant in late June through July, and had decreased to 70% of their maximum value by mid-September and declined further to only 30% of their maximum value by mid-October.

For BHC 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, and leaf expansion for deciduous species begins in March-April and finishes in November and December with senescence.

3.2.2 Previous Experimental Approaches

Isoprene emissions of vegetation have been measured by branch enclosure, leaf cuvette, relaxed eddy accumulation, surface layer gradient, mixed layer gradient and mixed layer mass balance techniques (Guenther et al. 1996a,b). A thorough review of previous experimental approaches is beyond the scope of this chapter and the reader may wish to refer to the critical review of Winer et al. (1995).

For this report, the recent compilation of Benjamin et al. (1996) was used as the primary reference for species-specific isoprene emission rates. The summary of Guenther et al. (1994) was also consulted.

3.2.3 Rationale and Approach for the Present Investigation

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 measure experimentally the isoprene emission rates of even a small fraction of the plant species found in California and other regions, although quantitative emission rate data for additional species have been accumulated during the BEMA project (Owen et al. 1997) and qualitative appraisals of emission rate behavior for previously unreported species have also been published (Guenther et al. 1994, Lerdau and Keller 1997, Klinger et al. 1998). However, a vast number of species remain to be evaluated, hence generalizations of BHC 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 BHC emissions inventories for urban areas (Geron et al. 1995).

An explicit link between isoprene and monoterpene emissions rates and plant taxonomic relationships has been proposed for species found in southern California (Benjamin et al. 1996) and was subsequently used (Benjamin et al. 1997) to compile a detailed BHC 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 BHC 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 emission rates for carefully selected plant species are required to test further the taxonomic predictive method. In response to this need, the present study expanded the measured isoprene emission rate database by more than sixty California species and provided data for further evaluating isoprene emission rates inferred from taxonomic relationships. Plants were sampled in situ and quantification of isoprene was made at a laboratory at the University of California's Shafter Research and Extension Center as described in detail below.

3.2.3.1 Availability and Location of Plant Specimens

Most urban tree and shrub species sampled in the 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 (CE), in city parks and in residential landscapes within the Bakersfield metropolitan area (BFD), on the campus of California State University, Bakersfield (CSUB), and on the grounds of the Shafter Research and Extension Center (SREC) located 35 miles northwest of Bakersfield. Plant genera more frequent in cooler climates, such as *Cornus* and *Viburnum*, were sampled within the Mourning Cloak Botanic Garden (MCBG), 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 (MTN) such as Caliente, approximately 15 miles east of Bakersfield (elev. ca. 1000 ft), and California Hot Springs, approximately 60 miles northeast of Bakersfield (elev. ca. 2300 ft). A few plants were sampled in other unirrigated locations, such as the Mojave Desert 60 miles east of Bakersfield (elev. ca. 2300 ft) and at the Eddy Arboretum at Placerville, east of Sacramento.

3.2.3.2 Criteria for the Selection of Plant Species Studied

Because the study was necessarily limited, candidate plant species were carefully selected to allow evaluation of the taxonomic predictive method and expansion of the isoprene emission rate database. 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 example, within the confused nomenclature of *Cytisus* (= *Genista*) within the Leguminosae.

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, as seen in Table 3-1.

Table 3-1. Plants measured for intrafamily comparison of isoprene emission rates.

Family	Genus-species	Common Name	Location
Bignoniaceae	Macfadyena unguis-cati	Cat's-Claw Vine	BFD
Compositae	Baccharis pilularis	Coyotebrush	CE
Euphorbiaceae	Sapium sebiferum	Chinese Tallow Tree	BFD
Lamiaceae	Rosmarinus officinalis	Rosemary	BFD
Leguminosae	Caesalpinia gillesii	Desert-Bird-of-Paradise	CE
	Ceratonia siliqua	Carob	BFD
Oleaceae	Syringa vulgaris	Common Lilac	MCR
Palmae	Syragus romanzoffianum	Queen Palm	BFD
Pinaceae	Abies concolor	White Fir	MCR
Rosaceae	Rosa hybrida	Rose	CE, BFD
Taxodiaceae	Sequoia gigantea	Giant Sequoia	MCBG
	Sequoia sempirvirens	Coast Redwood	BFD

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 (Table 3-2).

Several plant families, which contain genera and species common in urban landscapes and the natural communities of California, were not found in the compilation of Benjamin et. al (1996). Therefore, plants were also chosen to represent such families, as seen in Table 3-3.

Table 3-2. Plants measured for intrageneric comparison of isoprene emission rates.

Family	Genus-species	Common Name	Location
Anacardiaceae	Pistacia chinensis	Chinese Pistache	CE
Caprifoliaceae	Viburnum trilobum	American Cranberry	MCBG
Cupressaceae	Cypress leylandii	Leyland Cypress	CE
Fagaceae	Quercus palustris	Northern Pin Oak	BFD
	Quercus suber	Cork Oak	CE
Juglandaceae	Carya illinoinensis	Pecan	BFD
Lamiaceae	Salvia greggii	Salvia	BFD
Leguminosae	Acacia aneura	Mulga	BFD
Moraceae	Morus alba 'Fruitless'	Fruitless Mulberry	BFD
	Ficus carica	Edible Fig	BFD
Myrtaceae	Eucalyptus camaldulensis 'C2'	Red Gum	CSUB
	Eucalyptus grandis 'GCT'	Rose Gum	CSUB
Oleaceae	Fraxinus velutina 'Modesto'	Modesto Ash	SREC
Palmae	Washingtonia robusta	Mexican Fan Palm	BFD
Pinaceae	Picea glauca	Colorado Blue Spruce	MCBG
Salicaceae	Populus alba	White Poplar	BFD
	Populus nigra italica	Lombardy Poplar	CSUB
	Populus euramerica 'R111'	Hybrid Poplar	CSUB
	Populus euramerica 'R112'	Hybrid Poplar	CSUB

Table 3-3. Important plant families not reported in Benjamin et al. (1996) with candidate species for sampling for isoprene emission rates.

Family	Genus-species	Common Name	Location
Betulaceae	Betula papyrifera	Paper Birch	MCBG
	Betula nigra	River Birch	MCBG
Cornaceae	Cornus stolonifera	Redtwig Dogwood	MCBG
Hipposcastanaceae	Aesculus californica	California Buckeye	MTN
Malvaceae	Hibiscus rosa-sinensis	Hibiscus	BFD
Proteaceae	Grevillea robusta	Silk Oak	BFD
Steculiaceae	Brachychiton populneus	Bottle Tree	BFD
Verbenaceae	Lantana camara	Bush Lantana	BFD
	Vitex agnus-castus	Chaste Tree	CE

As shown in Table 3-4, additional species were selected because of their frequency of occurrence in native plant communities (*Chrysothamnus nauseosus* and *Spartium junceum*), in the extensive desert region of California (*Cassia* sp. and *Larrea tridentata*), in agriculture in the San Joaquin Valley (cotton) or in urban landscapes (the families Compositae and Leguminosae).

3.3 Experimental Methods

3.3.1 Introduction

Experimental methods were selected and developed during the course of the project, including protocols for enclosure sampling, sample transport from the field to the laboratory, and analysis of enclosure air samples.

3.3.2 Branch Enclosure Method

3.3.2.1 Enclosure Construction

Enclosure methods have been used in California studies (Winer et al. 1983, 1992, Arey et al. 1995), in other regions of the United States (Kempf et al. 1996), in other parts of the world (Street et al. 1996) and were also employed in the BEMA project (Seufert 1997, Owen et al. 1997). The Teflon enclosure method was adopted as the primary method for sampling isoprene emissions in this study, with a design similar to that utilized by Winer and co-workers (Winer et al. 1983, 1992) and Arey and co-workers (Arey et al. 1995). The enclosure chamber, with dimensions of 40 x 40 x 90 cm (16 x 16 x 36 in), was constructed with 2 mil Teflon sheeting formed into a bag that was heat sealed and supported by a framework of 1.3 cm (1/2 in) schedule 40 PVC pipe and fittings. Two and one-half cm (one inch) schedule 80 PVC was substituted for one of the 1.3 cm (1/2 in) legs, providing a smooth, sliding fit on 1.9 cm (3/4 in) thin-walled steel conduit. This design enabled the operator to slide the enclosure up and down on a cantilevered arm of conduit, allowing a good fit on the target. The enclosure was held stationary for measurements with a 1.9 cm (3/4 in) OD, hand tightened collet. An adjustable steel tripod was fabricated to suspend the enclosure horizontally to encase a branch and the enclosure could be held at angles from approximately 30° to 150° (0° vertical) and at heights from ground level to approximately three meters.

Table 3-4. Additional frequently-occurring plant species to be measured for isoprene emission rates.

Family	Genus-species	Common Name	Location
Chenopodiaceae	Atriplex spp.	Saltbush	SREC
Compositae	Chrysothamnus nauseosus	Rubber Rabbitbrush	MCBG
Leguminosae	Cassia nemophila	Desert Cassia	CE
	Cercidium microphyllum	Foothill Palo Verde	CE
	Prosopis alba 'Colorado'	Colorado Mesquite	CE
	Spartium junceum	Spanish Broom	MCBG
Malvaceae	Gossypium hirsutum	Cotton	SREC
Zygophyllaceae	Larrea tridentata	Creosote Bush	Mojave

In this study, analyzed air was used (Analyzed Ambient Air, Praxair Inc.) which was certified to contain 350 ppm CO_2, and verified using an infrared gas analyzer. The CO_2 content of air within the enclosure was also monitored during selected runs; an example is presented in Table 3-5. Therefore, in the present study isoprene production was not limited by CO_2 concentration surrounding the branch, especially considering the short duration of the enclosure runs.

Air was delivered to the enclosure from a tank using a two-stage regulator (Victor No. SR450D-540) and 0.64 x 0.95 cm (1/4 in ID x 3/8 in) OD Teflon tubing (Fisher Scientific No. 14-169-16G). The air passed through an activated carbon filter (Fisher Scientific No. 09-744-40) followed by a calibrated Cole-Parmer flow meter (Cole-Parmer No. E-03218-41) and entered the enclosure through an intake port (FEP Teflon bulkhead fitting Cole-Parmer No. H-06482-38) supported with two sheets of Teflon 7.6 x 7.6 x 0.32 cm (3 in x 3 in x 1/8 in). Air in the enclosure was mixed with a fan powered by a 12V battery. A sample port (Cajon Ultra-Torr Union, No. SS-4-UT-6, changed to SS-4-UT-6-BT at the beginning of the 1997 sample series) was installed on the same side of the enclosure as the intake port and supported with two sheets of Teflon 7.6 x 7.6 x 0.32 cm (3 in x 3 in x 1/8 in). The original sample port only allowed sampling of air flowing past the inner surface of the enclosure and did not always maintain a tight seal around the

Table 3-5. CO_2 concentration in enclosure air during a run made on September 26, 1997, with *Populus euramerica* 'R112' under conditions of full sun (PAR of 1510 umol m^{-2} sec^{-1}) and 31.0g dry leafmass.

Time (PDT)	CO_2 (ppm)	Notes
11:23	365	Check of ambient air
11:24		Enclosure moved into position
11:26		Enclosure secured, airflow begun
11:29	302	
11:30	298	
11:31	292	
11:32	290	
11:33	289	
11:34	287	
11:35	287	Sampling begun
11:36	288	
11:37	284	Sampling ended

glass sampling tube. When the sample port was changed to the second Ultra-Torr fitting a tight seal was made around the glass sampling tube, which protruded into the enclosure.

Differences between the enclosure used by Winer and co-workers (1983, 1992) and Arey and co-workers (1995) and the present system included the absence of a perforated copper tubing diffuser ring or humidifying chamber. Also, unlike the earlier studies, a metal stand was constructed to allow a range of motion in placing the enclosure over foliage.

3.3.2.2 Branch Enclosure Flow Characterization

As in previous studies (Winer et al. 1983, 1992, Arey et al. 1995), the enclosure acted as a continuous flow stirred tank reactor (CFSTR) and emitted BHC concentrations approached 95% of a final concentration asymptotically within approximately eight minutes, corresponding to three air exchanges. The concentration after three air exchanges is considered to be a satisfactory approximation of the final steady-state concentration (Tchobanoglous and Schroeder 1987), which would be attained

theoretically at time of infinity, and this report we use the term steady-state to indicate a BHC concentration attained after at least three air exchanges.

The time to steady state within the CFSTR was calculated from standard engineering equations. Specifically, the concentration of isoprene, or other tracer, in a CFSTR may be calculated by beginning with the materials balance equation for the system, where:

Accumulation = Inflow - Outflow + Generation

Expressed mathematically,

$$\frac{dCtV}{dt} = QCt_i - QCt_o + r_tV \qquad (1)$$

where

Ct is the concentration of a trace gas, in this case isoprene,

V is the volume of the CFSTR,

t is time,

Q is the flow, in units of volume per time,

Ct_i is the concentration of the tracer in the input stream, which in this case is analogous to isoprene production by leaves and insertion into the input air stream,

Ct_o is the concentration of the tracer in the output stream, and

r_t is the rate of generation, which is zero in this case since isoprene is nonreactive within the CFSTR.

Simplifying, since r_tV becomes zero, and integrating gives

$$Ct = Ct_i (1-e^{-t(Q/V)}) \qquad (2)$$

Since Q/V is the hydraulic detention time, it may be seen that after a time sufficient for three air exchanges the enclosure concentration will be equal to 95% of its final value because

$$Ct = Ct_i (1 - e^{-3}) \quad (3)$$

or $$Ct = Ct_i (1 - 0.5) \quad (4)$$

or $$\frac{Ct}{Ct_i} = 0.95 \quad (5)$$

Using an approach similar to Winer and co-workers (Winer et al., 1983) and prior to field sampling, the enclosure behavior was validated using ethylene as a tracer. As described above, the enclosure was connected to an air supply and the stirring fan was switched on. Ethylene from a diffusion tube apparatus was introduced at a constant rate via a delivery tube into the bottom of the enclosure and the ethylene concentration within the enclosure was measured with a dedicated gas chromatograph at regular time intervals (Figure 3-1). The enclosure behaved as expected and reached steady-state after three air exchanges.

3.3.2.3 Measurements of Environmental Parameters

A quantum sensor (LiCor 190SA) and digital meter (LiCor LI-250) were used to measure PAR. The quantum sensor was factory-calibrated (16 August 1996) with a National Institute of Standards and Technology (NIST)-traceable calibration of ±5%. Accounting for instrument drift (±2% over a one-year period) and the digital meter accuracy of ±0.6% yielded an overall PAR accuracy of ±8% of the reading. The sensor was checked against a second LiCor quantum sensor and meter was found to agree within the factory specified error of ±5.6 %. The sensor was mounted on a wood block and suitably oriented in the field for readings, which were 15 second averages of PAR calculated by the microprocessor in the meter. Transmissibility of the Teflon sheeting was also checked with the quantum sensor by comparing readings within and without the enclosure. PAR was found to be identical inside and outside the enclosure within the error of sensor. In fact, for about half the comparison measurements, readings were

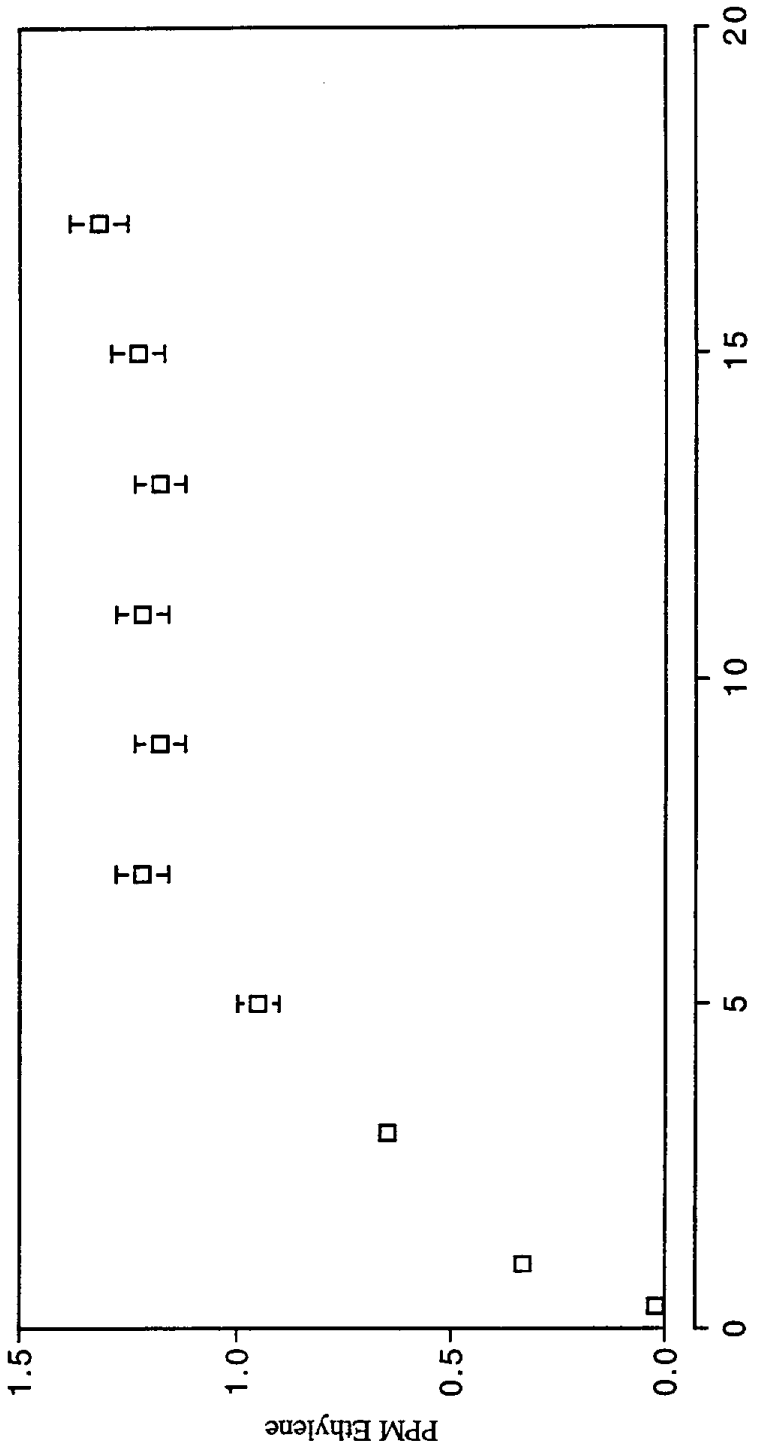

Figure 3-1. Validation of the branch enclosure using ethylene as a tracer. Incoming air flow rate was 35.9 L/min. Error bars show 5% confidence intervals.

slightly higher within the enclosure than without, perhaps due to internal reflection from the Teflon sheeting.

Temperature outside the Teflon enclosure was measured with a digital probe thermometer accurate to ±0.2 °C (Fisher Scientific No. 15-077-8) with an NIST-traceable calibration. The temperature readings were 15 second averages calculated by the microprocessor in the meter.

It would be extremely difficult to measure temperatures from all leaves during branch enclosure, experiment or to characterize the canopy position and incident light on each leaf. The necessary averaging of temperature and light intensity seen by leaves is one reason the enclosure method is not as rigorous as leaf-cuvette studies in characterizing specific leaf conditions. Also, the exact physiological condition of each leaf (e.g. stomatal conductance, photosynthetic rate) is not described during enclosure measurements. However, leaf cuvette data for a specific leaf condition must be scaled to provide an isoprene emissions rate estimate for the range of temperatures and multitude of leaf orientations found within a tree crown. So each approach has its strengths and limitations. From another perspective, the branch enclosure method has advantages because it provides data developed from multiple leaves in a system approximating field conditions, since self-shading by leaves occurs within tree crowns.

We used enclosure air temperature as a surrogate for leaf temperature. To check the representativeness of air temperature with respect to leaf temperature, additional measurements were made with insulated fast-response thermocouples (Omega 5SC-TT-T-36-72) and read with a microprocessor thermometer (Omega Model HH21). Thermocouples were checked and found to agree within 0.1 °C. During selected enclosure runs, thermocouples were attached to the undersides of five leaves and temperature measurements were taken at one-to-two minute intervals, and were compared to measurements of enclosure air temperature made with a sixth thermocouple and the temperature probe described below. Data from a representative run is presented in Table 3-6. For these enclosure runs, leaf temperatures were found to be similar to air temperatures. These results are consistent with reports of other investigators, who found enclosure air and leaf temperatures to be similar. For example, in a whole tree enclosure of a 8.2 m tall *Quercus alba* (white oak), about half the leaf temperatures measured at the

Table 3-6. Leaf, enclosure air, and outside air temperatures during a sampling run of *Quercus lobata* on September 9, 1997. A cirrus cloud passed overhead at 12:19.

Time (PDT)	Leaf Number 1	2	3	4	5	Enclosure Air	Outside Air
12:05	91.4	93.0	95.4	88.0	93.4	90.3	
12:06	92.8	94.2	96.5	88.5	92.8	91.2	
Enclosure was placed over a branch and air flow in the enclosure was began at 12:12							
12:12	100.6	100.5	104.9	97.7	100.3	98.3	92.5
12:13	98.8	98.9	103.4	97.7	100.5	98.7	91.8
12:14	99.0	99.1	103.2	97.9	100.3	98.5	92.2
12:15	98.6	99.4	103.2	97.8	100.3	98.7	91.8
12:16	98.8	99.4	103.2	97.7	100.0	98.4	91.4
12:17	98.4	98.9	103.6	97.1	100.1	98.4	91.2
12:18	98.5	98.7	104.0	97.4	100.3	98.2	90.1
12:19	97.7	97.9	101.4	96.1	98.3	97.3	90.4
12:20	97.0	97.1	100.3	95.4	97.6	96.4	90.1
12:21	94.8	94.6	96.1	92.6	94.7	94.0	89.8
12:22	93.5	94.4	98.2	92.9	94.9	95.5	93.8
12:23	93.7	93.8	97.7	93.0	96.7	95.6	90.5
12:24	94.6	95.0	98.8	93.7	95.8	94.4	89.6

very top of the canopy were within 1.5°C of the ambient air temperature. For leaves one meter or deeper into the canopy, median difference between air and leaf were 0.5 °C or less and the percentage of leaf temperatures within 1.5°C of air temperature increased with deeper penetration into the canopy (Pier and McDuffie 1997). In the study of Street et al. (1997), leaf temperatures within a 12 L enclosure were within $\pm$1°C of air temperatures.

Temperature and relative humidity measurements within the branch enclosure were made with a fast response digital thermometer-hygrometer (Fisher Scientific part no. 11-661-7A) with certification traceable to NIST. Accuracy was listed by the manufacturer as $\pm$0.2 °C for temperature and $\pm$1.5% for relative humidity. This instrument was checked for accuracy against a laboratory thermometer and the other Fisher digital probe thermometer. Humidity measurements were checked against readings from the CIMIS station located at the Shafter Research and Extension Center.

Although no water vapor was added to air entering the enclosure chamber, humidity within the enclosure was typically 30-50%, which was often greater than the 20-35% relative humidity found in outside air during midday hours in summer in the San Joaquin Valley.

3.3.2.4 Construction of Glass Sampling Tubes

The glass sampling tubes were made from Pyrex glass tubing 6 mm OD x 122 cm that was cut into lengths of 78 mm. An indentation was made approximately 5 mm from one end of the insert to hold the packing materials in place. The inserts were packed with a layer of pesticide grade glasswool (Alltech No. 4043), 4 mm of Carbosieve S-III 60/80 mesh, pesticide grade glasswool, 45 mm of Tenax TA 60/80 mesh or 80/100 mesh (changed to exclusively 80/100 mesh for the 1997 season) and a final packing of pesticide grade glasswool. The sampling tubes were pre-treated to remove contaminants by placing in an oven at 220°C for about 24 hours with a flow of helium through each tube of about 3 ml/min and then stored under a vacuum. A few tubes were checked periodically by GC runs to assure absence of contaminants.

3.3.2.5 Enclosure Sampling Protocol

After a plant had been selected for measurement, the enclosure was placed around a branch carefully to minimize any effects from rough handling and the bottom of the Teflon bag was loosely tied around the branch. The flow of air was begun, followed by the start of the stirring fan, and measurement of ambient temperature and PAR. If either the temperature or light intensity fluctuated appreciably during the measurement, a second or third measurement was made. The temperature and relative humidity inside the enclosure were recorded at five minutes, eight minutes (steady-state), and at the conclusion of syringe sampling. Temperatures used for normalization of emission rates were the means of the eight minute and final readings.

Shortly after eight minutes into a run, the first of three-to-five successive syringe samples of enclosure air was drawn. Sample volumes were chosen based on preliminary sampling and taxonomic predictions and were 300 cm^3 for preliminary samples. For quantitation, sample volumes were 100 cm^3 for plants observed to be isoprene emitters

but 300 cm^3 samples were repeated for plants observed to be very low or non-emitters. A retention time marker compound was added to sample tubes after the required enclosure air sample volume. An aliquot of 20-40 cm^3 of a 1 ppm standard of 2,2-dimethylbutane was taken with the glass syringe from a cylinder at the sampling site and pushed into the sample tube. Each sample tube was labeled and placed in a test tube, which was then placed in a cooler packed with dry ice and transported from the field to the laboratory. A travel blank was included with each day's samples. At the laboratory, the sample tubes were placed in a freezer at -20°C.

3.3.2.6 Dry Leafmass Measurements

Following syringe sampling, the branch was removed and placed in a paper bag. Leaves were removed and one-side leaf areas measured with a LiCor (No. LI 3100) leaf area meter. Some leaf areas could not be measured because either we did not have access to the leaf area meter during cotton harvest at the research center, some plants (e.g. *Cassia nemophila* and *Torreya californica*) had leaves very difficult to measure because of their morphology, or due to time constraints. Following leaf area measurement, leaves were dried by placing the sample bags in an adjoining greenhouse which had no cooling system, resulting in air temperatures of ca. 65°. Following drying of more than one week, leaves were weighed. Selected samples from the greenhouse were checked for complete drying by placing them in an oven at 70°C for at least 48 hr and reweighing them. In all cases the greenhouse provided complete drying of samples. The electronic balance was checked with standard weights and found to be accurate.

3.3.3 Gas Chromatograph Parameters and Calibration

A Hewlett-Packard 5890 gas chromatograph (GC), equipped with a flame ionization detector (FID) and a Hewlett-Packard 3396A recording integrator, was installed at the University of California's Shafter Research and Extension Center. A J&W Scientific GS-Q megabor column (0.53 mm ID x 30 meters and 0.0 um film thickness) was installed in the GC at the beginning of the study. The GC was cryocooled with liquid nitrogen. Initial oven temperature was 0°C held for 10 min and then ramped to 25°C at 10°C/min for 2.5 minutes and then ramped at 20°C/min to a final temperature of

225°C. The injection port and FID detector were held at 225°C. A complete listing of GC operating parameters for the emission rate data presented in this report may be found in Table 3-7.

The isoprene (2-methyl-1,3-butadiene) calibration procedure was designed to follow that used by Arey and co-workers (26) in which 100 cm^3 volume samples of air containing a known concentration of isoprene were analyzed. In this study, analyzed reference standards containing 1 ppm isoprene and 1 ppm 2,2-dimethylbutane were obtained from Scott Specialty Gas and used for the calibration of the HP 5890A. An additional cylinder of 2,2-dimethylbutane was obtained as a marker for field samples as described above.

A weekly five-point calibration was performed. Volumes of 1, 5 and 10 cm^3 were drawn into a gas-tight syringe (Hamilton Co.) and injected into glass sample tubes (described above). These volumes were equivalent to a mixing ratio of 10, 50 and 100 ppb of isoprene in 100 cm^3 of air, respectively. Volumes of 50 and 100 cm^3 were also drawn into a 100 cm^3 syringe and injected into the glass inserts. These volumes represented a mixing ratio of 500 ppb and 1 ppm of isoprene in 100 cm^3 of air, respectively. A response factor was generated by dividing the standard concentration by the peak area for the isoprene at that concentration and multiplying by 0.1 (the base volume in liters).

The response factor (RF) was calculated as:

$$RF = (C * A^{-1}) * V \qquad (6)$$

where

RF was the response factor generated by the concentration of the isoprene in the standard,

C was the concentration of the isoprene in the standard,

A was the area generated by the isoprene concentration,

and

V was the volume of the standard taken in liters (= 0.1)

Table 3-7. Gas chromatograph conditions employed in summer and autumn of 1997.

Oven Temp	0 °C
Initial Value	0 °C
Initial Time	10 min
Rate	10 °C/min
Final Value	25 °C
Final Time	0 min.
Rate A	20 °C/min
Final Value A	225 °C
Final Time A	5.5 min
Purge Valve	off
Purge Valve on	10 min
Purge Valve off	24.95 min
Signal Range 2	11
Signal Attn 2	10
Equib Time	0.5 min
Injection Temp	225 °C
Detector Temp	225 °C
Column Flow Rate	6 ml/min
Make-up Gas Flow Rate	20 ml/min.

All standards used for calibrating the GC were drawn into either a 10 cm^3 or a 100 cm^3 gas tight syringe and injected into the Tenax end of the inserts and all samples were injected through the same end (i.e., the Tenax end). When the inserts were placed into the GC for analysis, the glass sample tube was placed directly into the injection port and desorbed with the Tenax end directly above the column. To prevent any loss of the isoprene standard, less than three seconds elapsed between placing the glass sample tube in the injection port and placement of the cover, and less than 30 seconds usually elapsed between the placement of the insert into the injection port and the start of the run.

A 500 ppb standard on an insert was desorbed into the GC daily to confirm the analytical accuracy of the instrument. If not within the standard deviation range (i.e., 500 ppb standard = response factor $\pm$ standard deviation), then a second 500 ppb standard was drawn into a 100 cc gas tight syringe, injected into an insert and analyzed. If neither standard fell within the range, then a complete recalibration was performed and a new response factor was calculated and used for subsequent analyses.

3.3.4 Sample Analysis and Minimum Detection Limit

Field samples were stored at -20°C in a laboratory freezer prior to analysis. Samples were usually analyzed the day following acquisition and replicate samples were analyzed in the order taken in the field. Isoprene peak identification fell into three categories, listed in order of preference: (1) A peak was considered isoprene if it fell at ± 0.01 min from the 2,2-dimethylbutane retention time marker; or (2) the peak pattern of an ambiguous sample could be matched to a replicate sample from the same run and identified; or (3) the peak was within 0.01 minute of the retention time of isoprene in the standard. To avoid mis-identification of background noise in the chromatogram as an isoprene peak, the area reject was set at a count of 5000; peaks with areas less than this value were not considered to be isoprene even if they had an appropriate retention time. This area reject corresponded to an enclosure concentration of 5 ppbv sampled with a 100 cm^3 volume, or 1.7 ppbv sampled with a 300 cm^3 volume. Leafmass of the branch sampled affected the minimum isoprene emission rate which could be detected because the total amount of isoprene emitted from a branch of a given species is directly proportional to its leafmass. Therefore, for a branch with 20 g of leaves, the lowest isoprene emission rates which could be detected were 1 and 0.3 ug g^{-1} h^{-1} for enclosure air samples of 100 cm^3 and 300 cm^3, respectively. [GC/MS was not available at the laboratory; therefore, isoprene emission for key plant species (i.e. where no other members of the genus or sub-family have been reported) should be confirmed with GC/MS or other supplemental techniques.]

As seen in Appendix A, leafmasses of branches were often greater than 20 g, which lowered the detection limit below 1 μg g^{-1} h^{-1}. Detection limits for all enclosure runs are noted in Appendix A.

3.3.5 Sample Storage and Transport

A sample integrity study was part of the technical plan and vital in understanding the influence of sample storage and transport under conditions in the San Joaquin Valley where summer temperatures range between 20 and 40°C. Due to the geographic location of the analytical laboratory, it was important to determine how long isoprene would remain adsorbed on Carbosieve S-III and Tenax TA adsorbents, and under what

conditions the isoprene could be recovered quantitatively. The furthermost sites of sampling were in the mountains and desert approximately 100 miles distant, or 1 1/2 hours driving time from the laboratory (assuming immediate transport of the samples following collection).

For this purpose, a set of three 50 cm^3 volumes of the 1 ppm isoprene standard (Scott Specialty Gas) was drawn into a 100 cm^3 gas tight syringe (Popper and Sons, Inc.) and injected into a glass sampling tube. The storage times for the sample integrity study were 10 and 30 minutes, 1, 3 and 6 hours, and 1, 2 and 3 days. The samples were maintained at three different temperatures: ambient (25 °C), blue ice (0 °C to 6 °C) and dry ice (< -20 °C).

The sample integrity study was conducted over a two week period from October 2 to October 16, 1996. The expected isoprene concentration for the 50 cm^3 samples was 0.49 ±0.1 ppm and the measured concentrations are listed in Table 3-8.

Within overall experimental uncertainty, isoprene concentrations at ambient and blue ice temperatures remained approximately constant for the first 3 to 6 hours, but then decayed substantially over longer storage times. In contrast, measured concentrations of samples stored at dry ice temperatures were actually higher than expected values throughout the three day period. This may have been caused by not allowing the pressure in the syringe to reach ambient pressure before injecting the isoprene into the insert. Dry ice was chosen for sample transport and storage.

Calibration standards were treated in the same fashion, injecting the calibration gas into inserts packed with Carbosieve and Tenax and then freezing them until the time of insertion into the GC.

3.4 Isoprene Emission Rate Measurement Results

The isoprene emission rate data collected in this study are branch-level results, which are reported to be approximately 60% of leaf-level results obtained with a leaf cuvette apparatus (Guenther et al. 1994, Harley et al. 1997). In BHC flux models, different factors should be applied to branch-level emission rate data as compared to leaf-level data for scaling to whole plants crowns or to plant canopies.

Table 3-8. Mean isoprene concentration (ppm) in samples stored under three temperature conditions for eight time periods. Expected concentration was 0.49 ±0.1 ppm.

	Temperature Condition		
Duration	Ambient	Blue ice	Dry ice
10 min.	0.50	0.50	0.51
30 min.	0.46	0.48	0.55
1 hour	0.44	0.45	0.54
3 hours	0.51	0.56	0.52
6 hours	0.44	0.53	0.63
1 day	0.29	0.41	0.58
2 days	0.15	0.36	0.51
3 days	0.08	0.43	0.60

Mean isoprene emission rates were measured for 63 species within 29 families and 49 genera and normalized to standard conditions (see below). Sixty-one of the 63 plant species studied represent species not reported in the compilation of Benjamin et al. (1996). An overall uncertainty of about 50% is associated with these emission rate data for multiple samples taken for the same branch, based on means and standard deviations for results prior to senescence for the three species having the largest dataset, *L. styraciflua*, *Q. lobata* and *Q. douglasii*. The uncertainty estimate reported for enclosure measurements made during the BEMA project was 54% (Owen et al. 1997).

A complete description of emission rates and associated environmental parameters measured in the present study may be found in Appendix A. Unadjusted emission rates are also included in that appendix, as recommended in Winer et al. (1995), should an improved isoprene emission rate algorithm be subsequently developed for normalization to standard conditions of light and temperature.

3.4.1 Calculation of Isoprene Emission Rates

Isoprene emission rates were normalized to PAR and temperature of 1000 umol m^{-2} sec^{-1} and 30°C, respectively, using the algorithm proposed by Guenther et al. (1993)

and subsequently modified by Guenther (1997). Specifically, the first number in the denominator of the temperature correction term becomes 0.961 (Guenther, 1997) rather than 1.0 (Guenther, 1993), as seen in equation 10.

The normalization equation was of the form:

$$ER = \frac{ERM}{C_L * C_T} \quad (7)$$

where

ER was the normalized isoprene emission rate,

ERM was the measured isoprene emission rate,

C_L was the correction factor for light intensity, and

C_T was the correction factor for temperature.

The term for light intensity correction (C_L) was calculated as follows:

$$C_L = \frac{a * C_{L1} * L}{(1 + a^2 * L)^{1/2}} \quad (8)$$

where

L was the PAR (umol m^{-2} sec^{-1}),

C_{L1} was an empirical coefficient (= 1.066), and

a was an empirical coefficient (= 0.0027).

As light intensity drops, C_L declines and is prone to increasingly large errors; therefore, the algorithm should not be used for light intensities below 100 umol m^{-2} sec^{-1} (Street et al. 1997). In no cases in this study were light intensities at or below 100 umol m^{-2} sec^{-1}; rather, the lowest PAR recorded were two measurements at 350, one at 440 and a third at 710 umol m^{-2} sec^{-1}. Most PAR measurements were between 1000 and 1700 umol m^{-2} sec^{-1}.

Temperatures were converted from Fahrenheit to Kelvin using the equation:

$$K = ((F - 32) * 5/9) + 273 \quad (9)$$

where

K was the temperature in degrees Kelvin and

F was the temperature in degrees Fahrenheit.

The term for temperature correction (C_T) was calculated as follows:

$$C_T = \frac{\exp\left[\frac{C_{T1}(T - T_S)}{R * T_S * T}\right]}{0.961 + \exp\left[\frac{C_{T2}(T - T_M)}{R * T_S * T}\right]} \quad (10)$$

where

T was the leaf temperature in degrees Kelvin,

R was the gas constant (8.304 J/ K mole),

T_S was the normalizing temperature in degrees Kelvin,

T_M was an empirical constant (= 314 K),

C_{T1} was an empirical constant (= 95,000 J), and

C_{T2} was an empirical constant (= 230,000 J).

The unadjusted isoprene emission rate (ERM) was calculated as:

$$ERM = (MI * FR * 60 * 0.001) * LM^{-1} \quad (11)$$

where

ERM was the measured isoprene rate

MI was the amount of isoprene in the sample

FR was the flow rate through the enclosure (35.9 L min^{-1})

LM was the leaf mass on a dry weight basis

and the other numbers represent unit conversions from minutes to hours and liters to cubic meters, respectively.

The mass of isoprene (MI) was calculated as:

$$MI = 40.9 * MW * C \quad (12)$$

where

MI was the amount of isoprene in the sample,

MW was the molecular weight of isoprene (68.12), and

C was the mixing ratio of isoprene in the sample in ppm.

Isoprene concentration was measured by gas chromatography and calculated as

$$C = (A * RF) * V^{-1} \quad (13)$$

where

C was the mixing ratio of the isoprene in the sample in ppm,

A was the area generated by the isoprene in the sample,

RF was the response factor generated from the isoprene in the standard,

and

V was the volume of the sample taken in liters

3.4.2 Isoprene Emission Rates of the Plant Species Investigated

Isoprene emission rates may be expressed with several unit systems. In this report we prefer micrograms isoprene per gram dry leafmass per hour (ug g^{-1} h^{-1}) for comparison with Benjamin et al. (1996). An alternative unit system used for many BHC compounds is based on micrograms carbon per gram dry leafmass per hour (ugC g^{-1} hr^{-1}). Because the molecular weight of isoprene is 68.12 and the sum of the atomic weights for

the carbon fraction of the molecule 60.06, the carbon mass is 88.2% of the total molecular mass. Therefore, an isoprene emission rate expressed on a carbon basis (ugC g^{-1} hr^{-1}) will be equivalent to an isoprene emission rate expressed on an isoprene basis (ug g^{-1} h^{-1}) * 0.882. In comparing data from this study to other published works, we have converted literature isoprene emission rates expressed on a carbon basis to ug g^{-1} h^{-1}.

Guenther et al. (1994) placed leaf-level isoprene emission rates into four descriptive categories, each with a midpoint and range of ±50%. The categories were (ugC g^{-1} hr^{-1}) (1) negligible, <0.1; (2) low, 14 ±7; (3) moderate, 35 ±17.5, and (4) high, 70 ±35. Corresponding branch-level emission rate midpoints were also given (Guenther et al., 1994) of <0.1, 8, 20 and 40 ugC g^{-1} hr^{-1}. Branch level emission rates are reported to be approximately 60% of rates determined with leaf cuvettes (Guenther et al. 1994) because of self-shading of leaves within the enclosure. More specifically, for four oak species studied, the mean branch-level isoprene emission rates were 59% and 56% for sun leaves and shade leaves, respectively, of the leaf-level isoprene emission rates obtained with a leaf cuvette apparatus (Harley et al. 1997), bracketing the value of 57% used as an overall conversion factor by Guenther et al. (1994).

We have followed the example of Guenther et al. (1994) in describing isoprene emission rate ranges, with slight modifications: our ranges are based on branch-level data, we use the units of ug g^{-1} h^{-1} and we have assigned endpoints so ranges do not overlap. Quantitatively, our branch-level isoprene emission rate ranges correspond very closely to the leaf-level ranges of Guenther et al. (1994). In the following discussion we refer to four branch-level emission rate categories (ug g^{-1} h^{-1}): (1) negligible or below detection limit (BDL), <1; (2) low, 1-10; (3) moderate, 10-25; and (4) high, 25-70.

3.4.2.1 Isoprene Emission Rates Within Families

As seen from Table 3-9, all members sampled in this study within 19 families had isoprene emissions BDL. These results are consistent with the literature cited in Benjamin et al. (1996) for ten families, including Anacardiaceae (cashew), Bignoniaceae (bignonia), Caprifoliaceae (honeysuckle), Compositae (composite), Cupressaceae (cypress), Juglandaceae (walnut), Lamiaceae (mint), Oleaceae (olive), Rosaceae (rose) and Taxodiaceae (bald cypress), all of which may be regarded as containing mostly if not

Table 3-9. Plant families where all members sampled in the present study had mean adjusted isoprene emission rate measurements (ug g^{-1} h^{-1}) below detection limits (BDL).

Scientific Name	Common Name	Number of Enclosure Runs
Anacardiaceae		
Pistacia chinensis	Chinese Pistache	1
Betulaceae		
Betula nigra	River Birch	3
Betula papyrifera	Paper Birch	1
Bignoniaceae		
Macfadyena unguis-cati	Cat's Claw Vine	3
Caprifoliaceae		
Viburnum trilobum	American Highbush Cranberry	2
Chenopodiaceae		
Atriplex polycarpa	Saltbush	1
Compositae		
Artemisia ludoviciana	Silver Wormwood	2
Baccharis pilularis	Coyote Brush	2
Chrysothamnus nauseosus	Rubber Rabbitbrush	2
Euryops pectinatus	Euryops Daisy	3
Cornaceae		
Cornus stolonifera	Redtwig Dogwood	3
Cupressaceae		
x Cupressocyparis leylandii	Leyland Cypress	2
Euphorbiaceae		
Sapium sebiferum	Chinese Tallow Tree	3
Hippocastanaceae		
Aesculus californica	California Buckeye	2
Juglandaceae		
Carya illinoensis	Pecan	2

Table 3-9. (Continued)

Scientific Name	Common Name	Number of Enclosure Runs
Lamiaceae		
Rosemarinus officinalis	Rosemary	2
Salvia greggii	Autumn Sage	2
Malvaceae		
Gossypium barbadense	Cotton 'Pima'	1
Gossypium hirsutum	Cotton 'Maxxa'	1
Hibiscus rosa-sinensis	Hibiscus	1
Oleaceae		
Fraxinus velutina 'Modesto'	Modesto Ash	1
Syringa vulgaris	Common Lilac	2
Pinaceae		
Abies concolor	White Fir	1
Picea pungens glauca	Colorado Blue Spruce	1
Proteaceae		
Grevillea robusta	Silk Oak	2
Rosaceae		
Rosa hybrida	Rose	2
Steruliaceae		
Brachychiton populneus	Bottle Tree	2
Taxaceae		
Torreya californica	California Nutmeg	1
Taxodiaceae		
Sequoiaodendron giganteum	Giant Sequoia	2
Sequoia sempervirens	Coast Redwood	1
Verbenaceae		
Latana camara	Lantana	1
Vitex agnus-castus	Chaste Tree	1
Zygophyllaceae		
Larrea tridentata	Creosote Bush	2

all negligible-emitters. These results are important because the Rosaceae and Compositae are very large families, well-represented in agriculture, native plant communities and urban landscapes.

Additional families not reported in Benjamin et al. (1996) but sampled in this study and found to contain only negligible emitters included Betulaceae (birch), Cornaceae (dogwoods), Hippocastanaceae (buckeye), Malvaceae (mallow), Sterculiaceae (sterculia), Taxaceae (yew), Verbenaceae (verbena), and Zygophyllaceae (caltrop).

Needle evergreens may generally be thought of as low or negligible isoprene emitters. In this study, isoprene emissions were not detected from plants sampled from the Cupressaceae, Taxaceae and Taxodiaceae families, including *x Cupressocyparis leylandii* (leyland cypress), *Sequoiadendron giganteum* (giant sequoia), and *Sequoia sempirvirens* (coast redwood). Isoprene emissions have been previously reported as below detection limits or non-detected for plants sampled within these families (Lamb et al. 1985, 1987, Guenther 1994, Winer et al. 1983, Arey et al. 1995, Zimmerman 1979). We did not find isoprene emitted by *Torreya californica* (California nutmeg) of the Taxaceae family, a family not reported in Benjamin et al or *Abies concolor* (white fir) listed as a negligible emitter by Guenther et al. (1994). We did not find measurable isoprene from *Picea pungens* (blue spruce) although isoprene emission has been reported from four spruce species including *Picea pungens*, which had a moderate emission rate of isoprene of 14 ug g^{-1} h^{-1} (Kempf et al. 1996), and isoprene emission was also reported by Evans et al. (1982) for two *Picea* species. Emission for *Picea sitchensis* (Sitka spruce) was only 0.7 ug g^{-1} h^{-1} (not normalized for light and temperature) in June of 1992 followed by a 2-5 fold decrease in emissions from July to September (Street et al. 1996). It is possible the blue spruce we sampled was emitting isoprene, but at rates below our detection limit.

Deciduous and broadleaf evergreen plants within the Anacardiaceae, Compositae and Oleaceae families sampled in this study had isoprene emission rates which were below detection limits (Table 3-9), including *Pistacia chinensis* (Chinese pistache), *Baccharis pilularis* (coyotebrush), *Chrysothamnus nauseosus* (rubber rabbitbrush), *Euryops pectinatus* (euryops daisy), *Fraxinus velutina 'Modesto'* (Modesto ash), and *Syringa vulgaris* (common lilac). Our results are consistent with the reported isoprene

emissions of other plants within these families (Zimmerman 1979, Winer et al. 1983, Winer et al. 1989, Corchnoy et al. 1992, Arey et al. 1995). These species we have studied, like others reported as non-emitters or below detection limits, may emit isoprene but at very low levels (Rasmussen and Khalil 1997). Chinese pistache and Modesto ash are shade trees often planted in urban landscapes in California and euryops daisy is a common ornamental shrub. Coyotebrush is often used as a groundcover along freeways and is also found in native plant communities, while rubber rabbitbrush is a California native plant found at elevations of about 3000 ft, such as along I-5 north of the SoCAB.

The Betulaceae (birch) family contains *Betula* and *Carpinus*, genera with species reported to have negligible emissions of isoprene (Lamb et al. 1985, 1987) and *Betula nigra* (river birch) and *Betula papyrifera* (paper birch) sampled in this study were also found to have negligible isoprene emission rates.

Certain families appear to contain predominately negligible emitters, but with some moderate or high emitters, as seen in Table 3-10, although most members of Leguminosae (legume) family which have been studied have reported isoprene emission rates BDL, exceptions exist, such as *Robinia pseudoacacia* (black locust) (Lamb et al. 1983, Winer et al. 1983). All of the legumes sampled in the present study, including *Acacia aneura* (mulga), *Acacia melanoxylon* (blackwood acacia) *Caesalpinia gillessii* (desert bird-of-paradise), *Cassia artemisiodes* (feathery cassia), *Cassia nemophila* (desert cassia),*Ceratonia siliqua* (carob) *Cercidium floridum* (= *Parkinsonia floridum*) (blue palo verde), *Prosopis alba* 'Colorado' (Colorado mesquite) and *Cytisus spachianus* had emission rates BDL except *Sophora secundiflora* (Texas mountain laurel) and *Spartium junceum* (Spanish broom), for which we found values of 34 and 21 ug g^{-1} h^{-1}, respectively.

The Leguminosae may be divided into three subfamilies: Caesalpiniodeae, Mimosoideae and Papilionoideae. The two species found to emit isoprene in the present study, *Sophora secundiflora* (Texas mountain laurel) and *Spartium junceum* (Spanish broom), are found in the subfamily Papilionoideae (= Faboideae) of the Leguminosae family, which has been suggested to contain plants with moderate or high isoprene emission rates (Rasmussen and Khalil 1997) and 9 of 13 species in this subfamily found

Table 3-10. Summary of plants from urban and natural environments of California sampled in the present study where at least one species of the family had a mean adjusted isoprene emission rate (ug g^{-1} h^{-1}) above the detection limit.

Scientific Name	Common Name	Isoprene Emission Rate	Number of Enclosure Runs
Fagaceae			
Quercus chrysolepis	Canyon Live Oak	19	3
Quercus douglasii	Blue Oak[1]	27	3
Quercus kelloggii	California Black Oak[1]	54	2
Quercus lobata	Valley Oak[1]	23	3
Quercus palustris	Pin Oak	27	1
Quercus suber	Cork Oak	BDL	1
Hamamelidaceae			
Liquidambar styraciflua	Sweetgum[1]	26	6
Leguminosae			
Acacia aneura	Mulga	BDL	1
Acacia melanoxylon	Blackwood Acacia	BDL	3
Caesalpinia gilliesii	Bird of Paradise Bush	BDL	2
Cassia artemisiodes	Feathery Cassia	BDL	2
Cassia nemophila	Desert Cassia	BDL	2
Ceratonia siliqua	Carob	BDL	1
Cercidium floridum	Blue Palo Verde	BDL	2
Cytisus spachinanus	Broom	BDL	1
Lysiloma thornberi	Feather Bush	BDL	2
Prosopis alba 'Colorado'	Colorado Mesquite	BDL	1
Sophora secundiflora	Texas Mountain Laurel	34	2
Spartium junceum	Spanish Broom	21	2
Moraceae			
Morus alba 'Fruitless'	Fruitless Mulberry	BDL	2
Ficus carica	Edible Fig	18	1
Myrtaceae			
Eucalyptus camaldulensis 'C2'	Red Gum	28	4
Eucalyptus grandis 'GCT'	Rose Gum	21	4
Eucalyptus polyanthemos	Silver Dollar Gum	10	2

Table 3-10. (Continued)

Scientific Name	Common Name	Isoprene Emission Rate	Number of Enclosure Runs
Palmae			
Syagrus romanzoffiana	Queen Palm	BDL	2
Washingtonia robusta	Mexican Fan Palm	14	1
Salicaceae			
Populus alba	White Poplar	25	2
Populus euramerica 'R111'	Hybrid Poplar	31	2
Populus euramerica 'R112'	Hybrid Poplar	28	2
Populus fremontii	Western Cottonwood	43	2
Populus nigra italica	Lombardy Poplar	36	3

[1] The last measurements of the season were excluded from the mean because of senescence of leaves.

in Africa were isoprene emitters based measurements made with a portable instrument containing a photoionization detector (PID) (Klinger et al. 1998). Another member of the Papilionoideae subfamily examined in the present study, *Cytisus spachianus* (= *Cytisus racemosus*, = *Genista racemosus*) (broom), did not exhibit detectable isoprene, and resampling is recommended; a *Cytisus* species and *Genista scorpius* were found to be moderate isoprene emitters in the BEMA project (Owen and Hewitt 1997).

All the legumes of the Caesalpiniodeae subfamily sampled in the present study, *Caesalpinia gillessii*, the *Cassia* species, *Ceratonia siliqua*, and *Cercidium floridum* , did not emit detectable quantities of isoprene. Of the legumes in the Caesalpiniodeae subfamily studied in Africa, nine of 16 species studied were isoprene emitters as determined with a PID (Klinger et al. 1998). Of these 16 species, the only species with a genus corresponding to plants sampled in the present study was a *Cassia* species, which was classified as a non-emitter.

The Mimosoideae subfamily of the Leguminosae contains the *Acacia* species and *Prosopis alba* 'Colorado' sampled in the present study, which were found to be negligible isoprene emitters. The three *Acacia* species sampled in Africa with a PID were also found to be non-emitters (Klinger et al. 1998).

Based on limited data, certain families appear to contain approximately equal numbers of members with BDL or low isoprene emission rates and moderate-to-high rates. Variation within the Moraceae (mulberry) family may be seen by comparing *Ficus fistulosa*, with an isoprene emission rate of 27 ug g^{-1} h^{-1} (Cronn and Nutmagul 1982), to *Morus rubra*, which was a negligible emitter (Zimmerman 1979). In this study, within the Moraceae family, *Ficus carica* (edible fig) was a moderate emitter of isoprene at a rate of 17 ug g^{-1} h^{-1} but *Morus alba* 'Fruitless' (fruitless mulberry) exhibited negligible isoprene emissions (i.e. BDL). Of African plants sampled, seven of 12 were isoprene emitters, as determined by PID measurement. These included five *Ficus* species and of those, two were classified as high isoprene emitters, one was classified as a low emitter and two were classified as non-emitters (Klinger et al. 1998).

Certain families seem to be dominated by plants emitting isoprene at moderate-to-high rates. The Palmae family (palms) has members with isoprene emissions rates ranging from low to very high (Zimmerman 1979, Winer et al. 1983, Cronn et al. 1982). In this study, two palms common in California landscapes were sampled and one of the two, *Washingtonia robusta*, was a moderate isoprene emitter at a rate of 14 ug g^{-1} h^{-1}. The member of Euphorbiaceae (spurge) family sampled in the present study, *Sapium sebiferum* (Chinese tallow tree) had emissions BDL, while previously reported isoprene emission rates for three other members of the Euphorbiaceae family, but no other *Sapium* species, ranged from negligible to high (Cronn and Nutmagul 1982, Winer et al. 1983).

Certain families seem to contain mostly species with high emissions rates, such as the Salicaceae (willows and poplars) (Zimmerman 1979, Winer et al. 1983, Evans 1982). The poplars sampled in the present study, *Populus alba* (white poplar), *P. euramerica* 'R111' and 'R112' (hybrid poplars), *P. fremontii* (western cottonwood), a California native, and *P. nigra italica* (lombardy poplar) were clearly high isoprene emitters with mean emission rates of 25, 31, 28, 43, and 36 ug g^{-1} h^{-1}, respectively.

The Myrtaceae (myrtle) family also contains several genera with high isoprene emission rates, such as *Eucalyptus*, *Callistemon*, and *Myrtus* (Evans et al. 1982, Winer et al., 1983). The Eucalyptus species sampled in this study, *E. polyanthemos* (silver dollar gum), *E. grandis* 'GCT' (rose gum), and *E. camaldulensis* 'C2' (red gum) had moderate to high emission rates of 10, 21, and 28 ug g^{-1} h^{-1}, respectively.

3.4.2.2 Isoprene Emission Rates Within Genera

Genera which included two or more moderate-to-high emitting species sampled in this study included *Eucalyptus* (eucalyptus or gum trees) and *Populus* (poplar and aspen). The three eucalyptus species measured in this study had emission rates ranging from 10-28 ug g^{-1} h^{-1}. The four poplar species were high emitters, ranging from 25-43 ug g^{-1} h^{-1}. These results are consistent with previous reports (Evans et al. 1982, Winer et al. 1983, Guenther et al. 1994)

Isoprene emission rates were consistent within most genera with the chief exception of *Quercus* (oak), a frequently occurring genus in native stands as well as in urban landscapes in California For example, of the *Quercus* reported here, mean emission rates of isoprene emission ranged from negligible for *Q. suber* (cork oak) to moderate (19 ug g^{-1} h^{-1}) for *Q. chrysolepis* (canyon live oak) and high (27 ug $g^{-1}h^{-1}$) for *Q. palustris* (pin oak) to very high (54 ug g^{-1} h^{-1}) for *Q. kelloggii* (California black oak). These observations are consistent with the variability observed within the *Quercus* genus by other researchers. As has been noted by previous investigators, isoprene emission rates for *Quercus* range from low to very high (Zimmerman 1979, Lamb et al. 1983, Isidorov et al. 1985, Winer et al. 1989, Arey et al. 1995). Unfortunately, an illustrative subfamily categorization of the oaks, analogous to the legumes, is not available. From a geographic perspective, oaks native to North America include many species with high isoprene emission rates while lands surrounding the Mediterranean Sea seem to contain at least seven species with negligible isoprene emission rates, three with high isoprene emission rates, and several with high monoterpene emission rates, unlike any North American species reported thus far (Rasmussen and Khalil 1997, Seufert et al. 1997). In the present study, *Q. suber* (cork oak), which is native to the Iberian peninsula, was a negligible emitter of isoprene, whereas North American species, such as *Q. chrysolepis*, *Q. douglasii*, *Q. kelloggii*, *Q. lobata* and *Q. palustris* were moderate to high isoprene emitters. The first four of these five oak species are California native plants and two species, *Q. lobata* (valley oak) and *Q. douglasii* (blue oak), are especially common on the western slope of the Sierra Nevada above the San Joaquin Valley floor.

One *Quercus* species, *Q. ilex* (holm oak = holly oak), which is native to southern Europe, has been reported as a light-dependent monoterpene emitter but a negligible

isoprene emitter (Staudt and Seufert 1995, Kesselmeier et al. 1996, Loreto et al. 1996). In the present study, a tree which had been labeled in the nursery and sold as *Q. ilex* and had morphological features similar to *Q. ilex* was sampled and was found to be an isoprene emitter. However, the isoprene emission rate was the same as mean of previously reported values for *Q. virginiana*, southern live oak (Tingey et al. 1979, Zimmerman 1979). It is possible the tree in question was actually *Q. virginiana*, since that species and *Q. ilex* are similar in leaf form, acorn dimensions and growth habit. Therefore, we have not presented data for this plant pending confirmation by GC/MS or further confirmation of the actual species identity. For future emission rate studies of *Q. ilex*, a relatively popular urban species in California, we recommend using only authoritative identifications, such as found in arboreta or botanic gardens.

3.4.3 Variability in Isoprene Emission Rates

3.4.3.1 Plant-to-Plant Variability

As noted earlier, the isoprene emission rate will be affected by the isoprene synthase activity of individual leaves, determined in part by genetics which resulted in uncertainty as high as a factor of five when modeling isoprene emission of *Quercus robur* (English oak) leaves (Schnitzler et al. 1997).

Guenther et al. (1991) observed leaf-to-leaf variability of *Eucalyptus globulus* of about ±50% (the ratio of the standard deviation to the mean) for both isoprene and monoterpene emissions. Therefore, Guenther et al. (1994) developed emission categories centered around a midpoint and with an associated range of ±50% of the midpoint, an approach which has been used in considering data from the present study. The range of published emission rates for certain species exceeds this range, however. For example, isoprene emission rates (ug g^{-1} hr^{-1}) for *Liquidambar styraciflua* include 3.5 (Zimmerman 1979), 17.8 (Evans et al. 1982) and 35.3 (Corchnoy et al. 1992), with the high and low values differing by a factor of 10. Also, *Quercus dumosa* has reported values (ug g^{-1} h^{-1}) of 5.2 (Winer et al. 1983) and 54.4 (Arey et al. 1995), again differing by a factor of ten. Other species with dissimilar reported values (ug g^{-1} hr^{-1}) include *Q. virginiana* with 9.5 (Zimmerman 1979) and 30.9 (Tingey et al. 1979), and *Q. borealis* with 19.7 (Evans et al. 1982) and 40.4 (Flyckt 1979), although the values for each of these species are within

50% of means calculated from them. A confidence interval of ±50% appears to be reasonable for branch-level emission rate data from this study.

Some variability in published results may be attributable to early experiments in which the effects of light intensity and temperature upon isoprene emission rates were not well understood and therefore these environmental factors were expressed qualitatively (e.g. sun or shade) but not measured. Also, reported isoprene emission rates may have been normalized using earlier algorithms without report of the actual isoprene emission measurements (Winer et al., 1995).

In this study, *Liquidambar styraciflua* individuals varied from 13 ug g^{-1} h^{-1} for each of the two trees sampled at the Eddy Arboretum at Placerville to a high of 40 ug g^{-1} h^{-1} for a tree sampled at California Hot Springs. The mean of values found in this study was 26 ug g^{-1} h^{-1} compared to 19 ug g^{-1} h^{-1} as the mean of the three values found in Benjamin et al. (1996), a good agreement.

3.4.3.2 Branch-to-Branch Variability

Branch-to-branch variability is included in plant-to-plant variability. No significant difference ($P < 0.05$) was observed in 20 samples from two branches of a *Eucalyptus globulus* tree, 10 samples taken from each branch (Street at al., 1997). Branch-to-branch variability was not specifically addressed in this study.

3.4.3.3 Diurnal Variability

Diurnal variability of isoprene emission rate has been reported in many studies, with only a few cited here (Tingey et al. 1979, Winer et al. 1989, Ohta 1986, Helmig et al. 1997, Pier and McDuffie 1997, Street et al. 1997). Diurnal variability usually refers to the absolute change in isoprene emission rate, mostly due to changes in light intensity and temperature. Of interest was possible change of the normalized isoprene emission rate. However, the few samples taken morning and afternoon from the same tree of *Eucalyptus camaldulensis* 'C2' and *E. grandis* 'GCT' (both species taken 1 October), and *P. nigra italica* (taken 24 September) did not reveal diurnal variability of the normalized isoprene emission rate.

3.4.3.4 Seasonal Variability

We measured a decrease in isoprene emission rate for certain species at the end of the season, for example *Q. kelloggii*, which was sampled 13 October 1997 at an elevation of about 500 m (1600 ft) when leaves were clearly entering senescence. Emissions from a *Q. lobata* tree sampled 7 November 1997 dropped to BDL from a mean of 22 ug g^{-1} h^{-1} from the same tree sampled 3 September 1997, which was located on the San Joaquin valley floor and isoprene emissions from another *Q. lobata* sampled 3 November were 20% of the those measured from samples taken 19 August from the same tree. The emission from *L. styraciflua* sampled 3 November 1997 were less than one-half of the previously reported isoprene emission rate, and less than half of the *L. styraciflua* sampled in mid-October. However, for the period June 1 - September 15, when elevated ozone concentrations are most likely in the southern San Joaquin Valley and the SoCAB, the emission of isoprene should be relatively constant.

3.5 Implications for the Taxonomic Method

3.5.1 General Observations

In Linnean plant classification, species are primarily organized on the basis of physical similarities of morphology, particularly floral anatomy. Categorizing plant emission rates according to taxonomy presumes physiological similarities among members of a given species, genus and family. Because species may hybridize and are often graft-compatible, implying a degree of genetic similarity, such a physiological relationship is plausible. Hybridization may also imply that species-specific emissions rates may be difficult to determine for species within certain genera, such as the *Eucalyptus* genus, which contains more than 600 species, or the large *Quercus* genus. Hybridization or intraspecies variability may partly explain the range of emission rates reported for a single species, such as *Q. dumosa* (Winer et al. 1995, Arey et al. 1995).

The capability of species to hybridize implies a close taxonomic relationship. While hybridization is often possible among plant species, implying assignment to the same genus, hybridization between plants of different genera is uncommon. Therefore, other characteristics, such as floral morphology, must be used to group genera and place them into families. Families may represent a more tenuous association of plant genera

than genera do of plant species. Therefore, it should not be surprising that isoprene emission rates are often similar when considering members of the same genus, but families may contain both high- and low- emitters. Of course, it is desirable to base taxonomic predictions on the most closely related species for which data are available, and association of emitters generally occurs at the genus level (Monson 1997).

It may be possible to use emission rate data to develop a better understanding of plant taxonomy and phylogenetic relationships may be inferred from the presence and concentration of chemical compounds. For example, a scheme for organizing the *Citrus* genus has been developed based on contents of polymethoxyflavones in the fruit peels (Mizuno et al 1991) and herbaceous flowering plants of *Gaillardia* were separated into species and varieties based on presence of lactones and flavonoids (Petenatti et al. 1996).

3.5.2 Comparison of Results of the Present Study to Taxonomic Predictions

As shown in Table 3-11, the data obtained in the present study may be compared to specific emission rate predictions for plant species made on the basis of taxonomy in Table 3 of Benjamin et al. (1996). For *Euryops pectinatus* (Compositae family) the predicted isoprene emission rate was 0, assigned on the basis of family, and agreed with results of this study. Based on the literature and results from the present study, the family Compositae appears to contain plants with negligible isoprene emission rates.

For *Ceratonia siliqua* (Leguminosae) the predicted emission rate was 4 ug g^{-1} h^{-1} based on an average of species within the legume family while our measured value was BDL. Within the Leguminosae family a mean of all genera is probably unsatisfactory, although BDL is well within the factor or ten criterion established by Benjamin et al. (1996), because legumes of most genera appear to have negligible isoprene emission rates with exception of certain subfamilies, such as the Papilionoideae (= Faboideae) (Rasmussen and Khalil 1997). The predicted isoprene emission rate for *Sophora japonica* of 4 (Benjamin et al. 1996) should probably be replaced with a predicted rate of about 20, based on a mean of *Robinia pseudoacacia* (Lamb et al., 1983), and *Spartium junceum* and *Sophora secundiflora* measured in this study.

Table 3-11. Mean plant isoprene emission rates (ug g^{-1} h^{-1}) from the present study compared to the specific rates predicted on the basis of plant taxonomic relationships (found in Table 3 of Benjamin et al. (1996)).

Scientific Name	Common Name	Present Study	Predicted Rate	Ratio[1] (Pres. Study/ Predicted)
Anacardiaceae				
Pistachia chinensis	Chinese Pistache	BDL	0.0	1
Compositae				
Baccharis pilularis	Coyote Brush	BDL	0.0	1
Euryops pectinatus	Euryops Daisy	BDL	0.0	1
Fagaceae				
Quercus chrysolepis	Canyon Live Oak	19	24.8	0.8
Quercus kelloggii	California Black Oak	54	24.8	2.2
Quercus suber	Cork Oak	BDL	24.8	N/A
Leguminosae				
Acacia melanoxylon	Blackwood Acacia	BDL	0.0	1
Ceratonia siliqua	Carob	BDL	4.3	N/A
Cercidium floridum	Blue Palo Verde	BDL	4.3	N/A
Moraceae				
Ficus carica	Edible Fig	18	27.0	0.6
Morus alba 'Fruitless'	Fruitless Mulberry	BDL	0.0	1
Myrtaceae				
Eucalyptus camaldulensis	Red Gum	28	32.5	0.9
Eucalyptus polyanthemos	Silver Dollar Gum	10	32.5	0.3
Oleaceae				
Fraxinus velutina 'Modesto'	Modesto Ash	BDL	0.0	1
Rosaceae				
Rosa sp.	Rose	BDL	0.0	1
Palmae				
Washingtonia robusta	Mexican Fan Palm	14	9.9	1.4
Pinaceae				
Abies concolor	White Fir	BDL	1.4	N/A

Table 3-11. (Continued)

Scientific Name	Common Name	Present Study	Predicted Rate	Ratio[1] (Pres. Study/ Predicted)
Taxodiaceae				
Sequoia sempervirens	Coast Redwood	BDL	0.0	1
Sequoiadendron giganteum	Giant Sequoia	BDL	0.0	1

[1] Where emissions were BDL in the present study and a zero was assigned by Benjamin et al., the ratio is given as 1 indicating agreement. N/A = Not Applicable.

For *Acacia melanoxylon*, *Fraxinus velutina* 'Modesto' and *Morus alba* 'Fruitless', the predicted isoprene emission rates (Benjamin et al. 1996) were 0, assigned on the basis of genus and confirmed by this study. For *Ficus carica* (edible fig), the predicted isoprene emission rate and the rate found in this study were 27 and 18 ug g^{-1} h^{-1}, respectively, in good agreement. For unmeasured *Quercus* species, such as *Q. suber* and *Q. chrysolepis*, an isoprene emission rate of 25 was proposed by Benjamin et al. (1996), calculated as the mean of reported *Quercus* species. However, for the *Quercus*, a mean of the genus is probably not satisfactory because of the range in reported emission rates for species within that genus. For the *Quercus* species reported here (see Table 3-10), isoprene emission rates ranged from BDL for *Q. suber* (cork oak) to 54 ug g^{-1} h^{-1} for *Q. kelloggii* (California black oak).

In summary, for 13 of 19 "predictions" found in Benjamin et al. (1996) (Table 3-11) isoprene emission rates measured in the present study were within ±50% of the predicted rate. Nine of the nine species expected to have zero isoprene emission rates were measured as BDL (and the ratio of the predicted to the measured rate was considered to be one). By considering subfamily taxonomy of the Leguminosae, the predictive accuracy (±50%) rises to 15 of 19. In addition, if oaks are not considered, since *Quercus* is so variable, the proportion rises to 14 of 16. For the remaining two species, *Eucalyptus polyanthemos* and *Abies concolor*, it would be of interest to further test agreement with the genus-based prediction of Benjamin et al. (1996).

No predictions were made in Benjamin et al. (1996) for many other species measured within this study. However, species measured in this study may be compared

with mean values for families and genera as seen in Table 3-12. The family mean for Fagaceae and the genus mean for *Quercus* (oaks) were each 25 ug g^{-1} h^{-1} based on data from this study compared to 24.8 ug g^{-1} h^{-1} in Benjamin et al. (1996), excellent agreement, but isoprene emission rates of individual oak species varied from BDL to 54 ug g^{-1} h^{-1}, $\pm$100% of the genus or family means. For the Hamamelidaceae family and the *Liquidambar* genus, the means were 26 ug g^{-1} h^{-1} based on the present study compared to 18.9 calculated from the data in Benjamin et al. (1996), very good agreement. For the Salicaceae family, the family mean calculated from the data found in Benjamin et al. (1996) was 47.2 and the genus mean for *Populus* (poplar) species contained within this family was almost identical, 44 ug g^{-1} h^{-1}. The mean of *Populus* species measured in this study was 33 ug g^{-1} h^{-1} and individual poplar species were within $\pm$35% of this value.

As found in the previous compilation of Benjamin et al. (1996), comparison of species with the corresponding genus-level means provides generally good agreement, with an obvious exception of *Quercus* (oaks). Also, for families containing genera with a wide range of emission rates, such as Palmae (palms), Moraceae (mulberry) or Euphorbiaceae (spurge), consideration of genus means is distinctly preferable to family means. For example, for the Palmae (palms), the family mean (Benjamin et al. 1996) contains a value of 173 ug g^{-1} h^{-1} for *Elais guineensis* which raises the family mean to 36.5 ug g^{-1} h^{-1}, far above the 9.9 ug g^{-1} h^{-1} reported for *Washingtonia filifera* (Benjamin et al. 1996) and 14 ug g^{-1} h^{-1} reported for *W. robusta* measured in this study. For the legumes, classification into subfamilies is helpful for taxonomic isoprene emission rate assignment, although recent work by Klinger et al. (1998) has shown dissimilar isoprene emission rates within the subfamilies.

The taxonomic method is thus seen to provide a useful framework for organizing and understanding isoprene emission rates, especially for families and genera containing few if any anomalous species. The method is seen to work well in many cases but with exceptions (Seufert et al. 1997) and the most troublesome genus for taxonomic predictions at this time is *Quercus* (oaks) (Geron et al. 1995, Seufert et al. 1997) and further characterization of this genus is recommended. Oaks are very important for BHC emission inventories in California because of their wide distribution in both urban and

Table 3.12 Comparison of isoprene emission rates (ug g^{-1} h^{-1}) measured in the present study with values reported in the compilation of Benjamin et al. (1996) referred to in the table below as REF.

Family	Family Mean		Genus	Genus Mean		Species	Species Mean	
	REF	Pres. Study		REF	Pres. Study		REF	Pres. Study
Anacardiaceae	NED[1]	BDL[1]	Pistacia	NED	BDL	P. chinensis	NR	BDL
Betulaceae	NR[1]	BDL	Betula	NR	BDL	B. nigra	NR	BDL
				NR	BDL	B. papyrifera	NR	BDL
Bignoniaceae	NED	BDL	Macfadyena	NR	BDL	M. unguis-cati	NR	BDL
Caprifoliaceae	NED	BDL	Viburnum	NED	BDL	V. trilobum	NR	BDL
Chenopodiaceae	NR	BDL	Atriplex	NR	BDL	A. polycarpa	NR	BDL
Compositae	BDL	BDL	Artemisia	NED	BDL	A. ludoviciana	NR	BDL
			Baccharis	NR	BDL	B. pilularis	NR	BDL
			Chrysothamnus	NR	BDL	C. nauseosus	NR	BDL
			Euryops	NR	BDL	E. pectinatus	NR	BDL
Cornaceae	NR	BDL	Cornus	NR	BDL	C. stolonifera	NR	BDL
Cupressaceae	0.0	BDL	x Cupressocyparis	NR	BDL	x C. leylandii	NR	BDL
Euphorbiaceae	17.6	BDL	Sapium	NR	BDL	S. sebiferum	NR	BDL

Table 3.12 (Continued)

Family	Family Mean		Genus	Genus Mean		Species	Species Mean	
	REF	Pres. Study		REF	Pres. Study		REF	Pres. Study
Fagaceae	24.8	25	Quercus	24.8	25	Q. chrysolepis	NR	19
						Q. douglasii	8.7	32
						Q. kelloggii [2]	NR	54
						Q. lobata[2]	3.4	18
						Q. palustris	NR	27
						Q. suber	NR	BDL
Hamamelidaceae	18.9	26	Liquidambar	18.9	26	L. styraciflua[2]	18.9	26
Hippocastanaceae	NR	BDL	Aesculus	NR	BDL	A. californica	NR	BDL
Juglandaceae	NED	BDL	Carya	NED	BDL	C. illinoensis	NR	BDL
Lamiaceae	BDL	BDL	Rosemarinus	NR	BDL	R. officinalis	NR	BDL
			Salvia	BDL	BDL	S. greggii	NR	BDL
Leguminosae	4.3	5.5	Acacia	NED	BDL	A. aneura	NR	BDL
						A. melanoxylon	NR	BDL
			Caesalpinia	NR	BDL	C. gilliesii	NR	BDL
			Cassia	NR	BDL	C. artemisiodes	NR	BDL
						C. nemophila	NR	BDL
			Ceratonia	NR	BDL	C. siliqua	NR	BDL
			Cercidium	NR	BDL	C. floridum	NR	BDL
			Cytisus	NR	BDL	C. spachianus	NR	BDL

Table 3.12 (Continued)

Family	Family Mean		Genus	Genus Mean		Species	Species Mean	
	REF	Pres. Study		REF	Pres. Study		REF	Pres. Study
			Lysiloma	NR	BDL	L. thornberi	NR	BDL
			Prosopis	NR	BDL	P. alba 'Colorado'	NR	BDL
			Sophora	NR	34	S. secundiflora	NR	34
			Spartium	NR	21	S. junceum	NR	21
Malvaceae	NR	BDL	Gossypium	NR	BDL	G. barbadense	NR	BDL
						G. hirsutum	NR	BDL
			Hibiscus	NR	BDL	H. rosa-sinensis	NR	BDL
Moraceae	13.5	9.0	Morus	NED	BDL	M. alba 'Fruitless'	NR	BDL
			Ficus	27.0	18	F. carica	NR	18
Myrtaceae	21.2	20	Eucalyptus	32.5	20	E. camaldulensis 'C2'	NR	28
						E. grandis 'GCT'	NR	21
						E. polyanthemos	NR	10
Oleaceae	BDL	BDL	Fraxinus	BDL	BDL	F. velutina 'Modesto'	NR	BDL
			Syringa	NR	BDL	S. vulgaris	NR	BDL
Palmae	36.5	7.0	Syragus	NR	BDL	S. romanzoffiana	NR	BDL
			Washingtonia	9.9	14	W. robusta	NR	14
Pinaceae	2.3	BDL	Abies	NR	BDL	A. concolor	NR	BDL
			Picea	6.8	BDL	P. pungens glauca	NR	BDL

Table 3.12 (Continued)

Family	Family Mean		Genus	Genus Mean		Species	Species Mean	
	REF	Pres. Study		REF	Pres. Study		REF	Pres. Study
Proteaceae	NR	BDL	Grevillea	NR	BDL	G. robusta	NR	BDL
Rosaceae	NED	BDL	Rosa	NR	BDL	R. hybrida	NR	BDL
Salicaceae	47.2	33	Populus	44	33	P. alba	NR	25
						P. euramerica 'R111'	NR	31
						P. euramerica 'R112'	NR	28
						P. fremontii	NR	43
						P. nigra italica	NR	36
Sterculiaceae	NR	BDL	Brachychiton	NR	BDL	B. populneus	NR	BDL
Taxaceae	NR	BDL	Torreya	NR	BDL	T. californica	NR	BDL
Taxodiaceae	NED	BDL	Sequoia	NR	BDL	S. giganteum	NR	BDL
						S. sempervirens	NR	BDL
Verbenaceae	NR	BDL	Lantana	NR	BDL	L. camara	NR	BDL
			Vitex	NR	BDL	V. agnus-castus	NR	BDL
Zygophyllaceae	NR	BDL	Larrea	NR	BDL	L. tridentata	NR	BDL

[1]NR = not reported, BDL = below detection limit, NED = no isoprene emissions detected.

[2] The last measurements of the season were excluded from the mean because of senescence of leaves.

natural settings, and high leafmass. In this study we have reported isoprene emission rates for four additional native species and one exotic species found in urban settings.

3.6 Implications for Biogenic Emission Inventories

When developing BHC inventories, there are two possible approaches (Guenther et al. 1995). The first is to determine the coverage fraction and foliar mass of each species for a given landcover or landuse type and then assign species-specific emission rates, while the second is to assign a landscape-level emission rate. The first approach would be more easily accomplished if grid cells contained low species diversity, such as a single-species forest. The second approach might be necessary if the grid cell contained a montage of species of varying heights and foliar masses, such as found in some chaparral communities. This approach might also be possible if plant species assemblages found in certain stages, e.g. early to mid-successional stages (Martin and Guenther 1995, Klinger et al. 1998), could be characterized as having certain isoprene emission rates. Further work is needed to understand how to use these approaches in building BHC inventories in California, and when or whether each should be preferred.

An interesting feature of present and past results is the possibility of associating plant growth, site preferences or other characteristics with isoprene emission rates. For example, high emitting species include *Populus* and *Salix* (Salicaceae family) and the *Quercus* genera, all of which are wind-pollinated, and, except for *Quercus*, are often considered riparian plants, found within floodplains and along stream banks. The Myrtaceae family, containing exotic species from Australia, is another example of plants with similar emission behavior and site preferences including drought tolerance.

Ecological succession is the naturally-occurring gradual process of replacement of one species assemblage with another until a stable (i.e. climax) state is reached. Klinger et al. (1998) propose that mid-successional stages contain more plants which emit isoprene than earlier or later stages. If true, landscape-level isoprene emission rates could be calculated rather than summing species-specific emission rates. Klinger et al. cite *Populus*, *Salix* and *Quercus*, which are genera containing high isoprene emitters and are considered to be relatively early in plant succession. Based on the present study and recent references (Guenther et al. 1994, Benjamin et al. 1996), taxonomic comparisons

presently remain more useful for predicting isoprene emission rates than do comparisons based on site preferences or other characteristics.

Data from the present study represent a significant expansion of the published isoprene emission rate database, and will be useful for building BHC emissions inventories in California, as well as other regions where these plants are found, including other Mediterranean climate types of the world, and the arid southwestern U.S. where several of the species investigated in this study may be found. The BHC emissions estimates given by Guenther et al. (1995) for a Mediterranean ecosystem were based on the reports of Arey et al. (1991b) and Winer et al. (1992), which were primarily focused on terpenes emitted by agricultural species. The data generated in the BEMA project (Seufert et al. 1997) and those of this report may offer further guidance in considering plants within Mediterranean climates.

Given the enormous number of plant species in California and worldwide, a reference framework for understanding and categorizing emissions rates, and for assigning rates to unmeasured species, will be necessary. As Benjamin et al. (1996) emphasized, the taxonomic relationship they proposed to meet this need is possible because there is a range of almost four orders of magnitude in emission rates. Within an order of magnitude uncertainty, and for many genera within factors of two to five (or even $\pm$50% as shown above), plant taxonomy appears to be a reasonable framework for organizing isoprene emission rate information, and taxonomy seems to be increasingly useful when descending to the lower levels of hierarchical classification (i.e. to subfamilies and genera). Other researchers have also concluded the taxonomic method, in general, works well (Seufert et al. 1997). Although anomalies will undoubtedly be found (Staudt and Seufert 1995, Kesselmeier et al. 1996, Loreto et al. 1996), several investigators have used a taxonomic approach to assign BHC emissions rates (Guenther et al. 1994, Geron et al. 1995, Benjamin et al. 1996, although the phylogenetic relationships among isoprene-emitting plants are not definitive (Klinger et al. 1998). The data developed in the present study support taxonomic predictive methodology, especially if previous measurements within specific families, sub-families, genera and species are considered and compared, and results of such assignment treated with proper caution.

4.0 LEAFMASS AND LEAF AREA RELATIONSHIPS DETERMINED FROM SAMPLING AND WHOLE-TREE HARVEST: IMPLICATIONS FOR LEAFMASS ESTIMATION METHODS

4.1 Introduction and Background

Accurate leafmass determination is a critical factor in estimating the magnitude of biogenic hydrocarbon emissions from green plants. As discussed earlier, emission rates, expressed as ug BHC 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 BHC 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. Foliar estimates may be obtained through three types of methods: (1) use of allometric equations, (2) remote sensing, including light interception and photography; or (3) direct measurement methods, including the volumetric method (Campbell and Norman 1989).

4.1.1 Leafmass Estimation Methods Utilizing Allometric Equations

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 leafmass 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 leafmass above. This model, or a variation, may give the most accurate results for tree species. For example, Nygren and coworkers (1993) developed relationships between leafmass

and branch cross sectional area with $r^2 > 0.85$ for four clones of each of two tropical broadleaved tree species.

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 BHC 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 and limit the plant species investigated. Also, in many survey situations it is not permissible to remove trunks, branches or leaves, and the pipe method cannot be used for shrubs.

Attempts to increase the precision and accuracy of leafmass 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 will often be limiting for urban situations.

4.1.2 Indirect Leafmass Estimation Methods Utilizing Remote Sensing

The application of remote sensing methods for BHC inventory development for California was recently reviewed by Winer et al. (1995). Although remote sensing methods have not been shown to be amenable to direct measurement of BHC emissions or discriminating between emitting and non-emitting species (Winer et al. 1995), remote sensing methods have been used to estimate canopy photosynthesis and primary productivity (Kaufman and Tanre 1992, Myneni et al. 1992) although for heterogeneous canopies, such as found in many parts of California, the relationship between leaf area index and reflectance was confounded (Asrar et al. 1992). Remote sensing methods have been used to develop BHC emissions inventories for the eastern U.S. (Guenther et al. 1994, Guenther 1997, Kinnee et al. 1997) and the world (Guenther et al. 1995).

Leafmass may be inferred by remote sensing measurements (Ustin et al. 1991), and the difference in spectral reflectance between the red band (580-680 nm) and the near-infrared band (720-1100) of the Advanced Very High Resolution Radiometer may be used to calculate the normalized difference vegetation index (NDVI). Leaf area index (LAI) has been shown to be correlated with NDVI (Running et al. 1989) and leafmass density may be inferred from NDVI (Cheung et al. 1991). LAI may be thought of as the number of leaf layers directly above a given ground surface area, or be thought of as leaf column density. LAI is calculated as the non-dimensional ratio of the sum of the surface areas of leaves above a specified ground area, usually thought of as m^2 leaf surface per m^2 ground area. Leafmass estimates may be expressed as leafmass per unit ground area (g m^{-2}) or LAI. Although BHC emissions are usually expressed relative to leafmass, emissions may be expressed on the basis of either leafmass or leaf area, discussed further in Chapter 3 of this report.

4.1.3 Previous Use of the Volumetric Method

A volumetric approach for estimating leafmasses has relatively simple non-destructive data requirements in field surveys, has potential applicability to the enormous range of species found in urban landscapes, and has flexibility in modeling both tree and shrub morphology. Estimation of leafmass through a volumetric approach has been specifically utilized for generating BHC emission inventories in individual airsheds (Winer et al. 1983, Miller and Winer 1984, Horie et al. 1991, Chinkin et al. 1996 a,b, Benjamin et al. 1997, Karlik et al. 1998). In these studies, plant species identities were tabulated for stratified random samples of urban vegetation and crown shapes were modeled by geometric solids and then multiplied by the appropriate mass-to-volume ratio (the leafmass constant). Although modeling with simple geometric solids does not take into account the exact crown shape of trees, digital models similar in form to solids used in the present study were used in the BEMA project to scale up emission rate data of Italian stone pine and holm oak (= holly oak) to full tree crowns (Lenz et al. 1997). Species-specific leafmass constants have been experimentally determined through sampling within plant crowns (Miller and Winer 1984, Nowak 1991, 1997). However,

uncertainties in BHC inventory development which were associated with leafmass estimation based on a volumetric approach were not well characterized.

4.2 Evaluation of the Volumetric Method for Leafmass Estimation Through Whole-Tree Harvest

4.2.1 Rationale for the Present Study

Estimation of leafmass through a volumetric approach has been compared to light interception or measurement of trunk diameter in a forest environment, although the actual leafmasses of trees were not determined (Temple and Mutters 1995). Both terms of a volumetric calculation, i.e. the leafmass constant and the estimation of crown volume, represent sources of uncertainty in estimating whole-plant leafmass, although the uncertainties associated with these terms have not been well understood. 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. The principal goals of the present study were to evaluate the precision and accuracy of a volumetric approach, using geometric solids to compare estimated leafmasses to measured whole tree leafmasses; and to compare leafmass constants derived from selective sampling to whole-tree values. A related goal was to expand the very limited database of experimentally measured leafmass constants. Another goal of the study was to develop leafmass-leaf area relationships, which may then be used to bridge between leafmass-based and leaf area-based BHC emission rate and inventory data.

4.2.2 Experimental Methods

In 1996, nine deciduous trees which could later be harvested were selected from populations in the landscape of an office building and on the campus of the California State University, Bakersfield (CSUB). Of the trees available for the study based on accessibility and permission for harvest, specimens were chosen to represent a variety of species and growth forms. Several of the trees had columnar growth habits (Nos. 5-8). For trees and shrubs less than 4.5 meters tall, crown height was measured with a steel tape measure to an accuracy of 0.5 m. Taller trees were measured with a clinometer and

telescoping measuring pole. The crown radius was approximated by the average dripline, measured in four directions with a steel tape measure to an accuracy of 0.3 m, and the mean was calculated (Table 4-1).

In 1997, 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, five open-grown shade trees were selected which could be measured, sampled and harvested (Nos. 14-18). Five additional trees were chosen from the CSUB campus and two others from the courtyard of an office building for a total of 12 trees. All trees were measured with a telescoping measuring pole or tape measure as described above (Table 4-1). For each tree except the mulberry (No. 16), where dense foliage and the presence of telephone and electrical wires prevented access, ten samples were taken with an open cube, with edges made of plastic pipe and a volume of 0.028 m^3 (1 ft^3). Sampling locations within the crown were chosen based on a three-digit random coordinate system. The first digit identified the compass direction with 0 being due north, the second number gave the percentage of the distance from the trunk to the perimeter, and the third number expressed the percentage of the height from the base of the canopy to the top. A lift truck or ladder was used to reach the sampling locations. To investigate the uncertainties associated with a more rapid sampling protocol, an additional four samples were taken with the cube from locations around the base of the crown of each tree which did not require use of a ladder or lift truck: two at the dripline, one adjacent to the trunk, and another at the approximate midpoint between the trunk and dripline.

Four purpleleaf plum trees were chosen from the CSUB campus for a species intracomparison. Measurement and sampling were the same for these trees as for other trees selected for harvest in 1997 except only five within-crown samples were taken with the cube for each tree.

In both years, the geometric solid visually approximating the crown shape for each tree was chosen in the field and was subsequently referred to as the preferred solid. In 1996, painstaking leaf removal was accomplished by research staff, and trees required as much as one week for leaf removal with a crew of four. In 1997, the inmates from the

Table 4-1. Trees selected in 1996 and 1997 for leaf removal and measurement of total leafmass.

Tree No.	Genus, species and variety	Crown Height (m)	Crown Radius (m)	DBH (cm)	Leafmass (g)
1996					
1	*Prunus cerasifera* 'Krauter Vesuvius'	3.4	1.5		4330
2	*Prunus cerasifera* 'Krauter Vesuvius'	3.0	1.4		4110
3	*Prunus cerasifera* 'Krauter Vesuvius'	3.4	2.0		6850
4	*Prunus cerasifera* 'Krauter Vesuvius'	3.4	1.7		5390
5	*Eucalyptus camaldulensis* 'C2'	8.2	1.1		4320
6	*Eucalytpus camaldulensis* 'C2'	13	1.4		8020
7	*Eucalyptus grandis* 'GCT'	14	0.9		5200
8	*Populus euramerica* 'R112'	15	1.5		23200
9	*Koelreuteria paniculata*	1.8	1.2		3200
1997					
10	*Prunus cerasifera* 'Krauter Vesuvius'	3.6	2.3		2560
11	*Prunus cerasifera* 'Krauter Vesuvius'	2.8	1.3		1960
12	*Prunus cerasifera* 'Krauter Vesuvius'	4.3	2.3		4350
13	*Prunus cerasifera* 'Krauter Vesuvius'	4.0	2.3		3340
14	*Eucalyptus polyanthemos*	7.1	3.7	39	89600
15	*Fraxinus velutina* 'Modesto'	5.8	4.3	25	40500
16	*Morus alba* 'Fruitless'	6.9	5.2	37	84700
17	*Liquidambar styraciflua*	7.9	1.9	14	8010
18	*Acacia melanoxylon*	6.4	2.7	29	61000
19	*Populus euramerica* 'R112'	8.7	1.3	17	1530
20	*Koelreuteria paniculata*	2.9	2.2	11	2910
21	*Koelreuteria paniculata*	2.5	1.6	7.0	1680

county correctional facility provided approximately 800 hours of labor for leaf removal. Given the high labor requirements for leaf removal, it is not surprising very few similar datasets have been generated for urban trees. Leaves were placed in large paper bags and dried for at least two weeks in a vacant greenhouse with daily maximum temperatures of about 150°F and 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 4-1). Bags were spot checked after more than six weeks to verify complete drying and no decomposition was observed.

4.3 Results and Discussion

4.3.1 Whole Tree Leafmass Estimation

Using height and radius data for each tree crown, volumes for five geometric solids approximating tree shapes (McPherson and Rowntree, 1988) 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 was used if available (Miller and Winer 1984, Nowak 1991,1997); otherwise, a value for structural class, e.g. broadleaf deciduous, was used. The structural class values (Horie et al. 1991) were based upon experimental data for fewer than 10 species and we were not able to verify the calculations leading to these values.

Leafmasses were also calculated using the allometric equations of developed by Nowak (1996) for application to a wide variety of species. Equation 1 (Eqn. 1), uses crown dimensions and is of the form:

$$\ln Y = 1.9375 + 0.4184H + 0.6218D + 3.0825S - 0.0133C + \text{error} \quad (1)$$

and equation 2 (Eqn. 2) uses trunk diameter and is of the form:

$$\ln Y = 7.6109 + 0.0643X + \text{error} \quad (2)$$

where Y is dry leafmass, H is crown height (m), D is average crown diameter (m), S is a shading factor (percent 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. These 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; therefore, leafmass was not calculated using these equations. However, because crown dimensions are thought to be a good predictor of leafmass

(Nowak, 1996), we did use Eqn. 1 for the purpleleaf plums, which had crown dimensions within the suggested range but had a multiple leader structure not suited to dbh measurement. Trunk diameters were not measured in 1996, the purpleleaf plum trees harvested in 1997 did not have a central leader, and the goldenrain tree (No. 21) had a trunk too small, so Eqn. 2 was not applied to these trees.

Total measured leafmass for trees in this study (367 kg) may be compared to estimates of total leafmass derived from the geometric solids, which ranged from 167 kg (cone) to 501 kg (cylinder). For the preferred solid, the total leafmass estimate of 436 kg was a factor of 1.18 greater than the measured. For the cylinder, sphere, vertical ellipsoid, paraboloid and cone, total leafmass estimates were factors of 1.4, 0.92, 0.9, 0.68 and 0.46 of the measured, respectively. Therefore, two of the solids and the preferred solid gave estimates of total leafmass for all trees within 20% of the measured. Total leafmass estimates were not calculated using Eqn. 1 or 2 because these equations could not be applied to all trees in the study.

Plots were made of estimated leafmasses vs. the measured for trees using the geometric solids and Eqn. 1. As seen in Figure 4-1, the preferred solid overestimated leafmasses for smaller and medium-sized trees, but gave estimates close to the measured for the largest trees. The vertical ellipsoid solid (Figure 4-2) tended to overestimate leafmasses for smaller trees but underestimate leafmasses for larger trees. Data for the sphere solid were scattered, especially for small and medium-sized trees (Figure 4-3), while Eqn. 1 underestimated leafmasses for 11 of the 13 trees to which it could be applied (Figure 4-4). The paraboloid solid tended to overestimate leafmasses for smaller trees and underestimate them for larger trees (Figure 4-5). For most trees, the cylinder solid overestimated leafmasses (Figure 4-6) while the cone solid underestimated them (Figure 4-7).

For individual trees, leafmasses calculated by the above approaches were compared to the experimentally measured whole tree leafmasses. For trees harvested in 1996 (Nos. 1-9), field observation leading to selection of a preferred solid (starred in Table 4-2) to model the crown led to a leafmass estimate within $\pm$30% of the measured value for six of the nine trees. All preferred-solid estimates were within a factor of $\pm$3 of the measured value, and the solid selected in the field was the best choice for four of the

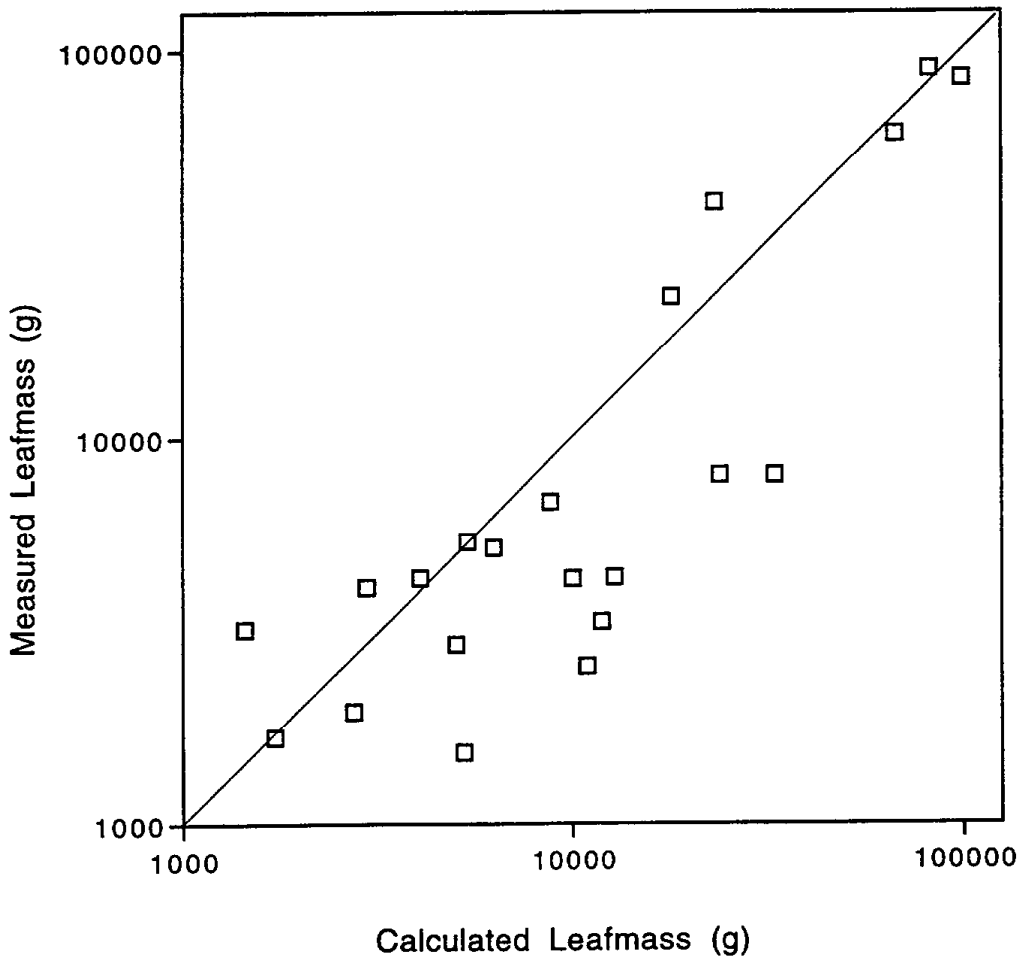

Figure 4-1. Comparison of measured leafmasses of urban trees to leafmasses calculated using the preferred solid.

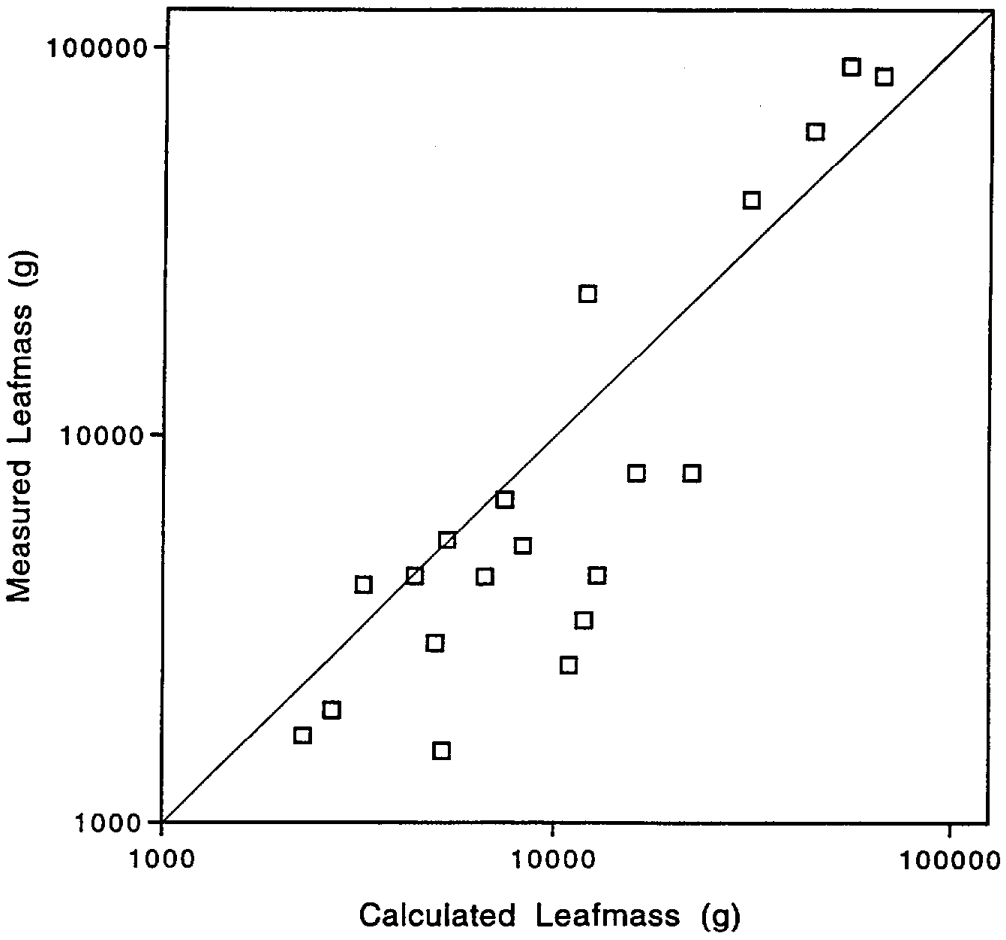

Figure 4-2. Comparison of measured leafmasses of urban trees to leafmasses calculated using the vertical ellipsoid solid.

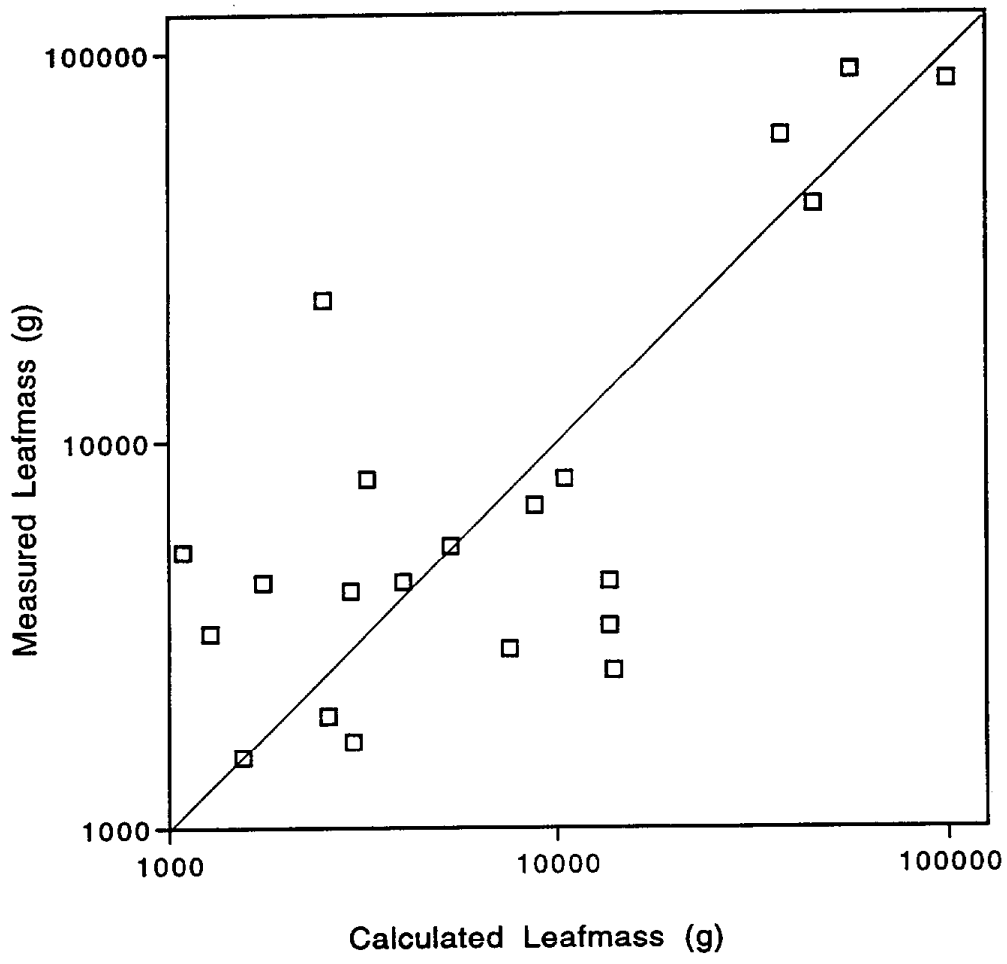

Figure 4-3. Comparison of measured leafmasses of urban trees to leafmasses calculated using the sphere solid.

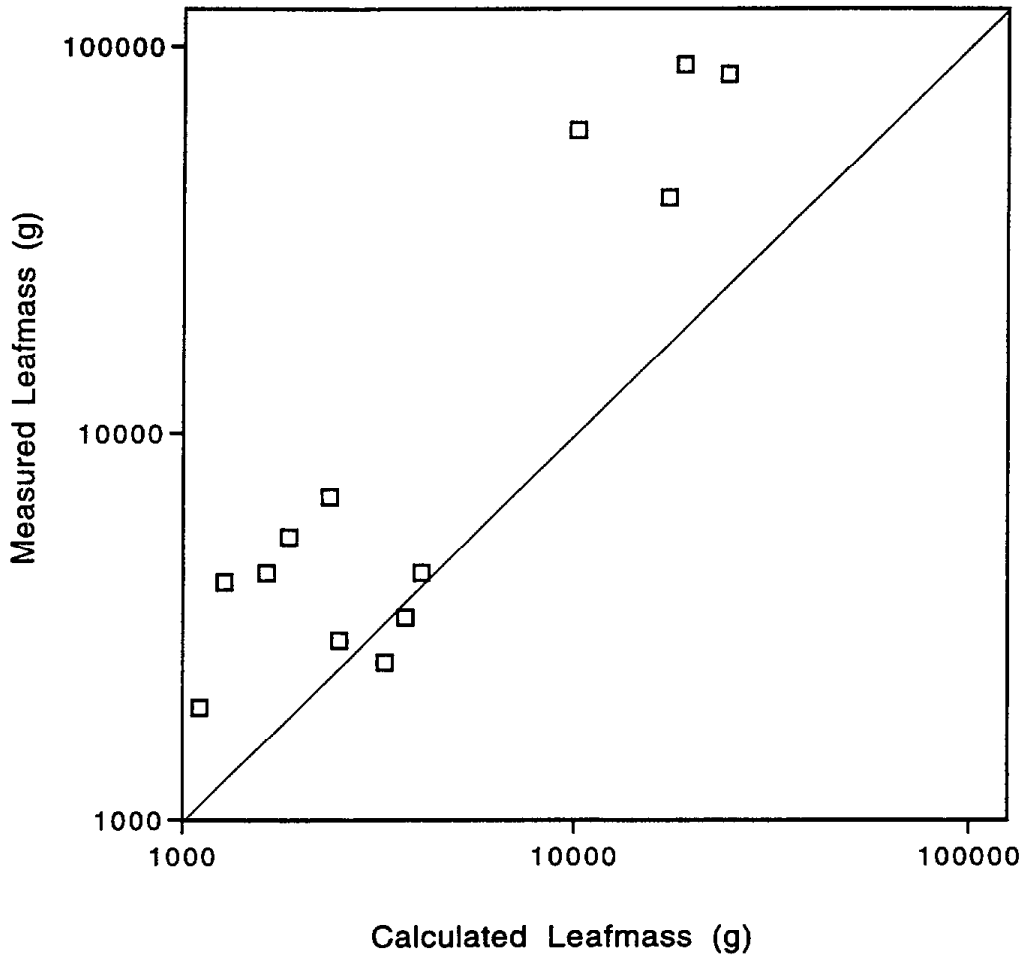

Figure 4-4. Comparison of measured leafmasses or urban trees to leafmasses calculated using Equation 1 of Nowak (1996).

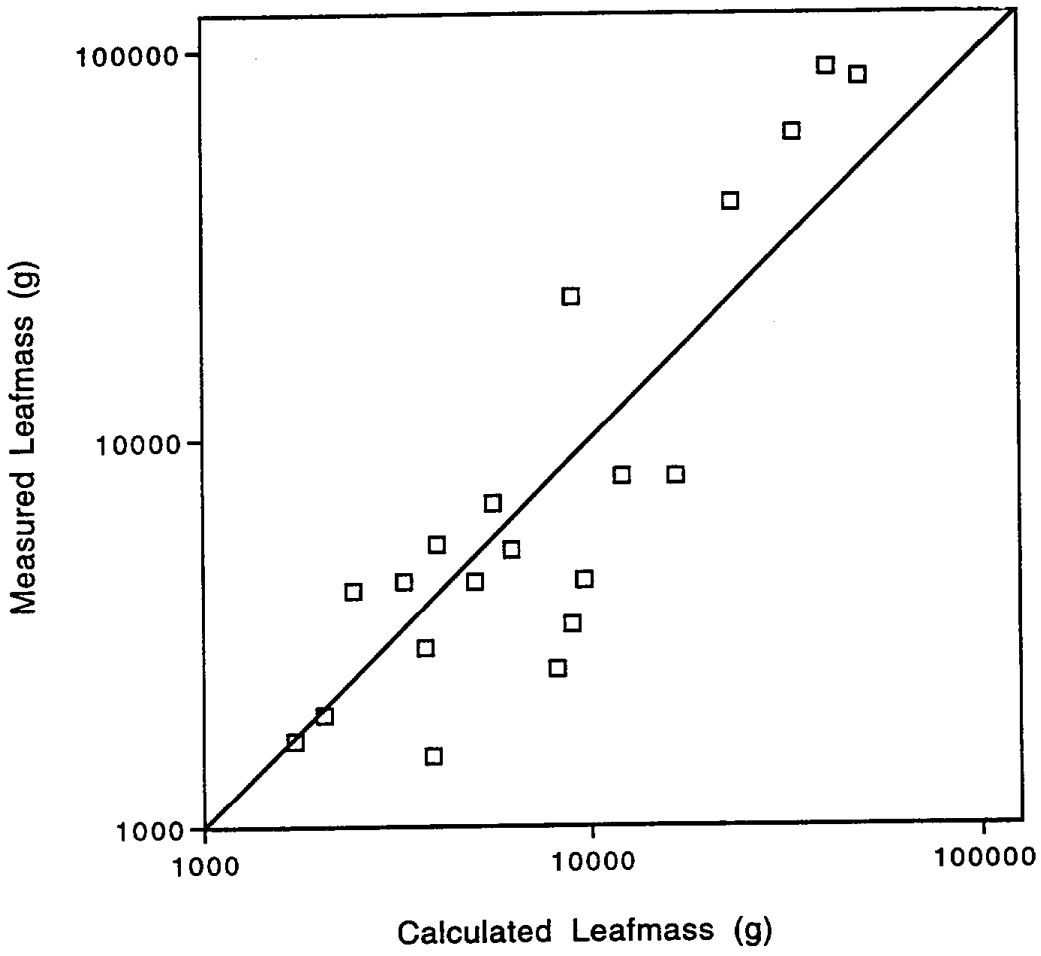

Figure 4-5. Comparison of measured leafmasses of urban trees to leafmasses calculated using the paraboloid solid.

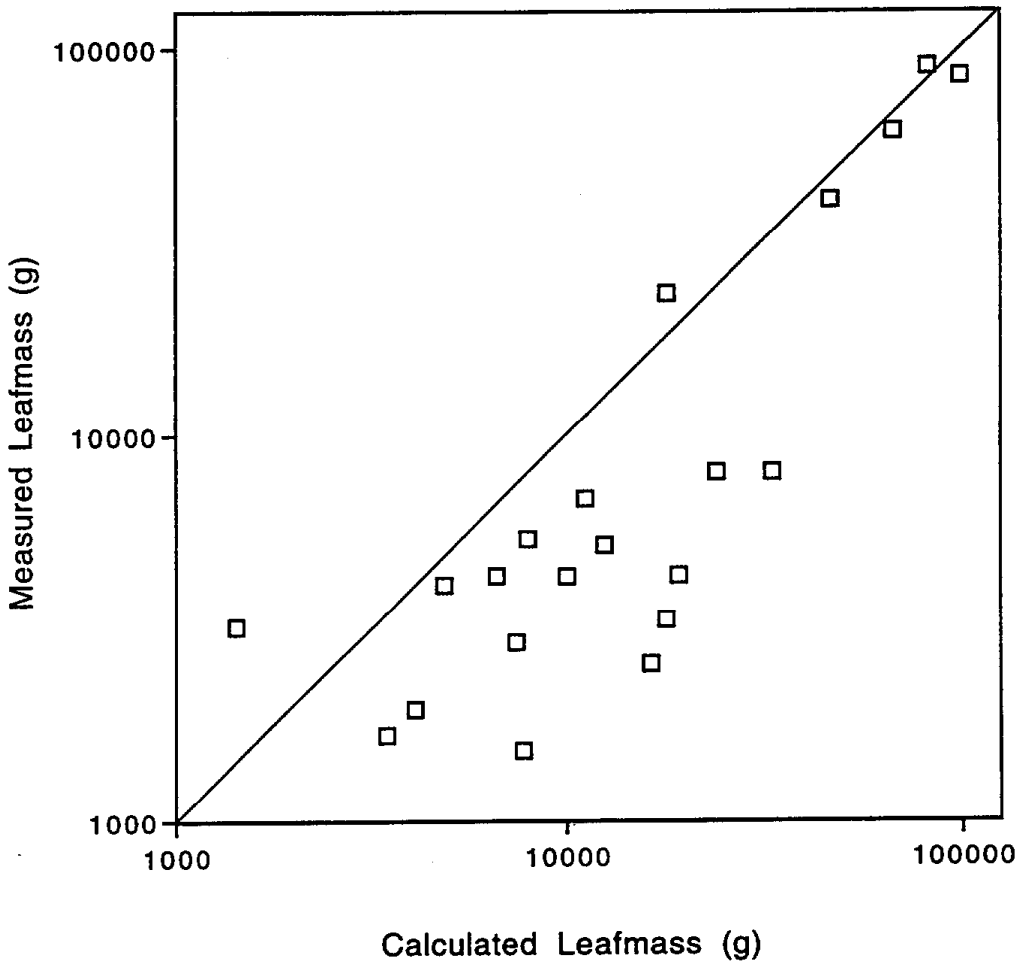

Figure 4-6. Comparison of measured leafmasses or urban trees with leafmasses calculated using the cylinder solid.

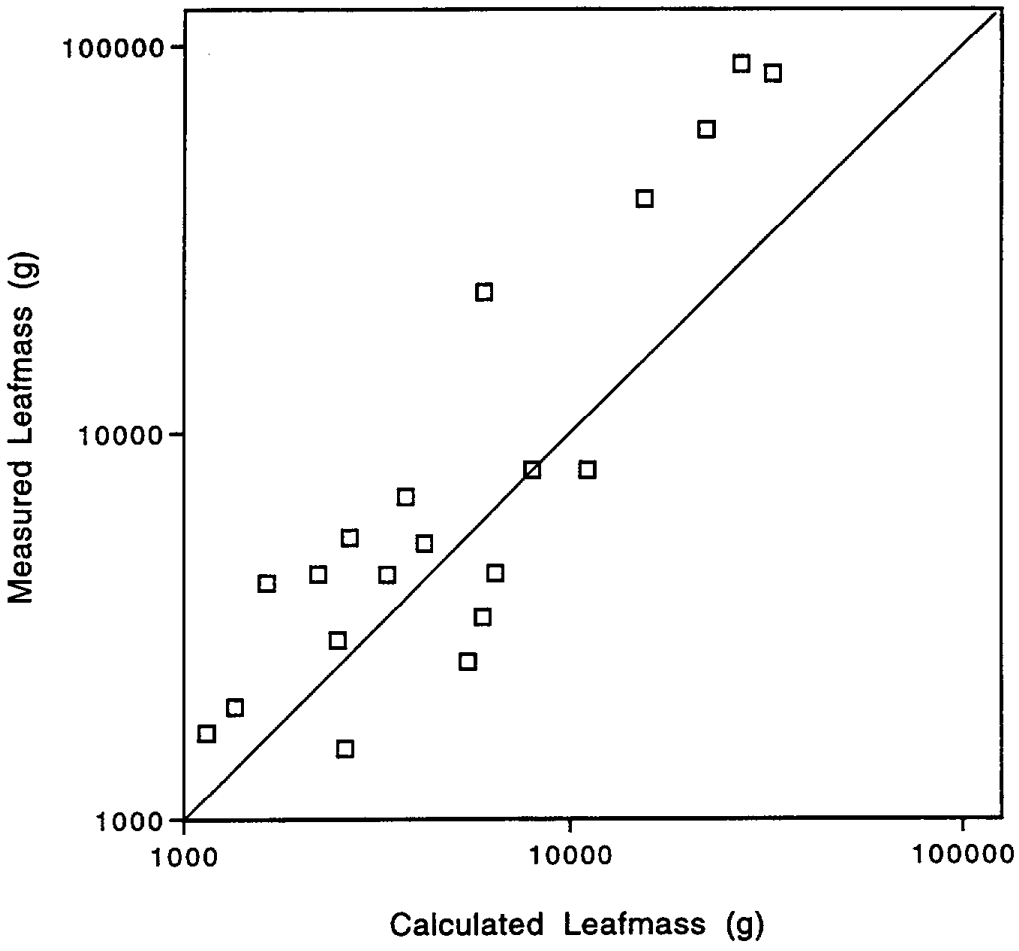

Figure 4-7. Comparison of measured leafmasses of urban trees with leafmasses calculated using the cone solid.

Table 4-2. Whole-tree calculated leafmasses for trees harvested in 1996 and 1997 using geometric solids to approximate tree volumes, and using crown dimensions in allometric equations, expressed as a fraction of experimentally measured whole-tree leafmass. The solid which was thought in the field to be the best fit is starred.

	Fraction of Measured Leafmass						
Tree No.	Cylinder	Vert. Ellips.	Paraboloid	Cone	Sphere	Eqn1	Eqn2
1	1.5	1.0	0.76	0.51	0.92*	0.38	N/A
2	1.2	0.79	0.59	0.40	0.71*	0.31	N/A
3	1.6	1.1	0.82	0.54	1.3*	0.35	N/A
4	1.5	0.99	0.74	0.50	0.99*	0.35	N/A
5	2.3*	1.5	1.2	0.77	0.40	N/A	N/A
6	3.0*	2.0	1.5	1.0	0.40	N/A	N/A
7	2.4	1.6	1.2*	0.80	0.21	N/A	N/A
8	0.77*	0.52	0.39	0.26	0.11	N/A	N/A
9	0.45*	0.30	0.23	0.15	0.40	0.23	N/A
10	6.4	4.3*	3.2	2.1	5.5	1.3	N/A
11	2.1	1.4*	1.0	0.69	1.3	0.57	N/A
12	4.4	3.0*	2.2	1.5	3.2	0.94	N/A
13	5.4	3.6*	2.7	1.8	4.1	1.1	N/A
14	0.92*	0.61	0.46	0.31	0.64	0.21	0.34
15	1.2	0.76	0.57*	0.38	1.1	0.42	0.31
16	1.2*	0.78	0.58	0.39	1.2	0.29	0.3
17	4.1*	2.8	2.1	1.4	1.3	N/A	N/A
18	1.1*	0.73	0.55	0.37	0.62	0.17	0.25
19	5.1	3.4*	2.5	1.7	1.0	N/A	N/A
20	2.6	1.7*	1.3	0.85	2.6	0.86	1.7
21	2.0	1.4	1.0*	0.68	1.8	N/A	N/A

nine trees. For the trees Nos. 5-8, leafmass estimates varied greatly depending on the solid selected, and tended to overestimate leafmass. The overestimation of leafmass has obvious implications for field studies where dimensions of large trees are measured and volumes calculated. It has been suggested the paraboloid is generally the best solid for representing the three dimensional shapes of trees (McPherson, 1996). As seen in Table 4-2, the paraboloid yielded the closest estimate for one of the nine trees, although it was either first or second for the three tall eucalyptus trees.

For trees harvested in 1997 (Nos. 10-21) (Table 4-2), the paraboloid solid gave the leafmass estimate closest to the experimentally measured leafmass for two of the 12

trees and was second-best for four others. The cone solid gave the closest estimate for five of the 12 trees and the cylinder solid was closest for four of the 12, including four of the five largest shade trees in the study (Nos. 14-18). For these trees (Nos. 14-18), the field choice for the preferred solid led to estimated leafmasses within ±45% of the measured leafmass for four of the five trees. The other tree, a sweetgum (No. 17), was healthy but open in growth habit and the measured leafmass was less than the calculated leafmass using any of the solids. The preferred solid led to an estimate greater than the measured leafmass by almost a factor of two for one of the goldenrain trees (No. 20) but the calculated leafmass for the other (No. 21) was almost the same as the measured leafmass. Calculated leafmass for the tall columnar poplar (No. 19) was overestimated by the preferred solid compared with the measured value by more than a factor of three and leafmasses of the purpleleaf plum trees (Nos. 10-13) were overestimated by most geometric solids. Trees Nos. 10-13 and 19 appeared to be drought stressed, which could have led to lower leafmasses. Irrigation to these trees had been reduced, according to site managers, and drought stress was inferred based on appearance of these trees in comparison to neighboring trees of the same species.

As seen in Table 4-2, Eqn. 1 and Eqn. 2 underestimated leafmasses for most of the trees in this study. These equations were developed using medium-sized trees of six deciduous species found in northern temperate climates, which may have had thinner leaves of relatively less mass per unit area than several species harvested in this study (Nowak, 1997). Thus, these equations may tend to underestimate leafmass for trees having thicker leaves, common in species adapted to dry climates, such as *Acacia melanoxylon* (blackwood acacia).

We can compare our data 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, 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.

4.3.2 Experimental Determination of Leafmass Constants

For the nine trees harvested in 1996, whole-plant leafmass constants (g m^{-3}) based on the entire tree leafmass and volume were calculated. Table 4-3 compares leafmass constants taken from the literature against leafmass constants derived from measured whole-tree leafmass and the assumed shape of each tree. Each tree was modeled as a paraboloid and as a preferred solid, with the preferred solid previously defined a priori in the field when dimensions of the trees were being measured. Whole- tree leafmass constants for the paraboloid differed from experimentally determined constants of closely related species (tree Nos. 1-7) by less than a factor of two. For the preferred solids, the whole tree values ranged from one-third to one-and-one-half times the literature value. These results agreed reasonably well the literature values for leafmass 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 leafmass constants.

In similar fashion, leafmass constants were calculated for trees harvested in 1997 and compared to experimentally-determined literature values where available (Table 4-4). The whole-tree values for the purpleleaf plums (Nos. 10-13) were lower than the literature value, possibly reflecting the drought stress of these trees. For the larger shade trees (Nos. 14, 15, 17, 18), the leafmass constants calculated on the basis of the preferred solid ranged from 0.74-1.6 (mean of 1.1) times the literature values.

The whole-tree value for the preferred solid values ranged from 0.3-2.2 (mean of 1.0) times the deciduous broadleaf structural class value of 168 g m^{-3} (Horie et al., 1991) for the trees for which it was assigned (nos. 8, 9, 16, 19-21).

For trees harvested in 1997, leafmass constants from within-crown selective sampling were also calculated and compared to values from the literature and to the present whole-tree determinations. For the purpleleaf plums (Nos. 10-13), within-crown sampling using five cubes placed randomly to characterize the leafmass-to-volume ratio

Table 4-3. Comparison between leafmass constants derived from literature values and those obtained from whole-tree measurements for trees harvested in 1996.

	Leafmass Constant ($g\ m^{-3}$)		
Tree No.	Literature Value	Whole Tree (paraboloid)	Whole Tree (preferred solid)
1	270[1]	350	290
2	270[1]	460	380
3	270[1]	330	210
4	270[1]	360	270
5	340[2]	290	150
6	340[2]	230	110
7	340[2]	280	280
8	168[3]	430	220
9	168[3]	750	370

1 Value for *Prunus blireana*, blireana plum and *Prunus* spp., green plum (Nowak, 1991).

2 Value for *Eucalyptus viminalis* (Miller and Winer, 1984), which has form similar to the eucalyptus measured. Other literature values are 740 for *E. globulus* (Nowak, 1991) and 270 for *E. polyanthemos* (Miller and Winer, 1984).

3 Structural class value assigned to broadleaf deciduous trees for which no leafmass constant has been measured for any closely related species (Horie et al., 1991).

Table 4-4. Comparison between leafmass constants derived from literature values, those obtained from whole-tree measurements, and those obtained from sampling ten random cubes within the crown. Trees harvested in 1997.

	Leafmass Constant ($g\ m^{-3}$)				
		Whole Tree		Crown Sampling	
Tree No.	Literature Value	(paraboloid)	(preferred solid)	5 or 10 cubes	4 cubes
10	270[1]	83	63	11	--
11	270[1]	260	200	40	--
12	270[1]	120	90	27	--
13	270[1]	93	76	95	--
14	270[2]	590	290	190	180
15	139[3]	220	220	150	210
16	168[4]	290	140	N/A	220
17	380[5]	180	280	300	610
18	450[5]	820	410	160	190

Table 4-4. (Continued)

	Leafmass Constant (g m^{-3})				
		Whole Tree		Crown Sampling	
Tree No.	Literature Value	(paraboloid)	(preferred solid)	5 or 10 cubes	4 cubes
19	168[4]	66	50	51	60
20	168[4]	130	98	37	370
21	168[4]	160	160	30	230

[1] Value for *Prunus blireana*, blireana plum and *Prunus* spp., green plum (Nowak, 1991).

[2] Miller and Winer, 1984.

[3] Mean of *Fraxinus uhdei* (Miller and Winer, 1984) and *F. pennsylvanica* (Nowak, 1997).

[4] Structural class value assigned to broadleaf deciduous trees for which no leafmass constant has been measured for any closely related species (Horie et al., 1990).

[5] Nowak, 1991.

within each tree gave values for leafmass constants lower than the literature value. This result is not surprising considering the likelihood of drought stress. Also, for three of the four trees the cube measurements were more than a factor of two less than corresponding whole-tree values, implying the cube measurements were not representative of the entire crown.

For the larger shade trees (nos. 14, 15, 17, 18), the 10-cube samples and four-cube samples resulted in leafmass constants ranging from factors of 0.36 to 1.08 (mean of 0.74) and from 0.42 to 1.6 (mean of 1.05), respectively, of experimentally-determined values for leafmass constants found in the literature. Similarly, the leafmass constants from 10-cube samples and from four-cube samples at the base of the crown ranged from factors of 0.39 to 1.1 (mean of 0.71) and from 0.46 to 2.2 (mean of 1.1), respectively, of the leafmass constants of the preferred solids. Therefore, for the larger shade trees, the four-cube sampling protocol gave values closer to those found in the literature and to those of the whole-tree preferred solid values than did 10-cube sampling protocol. When using the 10-cube random coordinate sampling protocol, it was not unusual to place the sampling cube in empty space, whereas all of the four-cube samples usually contained vegetation, resulting in higher values for leafmass constants from the four-cube sampling protocol.

For the poplar, which had a columnar growth habit and apparently uniform distribution of leaves, both 10-cube sampling and four-cube sampling gave similar results: ten-cube sampling gave a leafmass constant almost identical to that of the preferred solid and four-cube sampling resulted in a value 20% greater than that calculated using the preferred solid. For the small goldenrain trees (Nos. 20-21), values for leafmass constants from 10-cube sampling were less than whole-tree values for the preferred solid but values for the four-cube samples were much higher, probably because tree crowns contained noticeable open spaces surrounded by clumps of foliage. In such a situation, the 10-cube sampling protocol using the 0.0283 m^3 cube tended to underestimate and the four-cube sampling to overestimate leafmass per volume. Past selective sampling studies (Miller and Winer 1984, Nowak 1991, 1996) have used larger cube sampling volumes, which may better represent the non-uniform distribution of leaves within tree crowns.

4.3.3 Summary of Experimental Results for Assessment of the Volumetric Method

Summation of leafmass estimates generated using the preferred solid, vertical ellipsoid and sphere solid for all 21 trees in this study gave values within 20% of measured total leafmass. Although use of the sphere solid resulted in a total leafmass value within 10% of the measured total leafmass, data for individual trees were more scattered than those for the vertical ellipsoid, which was judged to be the best solid overall for modeling tree crowns in this study.

For individual trees, calculated leafmasses based on a paraboloid and leafmass constants from the literature resulted in leafmass estimates within ±50% for 12 of the 21 trees harvested. For the preferred solid, leafmass estimates were within ±50% for 11 of the 21 trees. Field choice of a preferred solid led to a leafmass estimate within a factor of three for all trees harvested in 1996 and, excluding the purpleleaf plums, for six of eight trees harvested in 1997. As a best case for individual trees (Nos. 14-16) judged from photographs and field observations to have most uniform foliage distribution and form, leafmass estimates generated using the preferred solid ranged from fractions of 0.57 to 1.2 of the measured leafmasses. Therefore, leafmass estimates developed for individual

trees for biogenic emissions inventories through a volumetric approach may be approximately ±50% of actual values.

Literature values for experimentally-determined leafmass constants appear to be reasonably accurate for the species tested. However, a larger dataset including additional tree species is clearly needed to more accurately quantify leafmasses of urban trees and to better understand structural class values. The sampling cube used in this study (0.028 m^3) was generally too small to adequately account for variability in foliage distribution. Previous studies have used sample volumes as large as one cubic meter and we recommend use of such larger volumes in future studies.

4.4 Leafmass and Leaf Area Relationships

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. The areas of leaves of needle evergreens, such as pines, cypress or spruces, are more difficult to measure and to model. For a single tree, 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 leaf layers will be strongly affected by the light compensation point (species-specific), which describes the light intensity needed to sustain at least a break-even energy balance between 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 of the tree to the outer leaves. 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. Therefore, for large trees, LAI probably provides a better representation of foliar distribution, and by extension, foliar mass, than does a description derived from leafmass per volume ratios of small-to-medium sized trees.

BHC emissions may be expressed on the basis of leaf area, as further discussed in section 3.2.1.4. Leaf area may also be more amenable to measurement by indirect methods based upon light interception (Peper and McPherson 1998).

4.4.1 Measurement of Leaf Areas

Crowns of 57 plant species were sampled with the 0.0283 m^3 PVC cube or a smaller 0.00354 m^3 PVC cube used for small shrubs, and the leafmasses and leaf areas of leaves from each cube sample were measured with a LiCor model LI3100 leaf area meter. The calculated mean ratios of leafmass to area and area to leafmass are listed in Table 4-5 for urban shade trees and shrubs, in Table 4-6 for palms, and in Table 4-7 for agricultural species. These data should be considered to be pooled values from both sun and shade leaves. A more complete description including crown location of subsamples may be found in Appendix B. In addition, leaves of trees sampled for emission rate measurements were often measured for leaf area, and mass was compared to leaf area, as seen in Table 4-8. Because the branch enclosure was placed around leaves located in the outer crown, and usually on the south side of plants, data in Table 4-8 should be considered to be from sun leaves. These data provide species-specific conversion factors from leaf area to dry leafmass and the inverse.

Table 4-5. Mean dry leafmass compared to green leaf area (one-sided) for tree and shrub species sampled. Data are based on four 0.0283 m^3 samples unless otherwise noted. To obtain actual values for specific leaf area multiply values in the table by 10^{-3}.

Scientific Name	Specific Leaf Weight ($g\ m^{-2}$)	Std. Dev.	Coeff. Var. (%)	Specific Leaf Area ($m^2\ g^{-1}$)x10^3
Acacia aneura	470	12	2	2.1
Acacia melanoxylon	163	9	6	6.2
Aesculus californica	89	12	14	11
Alnus rhombifolia	90	15	17	11
Atriplex polycarpa[1]	250	18	7	4.0
Baccharis pilularis[1]	190	27	14	5.2
Betula nigra	97	28	29	11
Betula papyrifera	77	6	7	13
Brachychiton populneus	88	7	8	11
Caesalpinia gillesii	98	34	34	11
Cassia artemisiodes[1]	190	29	15	5.4
Cassia nemophila	260	30	11	3.8
Chrysothamnus nauseosus[1]	260	47	18	4.0
Cornus stolonifera	59	13	21	18
E. camaldulensis 'C2'	140	18	13	7.2
E. grandis 'GCT'	120	18	15	8.6
Eucalyptus sideroxylon	140	10	7	7.2
Euryops pectinatus[1]	230	19	9	4.5
Garrya flavescens[1]	220	26	12	4.6
Grevillea robusta	120	11	9	8.2
Hibiscus rosa-sinensis	84	8	9	12
Koelreuteria paniculata	84	17	20	12
Liquidambar styraciflua	100	17	17	10
Lysiloma thornberi	120	40	34	9.4
Morus alba 'Fruitless'	72	16	22	14
Nerium oleander	150	26	17	6.7
Pistacia chinensis	78	12	16	13
Populus alba	88	12	14	12
Populus euramerica	85	13	16	12
Populus fremontii	88	10	12	12
Populus nigra italica	67	7	11	15
Prosopis chilensis 'Colorado'	220	31	14	4.7
Prunus cerasifera 'K. Vesuvius'	74	25	34	15
Quercus lobata	150	21	14	4.1
Quercus palustris	94	21	22	11

Table 4-5. (Continued)

Scientific Name	Specific Leaf Weight ($g\ m^{-2}$)	Std. Dev.	Coeff. Var. (%)	Specific Leaf Area ($m^2\ g^{-1}$)x10^3
Quercus robur	66	11	16	16
Querus rubra	87	13	15	11
Quercus suber	220	143	65	5.6
Quercus virginiana	180	35	20	5.8
Quercus wislizenii	180	32	18	5.7
Rhus lancea	130	40	30	8.2
Rhus ovata	321	17	5	3.1
Rosmarinus officinalis[1]	290	86	29	3.6
Salvia leucophylla	250	19	8	6.9
Sapium sebiferum	74	4	5	14
Spartium junceum	310	92	30	3.4
Ulmus parvifolia	120	37	30	8.8
Vitex agnus-castus	140	12	9	7.5

[1] Data were based on cube volumes of 0.00354 m^3.

Table 4-6. Mean dry leafmass compared to green leaf area (one-sided) for two palm species. To obtain actual values for specific leaf area multiply values in the table by 10^{-3}.

Scientific Name	Specific Leaf Weight ($g\ m^{-2}$)	Std. Dev.	Coeff. Var. (%)	Specific Leaf Area ($m^2\ g^{-1}$)x10^3
Syagrus romanzoffiana	180	2	1	5.4
Washingtonia robusta	170	59	36	6.4

Table 4-7. Mean dry leafmass compared to green leaf area (one-sided) for agricultural species sampled. Data are based on four 0.0283 m^3 samples unless otherwise noted. To obtain actual values for specific leaf area multiply values in the table by 10^{-3}.

Scientific Name	Specific Leaf Weight ($g\ m^{-2}$)	Std. Dev.	Coeff. Var. (%)	Specific Leaf Area ($m^2\ g^{-1}$)x10^3
Citrus limon 'Lisbon' Lemon	150	22	15	6.8
Citrus sinensis Orange	126	15	12	8.0
Gossypium hirsutum 'Maxxa' Cotton 'Maxxa'	70	5	7	14
Lycopersicon esculentum Tomato	89	6	7	11
L. esculentum 'Roma' Tomato 'Roma'	74	15	20	14
Juglans regia Walnut	47	19	42	24
Pistacia vera Pistacio	150	19	13	6.8
Prunus dulcis Almond	94	9	9	11
Prunus dulcis Almond (5 year)	120	21	19	9.0
Vitis vinifera 'Thompson Table Grapes	68	9	13	15
Citrullus lanatus Watermelon	86	8	9	12

Table 4-8. Mean dry leafmass compared to green leaf area (one-sided) for sun leaves. To obtain actual values for specific leaf area multiply values in the table by 10^{-3}.

Scientific Name	Specific Leaf Weight Mean ($g\ m^{-2}$)	Std Dev.	Specific Leaf Area Mean ($m^2\ g^{-1} x 10^3$)	Std Dev.	No. of samples
Acacia aneura	570	270	2.0	0.81	3
Acacia melanoxylon	180	N/A	5.4	N/A	1
Aesculus californica	89	28	12	3.2	4
Alnus rhombifolia	120	38	9.0	3.4	3
Atriplex polycarpa	190	82	5.8	2.5	2
Baccharis pilularis	180	N/A	5.6	N/A	1
Betula nigra	100	N/A	9.5	N/A	1
Brachychiton populneus	100	14	9.6	1.4	4
Callistemon viminalis	130	38	7.8	2.2	2
Carya illinoinensis	110	26	9.6	2.3	2
Ceratonia siliqua	160	54	6.8	2.8	3
Chrysothamnus nauseosus	270	230	5.5	4.5	2
Cornus stolonifera	100	31	10	3.3	4
Eucalyptus camaldulensis 'C2'	130	19	7.7	1.0	3
Eucalyptus grandis 'GCT'	140	8.9	7.4	0.47	3
Euryops pectinatus	120	33	9.0	2.6	2
Cytisus spachianus	330	12	3.1	0.11	2
Gossypium barbadense	170	N/A	6.0	N/A	1
Gossypium hirsutum	110	N/A	9.0	N/A	1
Grevillea robusta	420	430	5.1	5.2	2
Koelreuteria paniculata	160	74	6.9	2.6	4
Larrea tridentata	340	N/A	3.0	N/A	1
Latana camara	130	33	7.8	1.9	2
Liquidambar styraciflua	98	19	11	2.8	8
Lysiloma thornberi	220	N/A	4.5	N/A	1
Macfadena unguis - catii	84	42	14	8.0	3
Morus alba 'Fruitless'	100	5.0	9.6	0.46	2
Phoradendron villosum	520	37	1.9	0.13	3
Pistacia chinensis	150	9.3	6.6	0.41	2
Populus alba	100	18	10	2.0	3
Populus fremontii	100	4.6	9.7	0.44	3
Populus nigra italica	90	11	11	1.4	3
Prosopis alba 'Colorado'	330	43	3.0	0.40	3
Quercus douglasii	170	72	6.7	2.5	9
Quercus lobata	150	65	7.9	2.8	17
Quercus palustris	85	6.2	12	0.86	2
Quercus robur	120	N/A	8.6	N/A	1
Quercus suber	150	34	7.0	1.8	1
Quercus virginiana	100	63	13	7.9	3

Table 4-8. (Continued)

Scientific Name	Specific Leaf Weight Mean ($g\ m^{-2}$)	Std Dev.	Specific Leaf Area Mean ($m^2\ g^{-1}x10^3$)	Std Dev.	No. of samples
Rosa hybrida	120	11	8.7	0.87	4
Rosemarinus officinalis	240	150	5.3	3.3	2
Sapium sebiferum	130	60	8.3	3.7	2
Syagrus romanzoffiana	230	1.1	4.4	0.021	2
Syringa vulgaris	120	23	8.9	1.6	3
Viburnum trilobum	99	36	11	3.9	2
Vitex agnus-castus	140	40	7.4	2.4	3
Washingtonia robusta	180	N/A	5.4	N/A	1
Yucca brevifolia	910	N/A	1.1	N/A	1

4.4.2 Calculation of Leaf Area with Two Methods

Leaf area may be calculated using allometric equations, or by using leafmass to leaf area conversions. As seen in Table 4-9, leaf areas of harvested trees were calculated using the equations of Nowak (1996). Equation 3 (Eqn. 3), is based upon crown dimensions and is of the form:

$$\ln Y = -4.3309 + 0.2942H + 0.7312D + 5.7217S - 0.0148C + \text{error} \quad (3)$$

and equation 4 (Eqn. 4) is based upon trunk diameter and is of the form:

$$\ln Y = 0.2102 + 0.0586X + 4.0202S + \text{error} \quad (4)$$

where Y is leaf area (m^2). Consistent with the allometric equations for leafmass (section 4.4.1), 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; therefore, leaf area was not calculated using these equations.

Table 4-9. Comparison of leaf area, and corresponding leaf area index, for urban shade trees based on two allometric equations, with experimentally determined mass-to-leaf-area conversion factors.

	Leaf Area (m^2)			Leaf Area Index		
Tree No.	Eqn 3	Eqn 4	Eqn 5	Eqn 3	Eqn 4	Eqn 5
1996 Trees						
1	23	N/A	64	3.1	N/A	8.8
2	18	N/A	61	3.1	N/A	10
3	36	N/A	101	2.9	N/A	8.2
4	27	N/A	80	3.0	N/A	9.0
5	N/A	N/A	31	N/A	N/A	8.6
6	N/A	N/A	57	N/A	N/A	9.6
7	N/A	N/A	44	N/A	N/A	17
8	N/A	N/A	280	N/A	N/A	38
9	12	N/A	40	2.6	N/A	8.5
1997 Trees						
10	51	100	38	3.0	6.0	2.2
11	16	88	29	3.0	16	5.4
12	57	96	64	3.4	5.8	3.9
13	53	84	49	3.2	5.1	3.0
14	210	360	690[1]	5.0	8.4	16[1]
15	270	180	N/A	4.6	3.0	N/A
16	340	310	1230	3.9	3.6	14
17	N/A	N/A	82	N/A	N/A	7.5
18	110	200	400	4.8	8.4	17
19	N/A	N/A	18	N/A	N/A	3.5
20	43	73	36	2.8	4.8	2.4
21	N/A	N/A	21	N/A	N/A	2.5

[1] Specific leaf area used for calculation of the leaf area and LAI for tree No. 14, *Eucalyptus polyanthemos* was the mean of three *Eucalyptus* species (Appendix B).

Leaf areas of harvested trees were also calculated (Table 4-9) with leafmass-to-area conversion factors based on data in Tables 4.5-4.7, where:

$$Y = LM * SLA \quad (5)$$

and Y is leaf area (m^2), LM is leafmass (g) and SLA is specific leaf area ($m^2\ g^{-1}$).

LAI in a southeastern bottomland forest ranged from 4.4-5.8 when measured indirectly, and 5.2 when calculated by litterfall (Geron et al. 1997). The LAI values

calculated with Eqn. 3, where it could be applied (Tree Nos. 1-4, 9-16, 18, 20) had a range of 2.8 to 4.6, similar to the southeastern forest. However, the LAI for the columnar trees (Nos. 5-8) calculated with Eqn. 5 had a range of 8.6-38, from about two to six times higher than the forest. Columnar growth habit would favor higher LAI, because layers of leaves would be arranged over a relatively small area, assuming sufficient light was available to sustain leaves.

4.4.3 Check of Leaf Area Calculations

Leaf areas of two plants calculated using mass-to-area conversion factors with Eqn. 5 were compared to leaf areas measured with the leaf area meter. All the leaves of one tree No. 7, the *Eucalyptus grandis* 'GCT', were passed through the leaf area meter, a process requiring about one week, and the total measured leaf area was 47 m^2. The value for total leaf area for this tree calculated from Eqn 5 was 44 m^2, 94% of the measured leaf area of 47 m^2. The crown projection of the tree was 2.6 m^2 with a corresponding LAI of 17.9, higher than expected for shade trees; however, columnar tree forms, such as this *Eucalyptus* (height of 14 m, radius of 1.8 m) may have a higher LAI than broader forms, such as ellipsoids or spheres, containing the same volume.

All leaves of a *Rhus ovata* (sugar bush) shrub, a plant with a form approximated by a rectangular prism, were removed, measured for leaf area, dried and weighed. The plant measured 2.4 x 2.4 x 1.8 m in length, width, and height, respectively, with a calculated volume of 11 m^3. The measured leafmass of 14,400 g was multiplied by the experimentally determined factor of 0.00312 $m^2\ g^{-1}$ for this species to give a calculated leaf area of 45 m^2, 96% of the measured leaf area of 47 m^2. LAI for this plant using the measured leaf area was 7.6.

Thus, in this very limited comparison using only two plants, leaf areas calculated with mass-to-volume conversions were within about 5% of the measured leaf areas.

4.4.4 Leafmass per Projected Area of Tree Crowns

Leafmass per unit area of crown projection (g m^{-2}) was calculated for each tree based on measured leafmass and crown radius. As seen in Table 4-10, values ranged from 150 to 3200 with a mean of 650 g m^{-2} for deciduous trees. However, excluding the

Table 4-10. Comparison of leafmass per unit area of crown projection for urban shade trees.

Tree No.	Crown Diameter (m)	Crown Projection (m^2)	Measured Leafmass (g)	Leafmass per Unit Area ($g\ m^{-2}$)
1996 Trees				
1	3.0	7.3	4330	590
2	2.7	5.9	4110	700
3	4.0	12	6850	560
4	3.4	8.8	5390	610
5	2.1	3.6	4320	1200
6	2.7	5.9	8020	1400
7	1.8	2.6	5200	2000
8	3.0	7.3	23200	3200
9	2.4	4.7	3200	680
1997 Trees				
10	4.6	17	2560	150
11	2.6	5.4	1960	360
12	4.6	16	4350	260
13	4.6	16	3340	200
14	7.4	43	89600	2100
15	8.6	58	36500	630
16	10.4	85	84700	990
17	3.8	11	8010	720
18	5.4	23	61000	2600
19	2.6	5.3	1530	290
20	4.4	15	2920	190
21	3.2	8.2	1680	200

columnar poplar (no. 8) which had a value more than three times greater than the next closest value, the mean for deciduous trees measured in this study was 480 $g\ m^{-2}$. For the broadleaf evergreen species in the study, values ranged from 1200 to 2600 with a mean of 1900 $g\ m^{-2}$. These values may be compared to literature values of leafmass per unit of ground surface area ($g\ m^{-2}$) 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 for a broadleaf deciduous forest. In a model evaluation for southeastern bottomland forests, leafmass per unit ground area for a closed-canopy forest was estimated to be 416 $g\ m^{-2}$ using a litterfall method (Geron et al.,

1997). Data from the present study indicate the potential for broadleaf urban trees to contain more leafmass 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 leafmass than trees in temperate forests. Therefore, BHC emission inventories may underestimate leafmass 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 leafmasses.

4.5 Implications for BHC Emission Inventories

In urban areas with subtropical climates, including many cities of California, deciduous tree species are mingled with broadleaf evergreen species. For the urban trees in this study, mean leafmasses per unit projected crown area for deciduous and broadleaf evergreen trees were 1.7 and 5.0 times greater, respectively, than leafmass per unit surface area of eastern deciduous forests. Also, broadleaf deciduous trees should be distinguished from broadleaf evergreen trees in aerial photographic interpretation. Therefore, despite limited areal coverage, urban areas may contain a disproportionate amount of vegetation when compared to other landcover types.

Biogenic emission inventories for urban areas require leafmass estimation for plantings of large variability, including a wide range of ages and species of widely varying forms. A volumetric approach using previously established leafmass 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. A volumetric approach may not precisely account for clumping of tree foliage and the change in leafmass 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. Finally, a further advantage of a volumetric method is its applicability to shrubs.

Leaf area and LAI provide tools for describing crowns of trees and especially for describing plant canopies. Leaf areas are more likely to be measurable by remote sensing methods than are leaf masses. Indirect measurement methods for LAI using remote sensing technologies may be especially useful for the natural areas of California if problems associated with heterogeneity can be understood and overcome (Winer et al 1995). For example, LAI may be derived from NOVI, greenness index, or other ratios, and used to estimate leafmass. (Nikolov 1997). Leaf area to leafmass conversions provide a method for deriving leafmasses where leaf areas are known, and for linking data generated with the volumetric approach, which has been extensively used in urban areas of California, to the corpus of literature describing forests of other regions in terms of leaf area, leaf area index, specific leaf area and specific leaf weight. Conversion from LAI to leafmass for California plant species may be possible through data assembled from literature pertaining to plant geography and canopy structure, especially for plant communities of California. These data may also be useful in building plant inventories for other purposes (e.g. fire management).