INVESTIGATION OF THE ROLE OF NATURAL HYDROCARBONS IN PHOTOCHEMICAL SMOG FORMATION IN CALIFORNIA

Final Report

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ABSTRACT

A major uncertainty in present emission inventories for California's urban airsheds is the lack of data concerning reactive organics (ROG) from vegetation; the contribution of such emissions to formation of photochemical air pollution has been the subject of considerable controversy. In particular, an experimentally determined, "airshed-specific" estimate of such emissions has not been available for the California South Coast Air Basin (CSCAB) as an input to the Basin's Air Quality Management Plan.

In order to acquire the necessary data for the CSCAB, we designed and implemented a three-tiered, stratified, random sampling approach, which could be applied to other airsheds as well. This approach involved: (a) quantitative assessments of the area coverage of vegetation in randomly selected sample areas within the CSCAB urban area, using a combination of high altitude (NASA U-2) and low altitude, high resolution, color infrared imagery; (b) field determinations of the distribution and green leaf mass of the trees, shrubs and ground covers found in the selected sample areas; and (c) experimental measurements of emission rates of isoprene and monoterpenes from the most abundant natural and ornamental species found in the CSCAB. From these coordinated studies several significant data bases were generated which were not previously available. These include:

- Experimentally determined rates of emission of isoprene and monoterpenes for more than 60 plant species indigenous to Southern California.
- The first detailed survey of vegetation species composition and distribution in the urban portion of the Los Angeles Basin.
- Development of leaf mass constants for ~50 of the species identified in the study area.
- Acquisition of low altitude, high resolution color infrared imagery for 20 randomly selected areas of the Basin.
- Estimates of total green leaf mass and total percent cover by vegetation in the study area.

Using these data, estimates of emission strengths of isoprene and monoterpenes were derived for a 2600 km^2 urban area. These were combined with results for the native coastal sage and chaparral communities in the foothills surrounding Los Angeles. The total inventory for isoprene and monoterpenes emitted from vegetation in the 4500 km^2 study area during a summer day ranged from ~25 to ~80 tons day^{-1} depending upon the specific data analysis employed. The higher value, and a "worst case" upper limit of 93 tons day^{-1}, were obtained by assuming that all plants were emitters of both isoprene and the monoterpenes at levels corresponding to the detection limit of our chromatographic techniques. Since the study area encompassed 69.4% of the total anthropogenic ROG emitted in the Basin (1693 tons day^{-1} for an average summer weekday) these values for hydrocarbons emitted by vegetation may be compared to ~1200 tons day^{-1} of ROG emitted from anthropogenic sources in the same area.

So that detailed computer modeling of the impacts of ROG emissions from vegetation can be made, our emissions inventory is available in a format consistent with the grid system employed for the emission inventory assembled for anthropogenic sources in the 1982 AQMP for the CSCAB. While detailed airshed modeling was beyond the scope of this program, we have carried out "EKMA"-type calculations. The results suggest that isoprene and monoterpene emissions in the CSCAB will contribute no more than, and probably much less than, a few tens of a part per billion (ppb) of O_3, under conditions which correspond to the production of several hundred ppb O_3 from anthropogenic ROG.

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The statements and conclusions in this report are those of the contractor 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 either an actual or implied endorsement of such products.

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I. PROJECT SUMMARY

A. Introduction and Background

It is becoming increasingly recognized, at least for California's airsheds and the South Coast Air Basin in particular, that most, if not all, of the straightforward and relatively cost-effective measures available for controlling emissions of hydrocarbons from both mobile and stationary sources have either been implemented, or proposed for implementation in the near future. Unfortunately, the reductions in reactive organic gases (ROG) resulting from these present and proposed measures are inadequate to ensure compliance with Federal or State ozone air quality standards by 1987 or even by the end of the century (SCAQMD/SCAG 1982b). In view of this, there continues to be strong interest in improving emission inventories for reactive organics as well as other pollutant classes such as oxides of nitrogen (NO_x), and in quantitatively assessing the contributions of such emissions to the photochemical oxidant problem in California's air basins. One major gap in current emission inventories for ROG has been the lack of quantitative information concerning the amounts of reactive hydrocarbons emitted by vegetation in California's urban airsheds, and the role, if any, of these hydrocarbons in smog formation.

Although it is well established that some plants emit significant amounts of hydrocarbons (Rasmussen and Went 1965, Rasmussen 1970, Rasmussen 1972, Holdren et al. 1979, Zimmerman 1979a,b, Tingey et al. 1979, Graedel 1979, Tingey et al. 1980, Tingey and Burns 1980, Arnts and Meeks 1981), predominately isoprene and several monoterpenes, the atmospheric role of such emissions has been the subject of much discussion and analysis (Coffey 1977, Westberg 1977, Arnts and Gay 1979, Dimitriades 1981, Bufalini and Arnts 1981). Moreover, because of the complexity, cost and magnitude of such undertakings, there have been few previous attempts to assemble detailed emission inventories for natural organics in major air basins (Zimmerman 1979a,b,c, Hunsaker 1981, Hunsaker and Moreland 1981) and, prior to the present study, only an approximate estimate had been attempted for the California South Coast Air Basin (CSCAB) (Taback et al. 1978), and then only for natural vegetation.

In addition to the need for agencies such as the California Air Resources Board (CARB) and the South Coast Air Quality Mangement District (SCAQMD) to obtain reliable assessments of hydrocarbon emissions from vegetation as inputs to air quality management plans and state implementation plans for meeting air quality standards, a specific catalyst for the present study was a widely read report by Sandberg, Basso and Okin of the San Franciso Bay Area Air Quality Management District (BAAQMD) which appeared in 1978 (Sandberg et al. 1978). They argued that higher rainfall caused increased growth of vegetation biomass which, in the following summer, released larger quantities of organic material to the atmosphere, thus causing higher photochemical ozone formation.

In response it was argued (Miller, Pitts and Winer 1979, Bufalini 1979) that the proposal by Sandberg et al. (1978) did not give proper attention to important factors that determine the temporal and spatial concentrations of ozone in urban airsheds, including summer meteorological patterns, photochemistry, transport and hydrocarbon/NO_x ratios. Further, other workers had, by then, obtained recent ambient air data (Zimmerman et al. 1978, Lonneman et al. 1978, Arnts et al. 1978) which suggested that hydrocarbons from vegetation do not accumulate to sufficiently high concentrations to cause additional ozone over that produced from anthropogenic sources. However, such conclusions were challenged in the published literature (Sculley 1979, Ludlum and Bailey 1979). The absence of detailed, reliable emission inventories and ambient measurements of natural organics for any of California's urban airsheds compounded the questions being raised in the refereed literature. It was recognized that the lack of this information might leave certain of the CARB's emission control programs open to challenge and might then hinder development of defensible state implementation plans.

To attempt to address these needs, the CARB initiated, in October 1979, a study by SAPRC/UCR researchers designed to assess the potential contribution of organics from vegetation to the formation of photochemical air pollution in the California South Coast Air Basin. Although, between the initiation and completion of this program new data became available from other laboratories (e.g., Zimmerman 1979a,b,c, 1980, Holdren et al. 1979, Peterson and Tingey 1980, Arnts and Meeks 1980), as discussed in two recent reviews by Tingey and Burns (1980) and Dimitriades (1981), these

did not resolve the general issues, nor did they provide the data required for specific assessments of the situations in California's urban airsheds. However, in several cases they did suggest that hydrocarbons from vegetation were not of great importance.

Assessments of the "air pollution" impact of ROG emitted from vegetation in a specific air basin require knowledge of the ROG emission strength (during the smog season and in the source region of that basin), ambient concentrations and oxidant- and aerosol-forming potential. For the CSCAB, little or no data of this kind were available. Thus no leaf mass inventory was available, few emission rate measurements had been made for species indigenous to the Los Angeles Basin, few ambient measurements had been made specifically for isoprene and monoterpenes and the most recent color IR imagery suitable for analysis of vegetative cover dated to 1968. Accordingly, the original objectives of this study included (a) determination of the kinds and amounts of hydrocarbons emitted by dominant species in various plant communities in the CSCAB; (b) determination of oxidant-precursor relationships for selected hydrocarbons emitted by vegetation; (c) measurement of ambient concentrations of such hydrocarbons in urban airsheds; and (d) based on the results of these experimental measurements, assessments of the contribution of hydrocarbon emissions from plants to photochemical air pollution.

The first year of this program involved a substantial amount of developmental and exploratory work needed to lay the foundation for achieving these objectives. However, during the initial study period significant progress was made, including (a) development of oxidant-precursor relationships for α-pinene using the SAPRC 40,000 ℓ dual-mode outdoor irradiation chamber (Fitz et al. 1981); (b) initial measurements of the ambient concentrations of hydrocarbons emitted by relevant vegetative communities in areas free of anthropogenic emissions; (c) development of plant enclosure and analytical methodologies for measuring the emission rates of isoprene and the monoterpenes from such vegetation; and (d) analysis of the feasibility of applying remote imagery capabilities available on the UCR campus (including Landsat, U-2 and low altitude photography) to the task of quantifying the extent and estimated mass of vegetation types characteristic of the western portion of the CSCAB. Results from these efforts have been described in detail elsewhere (Winer

et al. 1981, Fitz et al. 1981) and are included in the present report only as required for clarity. We focus here on the methods of procedure, results, and conclusions for work carried out between November 1981 and June 1982. A preliminary description of this phase of the program has been presented (Winer et al. 1982).

B. Methods of Approach

As discussed in detail in Sections II through VI, one of the major objectives of this study was to obtain an airshed-specific estimate of the emission inventory for hydrocarbons emitted from vegetation in the region of the CSCAB encompassing a large majority of anthropogenic sources, and the surrounding foothills. (This area is defined here as the "source" region of the CSCAB and as the "study area"). Previous determinations of natural hydrocarbon emission inventories (see Section II) have used various data bases to obtain information on vegetation (Zimmerman 1979a, 1980, Schulting et al. 1980, Hunsaker 1981, Hunsaker and Moreland 1981). In reviewing these previous studies it became apparent that while in most cases considerable emphasis was placed on the measurement of emission rates, relatively minor consideration was given to a reliable calculation of the total green leaf mass of the study area. Since this is a critical link in the ultimate emission inventory calculation, it was decided that a greater emphasis should be placed upon vegetation mapping and field assessments, especially for the urban portion of the Basin.

Thus the four major experimental elements of the urban phase of the program consisted of: (1) the use of high resolution aerial photography (1:3,000) to map the distribution of vegetation in sample cells randomly selected in twenty broad contiguous polygons, each encompassing a relatively homogeneous vegetation composition as determined from low resolution (1:131,000) NASA U-2 imagery; (2) on-site studies of a randomly chosen 1 to 5% subset of each of the 20 sample cells, from which leaf mass and species composition was determined and extrapolated to the entire polygon; (3) direct measurements of the isoprene and monoterpene emission rates for the ornamental and native plants in the most frequently encountered "source" portion of the CSCAB, using specially developed enclosure and sampling techniques; and (4) experimental measurements of the ambient

concentrations of isoprene and the monoterpenes at several locations in the study area.

As indicated by Figure I-1, these coordinated studies constituted a stratified, random sampling approach which was used to estimate the hydrocarbon emission inventory for ornamental vegetation in the urban portion of the study area. The results for the urban portion of the study area were then added to an estimate of emissions from vegetation in the coastal sage and chapparal communities surrounding Los Angeles (which were obtained as described in Section V). These emissions data were then used to estimate their impact on photochemical ozone formation in the CSCAB.

A summary of the specific methods of procedure used in this program and the results obtained follows. Detailed descriptions may be found in Sections III through VIII.

1. Delineation of the Study Area

The area investigated in this study (Figure I-2) was that portion of the CSCAB containing the large majority (69.4%) of anthropogenic sources of ROG in the Basin (with the remaining ~30% of ROG sources being in the "receptor" areas of the Basin). In addition, based on geographical and meteorological factors, the study area was defined as the Los Angeles coastal plain bounded by the Santa Monica and San Gabriel mountains on the north, the Santa Ana mountains and San Joaquin hills on the east and southeast, and the Pacific Ocean on the west. The boundaries included the ridgeline of the Santa Monica mountains and the 3,600 foot contour line of the San Gabriel and Santa Ana mountains. The latter height was conservatively chosen as being well above the average height of the summer temperature inversion layer in which air pollutants are trapped.

The predominant summer wind pattern in this airshed is a daytime onshore breeze and an offshore flow at night (DeMarrais et al. 1965). Thus relatively clean marine air is transported into and through the source area in the morning, accumulates hydrocarbon and oxides of nitrogen emissions, and then moves to air pollution receptor sites east and north of the Los Angeles coastal plain.

2. Determination of Vegetation Cover in Urban Areas

Low Resolution Mapping. The first step in this phase of the investigation was to divide the defined study area into four broad categories of vegetation: urban (ornamental), natural, agriculture and

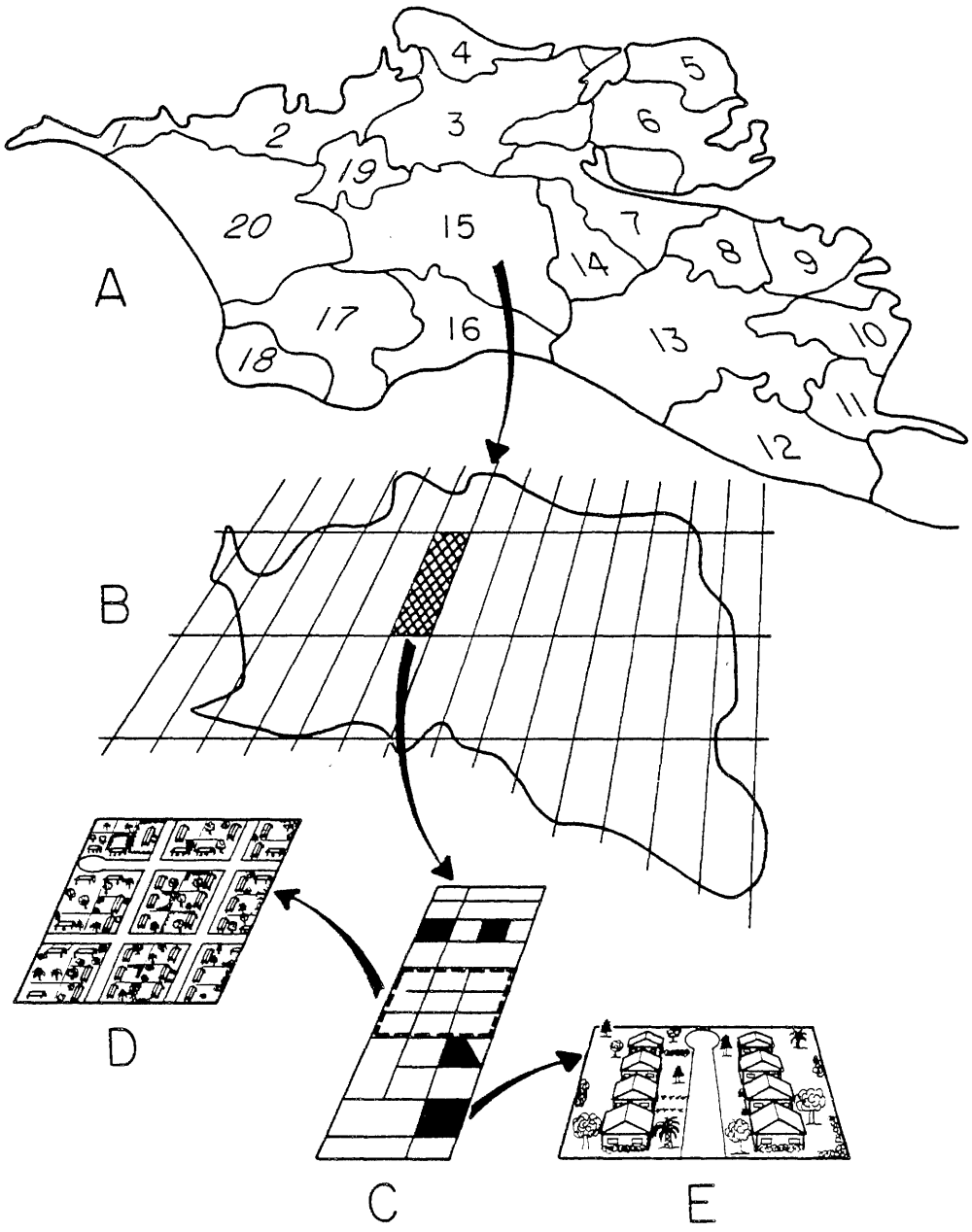


Figure I-1. Depiction of the three-stage, stratified, random sampling design used in this study. A. Twenty stratified polygons covering urban portion of study area; B. Polygon with sample cell grid and randomly selected cell; C. Randomly selected sample cell showing center frame of color infrared imagery (dashed line) and randomly selected subplots (darkened); D. Color infrared imagery area mapped for vegetation cover; E. Subplot randomly selected for vegetation inventory.

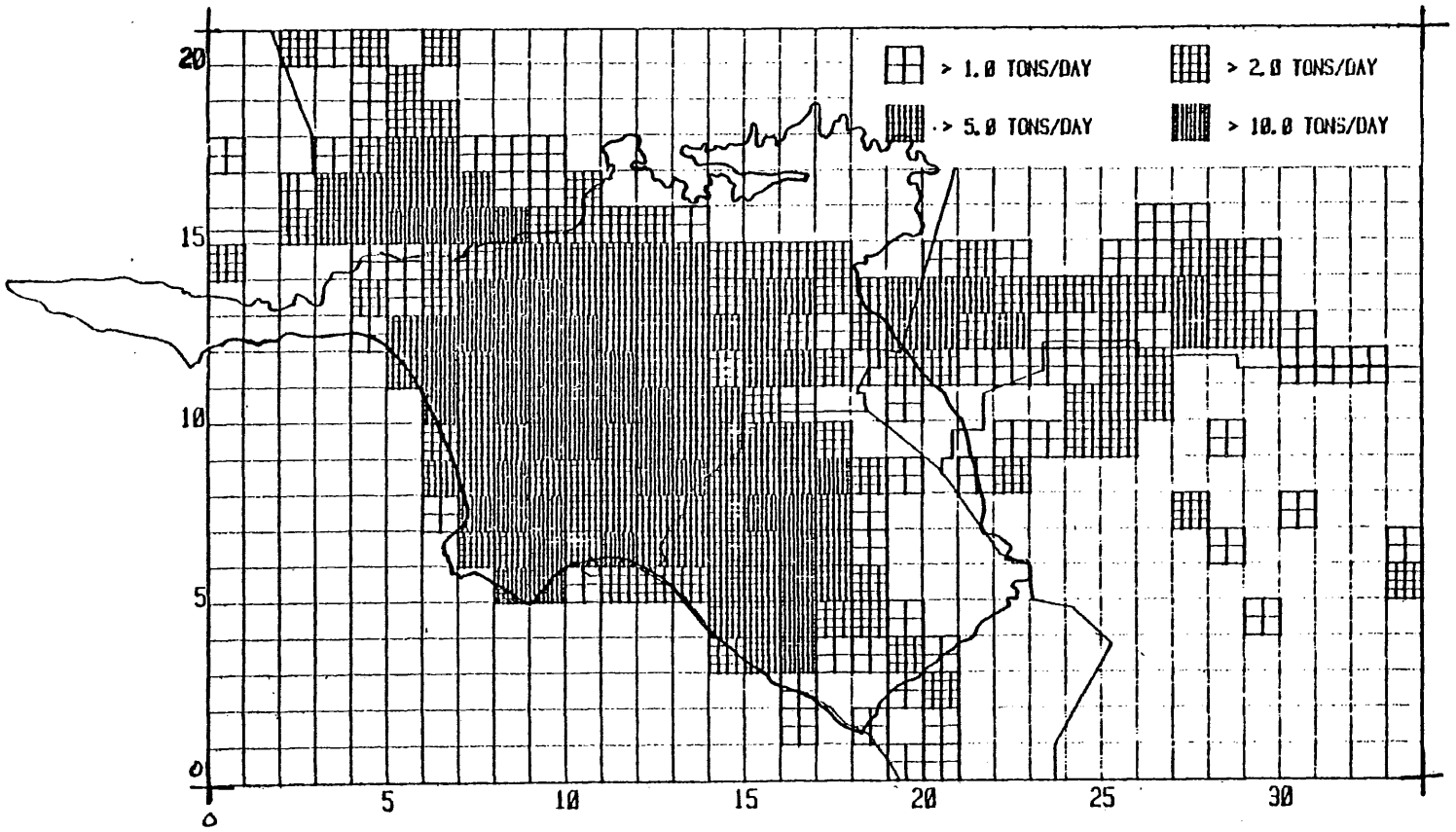


Figure I-2. Spatial distribution of reactive organic gas emissions from anthropogenic sources; 1979 average summer weekday. Each grid element is 5 km on a side (from SCAQMD/SCAG 1982a). The boundary of the study area used in this program is shown.

non-vegetated. Two forms of imagery immediately available for the study area were satellite (Landsat) imagery and high altitude (NASA U-2) photography. The Landsat imagery was not satisfactory for our purposes due to its low resolution and the fact that reflective tones are averaged over a large area. It was therefore decided to use the NASA U-2 color infrared (CIR) imagery for a regional analysis of vegetation by structural class (e.g., trees, shrubs and ground cover).

A mosaic of fifteen CIR images taken in July 1972 by a NASA U-2 aircraft at a scale of 1:131,000, were used to determine boundaries of urban, natural and agricultural vegetation along with non-vegetated areas in the study area. Boundary changes since 1972 were updated by analysis of current (June 1981) Landsat imagery on an International Imaging Systems color combiner. These boundary variations were found to be limited, involving primarily the urbanization of small agricultural areas.

The three vegetation categories and the non-vegetated areas are delineated in Figure I-3. Area sums for the four categories are shown in Table I-1. Urban vegetation is the largest class of vegetation in the study area (~58%) followed by natural vegetation (~33%). Agricultural areas were not a significant fraction and these were eliminated from further consideration.

Stratified Random Sampling Approach. Although a number of studies have been made of the natural vegetation of Southern California (Munz and Keck 1968, Mooney 1977), no detailed, quantitative study of the urban vegetation had been conducted prior to the present study. Previous studies of hydrocarbon emissions from plants have dealt primarily with

Table I-1. Area Totals for Natural, Agricultural and Urban Vegetation

	Area		
	km^2	mi^2	Percent of Study Area
Urban	2626	1014	58
Natural	1476	570	33
Non-vegetated	297	114	7
Agricultural	105	40	2
Total study area	4504	1738	100

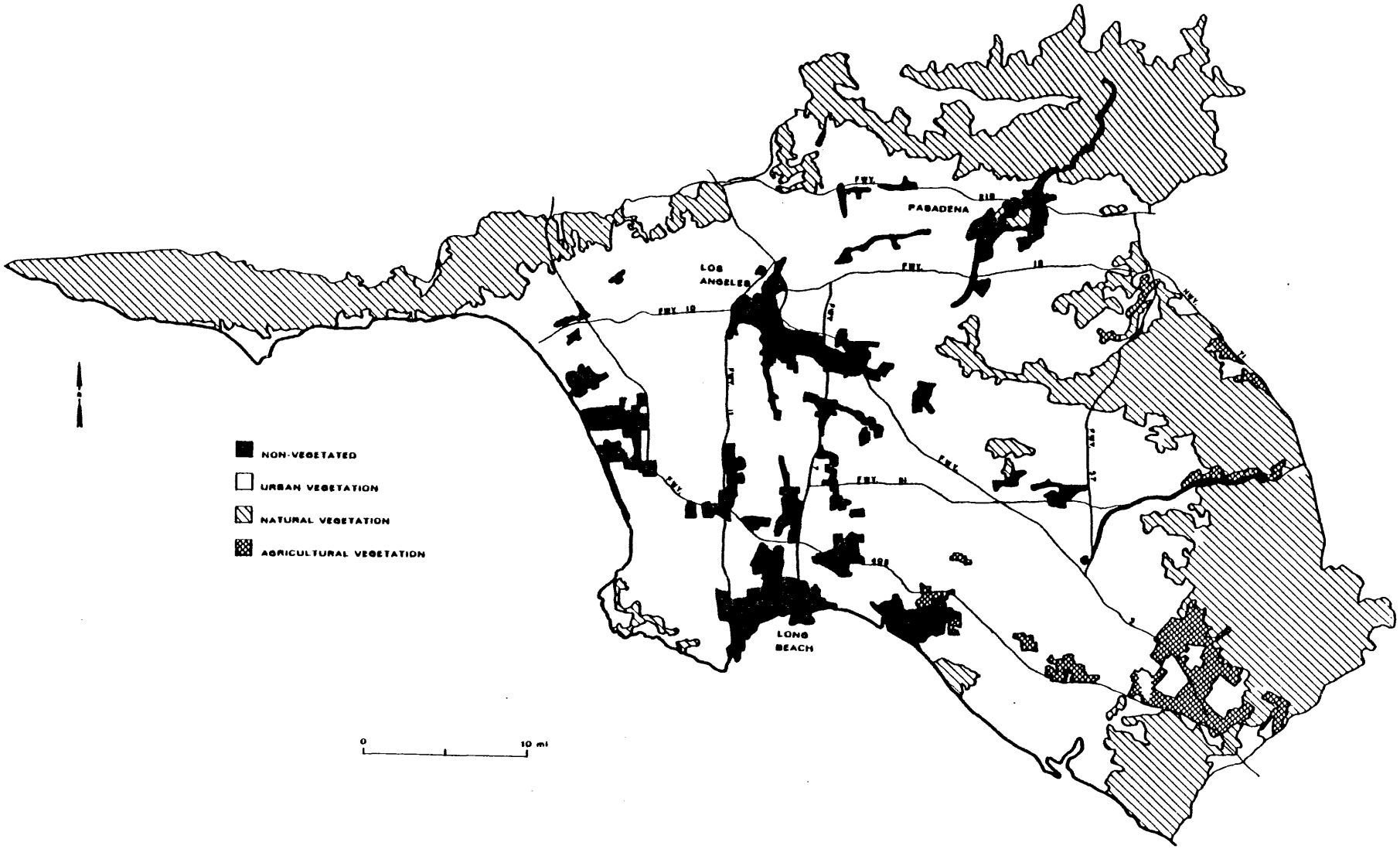


Figure I-3. Urban, natural and agricultural vegetation areas of the CSCAB as determined from a mosaic of 15 NASA U-2 color infrared images.

natural and agricultural vegetation (Zimmerman 1979a,c, Hunsaker 1981, Hunsaker and Moreland 1981, Taback et al. 1978), while urban vegetation has typically been ignored or given minor consideration. However, urban vegetation is the major component on an area basis in the present study. It was therefore decided that a detailed analysis of the urban component was required and that it should be based on random sampling procedures designed to be as comprehensive and statistically valid as possible within the limited time and resources of this investigation.

Simple random sampling usually provides good estimates of population quantities. As depicted in Figure I-1, a stratified random sample is one obtained by separating the population elements into non-overlapping groups called strata, and then selecting a simple random sample from each stratum (Mendenhall et al. 1971). From the U-2 CIR imagery, distinct variations in reflective intensity and tone were noted in the urban areas. These variations were interpreted as arising from differences in green leaf mass and species composition. On this basis the urban vegetation class was subdivided into 20 polygons (Figure I-4). These polygons were assumed to be relatively homogeneous in vegetation composition to permit a stratified random sampling analysis of urban vegetation.

High Resolution Mapping. To implement the stratified random sampling of the urban vegetation it was necessary to randomly select a sample cell for each of the 20 polygons. Thus, a grid was constructed over the entire urban area, with each grid cell the size of the area to be covered by photography taken from a low altitude flight. The grid was laid out by latitude and longitude over four 1:250,000 scale U. S. Geological Survey quadrangles covering the study area. Random numbers (Rand Corporation 1955) were converted by computer to latitude and longitude coordinates of sample cell size. Randomly selected cells were then consecutively plotted on the grid overlaying the urban study area and the 20 polygons, resulting in the 20 sample sites shown in Figure I-5.

3. Field Survey of Species Composition and Determinations of Leaf Mass Constants for Urban Vegetation

Field data for five vegetative classifications were obtained as an integral element of the stratified random sampling approach. To accomplish this each sample cell was positioned on a street map so that it

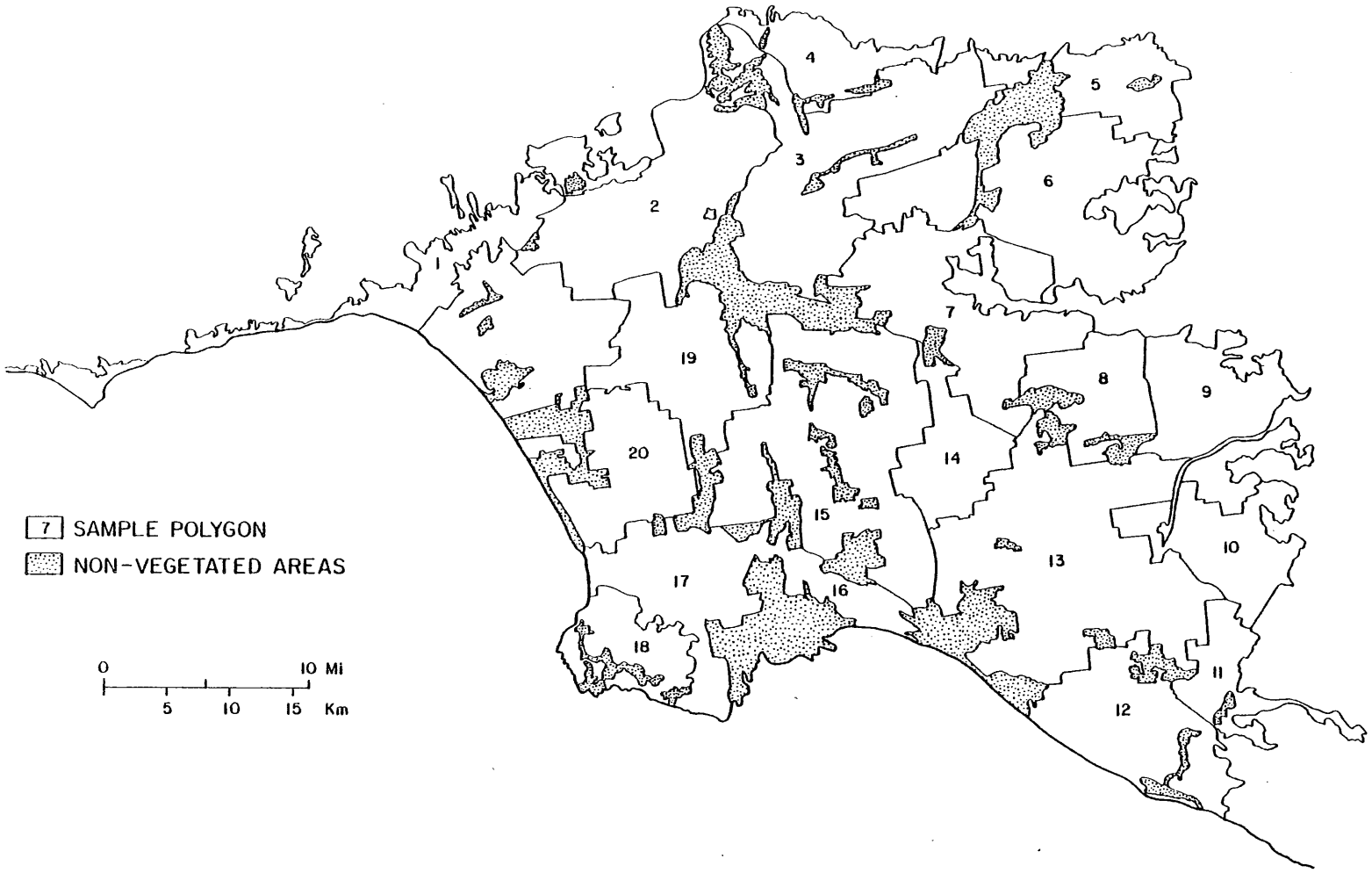


Figure I-4. Polygons for stratified sampling of urban vegetation.

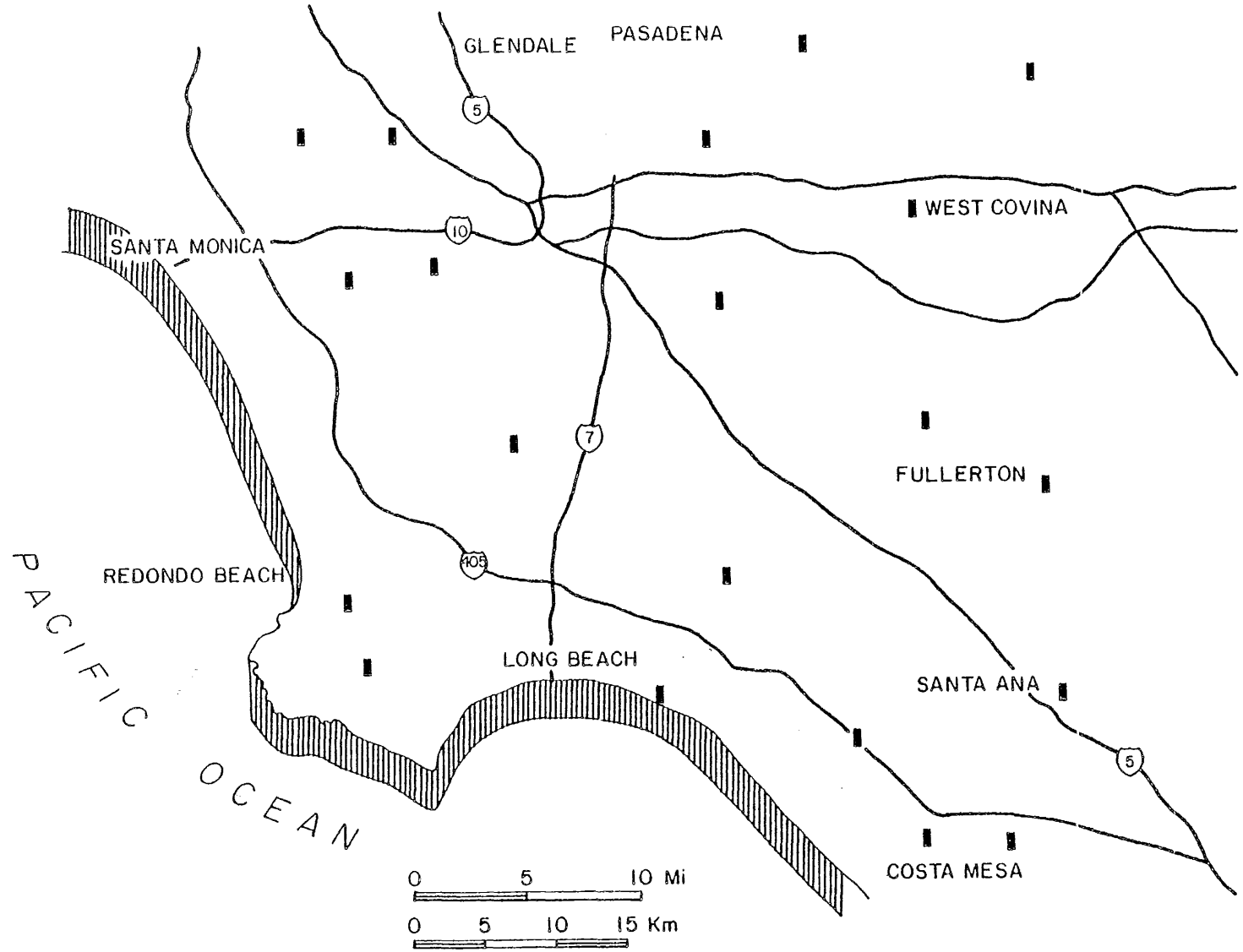


Figure I-5. Randomly selected sample areas.

could be subdivided into as many serially numbered subplots as practical, using city streets as the major reference points for division. The subplots were taken in serial order from this list until their total area exceeded ~1 to 5% of the plot area.

The frequency and dimensions for each species were recorded for all visible vegetation. If a plant could not be identified in the field, a small portion was brought back to the laboratory and later identified at the University herbarium. The dimensions of the leafy crown or canopies of trees and shrubs were measured or estimated. A number of geometric shapes were used as models for this purpose, the most common being either spheres or ellipsoids with varying densities. From these data a canopy volume was estimated for each species.

Only two dimensional data were taken in the analysis of ground cover. Only the surface areas of the vegetation were recorded. All grasses (lawns, playing fields, etc.) were lumped into a general category of "grass" because their usually highly mixed nature made species identification impossible. Other forms of ground cover (dichondra, ice-plant, ivy, flowers, etc.) were recorded under separate specific titles only if large, uniform patches were encountered.

To develop a leaf mass per unit crown volume (g m^{-3}) constant for each important species, samples of foliage were taken from representatives of these species found in accessible locations. Dry weights were measured for leaf and frond materials. The dry leaf mass per unit volume was then computed as an average of all the samples for each species of broad-leaf tree, conifer and shrub (g m^{-3}). Since fronds were counted for each palm, the units of leaf mass constant were g $frond^{-1}$. The units of leaf mass constants for ground cover were g m^{-2}.

4. Acquisition of Natural Vegetation Data Base

Data similar to that required for the urban area were also needed for the naturally occurring vegetation within the study area. After assessment of the urban vegetation, an evaluation was therefore made of the natural vegetation which, as previously shown, constitutes 33 percent of the study area.

A study like that made for the urban area was neither practical or necessary to obtain the data needed for the natural vegetation. Fortunately, a set of vegetation maps published by the U. S. Forest Service in

the 1930's was available. These detailed maps were made exclusively from field surveys and show vegetation as it existed in its natural communities or types (these maps are subsequently called Vegetation-Type maps). For reasons discussed in detail in Section IV, plant geographers and other researchers currently using these maps feel that for the most part they are still applicable today.

Having established the current credibility of these Vegetation-Type maps, it was also recognized that more information than type distributions would be needed for biomass calculations. As with urban vegetation data, actual plant cover by each species would be necessary. Original data compiled by the Forest Service for the Type maps included hundreds of field sample plots covering the areas mapped. The sample plot data, which are currently held at the Pacific Southwest Forest and Range Experiment Station in Berkeley, California, include information concerning species composition and percent cover. These data, when combined with area calculations from the Type maps, gave areal cover by species suitable for the biomass calculations.

Data for species and percent cover were transcribed from the sample plot cards (see for example Figure IV-11) for a total of 106 plots within the study area boundaries. These data included field plots within all vegetation types described. Each sample plot covered 100 milacres, the total of 106 giving a combined field sample of 10.6 acres or 0.04 km^2. Because the species composition may change within a type that occurs in a different geographical area, the data were grouped into five sets, one for each naturally vegetated region within the study area. These were the Santa Monica mountains, San Gabriel mountains, Chino hills, Santa Ana mountains and San Joaquin hills.

For each of these regions, the percent cover for each species was averaged for all sample plots within each vegetation type. This gave an average percent cover by species within the type. The Type maps were then used to gain areal data. Vegetation types from the maps were digitized to provide an acreage for each type within their respective geographical region. For example, 202 km^2 of chamise, 92 km^2 sage, 22 km^2 chaparral and 15 km^2 of woodland were found for the Santa Monica mountains. By multiplying the percent cover for each species (taken from the sample plots) times the area of the type it occurs in (from the maps), an acreage

for each species was obtained. The percent cover and area for each of the naturally occurring species reported for the five naturally vegetated regions within the study area are given in Tables IV-4 to IV-8.

The acreage of each individual species was then summed for the five geographical regions to provide a total area covered by each naturally occurring species. These data were then available for use in the leaf mass computations.

5. Measurements of Rates of Emission of Hydrocarbons from Vegetation

Emission rates of hydrocarbons from the most abundant plant species found in the urban field survey, and from the natural vegetation Type maps, were measured dynamically by enclosing a plant or branch in a 2 mil FEP Teflon film chamber supported by a rigid frame of PVC pipe. The sampling apparatus and associated equipment are described in detail in Section III. Ground cover plants and grasses were grown in plastic flats and the entire flat was placed in the chamber. After a 10 minute purge with ultra-pure air at a known flow rate, samples were taken using 100 mℓ all-glass gas-tight syringes and immediately analyzed by flame ionization gas chromatography (GC).

A Hewlett-Packard 5710A GC was equipped with a six-port gas sampling valve using a 9 mℓ glass loop. Samples were transferred from this loop by nitrogen carrier gas to the head of a 0.25 mm x 30 m SE 54 coated silica column cooled to -90°C. The oven was then temperature-programmed to heat to 200°C. Hydrocarbons containing five to fifteen carbons could be reliably detected at the 1-5 ppbC level. Calibrations were conducted using a 26 component mixture diluted to about 50 ppbC of each compound with nitrogen. Identification was made by measurement of retention times, with occasional verification by a Finnigan 3100 GC-mass spectrometer.

With the exception of ground covers, all plants were tested under field conditions. Sampling of urban ornamentals was conducted at the Los Angeles County Arboretum where proper plant maintenance was assured. Native species were sampled in their natural habitat during the summer of 1981 (either at the U. S. Forest Service San Dimas Experimental Forest or the Paramount Ranch in Agoura). Three replicate measurements were normally made for each plant species. After the GC measurements the plant or branch portion in the chamber was cut off and transported to the laboratory where the leaves were then removed, dried and weighed as described above.

C. Results

1. Areas Covered by Five Vegetation Classes in Urban Region

The 20 sample cells (one in each polygon) were photographed on October 6, 1981 at approximately 1:3,000 scale with color infrared film. The resulting high resolution photographs were used to digitize the areas covered by trees (broad-leaf and conifer), palm trees, shrubs, ground cover and grass. These vegetation groups could be distinguished on the basis of color, tone, size, shape, shadow, texture and height (coded by stereoscope viewing). The center frame of the five frames of imagery taken for each sample cell was digitized for each polygon. The results for the 20 polygons are shown in Table I-2.

2. Properties of Urban Vegetation in CSCAB Study Area

The field studies of the subplots within each of the 20 sample cells resulted in the identification of a total of 184 distinct plant species. These included 64 species of broad-leaf trees, 8 of conifers, 35 of ground cover, 4 of palms, 2 of lawns or grasses and 71 of shrubs. An additional 8 species could not be identified, giving a total of 192 observed species.

The detailed data for the dominant species in each of the five vegetation groups for all 20 polygons are summarized in Table I-3. These include the total number of times a given species was observed in the field, and the total area and volume. Also shown are the experimentally determined leaf mass constant and the leaf mass of the plants observed for each species. The sub-totals for each of these properties for the less-dominant species of broad-leaf trees, shrubs and ground covers, and the grand totals for each vegetation group are also given in Table I-3.

3. Rates of Emission of Hydrocarbons from Vegetation

Hydrocarbon emission rates were determined for more than 60 plant species common to the CSCAB. Of those, approximately half exhibited measurable rates of emission of either isoprene or monoterpenes. (For a list of the non-emitting species studied see Tables III-17 and III-18.) The measured rates of emission are summarized in Table I-4 in units of $\mu g\ g^{-1}$ of dry leaf weight per hour ($\mu g\ g^{-1}\ hr^{-1}$), except for ground cover which is in units of $\mu g\ m^{-2}\ hr^{-1}$.

Isoprene and the monoterpenes are grouped separately because of the dependence of the isoprene emission rate on both sunlight intensity and

Table I-2. Areal Cover (m^2) by Vegetation Group (Center Frame of Imagery)

Polygon Sample No.	Trees	Palm Trees	Shrubs	Ground Cover	Grass	Area Mapped	Total Area of Vegetation	Percent Vegetative Cover
1	87,310	2,904	21,362	1,188	71,887	392,757	184,651	47.0
2	17,006	605	4,920	1,895	7,277	373,549	31,703	8.4
3	38,045	807	7,095	1,297	40,553	288,456	87,796	30.4
4	16,690	675	6,504	2,669	6,274	361,880	32,812	9.1
5	20,539	1,119	7,021	1,657	47,051	342,892	77,387	22.7
6	28,963	806	6,523	1,148	27,875	286,449	65,315	22.8
7	20,185	143	4,075	131	55,897	280,137	80,431	28.7
8	1,907	25	3,505	999	18,783	194,157	25,219	13.0
9	26,618	632	5,880	2946	75,618	296,276	111,694	37.7
10	10,716	0	4,355	0	21,885	272,186	36,956	13.6
11	18,701	0	3,528	940	28,004	325,670	51,173	15.7
12	22,605	431	5,773	29	77,611	339,654	106,449	31.3
13	12,882	309	4,374	2,517	32,452	166,865	52,534	31.5
14	17,499	145	9,985	6,858	146,602	311,229	181,089	58.2
15	17,075	802	3,258	59	46,836	231,852	68,030	29.3
16	573	73	5,965	5,862	1,866	346,997	14,339	4.1
17	33,428	27	11,237	16,436	13,672	215,341	74,800	34.7
18	155,784	271	47,382	30,578	21,188	641,863	255,202	39.8
19	15,352	1,878	3,746	0	20,256	227,948	41,232	18.1
20	34,020	230	10,814	16,795	37,649	337,477	99,508	29.5

Table I-3. Summary of Field Survey Data for All Subplots and Leaf Mass Determinations

COMMON NAME	NUMBER OF SPECIMENS	AREA[a] sq m	VOL[a] cu m	LEAF MASS CONSTANT[b] g/cu m	LEAF MASS[a] kg
CONIFERS					
MONTEREY PINE	219	3400	8200	390	3200
CANARY ISLAND PINE	145	1100	2400	470	1100
ITALIAN CYPRESS	325	600	1000	5100	5100
DEODAR CEDAR	10	440	870	920	800
ARAUCARIA	18	100	200	--	--
REDWOOD	3	47	130	--	--
SAGO PALM	6	8	8	--	--
OTHERS	2	4	1	NA	--
TOTAL	728	5700	13000	NA	10000
BROAD-LEAF TREES					
RIBBON GUM	457	9800	14000	340	4800
ASH	145	4100	18000	170	3100
CALIFORNIA LIVE OAK	58	2200	8700	310	2700
CHINESE ELM	75	2200	11000	25	280
AMERICAN ELM	99	1800	10000	28	280
MAPLE	66	1600	11000	44	480
CALIFORNIA SYCAMORE	101	1400	5600	86	480
PERUVIAN PEPPER	41	1300	3100	150	470
JACARANDA	43	1200	3800	90	340
VICTORIAN BOX	66	840	770	2700	2100
BLACK LOCUST	40	760	2000	19	38
CRAPE MYRTLE	117	700	1600	950	1500
AVOCADO	39	650	2300	59	140
CAMPHOR	40	590	1200	75	90
MAGNOLIA	55	540	1700	350	600
OTHERS	852	9200	25000	NA	1300
TOTAL	2294	39000	120000	NA	18000
PALMS					
COCOS PALM	38	970	350	--	--
CALIFORNIA FAN PALM	82	830	2500c	520d	1300
CANARY ISLAND PALM	17	430	1600c	550d	880
DATE PALM	2	51	180c	--	--
TOTAL	139	2300	4700c	NA	2200
SHRUBS					
CALIF. SAGE BRUSH	640	2000	2600	52	140
SYDNEY GOLDEN WATTLE	7	1700	7600	150	1100
JUNIPER	389	1400	1300	3700	4800
GLOSSY PRIVET	176	1100	2300	230	530
BOTTLEBRUSH	219	1100	1800	470	850
CHINESE JUNIPER	556	890	580	3700	2100
CAMELLIA	365	770	970	1600	1600
OLEANDER	106	720	1300	230	300
HIBISCUS	184	710	1400	400	560
ROSE	762	700	650	360	230
SHINY XYLOSMA	282	560	700	470	330
COYOTE BUSH	173	540	710	--	--
JAPAN. PITTOSPORUM	394	510	400	2700	1100
TOYON	35	460	1300	--	--
OTHERS	3579	6300	7900	NA	790
TOTAL	7867	19000	32000	NA	15000

Table I-3 (continued) - 2

COMMON NAME	NUMBER OF SPECIMENS	AREA sq m	VOL cu m	LEAF MASS CONSTANT g/cu m	LEAF MASS kg
LAWNS & GRASSES					
GRASS (unid.)	NA	120000	NA	NA	NA
DICHONDRA	NA	3000	NA	NA	NA
TOTAL	NA	130000	NA	NA	NA
GROUND COVER					
IVY	NA	11000	NA	NA	NA
AFRICAN DAISY	NA	3300	NA	NA	NA
ICE PLANT	NA	1800	NA	NA	NA
FIVE FINGER	NA	180	NA	NA	NA
PERIWINKLE	NA	170	NA	NA	NA
GERANIUM	NA	160	NA	NA	NA
LILY	NA	130	NA	NA	NA
JADE PLANT	NA	120	NA	NA	NA
AFRICAN LILY	NA	55	NA	NA	NA
BELLFLOWER	NA	37	NA	NA	NA
BACHELOR BUTTON	NA	37	NA	NA	NA
WANDERING JEW	NA	33	NA	NA	NA
IRIS	NA	32	NA	NA	NA
TULE	NA	25	NA	NA	NA
OTHERS	NA	1600	NA	NA	NA
TOTAL	NA	18000	NA	NA	NA

a Area, volume and leaf mass rounded to 2 significant digits
b Dry weight of green tissue per unit volume
c Number of fronds -- Not measured
d g/frond NA Not applicable

Table I-4. Mean Emission Rates and Standard Deviations for Urban and Naturally Occurring Vegetation[a]

Common Name	Genus and Species	Mean Isoprene Emission Rate $\mu g\ g^{-1}\ hr^{-1}$	Mean Monoterpene Emission Rate $\mu g\ g^{-1}\ hr^{-1}$
Urban			
Broad-Leaf Trees			
Black locust	Robina pseudoacacia	11 ± 7	
Brazilian pepper	Schinus terebinthifolius		9 ± 9
California live oak	Quercus agrifolia	49 ± 37	
California sycamore	Platanus racemosa	11 ± 3	
Magnolia	Magnolia grandiflora		6 ± 3
Olive	Olea europaea		0.4 ± 0.3
Ribbon gum	Eucalyptus viminalis	7 ± 1	
Silver maple	Acer floridanum		2 ± 0.5
Weeping willow	Salix babylonica	233 ± 46	
Conifers			
Aleppo pine	Pinus halepensis		0.6 ± 0.4
Canary Island pine	Pinus canariensus		2 ± 2
Deodar cedar	Cedrus deodara		1 ± 1
Italian cypress	Cupressus sempervirens		0.1 ± 0.0
Monterey pine	Pinus radiata		0.6 ± 0.2
Flower and Ground Cover			
African daisy	Osteospermum fruticosum		350[b] ± 28
Palms			
California fan palm	Washingtonia filifera	11 ± 12	
Date palm	Phoenix dactylifera	15 ± 1	
Shrubs			
Bottlebrush	Callistemon citrinus	15 ± 6	
Chinese juniper	Juniperus chinensis		0.7 ± 0.7
Common myrtle	Myrtus communis	44 ± 39	
Heavenly bamboo	Nandina domestica	20 ± 5	
Shiny xylosma	Xylosma congestum	8 ± 3	
Natural			
Black sage	Salvia mellifera		12[c]
California sage brush	Artemesia californica		8 ± 9
Encelia	Encelia farinosa		6 ± 3
Rhamnus ceanothus	Rhamnus crocea	37 ± 12	
Scrub oak	Quercus dumosa	35 ± 10	
Woolly blue curls	Trichostema lanatum		21[c]

[a]Corrected to 30°C.
[b]$\mu g\ m^{-2}\ hr^{-1}$.
[c]Values from one measurement.

temperature (Tingey et al. 1979); isoprene is not emitted in the dark. Monoterpene emission rates have been shown to be primarily temperature-dependent (Tingey et al. 1980) and were corrected to 30°C for daylight hours and 25°C for nighttime hours (see Section VI.B.2). The detection limits for isoprene and the monoterpenes in these measurements were generally in the range 0.1 to 1 $\mu g\ g^{-1}\ hr^{-1}$.

4. Integration and Analysis of Emission Rate and Leaf Mass Data

Emission inventories for isoprene and selected monoterpenes were developed for (a) urban vegetation based on cover areas analyzed from aerial imagery and field survey data, and (b) naturally occurring vegetation using the available field plot data of the U. S. Forest Service.

Many approximations and subjective measurements were necessary in order to calculate the emissions in the urban region of the study area and these are enumerated in detail in Section VI. Among the major factors which became clear in the course of the study was the fact that although the polygons were outlined as homogeneous regions on the basis of the NASA U-2 imagery, on a much finer scale, individual field subplots within the same sample cell of a polygon contained differing distributions of vegetation. The small number of samples at each stage (i.e., one sample cell per polygon and as few as 1 or 2 subplots per sample cell) did not permit the calculation of variances at each stage, or the accumulation of variances from several stages. Given these inherent limitations, it was decided to calculate the emission inventory by a number of different methods in order to assess the sensitivity of the calculated total emissions to various statistical techniques, and to obtain an estimate of the range of possible uncertainties in the final inventory values. A total of 13 different methods of calculation were used to fully exploit the available data. These methods are described in detail in Section VI.

Daytime isoprene and monoterpene emissions ($kg\ hr^{-1}$) were calculated and summed with the nighttime monoterpene emissions (as noted earlier, isoprene is not emitted at night). The results are given in kg of hydrocarbons per day. This was done for all 13 of the methods described above. For purposes of comparison with anthropogenic ROG emissions these data were also converted to tons. Table I-5 summarizes the total emissions of isoprene and monoterpenes from the urban study area in tons per day for each of the calculation methods. Note that the emissions

Table I-5. Summary of Emission Inventory for Study Area in Tons Per Day: Lower Limits[a,b]

Method	Isoprene	Monoterpenes[c]	Total
Based on Aerial Imagery and Ground Survey Data			
1	8.2	3.6	11.8
2	7.5	3.8	11.3
3	8.4	2.9	11.3
Based on Ground Survey Data Only			
4	6.0	1.7	7.7
5	6.2	2.9	9.1
6	9.4	1.9	11.4
7	10.8	3.4	14.2
8	8.5	1.9	10.4
9	10.5	3.5	14.0
10	17.8	2.7	20.5
11	20.5	3.3	23.8
12	9.8	2.9	12.7
13	14.2	4.1	18.3
Naturals	4.8	9.3	14.1

[a]Species with emission rates below the detection limit were considered to be non-emitters.
[b]15 hour daylight at 30°C, 9 hour dark at 25°C.
[c]Sum of selected monoterpenes.

labeled 1 to 13 are for the urban region, and Naturals refers to the naturally vegetated region.

The values listed in Table I-5 were obtained by assuming that the emission rates were zero when no emissions were observed above the detection limit of the gas chromatographs. The values listed for Naturals were based on the lower limit for dimensions in the leaf mass constant adjustment. Combining the lowest estimate for the urban region with the estimate for the naturally vegetated region yields a total of 22 tons day^{-1}. The highest estimate for the urban region, when combined with the estimate for the natural region yields, a grand total of 38 tons day^{-1}.

A simple average of the highest and lowest values is 30 tons day^{-1} with a range of ±8 tons day^{-1}. A better total emissions value is probably obtained by adding the average of the totals for Methods 1-3 to the

Naturals total; this gives 26 tons day^{-1}. Methods 1-3 were based only on aerial imagery data, which covered a much larger sample of urban vegetation than the field survey data used in the remaining calculations, and the good agreement for the three different methods suggests that a higher level of confidence may be placed on this result.

Table I-6 gives results from calculations where those species showing no measurable emissions were considered to emit at the detection limit of the gas chromatographic analyses (rather than zero), and the values for Naturals were based on the upper limit of size dimensions. Again, combining the lowest estimate for the urban region with the estimate for the naturally vegetated region yields a total of 67 tons day^{-1}. When the highest estimate for the urban region is combined with the total for

Table I-6. Summary of Emission Inventory for Study Area in Tons Per Day: Upper Limits[a,b]

Method	Isoprene	Monoterpenes[c]	Total
Based on Aerial Imagery and Ground Survey Data			
1	14.5	7.7	22.2
2	13.6	7.3	20.9
3	14.4	6.9	21.3
Based on Ground Survey Data Only			
4	10.3	4.8	15.1
5	10.9	5.9	16.8
6	15.3	6.2	21.5
7	18.3	8.2	26.5
8	13.6	5.6	19.1
9	16.8	7.6	24.4
10	25.3	8.2	33.4
11	30.8	10.4	41.2
12	14.1	5.3	19.4
13	20.9	7.8	28.7
Naturals	20.8	31.3	52.1

[a]Species with emission rates below the detection limit were considered to emit at the detection limit.
[b]15 hour daylight at 30°C, 9 hour dark at 25°C.
[c]Sum of selected monoterpenes.

Naturals, a value of 93 tons day^{-1} is obtained. A simple average of the upper and lower values results in emissions of 80 tons day^{-1} with a range of ±13 tons day^{-1}. Taking the average of Methods 1-3 (as above) and adding it to the total for Naturals yields a value of 74 tons day^{-1}.

In summary, the results from this study suggest that total daily (summer day) emissions of isoprene and the monoterpenes in the study area are in the range of ~25 to ~80 tons. This can be compared to the total daily (average summer weekday) emissions of ROG from anthropogenic sources in the Basin of ~1700 tons and in the study area of ~1200 tons (SCAQMD/SCAG 1982a). It is recommended that those interested in modeling the impacts of isoprene and monoterpene emissions from vegetation on photochemical air pollution in the CSCAB investigate the effects of such emissions over the range from 25 to 80 tons day^{-1}.

5. Implications for Photochemical Ozone Formation in the California South Coast Air Basin

The isoprene and monoterpene emissions data obtained in this study will be made available (see Appendix D) in a format consistent with the UTM grid system used for the ARB/SCAQMD anthropogenic ROG emission inventory prepared for the 1982 AQMP revision. Thus, they can be used as input data for urban airshed model calculations designed to estimate the extent to which ROG emissions from vegetation contribute to the photochemical oxidant problem in the California South Coast Air Basin. Although a comprehensive grid or trajectory modeling study was clearly beyond the scope of this program, estimates of the magnitude of the contribution of vegetative emissions were made using a more approximate approach.

Methods of Approach and Results. The simplest approach currently employed which incorporates chemistry in estimates of the effects of hydrocarbon emissions on O_3 formation is the "EKMA" technique. This involves analyses of O_3 isopleth plots produced by floating "box"-type photochemical model calculations, and is discussed in more detail in Section VIII and elsewhere (U.S. EPA 1977, 1978, Dodge 1977a,b, Dimitriades 1977, Whitten and Hogo 1978).

If we restrict our consideration to relatively small percentage increases ($\lesssim$~20%) in total hydrocarbon emissions (as is the case when considering the effect of adding isoprene and monoterpene emissions to total anthropogenic ROG emissions in the study area), then it can be shown

that the change in O_3 predicted by this type of EKMA analysis is approximately proportional to the increases in hydrocarbon levels. The specific proportionality constant depends on the HC/NO_x ratio and the O_3 level assumed to be characteristic of the particular airshed in question. This can be expressed by the following formula,

$$\frac{\Delta O_3}{O_3} = f(HC/NO_x, O_3) \frac{\Delta HC}{HC} \qquad (I)$$

where $(\Delta O_3/O_3)$ is the fractional change in O_3 levels resulting from a fractional change of hydrocarbon levels given by $(\Delta HC/HC)$. This approach ignores chemical differences between biogenic and anthropogenic organics, as well as meteorological, topographical and spatial factors. Thus, in this case $(\Delta HC/HC)$ represents the fraction of total hydrocarbon emissions which come from vegetation, and $\Delta O_3/O_3$ is the fraction of the O_3 formed which results from those emissions.

As noted above, based on the emissions inventory compiled by SCAQMD/SCAG and the CARB for use in detailed airshed calculations for the CSCAB (SCAQMD/SCAG 1982a), total emissions of all classes of reactive organics from anthropogenic sources on an average summer weekday in our study area amount to ~1200 tons day^{-1} (i.e., 69.4% of 1693 tons day^{-1} = 1175 tons day^{-1}). In comparison, the best estimate obtained in this study of hydrocarbon emissions from vegetation for the summer solstice amounted to ~30 tons day^{-1} of isoprene and monoterpenes (i.e., about 2.5% of total ROG emissions), and the best estimate of the upper limit (or "detection level" limit - see above) for emissions for the same day are ~80 tons day^{-1}, or ~6% of the total ROG emissions. The "worst case" upper limit value obtained was 93 tons day^{-1}, or ~7% of total ROG emissions in the study area. Thus with a knowledge of the proportionality factor, f, the effect of increased hydrocarbon emissions, or the impact of emissions from a particular source (such as vegetation) on O_3 formation can be estimated.

Two different kinetic mechanisms and representations of reactive organics, designated models "E" and "S" in the subsequent discussion, were used to derive the proportionality factors for equation (I). These

mechanisms, the hydrocarbon representation, and the conditions employed in the EKMA simulations are discussed in detail in Section VIII.

A comparison of the O_3 isopleths calculated with the two models is shown in Figure I-6. As discussed previously (Carter et al. 1982), the models indeed give significantly different predictions. Plots of the proportionality factor, f, for equation (I) against the $NMHC/NO_x$ ratio calculated using the two models for assumed ambient O_3 levels of 0.2, 0.3, and 0.4 ppm are shown in Figure I-7. It can be seen that the proportionality factor is not particularly sensitive to the base O_3 level assumed (indeed, for model "E" it is almost completely insensitive - only a single curve is shown), but both models predict a significant dependence on the $NMHC/NO_x$ ratio, with the f-values approaching ~3 at low HC/NO_x ratios, and leveling off at ~0.3-0.4 at high HC/NO_x conditions. However, since model "S" predicts that NO_x is significantly more efficient in inhibiting O_3 formation than does model "E" (see Figure I-6), the models differ considerably in the $NMHC/NO_x$ levels below which the proportionality factor starts to increase rapidly. In addition, model "S" predict that no significant O_3 formation will occur at HC/NO_x ratios below ~6, and thus the analysis based on that model breaks down if ratios of 6 or lower are assumed. On the other hand, model "E" predicts significant O_3 can be formed at ratios as low as 3. Thus, except at HC/NO_x ratios above ~9, the calculated proportionality factors for equation (I) must also be considered to be highly sensitive to the kinetic mechanism and hydrocarbon representation employed in the EKMA analysis.

Although the HC/NO_x ratio most appropriate for use in EKMA analyses of the CSCAB is still uncertain (EQL 1980), it is generally believed to be in the range of 8-12, based on data for 6:00-9:00 a.m. NMHC and NO_x ambient air concentrations (EQL 1980). Within this range, model "E" predicts f $\cong$ 0.3-0.4 independent of the HC/NO_x ratio assumed, while model "S" predicts that f may be as high as ~1.7 if the ratio at the low end of this range is assumed.

Based on considerations (see Section VIII) concerning the probable range of values for the proportionality factor, f, equation (I) can then be used to estimate the contribution of the biogenic emissions to the maximum O_3 levels observed in the CSCAB. Since, as discussed above, our "lower limit" for ROG emissions from vegetation corresponds to ~2-3% of

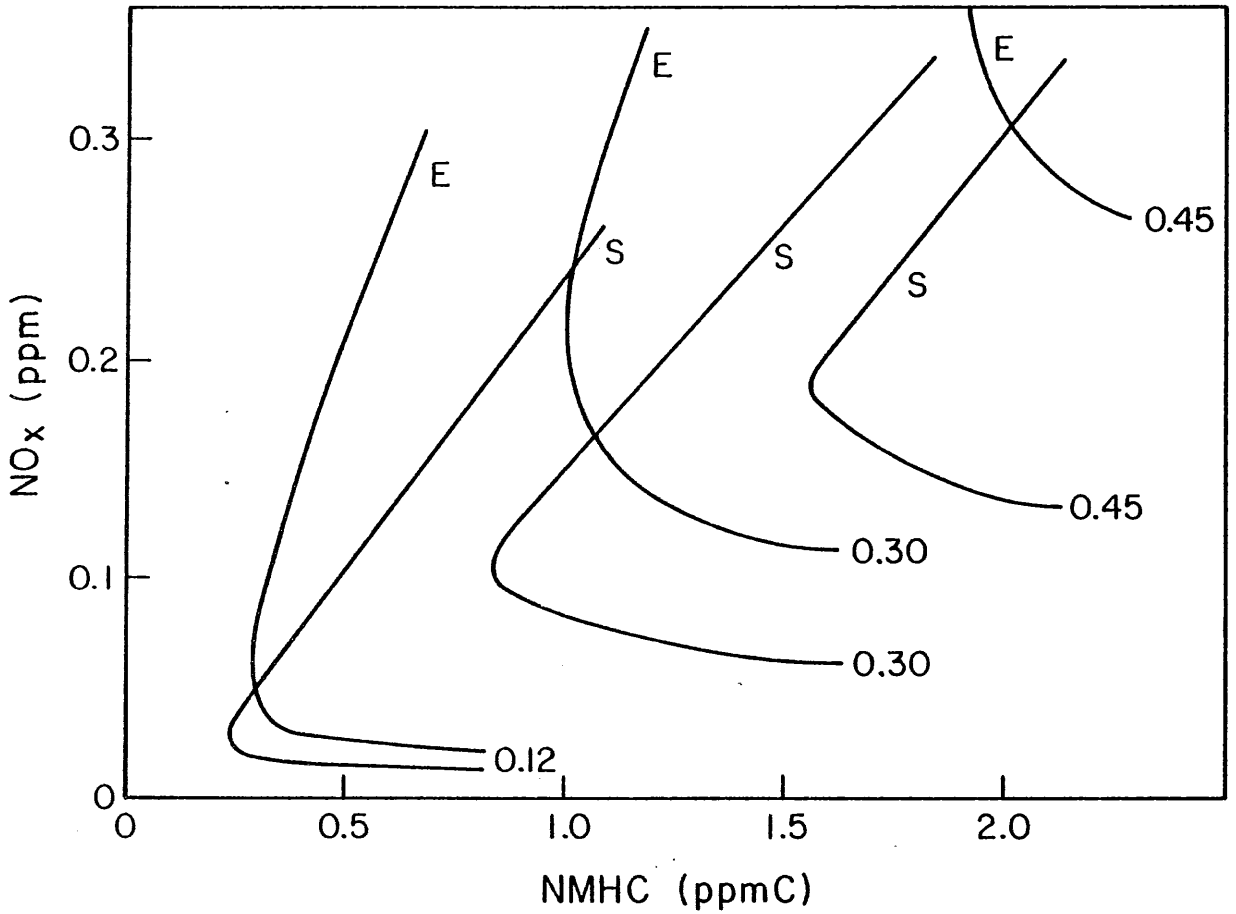


Figure I-6. Isopleth plots for O_3 = 0.12, 0.3 and 0.4 ppm calculated using the standard EPA EKMA model (E) and the SAPRC EKMA model (S). Note that axis labels refer to molar quantities.

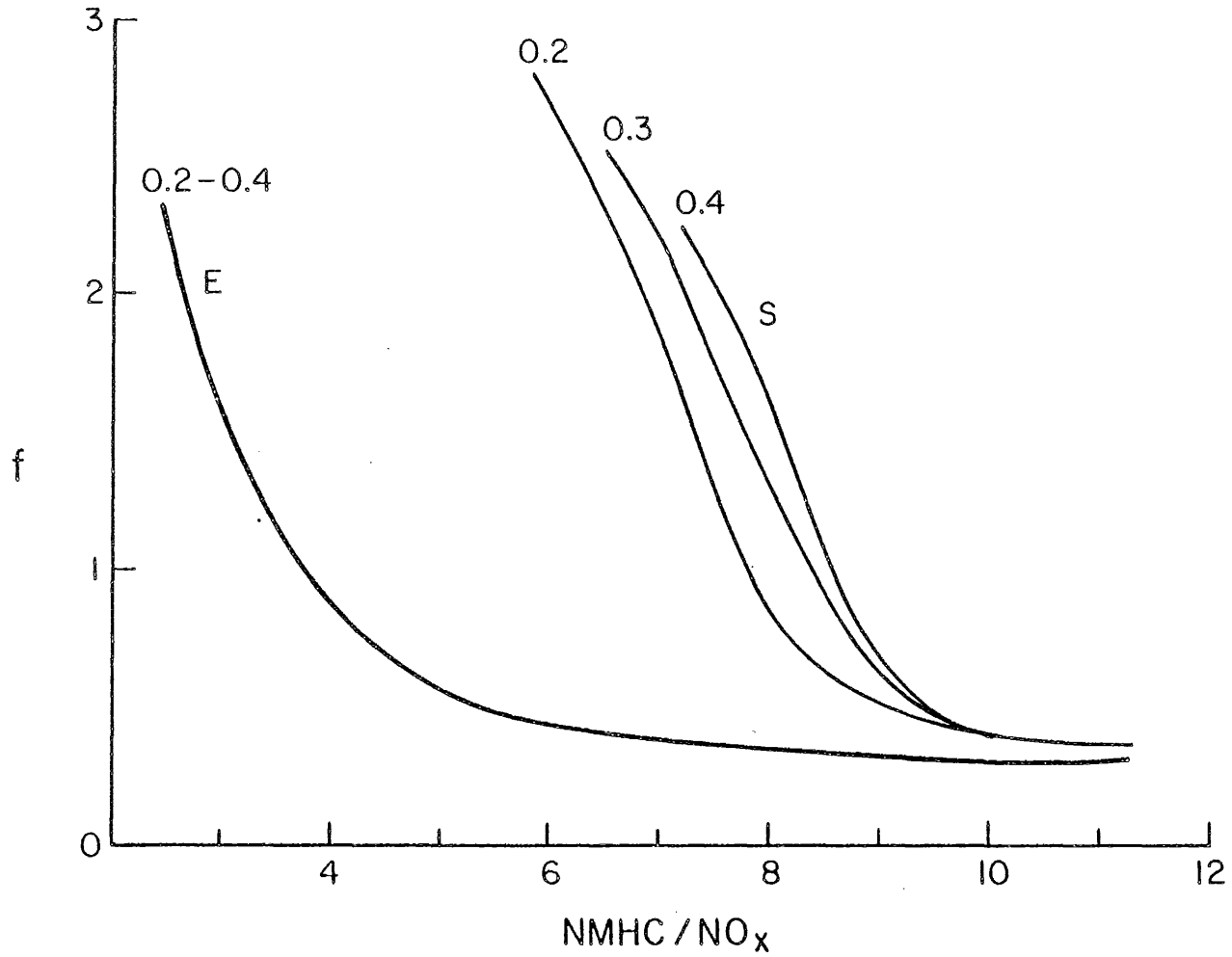


Figure I-7. Proportionality factor, f, for equation II plotted against HC/NO_x ratio for O_3 = 0.2, 0.3 and 0.4 ppm calculated using the standard EPA EKMA model (E) and the SAPRC EKMA model (S). Note that the abscissa units refer to mole ratios (ppmC/ppm) which must be divided by ~3.5 to give weight ratios.

the total ROG emitted from anthropogenic sources in the study area, this means that the isoprene and monoterpene emissions could contribute from <1% to ~3% of the O_3 formed, depending on which model and specific HC/NO_x ratio (within the limits specified above) is assumed. Likewise, if the "worst case" upper limit emission rate of 93 tons day^{-1} of ROG from vegetation is assumed (corresponding to to ~8% of the total anthropogenic organic emissions in the study area), the isoprene and the monoterpenes could contribute to between ~2% to ~8% of the O_3 formed. Thus, a "worst case" EKMA analysis predicts that the ROG emissions from vegetation in the "source" area will contribute less than 10% of the O_3 formed in the CSCAB.

Discussion and Conclusions. It should be re-emphasized that the analyses discussed above do not take into account spatial or temporal effects of emissions, factors relating to meteorology or transport of pollutants, or considerations relating to differing reactivities of isoprene and the monoterpenes relative to anthropogenic hydrocarbons. Thus these calculations must be considered highly approximate at best. However, the comparatively low emission inventory determined for isoprene and the monoterpenes from vegetation is consistent with the very low ambient levels observed for these compounds. Further, outdoor chamber experiments have shown that replacing up to ~20% of an urban-like hydrocarbon mixture with a corresponding amount of α-pinene results in no significant change in O_3 formation (Kamens 1981), and that isoprene is less reactive, in terms of O_3 formation, than propene (Arnts and Gay 1979). Thus reactivity considerations may be unimportant. On the other hand, temporal and spatial variations in vegetation and anthropogenic emissions may be such that vegetative emissions may have a non-negligible effect on O_3 levels in localized areas, even if their effects on average O_3 levels throughout the basin are small.

Clearly, more sophisticated model calculations are required to fully elucidate the effects of emissions of hydrocarbons from vegetation on the formation of photochemical smog in the CSCAB. However, the available evidence indicates that hydrocarbon emissions from vegetation in the study area are unimportant relative to reactive organic compounds emitted from anthropogenic sources in producing the high levels of photochemical oxidant observed in the CSCAB.

In view of this, any further efforts should be focused on refining and improving the anthropogenic ROG and NO_x emission inventories. The apparent discrepancy between the NMHC/NO_x ratio for the anthropogenic emissions inventory (SCAQMD/SCAG 1982a) vs observed ambient 6:00-9:00 a.m. concentrations (EQL 1980) suggests that the anthropogenic ROG inventory may be significantly low. If this is the case, then hydrocarbons emitted by vegetation would be an even smaller contributor to the photochemical oxidant problem in the CSCAB than our present results indicate.

II. INTRODUCTION

A. Statement of the Problem

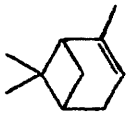
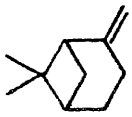
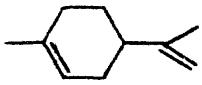
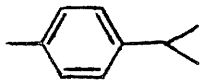
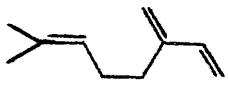
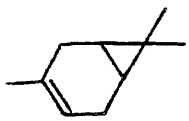
Concern over the possible role in photochemical air pollution of organic emissions from vegetative sources has been growing for two decades since early measurements by Went (1960) and Rasmussen and Went (1965) suggested that emissions of gaseous organics on a global or continental scale exceed those from anthropogenic sources. Although such natural emissions are generally segregated geographically from anthropogenic emissions it has been suggested that, due to their high reactivity and large emissions, hydrocarbons from vegetation could be responsible, at least in part, for elevated levels of ozone observed in rural areas, and indeed for a portion of photochemical air pollution in urban airsheds.

The major compounds emitted by plant species are isoprene and the monoterpenes α-pinene, β-pinene, camphene, limonene, myrcene and β-phellandrene (Rasmussen 1972, Graedel 1979) (see Table II-1). Rasmussen (1970, 1972) has identified isoprene as a compound emitted by many hardwood trees and α-pinene as a ubiquitous emission of softwood-type forests. Indeed, Zimmerman et al. (1978) have estimated that isoprene accounts for approximately 30% of plant emission in the U.S., and ~40% worldwide. A study of vapors from white pines and their hybrids by Gerhold and Plank (1970) indicated that the composition of monoterpene emissions were composed of 24-69% α-pinene, 12-38% β-pinene and 0-15% limonene.

While estimates of global emissions of terpenoid hydrocarbons appear to be uncertain by an order of magnitude, anthropogenic emissions of nonmethane hydrocarbons are somewhat more reliably known, with rates of ~30 MT yr^{-1} in the U.S. and 80 MT yr^{-1} worldwide (Duce 1978). Robinson (1978) has pointed out that since 95% of the world's energy is consumed in the northern hemisphere, with 85% being consumed between 30°N and 60°N latitude, these anthropogenic emissions are highly concentrated and thus should dominate the atmospheric trace gas chemistry in urban areas of the United States and Europe.

If natural organics do in fact contribute significantly to the formation of photochemical oxidants, then the effectiveness of hydrocarbon emission control strategies in reducing ozone levels is questionable,

Table II-1. Natural Organics Observed in the Troposphere

Compound	Structure	Occurrence
Isoprene		Measured in ambient air in rural areas. Emitted by deciduous trees and shrubs.
α-Pinene		Measured in ambient air in rural areas. Emitted by numerous conifers.
β-Pinene		Measured in ambient air in rural areas. Emitted by California Black Sage and general conifers.
d-Limonene		Measured in ambient rural air. Emitted by Loblolly pine, California Black Sage, and "disturbed" Eucalyptus.
p-Cymene		Emitted by California Black Sage and from "disturbed" Eucalyptus foliage.
Myrcene		Measured in air above pine needle litter. Emitted by Loblolly Pine, California Black Sage and Redwood.
Δ^3-Carene		Measured in ambient air. Found in the gum turpentines of some pines.

particularly in the United States where stringent hydrocarbon control has been adopted as the optimum strategy for meeting the Federal air quality standard for ozone.

The discourse between Coffey (1977) and Westberg (1977), undertaken in the context of the U. S. Environmental Protection Agency's International Conference on Oxidants, summarized most of the available published literature at that time, but left unresolved many of the major questions involved in this issue. The controversy was heightened with publication of a report by Sandberg, Basso and Okin in 1978, postulating that there is a significant relationship in the San Francisco Bay Area Air Basin (SFBAAB) between biomass increase resulting from wet winters and greater numbers of days with high ozone concentrations during the following summer. Reactive hydrocarbons volatilized from supposedly greater biomass were suggested to be the primary factor responsible for the observed increase in days with ozone concentrations exceeding the former Federal air quality standard of 0.08 ppm.

It was argued (Miller et al. 1979, Bufalini 1979) that the proposal by Sandberg et al. (1978) did not give proper attention to important factors that determine the temporal and spatial concentrations of ozone in urban airsheds, including summer meteorological patterns, photochemistry, transport and hydrocarbon/NO_x ratios. In addition, other workers had, at that time, obtained ambient air data (Zimmerman et al. 1978, Lonneman et al. 1978, Arnts et al. 1978) which suggested that hydrocarbons from vegetation do not accumulate to high enough concentrations to add significantly to the ozone which is produced from anthropogenic sources. However, such conclusions were challenged in the published literature by Sculley (1979) and Ludlum and Bailey (1979).

Generation of the experimental data (e.g. emission rates, leaf mass estimates, ambient concentrations) needed to assess the atmospheric role of vegetative organics, and the application of such data in conjunction with computer models, are difficult problems, pressing the current capabilities of both experimental and modeling techniques. It is perhaps not surprising then that despite a growing number of studies related to this issue, the question of whether or not natural organics contribute significantly to oxidant formation in urban or suburban areas had not been resolved at the time this study was initiated.

Based upon a review of the data in 1977, the EPA (1978) concluded (perhaps prematurely, given the limited evidence then available) that the contribution of "natural" organics is small at best and probably negligible. This assessment was based almost entirely on evidence that ambient concentrations of the monoterpenes were negligible relative to those of anthropogenic organics. However, on a regional (or larger) scale, emissions data for natural and anthropogenic organics appear to be inconsistent with ambient concentration data. Thus, as discussed above, natural organic emissions have been estimated to exceed anthropogenic emissions by factors of ~4 to 10, while the ambient concentration of natural organics are far lower than anthropogenic hydrocarbons even in rural areas.

Four possible reasons for this inconsistency have recently been discussed in detail by Dimitriades (1981). These were that: (1) ambient measurements of natural organics are erroneously low; (2) natural organic emission rates are erroneously high; (3) anthropogenic hydrocarbon emission measurements are erroneously low; and (4) ambient measurements of organics do not represent all emitted material, but rather reflect the residual amount after reactions with O_3 and OH radicals. A fifth possibility has been raised by very recent kinetic measurements in this laboratory (Atkinson et al. 1983) which show that isoprene and especially the monoterpenes react rapidly with the nitrate (NO_3) radical. These rate data, when coupled with the recent measurement of significant concentrations of the NO_3 radical in both clean (Platt et al. 1983) and polluted atmospheres (Platt et al. 1980), suggests that reaction with NO_3 radicals will be an important if not dominant nighttime reaction pathway for the monoterpenes. This represents a previously unrecognized loss process for organics emitted from vegetation.

Based upon the most recent data (Grimsrud et al. 1975, Winer et al. 1976, Atkinson et al. 1982b, Kleindienst et al. 1982, Atkinson et al. 1983), the lifetimes of isoprene and the monoterpenes in the atmosphere are indeed determined by reaction with ozone and OH and NO_3 radicals. From rate constants for these reactions and the estimated ambient concentrations of O_3 and OH and NO_3 radicals for atmospheres containing varying amounts of pollutants, atmospheric half-lives for isoprene and four of the monoterpenes can be calculated. These are shown in Table II-2. These short atmospheric half-lives (as short as a few minutes for reaction with

Table II-2. Calculated Lifetimes of Isoprene and Four Monoterpenes Studied Here Due to Reaction with O_3 and OH and NO_3 Radicals[a]

Organic Compound	Organic Lifetimes					
	"Clean" Atmosphere[b]			"Moderately Polluted"[c] Atmosphere		
	τ_{O_3} 24 hour	τ_{OH} Daytime	τ_{NO_3} Nighttime	τ_{O_3} 24 hour	τ_{OH} Daytime	τ_{NO_3} Nighttime
Isoprene	32 hr	2.9 hr	3.6 hr	10 hr	1.4 hr	22 min
α-Pinene	4.6 hr	4.6 hr	20 min	1.4 hr	2.3 hr	2 min
β-Pinene	18 hr	3.6 hr	50 min	5.5 hr	1.8 hr	5 min
Δ^3-Carene	3.2 hr	3.5 hr	12 min	1.0 hr	1.7 hr	1.2 min
d-Limonene	36 min	2.0 hr	9 min	11 min	1.0 hr	0.9 min

[a]From Atkinson et al. 1983.
[b]Assuming 30 ppb of O_3 (24 hr average), 1 x 10^6 cm^{-3} (0.04 ppt) of OH during daylight hours and 10 ppt of NO_3 during nighttime hours.
[c]Assuming 200 ppb of O_3 (24 hr average), 2 x 10^6 cm^{-3} (0.08 ppt) of OH during daylight hours, and 100 ppt of NO_3 during nighttime hours.

the NO_3 radical) may account in part for the apparent discrepancies found in previous studies between "high" emission rates and "low" ambient concentrations (even in vegetative canopies) of organics from vegetation. Because current airshed models used to formulate oxidant control strategies employ emission rates, rather than ambient concentrations, as precursor inputs, it is important to resolve this inconsistency.

B. Brief Description of Recent Related Studies of Urban or Regional Airsheds

Since the 1977 review by the EPA, numerous studies, both in the U.S. and abroad, have been conducted for regions incorporating urban airsheds. Several other studies have been conducted for regions encompassing nonurban areas, but these will not be discussed as they are outside the scope of the present program. The methods and conclusions for the urban investigations are briefly summarized below.

Zimmerman (1979a) determined a biogenic emission inventory for the Tampa/St. Petersburg area of Florida. Emission strengths of hydrocarbons from indigenous species were determined, and vegetation types and distribution were found primarily from Level II land-use and planning maps. These maps were developed by the U. S. Geological Survey for the Land-Use and Land-Cover Data Analysis system (LUDA). The study area was divided into a grid and overlayed on the 1:250,000 LUDA maps. The percentage occupied by each land-use category was then visually estimated for each grid cell. The result was a set of LUDA categories and their percent coverage of each grid cell in the study area. These results were combined with emission rates experimentally determined for vegetation indigenous to the Tampa/St. Petersburg area. Although Zimmerman found it to be comparable to the anthropogenic emission inventory, he calculated the ozone mixing ratio from vegetative isoprene emissions to be only ~10 ppb.

Zimmerman compiled another vegetation inventory in a study on natural sources of ozone in Houston (Zimmerman 1979c, 1980). The approximate vegetative composition was visually estimated from 1:20,000 scale aerial photographs for the 1,610 km^2 study area. Although it was recognized that land use changes had taken place since the aerial photographs were taken, no updating was carried since better data were not then available. The percent ground cover was visually estimated for trees, pasture, cropland

and lawn, water surfaces and barren land. Again, these data were combined with appropriate hydrocarbon emission rates. The total natural organic emission rate within this heavily developed area was estimated to be 32.4 metric tons per day. Recently Davis and Trijonis (1981) estimated the anthropogenic emission rate for roughly the same area to be 720 metric tons per day. Thus, the fraction of organics due to natural sources within the Houston city and ship channel area was estimated to be ~4% of anthropogenic emissions. Interestingly, the latter value is consistent with ambient concentration fractions of 0-7% measured by Zimmerman (1979c, 1980) in the same area. Using a greatly simplified box model, Zimmerman calculated that the total ozone produced by the daily emission of isoprene (~70% of total natural hydrocarbons) in the Houston study area was ~22 ppb.

Lloyd and co-workers (Lurmann et al. 1983a,b) have recently modeled the potential ozone impacts of biogenic hydrocarbon emissions using a chemical mechanism for the NO_x-air photooxidations of isoprene and α-pinene (Lloyd et al. 1983) as well for anthropogenic hydrocarbons. They calculated ozone levels under "worst case" meteorological conditions for various combinations of natural and anthropogenic emissions in both rural and urban environments. Their results showed ozone production by emissions from vegetation to be small or "negative" in rural environments due to low NO_x levels, and only a slight enhancement of ozone production in urban areas due to upwind sources of biogenic hydrocarbon emissions.

Schulting et al. (1980) investigated the emissions of hydrocarbons from vegetation and their contribution to air pollution in the Netherlands. They obtained emission rates for grasses, conifers and deciduous plants and, from estimates of the vegetative distribution in the Netherlands, obtained a countrywide estimate of natural organic emissions of 100,000 tons per year. This represents 70% of the total estimated hydrocarbons from all sources. However, for an industrialized area in South Holland the contribution of vegetative hydrocarbons was determined to be <1%. Based upon an extension of the literature data for oxidant precursor relationships and the emitted quantities and measured concentrations of the natural hydrocarbons, the contribution of these compounds to ozone formation was estimated to be less than 10%, or less than 10 ppb (Schulting et al. 1980).

Derwent and Hov (1980) have investigated the contribution from natural hydrocarbons to photochemical air pollution in the United Kingdom using numerical simulation techniques. A computer model was developed to predict the formation of ozone, PAN and sulfate aerosol from photochemical reactions involving NO, CO, SO_2 and 35 organic compounds from various anthropogenic and natural sources. The calculated results for a multi-day photochemical episode agreed reasonably well with observations of secondary pollutant concentrations in the United Kingdom. The effect of natural hydrocarbons "injected" during the second and third days was clearly evident in the concentration-time profiles for O_3, PAN and SO_4 aerosol. In the model, the consumption of the natural hydrocarbons stimulated OH radical production, leading to an ~10% increase in secondary pollutant concentrations. Thus, Derwent and Hov (1980) concluded that natural hydrocarbons could account for only about 10% of photochemical air pollution formation in the United Kingdom.

The Association of Bay Area Governments (ABAG), in preparing a biogenic hydrocarbon emission inventory for the San Francisco Bay Area, relied upon digital Landsat data for a vegetation inventory (Hunsaker 1981, Hunsaker and Moreland 1981). Land cover classification was based on Landsat spectral data which had been clustered by the California Department of Forestry. The Landsat data were used to describe location, area and percent composition of 23 different land cover classifications. Most of these were expressed as percentages of four basic vegetation types: hardwood, conifer, grass and brush (Hunsaker 1981, Hunsaker and Moreland 1981). Final results from this study are not yet available.

For additional discussions of this and other aspects of the issue of the role of vegetative hydrocarbons in photochemical air pollution formation, the reader is referred to recent articles by Tingey and Burns (1980) and Dimitriades (1981) and to an important collection of papers published in a two-volume series entitled "Atmospheric Biogenic Hydrocarbons" (Bufalini and Arnts 1981). A representative listing of the primary literature in this area is provided in Section IX.

C. Selection of the Study Area

The area investigated in this study was that portion of the CSCAB containing the large majority (~75%) of total anthropogenic sources of

hydrocarbons and essentially 100% of the reactive organic emissions in the western and middle portions of the Basin (i.e., the "source" region), plus surrounding areas of natural vegetation. On the basis of geographical and meteorological factors, the study area was defined as the Los Angeles coastal plain bounded by the Santa Monica and San Gabriel mountains on the north, the Santa Ana mountains and San Joaquin hills on the east and southeast, and the Pacific Ocean on the west. The boundaries included the ridgeline of the Santa Monica mountains and the 3,600 foot contour line of the San Gabriel and Santa Ana mountains. These natural boundaries were connected by imaginary lines which were consistent with treating this portion of the air basin as a source area for primary air pollutants. The resulting study area is shown plotted on a Universal Transverse Mercator (UTM) grid map in Figure II-1.

The predominant summer wind pattern in this airshed is a daytime onshore breeze and an offshore flow at night (DeMarrais et al. 1965). Thus relatively clean marine air is transported into and through the source area in the morning, accumulates hydrocarbon and NO_x emissions, then moves to receptor sites east and north of the Los Angeles coastal plain. Obtaining the data necessary to assess the contributions that hydrocarbons from vegetation may make to manifestations of photochemical smog in the CSCAB was the overall goal of this investigation.

D. Rationale and Approach for the Present Investigation

In reviewing the previous studies (Section II.B), it became apparent that while, in several cases, considerable emphasis was placed on the measurement of emission rates, relatively minor consideration was given to a reliable calculation of the total green leaf mass of the study areas. Since this is a critical link in the ultimate emission inventory calculation, it was decided that, in this study, a greater emphasis should be placed on vegetation mapping and field assessments. Thus, for urban vegetation the three principle experimental elements of this study consisted of: (1) direct measurements of the isoprene and monoterpene emission rates for the most frequently encountered ornamental and native plants in the "source" portion of the CSCAB (described in Section III); (2) the use of high resolution (1:3,000) aerial photography to map the vegetative distribution in sample cells randomly selected in twenty broad contiguous

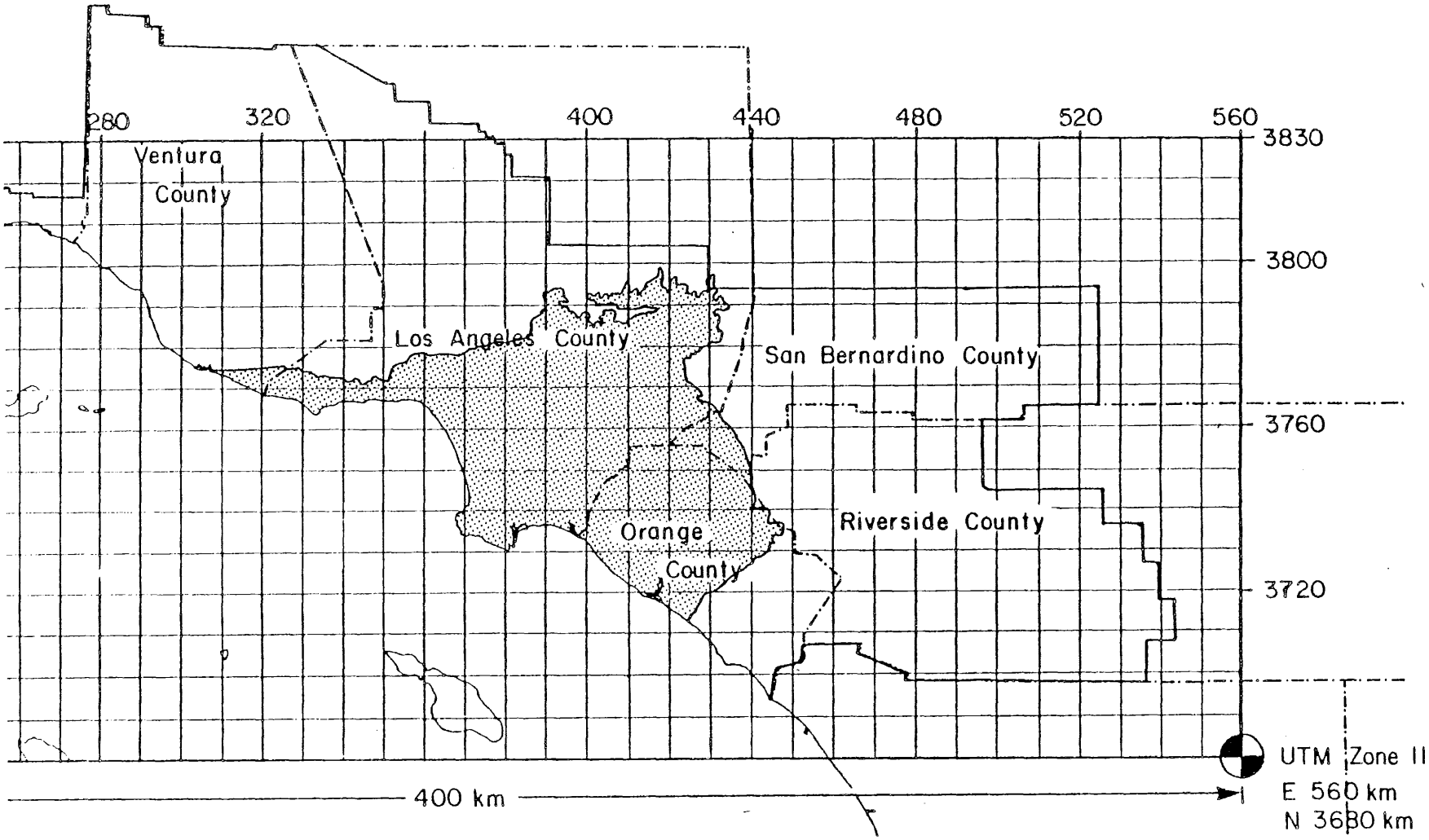


Figure II-1. Study area plotted on UTM grid map.

polygons each encompassing a relatively homogeneous vegetative composition (described in Section IV); (3) on-site studies of randomly chosen subplots of each of the 20 sample cells, from which leaf mass and species composition were determined and extrapolated to the cell and the entire polygon (described in Section V). These coordinated studies, constituting a stratified, random sampling approach were used to estimate the hydrocarbon emission inventory for urban ornamental vegetation in the study area.

The analysis of the naturally vegetated component of the CSCAB was accomplished by an approach similar to that used for the urban vegetation. In this case, however, available field data and maps were used rather than aerial photographs. These data consist of field plot data and Vegetation Type maps published by the U. S. Forest Service (1930-1940). This areal Type data, when combined with percent species cover, provided an areal cover for each naturally occurring species within the study area. This information was combined with field data for leaf mass of those species.

The three remaining elements of this program were: (1) statistical calculations of the total emission fluxes of isoprene and monoterpenes (described in Section VI), taking into account the dependence of such emissions on light intensity and temperature; (2) measurements of ambient concentrations of isoprene and the monoterpenes at several locations in the study area (described in Section VII); and (3) calculations, using simple models, of the impact of the estimated emissions of reactive organic gases from vegetation on photochemical O_3 formation in the study area (described in Section VIII). The interrelationship of the six elements of this program are shown in Figure II-2.

E. Limitations and Uncertainties in the Present Study

The study area chosen in this program is more than twice as large as the entire area covered by the cities of Baltimore, Chicago, Cincinnati, Detroit, Philadelphia, Pittsburg and St. Louis combined. Given the millions of individual sources of isoprene, monoterpenes and other organics (e.g., individual plants ranging from blades of grass to large trees) distributed over this 4500 km^2 area, many compromises were necessary in order to carry out this program. The difficulties and limitations encountered in attempting to experimentally establish an emission inventory for

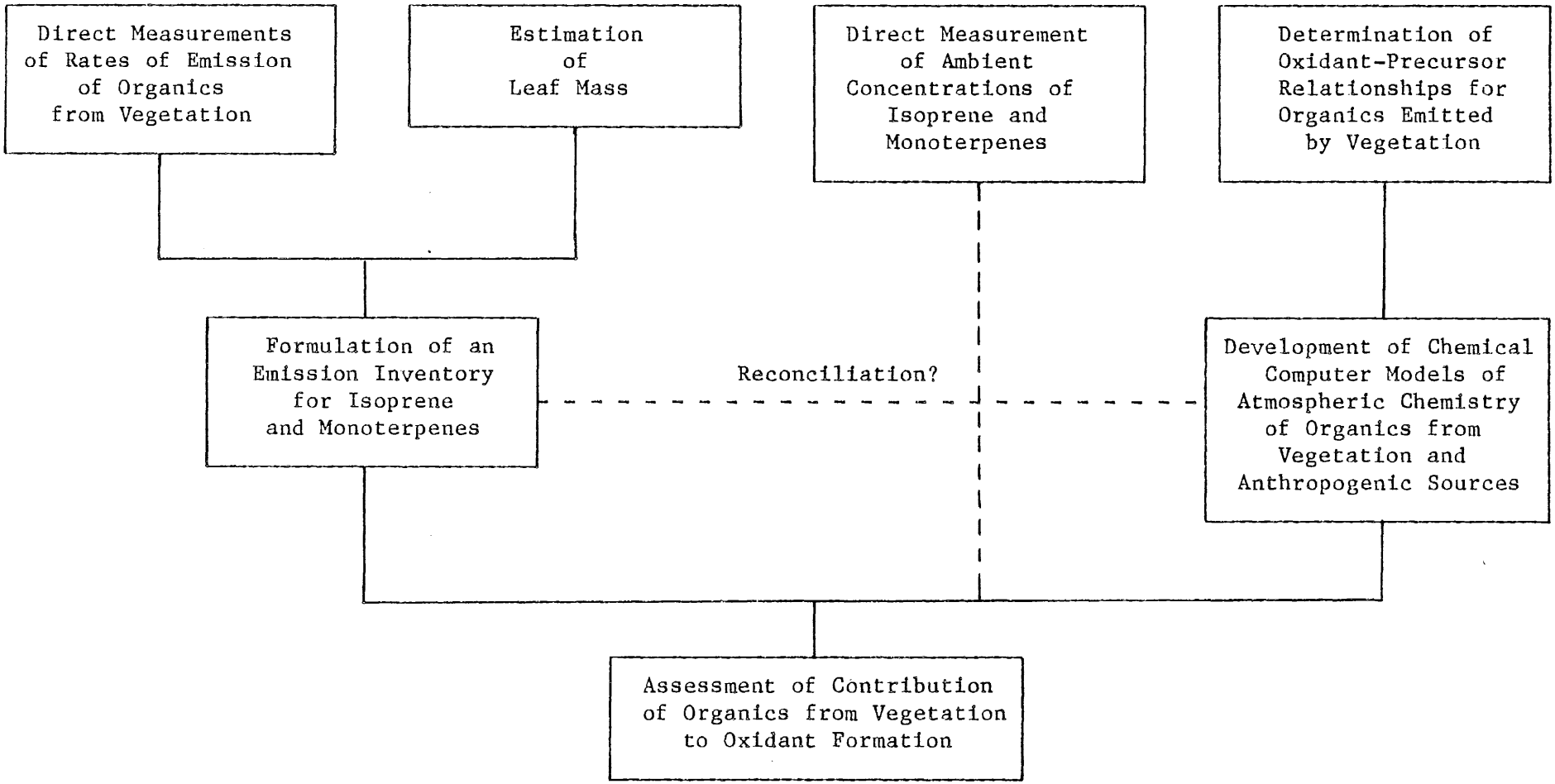


Figure II-2. Protocol for assessing role of organics from vegetation in photochemical air pollution.

vegetative hydrocarbons, and assess the influence of these emissions on air quality, in many respects mirrored those which have been encountered in analogous efforts for anthropogenic hydrocarbons. Necessarily then, the results of this study are open to the same criticisms (many of which we ourselves have articulated) concerning accuracy, precision and comprehensiveness which have been aimed at emission inventories for anthropogenic sources of reactive organics.

The experimental and calculational problems associated with this program have, of course, been encountered in previous studies of this kind. Measurements of hydrocarbon emission rates for each species are influenced by many variables such as temperature, sunlight, humidity, condition of individual plant and perturbations caused by the enclosure chamber, as well as the difficulties of making chromatographic measurements at or near the achievable detection limit. Thus the standard deviations of such measurements have been large, and factors of up to ten between the results of different workers have been observed for the emission rates assigned to the same species (see Section III). The measurement of extent and composition of plants in an air basin of this size is an even more complex task and is subject to even greater error. Vegetation is extremely varied in composition and spread over such a large area that total direct measurement is not feasible. Given these factors, a statistically valid method of estimation was used in this study, based on random sampling which involved direct ground measurement of vegetation in 0.02% of the study area and measurement by aerial mapping of vegetation in 0.4% of the total study area. Field measurements of green leaf mass could be based only on visual estimations. An understanding of the difficulties involved in a study of this kind can be obtained from the two-volume compendium entitled "Atmospheric Biogenic Hydrocarbons" (Bufalini and Arnts 1981), particularly from the unedited discussions published at the end of each paper in which many candid assessments of these problems were given by the investigators involved.

After consideration of the inherent limitations, as well as time and funding constraints, we adopted three principles for this investigation. First, that we would attempt an experimental program (rather than a "paper" study) in which we would exploit the expertise of chemists, earth scientists and plant scientists available at UCR. Second, that we would

try to insure that the primary data collected would be the best we could obtain, so that if a more extended or comprehensive approach were possible in later years the present data could be extended rather than have to be re-obtained. Third, that we would adopt a stratified, random sampling methodology and subject the resulting data to a variety of statistical analyses which would permit: (a) assessing the bounds of uncertainties associated with a "recommended" total emissions estimate, and (b) determination of a "worst case" upper limit to the emissions from vegetation, and their impact on air quality.

Although the uncertainties and limitations encountered in each phase of this study are treated separately in the appropriate sections of this report, a list of those which particularly require consideration has been compiled (Table II-3). They are divided into two categories: those which may (but do not necessarily) have a major impact on the final output of this study, and those which are believed to have minor impact on the final output (but for some of which a major effect cannot be ruled out). For discussions of these factors and their importance, see Sections III-VIII (particularly Section VI).

Table II-3. Uncertainties and Limitations Identified in This Study

A. Potentially Major Limitations or Uncertainties

1. Assumption that vegetation is homogeneous within the "polygons" defined from NASA U-2 CIR imagery.

2. Limited area covered by high resolution CIR aerial imagery used to assess vegetation cover in urban portion of the study area.

3. Difficulties in measurements of hydrocarbon emission rates for ground cover.

4. Potential uncertainty in published algorithms used for temperature corrections for emission rates.

5. Only the hydrocarbons readily observed were measured; not all possible compounds emitted.

6. Use of oversimplified models relating precursor emissions to photochemical O_3 production.

7. Inability to measure rates of emission of hydrocarbons from the same species in spring, summer and fall seasons.

B. Limitations or Uncertainties Believed to be Minor

1. Difficulties in identifying and measuring emitted compounds at the ppbC level.

2. Limited areas sampled by field botanists to determine species composition and distribution.

3. Ability to determine emission rates for only ~25% of the ~200 species observed in the urban region, and then only for a given set of plant conditions. Need, in some cases, to apply emission rate for a specific species to an entire genus.

4. Only ~25% of leaf mass constants could be determined experimentally. In some cases, forced to apply leaf mass constants for a specific species to an entire genus.

5. Determination of emission rates at only one location (i.e., for a given set of environmental conditions).

6. Necessity to assume certain diurnal variations in emission profiles based on published data.

7. Inability to experimentally determine the present species composition and area cover in the naturally vegetated portion of the study area.

8. Hydrocarbon emissions from stems, leaf litter, soils, and aquatic vegetation not included.

III. EXPERIMENTAL DETERMINATION OF EMISSION RATES OF HYDROCARBONS FROM DOMINANT NATURAL AND ORNAMENTAL SPECIES IN THE CALIFORNIA SOUTH COAST AIR BASIN

A. Introduction and Background

1. Previous Estimates or Measurements of Emission Rates

Microscale Estimates. A survey of the results of eight studies of hydrocarbon emissions from various plant species carried out prior to the beginning of this program in 1979 is summarized in Table III-1. These studies were representative of the various methods of sampling, and the units chosen for reporting the results during that period. The sampling environments represented in these studies ranged from temperature and light controlled chambers (Rasmussen 1972) to calculations of the flux from a canopy of loblolly pine (Pinus taeda) in uncontrolled ambient conditions (Arnts et al. 1978). The units of measurement are unique to each investigation making it very difficult to compare the studies. Both concentrations and rates are reported but rarely in the same study; the former may be based on the weight of foliage and surface area of foliage, but in some cases only volume/volume units are presented.

The heterogeneity of the present information in this sample of the literature suggested the need for standardization in reporting as well as in methods of measurement. For example, basing emission rates on plant tissue weight was felt to be highly desirable. Furthermore, it seemed clear that measurements in static air chambers might cause serious deviations in the plant environment from natural conditions and hence that such an approach should be avoided, except for special purposes. Finally, it was recognized that the ambient temperature, relative humidity and light intensity should be measured continuously during sampling.

Macroscale Estimates. Using biogenic hydrocarbon emission rates for various plant species and biomass estimates, Tingey and Burns (1980) compiled both global and regional estimates of total natural hydrocarbon emissions, as shown in Table III-2. The global estimates varied over approximately a factor of five. Such variations are perhaps not surprising given the variability in emission rates data and the large extrapolations required to obtain total emission rates. The global emission rates obtained are substantially greater than those for anthropogenic hydrocarbons.

Table III-1. Survey of Terpenoid Emission Estimates for Various Plant Species

Plant Community	Species	Position	Temperature	Compounds Measured	Sampling Method	Concentration or Rate	Reference
Coniferous Forest	Loblolly pine (*Pinus taeda*)	Above canopy	29.7°C	α-Pinene	Ambient (calculated flux)	52.8 μg m^{-2} min^{-1}	Arnts et al. 1978
Coastal Chaparral	Calif. Black Sage (*Salvia mellifera*)	---	9-16°C	Camphor	Branch	13.3 μg m^{-2} d^{-1} 3.1 kg km^{-2} d^{-1}	Tyson et al. 1974
Interior Sage	Sagebrush (*Artemisia tridentata*)	Above canopy	unspecified	unspecified	Ambient	50 kg km^{-2} d^{-1}	Went 1960
Coniferous Forest	Balsam fir (*Abies balsamea*) and red spruce (*Picea rubens* birch (*Betula popyrifera*) Maple (*Acer saccharum*)	Below canopy down wind from forest	27°C	"Lighter species"	Ambient	23.7 to 81.8 μg m^{-3}	Whitby and Coffey 1977
				"Terpene species"	Ambient	3.5 to 47.8 μg m^{-3}	
Citrus	Orange	Within canopy	unspecified	Isoprene	Ambient	<0.1 to 4.5 ppbC	Lonneman et al. 1978
	Mango (*Mangifera indica*)	Above canopy	unspecified	Isoprene	Ambient	0.5 to 24 ppb in 5 mℓ of air	Rasmussen 1970

Table III-1 (continued) - 2

Plant Community	Species	Position	Temperature	Compounds Measured	Sampling Method	Concentration or Rate	Reference
Ornamental Planting	Juniperus sp. (shrubs)	Inside canopy	unspecified	"Volatile aromatics"	Branch chamber	5 to 18 ppb/?	Rasmussen and Went 1965
	"	Above canopy		"	Ambient	5 to 8 ppb/?	
	"	Several meters from shrubs		"	"	3 to 6 ppb/?	
	White pine (P. monticola)	Laboratory	17-32°C	α-Pinene	Leaf chamber	0.4 to 2.0 ppb min^{-1} g^{-1}	Rasmussen 1972
	Ponderosa pine (P. ponderosa)		"	"	"	0.3 to 1.2 ppb min^{-1} g^{-1}	"
	Loblolly pine (P. taeda)	"	"	"	"	0.5 to 3.5 ppb min^{-1} g^{-1}	"
	White fire (Abies concolor)		"	"	"	0.2 to 1.5 ppb min^{-1} g^{-1}	"
	Oak (Querous) sp.	"	28°C[a]	Isoprene	Leaf chamber	1.7 ppb min^{-1} in^{-2}	"
	Sweet Gum (Liquidambar styraciflua)	"	"	"	"	0.7 ppb min^{-1} in^{-2}	"
	(Eucalyptus) sp.	"	"	"	"	0.83 ppb min^{-1} in^{-2}	"
	Cottonwood (Populus) sp.	"	"	"	"	1.2 ppb min^{-1} in^{-2}	"

[a]Light intensity = 700 foot candles.
? Basis for reported value not stated.

Table III-2. Estimated Emissions for Biogenic Hydrocarbons (Tingey and Burns 1980)

Location	Emissions (Metric Tons)	Emission Factors (kg km^{-2} day^{-1})	References
World	1.75×10^{8} yr^{-1}		Went 1960
World	4.38×10^{8} yr^{-1}		Rasmussen and Went 1965
World	8.30×10^{8} yr^{-1}		Zimmerman 1979b
United States	$0.23\text{-}4.64 \times 10^{7}$ yr^{-1}		Rasmussen 1972
United States	6.5×10^{7} yr^{-1}		Zimmerman 1979b
Florida (81 x 60 km)	157 day^{-1}	32.2	Zimmerman 1979a
Texas (38 x 31 km)	32.4 day^{-1}	27.5	Zimmerman 1979c
Pennsylvania	3,580 day^{-1}	30.7	Flyckt et al. 1980

It is important to recognize, however, that due to perturbation of the plant, the emission rates obtained for individual species in enclosed atmospheres may be higher than the actual emission rates occurring in ambient air. If this is the case, then the total emissions calculated on global and regional bases may be significantly overestimated. Possible evidence that this is the case is the incompatibility between the high emission rates and very low ambient concentrations of natural hydrocarbons such as isoprene and the monoterpenes reported to date (Dimitriades 1981).

2. Factors Influencing Hydrocarbon Emissions from Vegetation

Time of Year. Several researchers have recorded large seasonal variations in rates of emission of hydrocarbons from vegetation. Rasmussen and Went (1965) measured volatile hydrocarbons at a sample location in the summer to be 10-20 ppb compared with 2 ppb for the winter period. Holzer et al. (1977) also observed a large difference in emissions depending on seasons. Rasmussen and Went (1965) suggested that emissions are low in the spring from young foliage. They also observed two peaks in hydrocarbon emission in the vicinity of a mixed hardwood forest in autumn; these peaks were associated with leaf drop from two species of trees. It is possible that the fallen leaves were the major source of the observed peaks. Tyson et al. (1974) also suggested that the

period of leaf fall from the coastal black sage (Salvia mellifera) may be a time of increased camphor emission as a result of high summer temperatures which are coincident.

Flyckt (1979) has reported sinusoidal behavior for monoterpene emissions from ponderosa pine with a maximum in May/June and a minimum in November. Isoprene emissions from red oak were observed to be maximum during the fall decreasing to zero in the winter.

Time of Day (Influences of Light and Temperature). There is an important difference between the diurnal concentration profiles of isoprene and the monoterpenes. Isoprene emission appears to be light dependent (Rasmussen and Jones 1973, Sanadze and Kalandze 1966). Chatfield and co-workers (Chatfield et al. 1979) measured the highest concentrations at 1800 hr and the lowest at 0600 hr. The influence of varying light intensity on isoprene emission rate at various leaf temperatures is shown in Figure III-1 (Tingey et al. 1978). In contrast, monoterpenes from slash pine and black sage are emitted at similar rates in the light and dark (Tingey et al. 1980, Dement et al. 1975, Rasmussen 1972). Thus, monoterpene concentrations are estimated to be highest during the night and lowest during the day (Figure III-2) when the rates of dilution, photooxidation and ozonolysis are highest (Tingey et al. 1978, 1980).

There is general agreement among several investigators observing many plant species that isoprene and terpenoid emissions increase with increasing temperature (Figure III-3). These reports include Rasmussen (1972) with several conifer species; Dement et al. (1975) and Tyson et al. (1974) with Salvia mellifera; Kamiyama et al. (1978) with cryptomeria; and Arnts et al. (1978) with loblolly pine. Above 43°C isoprene emissions drop dramatically (Tingey et al. 1979, 1980). Generally, isoprene emissions increase sigmoidally with temperature while monoterpene emissions increase exponentially.

Tingey and co-workers (Tingey et al. 1978, 1980) estimated that for average summer days in Tampa, Florida, the net influence of light and temperature would result in more than 80% of the isoprene emissions occurring after mid-morning and ceasing at night (Figure III-4), while approximately 55% of the total daily monoterpene emissions were expected to occur during daylight hours between 0600 and 1800 with an additional 25% emitted between sunset (1800) and midnight.

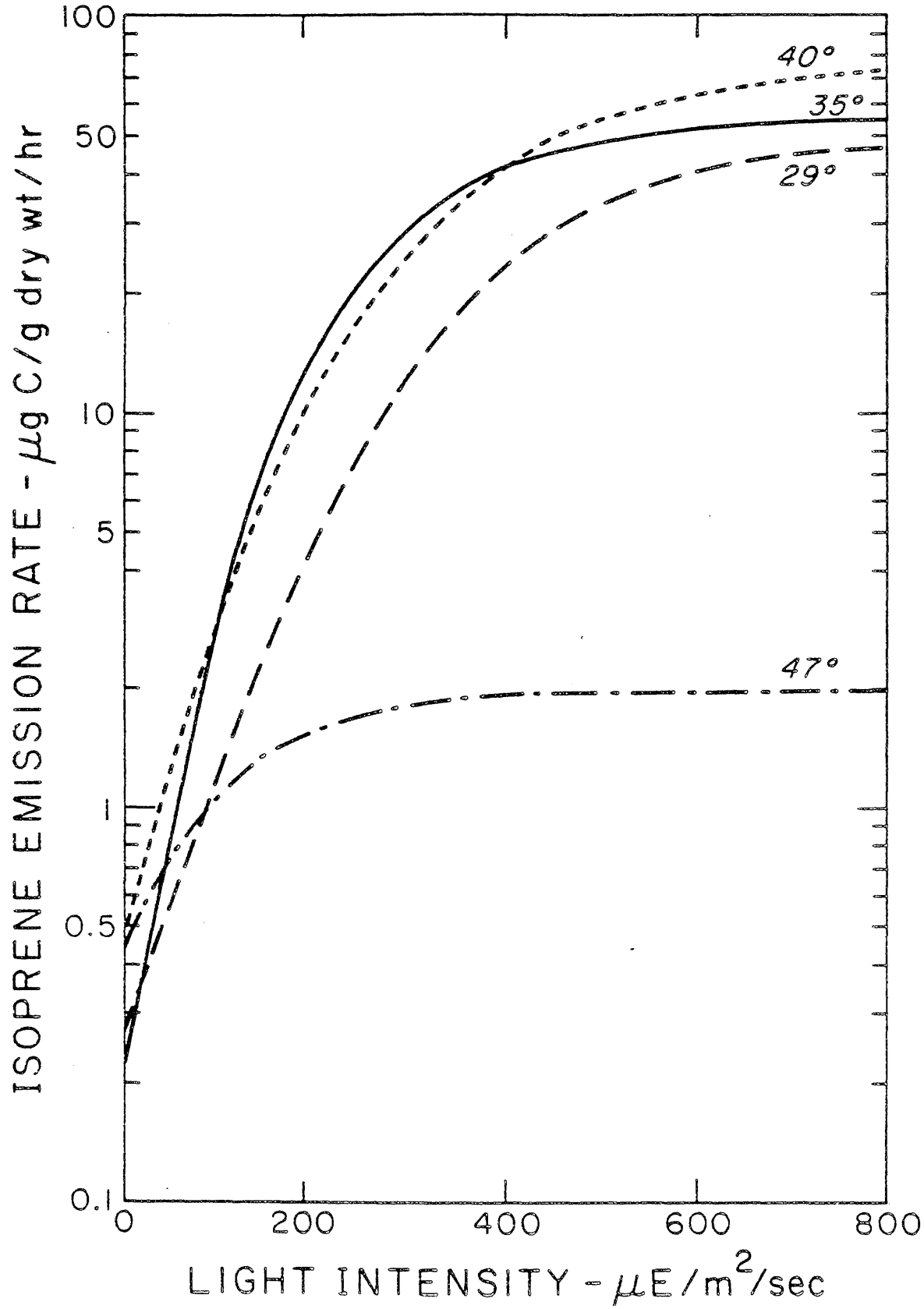


Figure III-1. The influence of varying light intensity on isoprene emission rate at various leaf temperatures (Tingey et al. 1978).

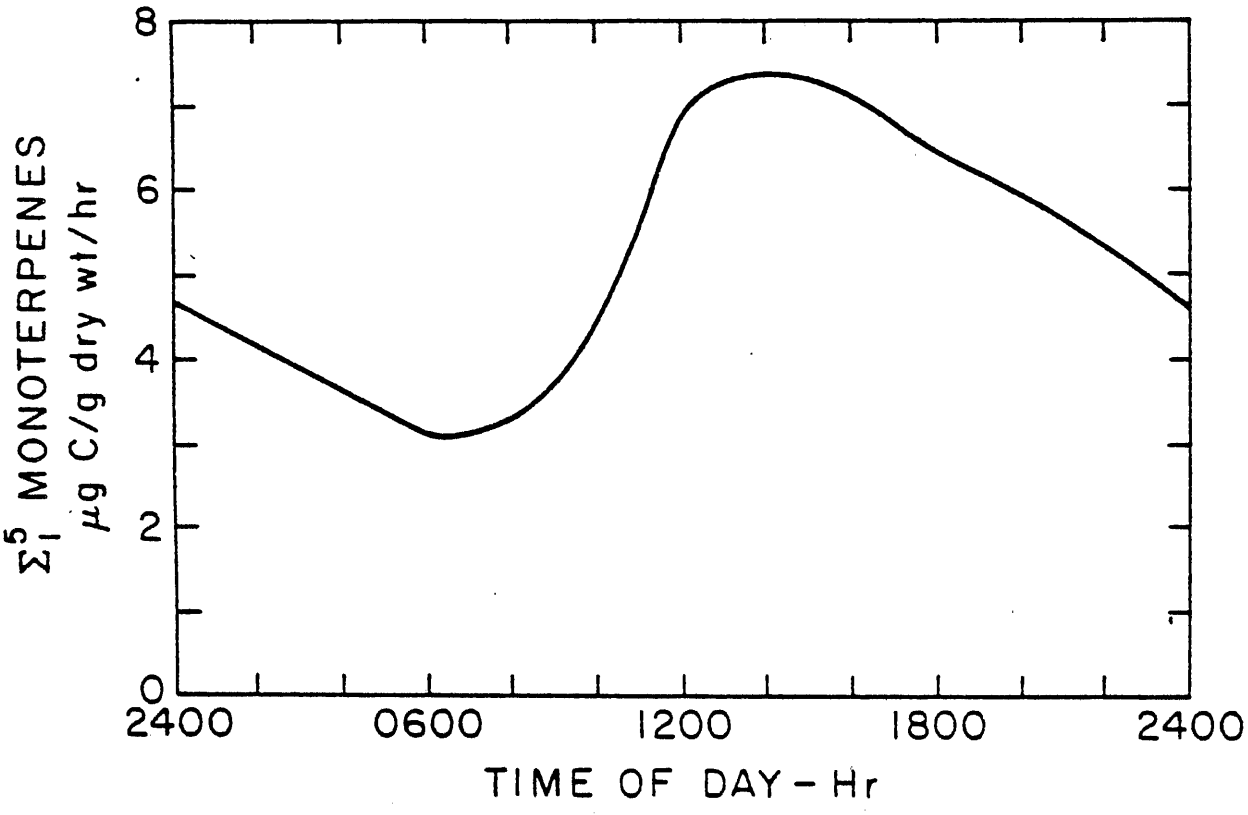


Figure III-2. Estimated diurnal emissions of five monoterpenes for slash pine in Tampa, Florida, for an average of summer days (Tingey et al. 1978)

Relative Humidity. Dement et al. (1975) observed increased camphor emissions as relative humidity increased. It was also suggested that during cool, foggy days the oil accumulated on the leaf surface and then volatilized rapidly when warm, sunny weather resumed.

Stomatal Control. Jones and Rasmussen (1975), working with leaf discs, and Dement et al. (1975), following observations of Salvia mellifera were unable to show that stomatal resistance was an important factor controlling terpenoid emission rate. Furthermore, Arnts et al. (1978) suggested that emissions from loblolly pine were greater during periods of water stress (when stomates are expected to be closed).

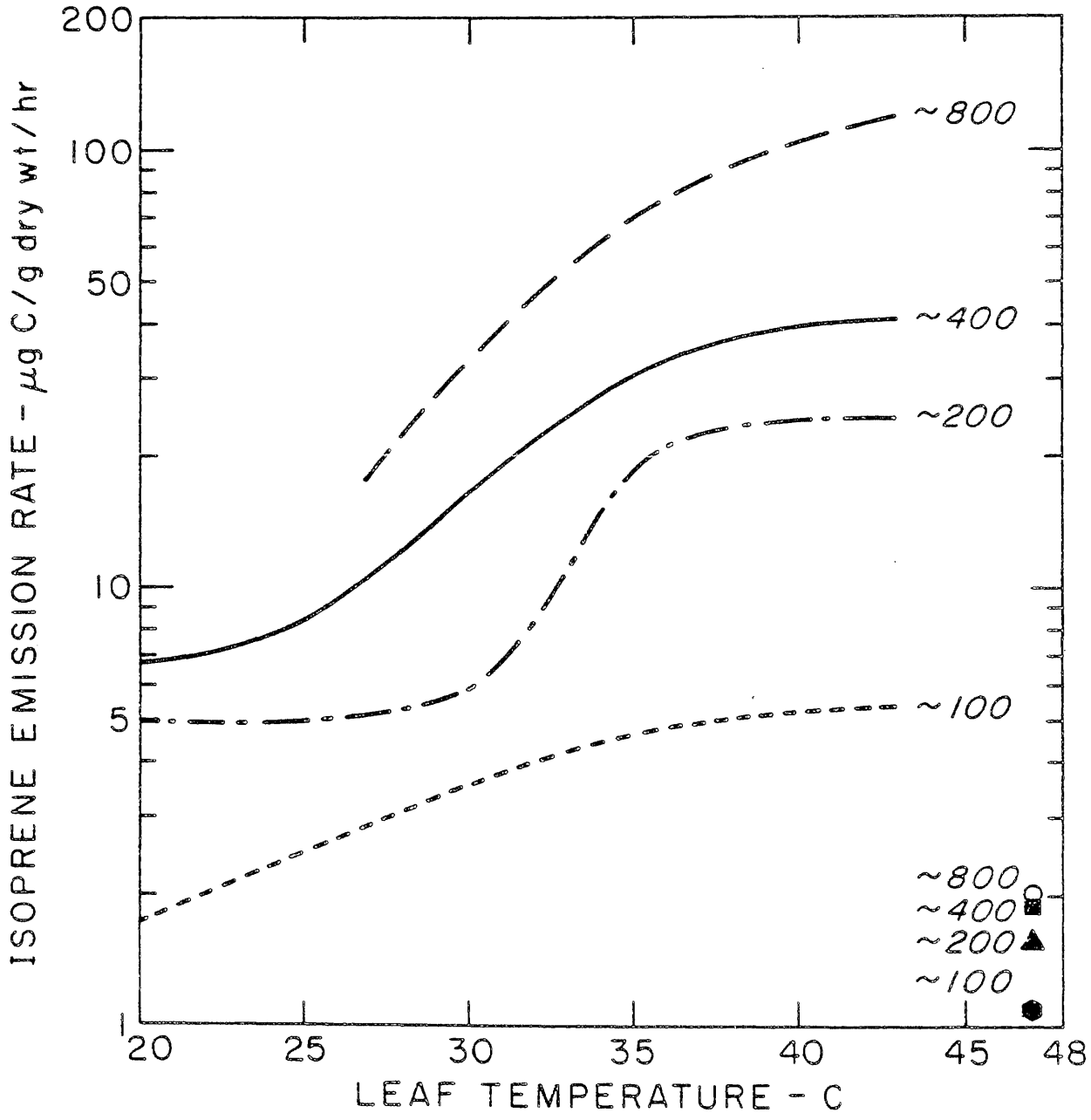


Figure III-3. The influence of varying temperature on isoprene emission rate at various light levels (Tingey et al. 1978).

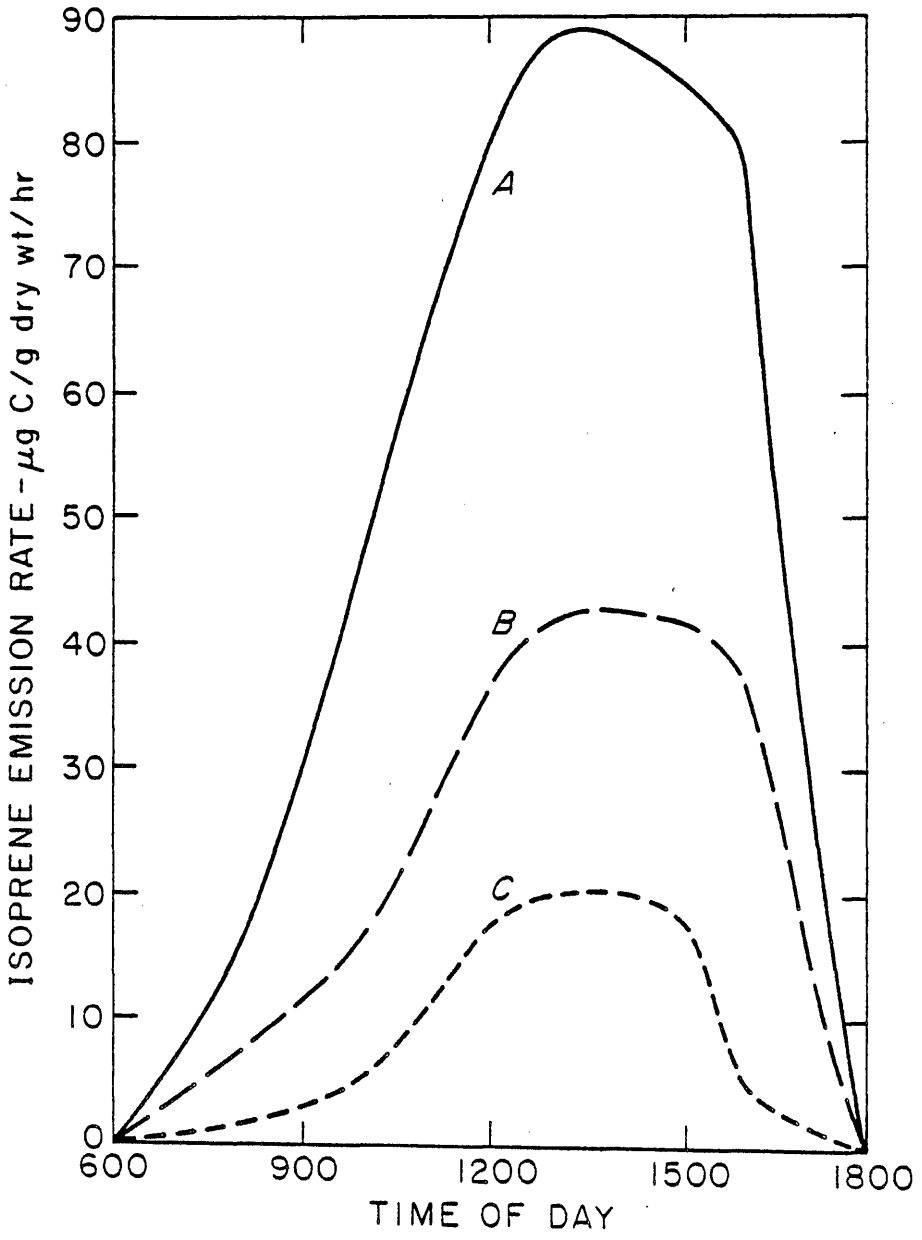


Figure III-4. Estimated isoprene emission rates for oak leaves in Tampa, Florida, for an average of summer days (Tingey et al. 1978). A - sunlit leaves; B - shaded leaves (one-half ambient sunlight); C - shaded leaves (one-fourth ambient sunlight).

3. Previous Experimental Approaches

Previous measurements for ambient concentrations of isoprene and monoterpenes in urban areas have found levels very near or below the detection limit of present analytical methods. This may be due to the high photochemical reactivity or low emission rates of these species, or both. The very low ambient levels of these compounds and their high chemical reactivity make it impossible to obtain reliable estimates of their emission strengths for an entire airshed from ambient air data. Rather, such estimates must be based on individual experimentally determined plant emission rates combined with estimations of the distribution and biomass of individual plant species.

As noted above, several different experimental approaches have been used in the past to estimate the emission rates of organics from vegetation. Semi-quantitative estimates were made by Rasmussen (1970, 1972) and by Sanadze and Kalandze (1966) using static gas exchange chambers containing either detached leaves, twigs or whole plants. Zimmerman (1979a,b,c) enclosed tree branches or small plants in a large Teflon bag which was sealed, evacuated and refilled with hydrocarbon-free air. After a period of time the head space of this static system was analyzed by gas chromatography to determine the gas phase concentrations of organics.

Dynamic mass-balance, gas-exchange chambers which attempt to simulate the gaseous environment of plants in the field have been employed (Kamiyama et al. 1978, Tingey et al. 1978, 1979, Tyson et al. 1974) in emission rate measurements as well as in determining the influence of environmental factors on these rates (see below).

Tingey and Burns (1980) have placed the more recent emission rate data of Zimmerman (1979a), Tingey et al. (1980), Arnts et al. (1978), Kamiyama et al. (1978) and Flyckt et al. (1980) on a common basis and the emission rates determined by them for a variety of species are shown in Table III-3. Normalized to dry leaf weight, these rates cover a range of more than a factor of 10.

It should be noted from Table III-3 that for the one common species studied by two investigators (live oak), the isoprene emission rates reported differ by more than a factor of four. It can also be concluded from Tables III-1 and III-3 that few if any measurements have been made

Table III-3. Biogenic Hydrocarbon Emission Rates Estimated at 30°C (Tingey and Burns 1980)

Species	μg (g dry weight[a])$^{-1}$ hr^{-1} TNMHC[b]	Iso-prene	Mono-terpenes	References
Slash Pine	4.1		2.6	Zimmerman 1979a
Longleaf Pine	7.3		5.6	Zimmerman 1979a
Sand Pine	13.6		11.0	Zimmerman 1979a
Cypress	14.2		8.1	Zimmerman 1979a
Slash Pine			6.4	Tingey et al. 1980
Loblolly Pine			3.7	Arnts et al. 1978
Cryptomeria			3.0	Kamiyama et al. 1978
Laurel Oak	12.6	10.0		Zimmerman 1979a
Turkey Oak	26.5	23.4		Zimmerman 1979a
Bluejack Oak	56.4	43.9		Zimmerman 1979a
Live Oak	10.8	9.1		Zimmerman 1979a
Live Oak		41.2		Tingey et al. 1980
Willow	22.1	12.4		Zimmerman 1979a
Saw Palmetto	11.5	8.6		Zimmerman 1979a
Mean 7 Hardwood Trees - Isoprene	20.0	15.7		Flyckt et al. 1980
Wax Myrtle	7.5			Zimmerman 1979a
Persimmon	2.9			Zimmerman 1979a
Orange	9.4			Zimmerman 1979a
Grapefruit	4.3			Zimmerman 1979a
Red Maple	6.5			Zimmerman 1979a
Hickory	3.2			Zimmerman 1979a
Mean 10 Hardwood Trees - Non-Isoprene	7.3			Flyckt et al. 1980

[a]Leaves only.
[b]Total non-methane hydrocarbons.

under the mediterranean climate regime of Southern California, or for plant species which are dominant or abundant in that region.

4. The Present Approach

Teflon Bags. Our first efforts to determine emission rates of natural hydrocarbons from selected plant species involved the use of simple Teflon bag enclosures. These were placed around branches of wild-growing shrubs for short time intervals. Preliminary sampling of several

native shrub species permitted testing of the analytical techniques which had been developed as well as the determination of the kinds of compounds emitted by each species. Members of the native soft chaparral community present on the UCR campus or on the nearby Box Springs mountains were selected because of their relative abundance in typical shrub stands. These species included California encelia (Encelia farinosa), California sage brush (Artemesia californica), chamise (Adenostoma fasciculatum) and California buckwheat (Eriogonum fasciculatum).

Portions of branches of the subject shrub were enclosed in a Teflon bag equipped with a side port to allow for insertion of a thermister probe and a Teflon tube connected to a 1-liter glass and Teflon syringe. The bag remained over the branch for periods of time ranging from 3-10 minutes. A seal was maintained by holding the gathered film of the open end around the branch by hand.

The changes of temperature in the sunlit bag and the first evidence of water condensation on the interior of the bag were observed. The results obtained suggested that in order to minimize modifications of the leaf environment due to increases in temperature and relative humidity, sampling should be conducted either early or late in the day and with enclosure times not exceeding five minutes.

The procedures described above for sampling natural hydrocarbons produced some high concentrations of monoterpenes. However, this procedure was found to have several drawbacks with respect to obtaining reliable emission rates. Factors which can affect emissions using this technique are mechanical injury, heat stress and contact with the Teflon film by the enclosed branch. Additionally, physical factors such as the volume of the bag, time period or surface area to be charged with the emissions were perhaps not as well defined as is desirable.

Rigid-Frame, Flow-Through Chambers and Sampling Protocols. In order to address some of the problems encountered with use of static-mode, Teflon film enclosures, several rigid-frame, flow-through chambers were designed and constructed, and a sampling protocol was devised to minimize deviations of the plant environment from ambient conditions. The principal elements of this protocol were: use of Teflon enclosures which were transparent to sunlight and relatively inert with respect to organics; use of a dynamic flow system to moderate temperature increases

and prevent accumulation of vegetative organics; maintenance of ambient concentrations of carbon dioxide and water. Details concerning the design, construction and use of rigid, flow-through chambers are given in the following section.

B. Experimental Methods

1. Plant Enclosure and Sampling Protocol

Chamber Design and Properties. The enclosure design used for emission rate determinations for either the whole plant or branches of free-standing shrubs and trees is shown in Figure III-5. A rigid outer frame of 0.5 in PVC pipe supported a chamber which was constructed of 2 mil thick FEP Teflon by heat-sealing the seams and then taping them with Mylar tape.

To ensure good mixing the chamber was equipped with a Teflon coated stirring fan driven by a 1300 RPM, 1/15 hp motor (Dayton Model 3M500) and,

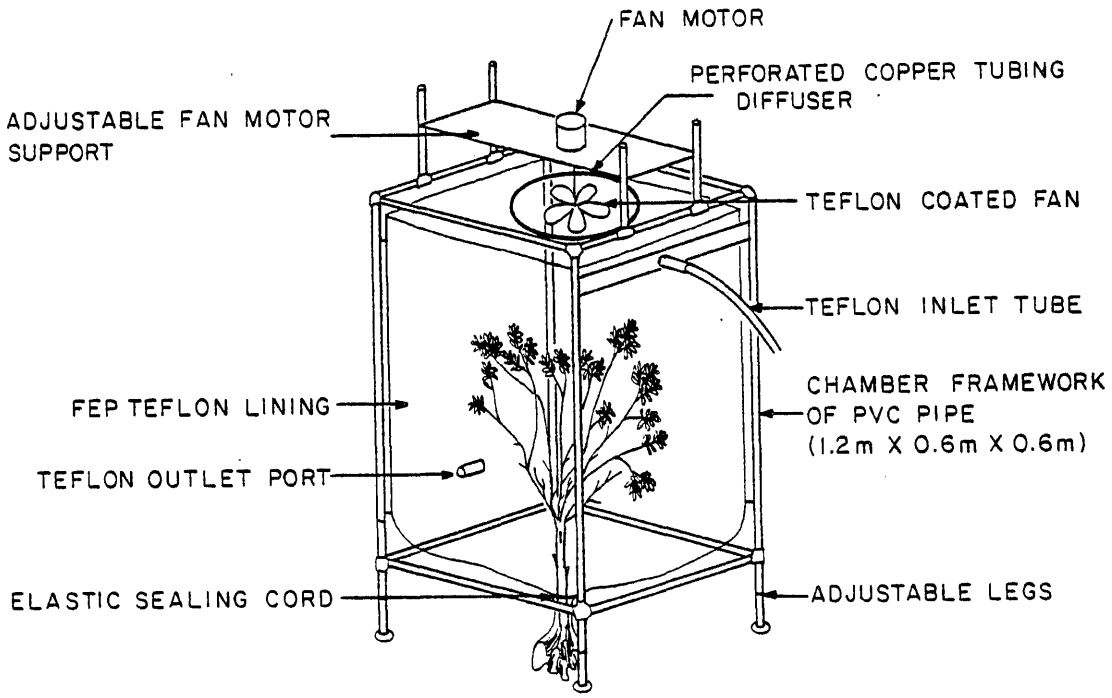


Figure III-5. Rigid flow-through enclosure for measuring rates of emission of hydrocarbons from vegetation.

in close proximity, a perforated copper tube (0.5 in OD) bent into a loop, through which air could be introduced. A Teflon outlet port located ~1/3 of the way up from the bottom of the chamber was used to exhaust the air flow, withdraw gas samples and to insert both a thermocouple and dew point sampling line.

Several sizes of chambers were constructed to facilitate the enclosure of various types of plant specimens. The dimensions of the most commonly employed chamber were 0.43 cm x 0.43 cm x 0.76 cm with a chamber volume of ~140 ℓ. With the proper supports or while held manually, the chambers could be oriented in any direction as dictated by the plant sample.

The time to reach a steady-state concentration of organics for a given flow rate of purified air through the chamber was measured by releasing a low, constant flow of ethane in a bottom corner of the chamber. This procedure should have represented a worst case for uniform mixing, since it involved a point source at the most remote position from the air inlet. Samples were taken at the exhaust port at approximately one minute intervals and analyzed by gas chromatography. With the fan off, the ethane concentration slowly increased but after five exchange volumes steady state was not achieved and the observed concentration was well below that calculated from the measured flow rates. However, as shown in Figure III-6, with the fan on the measured ethane concentration approached a steady-state value (and the expected concentration). This required 8-10 minutes or about three exchange volumes. Similar results were obtained with the other sized chambers.

Ground cover vegetation chambers as described by Zimmerman (1979a) were tried but abandoned for several reasons. The most significant problem was with placing a ring over the ground cover. This almost always resulted in some damage to the enclosed plants with the attendant possibility that anomalously high emission rates would be obtained. Mixing was also a problem when using a flexible chamber since emissions would be expected to accumulate in the lower areas closest to the plants. The final reason was that hammering the outer ring in place would leave objectionable markings in the public and private areas sampled in this program.

For these reasons measurements were made on ground cover species grown in plastic flats either in commercial nurseries or at SAPRC. By placing the flats on a pedestal, the enclosure chambers could be tightly sealed around the base of the pedestal without damaging the plant. Use of the same enclosure method for ground cover as employed for shrubs and trees was also expected to produce comparable results since the same flow systems were used in each case. Temperature increases were also moderated using the dynamic flow technique.

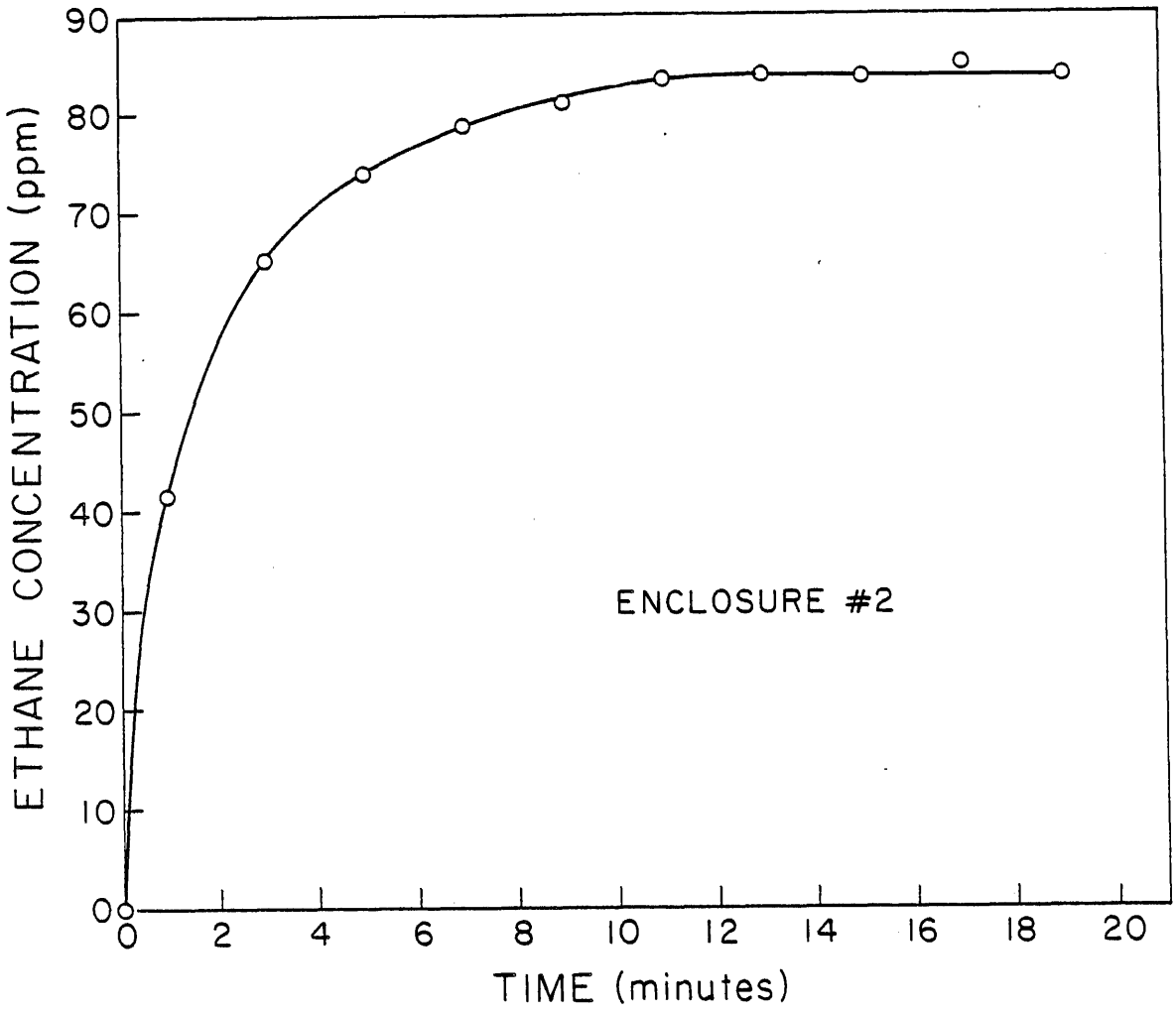


Figure III-6. Demonstration of mixing time in flow-through chamber using ethane as a tracer.

Pure Air Sources. Several sources of pure air were evaluated and employed. Scott-Marrin ultra-zero air (tank size 100) with 360 ppm added CO_2 (approximating ambient conentrations) was initially used prior to completion and testing of the humidification and carbon dioxide metering systems described below. Although this air was quite satisfactory with respect to its purity, it was found to be more cost-effective to purchase ultra-zero air and add CO_2 separately (see below).

A second source was an Aadco pressure-swing, adsorption-type pure air generator (Model No. 737, 250 ℓ min^{-1}), originally purchased as a further cost-effective measure. Unfortunately, it was not delivered until the emission rate measurements program was well under way and the necessary compressor and resulting electrical power requirements made its use less practical than had been anticipated for the major sampling site chosen. Specifically, a minimum of 20 amps was necessary to power the system but only 15 amps were available at the Los Angeles Arboretum. The use of an electric generator was considered, but this would have added to the already heavy burden of equipment.

For the emission rate measurements made in the field, cylinders of Scott-Marrin ultra-zero air were employed. These provided an adequate supply of air for up to four enclosure experiments, weighed less than the Aadco unit and its accompanying compressor and holding tank, and eliminated the need for electrical power.

The Aadco air purifier, however, received substantial use in measuring hydrocarbon emission rates for ground cover vegetation at UCR. Its output air was generally of the same or higher purity than the commerical zero-air cylinders. An additional advantage of this air purifier was that CO_2 was not attenuated. Thus it was not necessary to add CO_2 in experiments employing the Aadco system. In practice it was found to be convenient and cost-effective to use cylinders of compressed air in conjunction with the Aadco system.

Humidifier. In order to provide purified matrix air whose properties were as nearly those of ambient as possible, it was necessary to add water and carbon dioxide equivalent to typical ambient concentrations. This was done by means of a combined humidifier and a carbon dioxide metering system as shown in Figure III-7. All plumbing in this system was constructed of glass or Teflon tubing with brass Swagelock fittings and

valves which had been washed with a methanol/dichloromethane mixture followed by thorough purging with nitrogen. Analysis of the ultra-zero air prior to and after humidification showed no contamination within the range of the normally observed pure air chromatograms. The entire humidifier system was packaged in a wooden box (with an aluminum control panel) to facilitate portability and resistance to physical shock when used in field operations.

The large rotometers (Gilmont F1500) used in this system were calibrated up to a flow of 120 ℓ min^{-1} with a dry test meter. The humidity was controlled by using needle valves (A and B in Figure III-7) in order to control the fraction of air passing through the humidifier. At a given total rotometer reading, the ratio of wet to total flow was varied from 0.0 to 1.0. The humidity of the output air was measured by means of wet and dry bulb thermometers placed in the airstream.

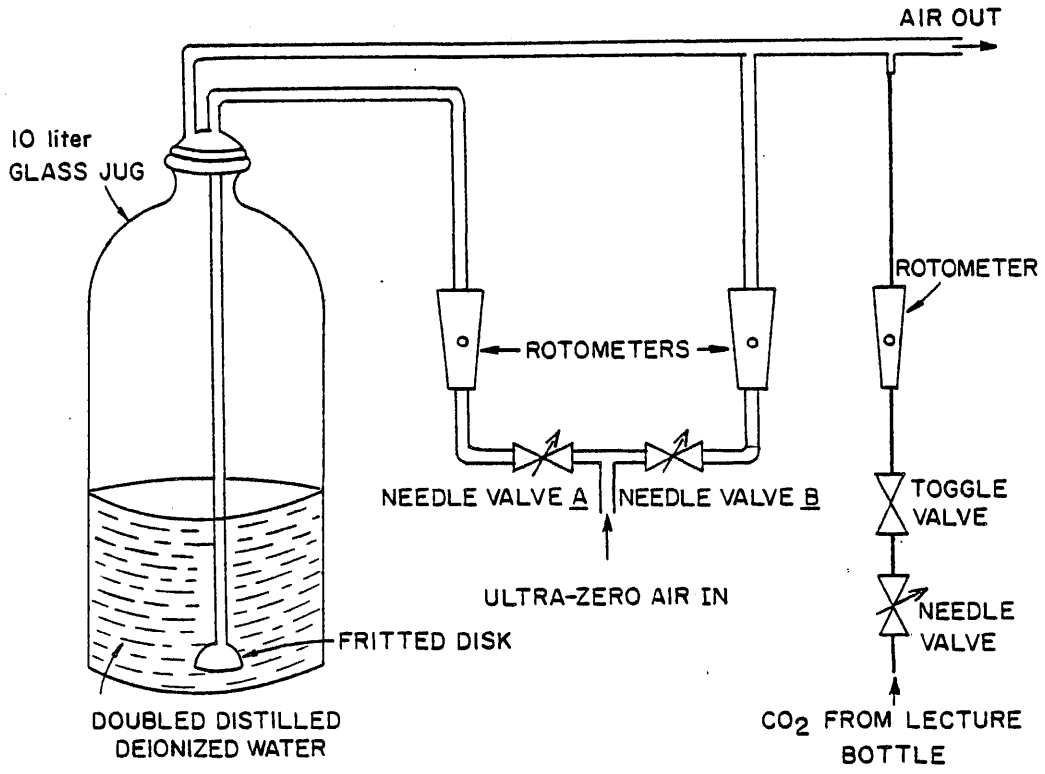


Figure III-7. Humidifier with CO_2 metering device.

Addition of CO_2. Pressure-regulated carbon dioxide obtained from a lecture bottle (Matheson bone dry) was added to the humidified ultra-zero air as shown in Figure III-7. The CO_2 concentration could be calculated from a knowledge of both flow rates. The total flow was routinely measured with a dry test meter (American Meter Company Model No. 806) before and after each run. Thus it was only necessary to calibrate the CO_2 rotometer in order to be able to adjust the flow to obtain a CO_2 concentration of 360 ppm characteristic of ambient air. A calibrated Byron (Model 401) hydrocarbon analyzer was used to validate the calculated CO_2 concentration. Results obtained with this instrument demonstrated that the metering system was sufficiently accurate to obtain CO_2 concentrations within 10% of the desired value. This was considered adequate in view of the variability of CO_2 concentrations in ambient air and the relatively slow response of plants to small changes in CO_2 concentrations (compared with the measurement periods).

Additional Measurements. Ambient temperatures were measured by both a thermistor-type digital thermometer (either an ECD Corporation T-Meter or a Markson Model 20) and the dry bulb of an automatic sling psychrometer (Cole-Parmer Model 3312-40). The ambient relative humidity was derived from either the wet bulb temperature obtained with the psychrometer or by measuring the dew point with an EG&G Model 880 thermoelectric meter.

Internal Teflon enclosure temperatures were monitored by placing the thermister in the exhaust outlet of the chamber. This point was most suitable because it provided shade from direct sunlight, an average temperature of the chamber air and a high rate of air mass transfer. The air velocity at the outlet port also made it possible to obtain wet bulb temperatures by placing the thermometer bulb within the port. In addition, the dew point was determined by inserting the inlet of the EG&G device into this port.

Samples for gas chromatographic analysis (see Section III.B.2) were obtained with 100 mℓ all-glass syringes attached to a short piece of stainless steel tubing which was placed through the outlet port into the interior of the chamber. The syringe was flushed with sample twice before the final filling. The filled syringe was brought to the gas chromatograph in approximately one to ten minutes depending upon the distance

between the vegetation being studied and the mobile laboratory (see below).

General Procedures. One specific chamber size (43 cm x 43 cm x 76 cm) was used for most of the emission rate studies. In order to enclose a vegetative sample, a single branch, or several small branches, would be chosen so that they would fit into the chamber without contacting the walls. Great care was taken to minimize any contact while placing the chamber over the plant and during the purge period. For some species it was difficult to make the seal at the base since there were no locations on the branch devoid of leaves. In these cases several leaves were removed and an attempt was made to make the seal such that the injured part of the branch was not within the chamber. Also, some plant types were so flexible in nature that the fan could not be used even at the lowest speed without buffeting the leaves against the chamber walls. In these cases short periods of stirring were used.

The chamber of these dimensions was quite flexible with respect to orientation. It could be used sideways, upside down and at various angles in between. It was necessary to fabricate new Teflon enclosures for this PVC frame only twice: once due to wear and a second time because of excessive hydrocarbon contamination.

The components of a typical sampling system are shown in Figure III-8. In this case an inverter with a 12 V DC battery was used to supply electrical power. A typical emission rate measurement sequence proceeded as follows.

1. The ambient and wet bulb temperatures, along with the dew point, were measured.

2. The relative humidity was calculated in two separate ways. First from the wet bulb and dry bulb measurements and second, using the dew point depression data from the EG&G instrument.

3. The wet and dry air flows were chosen from the calibration of the rotometer readings with humidity. For plants that emitted a great deal of water vapor this step was not necessary since dry air alone resulted in approximately the desired humidity.

4. The flow of ultra-zero air and CO_2 was started and all three rotometers were appropriately adjusted.

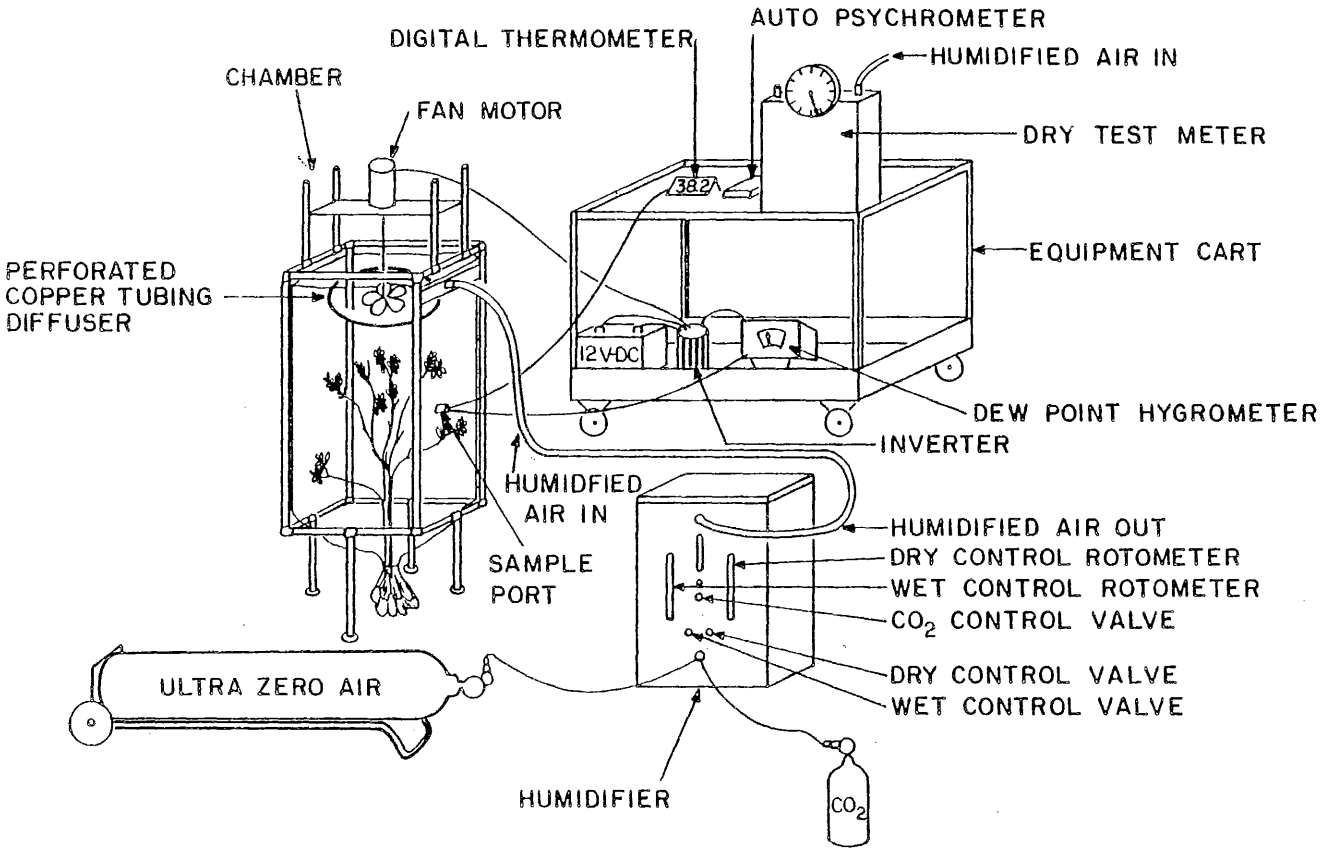


Figure III-8. Apparatus for direct measurement of rates of emission of natural hydrocarbons.

5. The total flow of ultra-zero air was measured with the dry test meter and the ultra-zero air output was attached to the chamber.

6. The chamber was placed over a suitable selected plant or branch and sealed with elastic cord.

7. The fan was turned on and the stopwatch started.

8. The thermister sensor was placed in the outlet port, and the air temperature was measured and recorded every 60 sec for three minutes.

9. The wet bulb temperature was monitored every 60 sec for three minutes using a mercury thermometer with a moistened sock over the bulb which was placed in the outlet port.

10. The thermister and dewpoint meter inlet in the port were replaced and the temperature was recorded every 60 sec for four minutes. The sample dew point was recorded after three minutes.

11. The necessary gas samples were withdrawn for chromatographic analyses after a total of 10 minutes.

12. The chamber was removed from the plant and the flow of ultra-zero air was remeasured using the dry test meter.

13. All flows were shut down.

The data were entered on the Sample Sheet as shown in Figure III-9. These were later recorded on a Field Data Sheet (e.g., Figure III-10) which also contained meteorological and plant conditions along with the chromatographic analysis on the reverse side (e.g., Figure III-11).

Photographs (35 mm slides) were taken of each separate sample plant. A card with the appropriate run number was placed adjacent to the plant before the picture was taken to ensure the correct identity of the plant in each photograph. The section of the plant studied in the chamber was then cut off and placed in a sealed plastic bag. It was later oven-dried and the leaf weight was obtained (see below).

2. Evaluation of Sample Collection and Storage Methods for Gas Chromatographic Analyses

Early in this program it was planned that vegetative emission rate samples (as well as ambient air samples) would be collected in the field (at various locations in the study area) and brought to the SAPRC laboratories for analysis by gas chromatography. However, although it involved substantial logistical and technical problems, it was deemed important to sample vegetation at the site where it was growing within the

Sample # 326 & 132

Species Allepo Pine

Type: Ambient Emission Blank (Loop) Trap

Ambient Measurements

Temp 21.6 °C

Dry bulb 22.5 °C

Wet bulb 18.0 °C

RH% 66 %

Dew Point 14 °C

Rotometer Settings

Dry 295

Wet .5

CO_2 initial 4.0

final

Initial flow 1 cuft/255 sec

Sample Dew Point -15 °C

RH 12%

Date 1981 Sept 3

Uz tank # CC28682

CO_2 tank # RR36663

Start time 0821 pst

Time	Temp	
1		
2	25.8	
3	18.6	wet
4	15.7	wet
5	15.5	wet
6	15.7	wet
7	26.3	
8	26.6	
9	26.9	RH 31%
10	26.9	

Sample time 0831 pst

Final flow 1 cuft/250 sec.

67.9

35

chamber is in complete sunlight

weather warm, clear, calm

coordinates K-5NE by roadside

Figure III-9. Sample data sheet for emission rate measurements.

Field Data

Date 1981, Sept 3 Sample # 326 & 132

Location L.A. Arboretum

Sample type Emission u/z tank # CC28682 CO_2 tank # RR3dd3

CO_2 rotometer 4.0 Dry rotometer 29.5 Wet rotometer .5 Enclosure # 2B

Site description coordinates K-5 NE by roadside

Weather, general warm, clear, calm

Weather, site Chamber was in complete sunlight

Cloud cover 0 % RH 66% Ambient air temperature 21.6°C Wet bulb 18.0°C Dry bulb 22.5°C

Wind: direction — speed —

Vegetation type, age, physiological state Pinus halepensis young and healthy. Same tree as sample # 303 & 114

Start flush, T = 0 0821 pst Sample wet bulb 15.7°C Sample dry bulb 26.9°C

Sample time 0831 pst Sample RH 30 % Flush flow rate 1 cuft/25.0 sec

No. of branches _____ Height _____ Girth _____

Representativeness of branch young and healthy

Analysis: Date 1981 Sept 3 Time 0835 pst Instrument # HP 5711A #3

Analysis method Standard 9.0ml glass loop procedure

Integrator # 3390A Location Blue Whale

Operator M. Dodd / D. Fitz

Dry leaf weight 20.6 ← total 12.7

Comments:

Figure III-10. Example of field data sheet for emission rate measurements.

Calibration date: 1991 September 2 Sample # 326/132

	E'	Area	ppbC	Corrected for [illegible]
Isoprene				-1.3
α-Pinene				
β-Pinene				
Myrcene				
Δ^3-Carene				
p-Cymene				
d-Limonene	13.19	3209	7.7	[illegible]
N-Hexane	7.43	3234	23.2	[illegible]
Benzene	9.33	1190	7.5	[illegible]
N-Heptane	10.58	6007	34.2	[illegible]
Methylcyclohexane	11.11	719	4.4	[illegible]
Toluene	12.47	11114	58.9	[illegible]
N-Octane				
Ethylbenzene	15.07	711	3.8	[illegible]
m-Xylene	15.37	1137	4.7	[illegible]
o-Xylene				[illegible]
N-Nonane				
Isopropylbenzene				
N-Propylbenzene				
1,2,4-Trimethylbenzene				
N-Decane				
N-Undecane	20.73	602	1.0	[illegible]
N-Dodecane	30.82	1197	1.5	[illegible]
N-Tridecane	34.79	3465	5.0	[illegible]
N-Tetradecane	36.62	4132	22.1	[illegible]
N-Pentadecane	39.00	5656	69.5	[illegible]
Isoprene (Varian 1400)	6.80	0.056mv	0.6	[illegible]
Unknown				
Unknown				

Comments:

Figure III-11. Reverse side of field data sheet for emission rate measurements.

study area, i.e., the Los Angeles coastal plain, rather than at UCR which is approximately 40 miles further inland. Only in this way, it was believed, could species be unambiguously sampled under applicable conditions of temperature, rainfall, elevation, etc.

Considerable effort was therefore devoted to developing and evaluating several methods for collecting and storing such hydrocarbon samples with particular attention to the issues of compound stability and avoidance of contamination effects over a series of experiments. Three different methods were evaluated involving use of (a) glass loops or traps, (b) silylated glass bulbs and (c) polished stainless steel cannisters. All three approaches were ultimately found to suffer from significant limitations or problems.

A major problem encountered early in the program concerned loss of the higher molecular weight hydrocarbons (i.e., $\geq C_{10}$). Calibration mixtures containing 19 individual hydrocarbons in calculated concentrations gave excellent repeatability for emergence time, peak height and peak area for all molecules except the higher molecular weight compounds for which poor peak size consistency was observed. Some peaks, especially C_{14} and C_{15} alkanes sometimes failed to appear while others (C_{10}-C_{12}) were larger than normal. One explanation which might account for this behavior was the occurrence of adsorption/desorption phenomena which would be more pronounced for low volatility hydrocarbons. The six-port sampling valve used on the gas chromatograph was suspected because it was sealed with a slider made of graphite-filled Teflon. Graphite is well known for its gas adsorption capacity. To remedy this, the valve was enclosed in an oven heated to 75-85°C. Changing from trap sampling to loop sampling also contributed to the resolution of this problem.

Several different sampling schemes employing the six-port valve were tried as shown in Figure III-12. The sample was either trapped directly or transferred using a 100 mℓ all-glass syringe into either a glass bead-filled metal trap (which was chilled with liquid argon), or into a silylated Pyrex loop of 10 mℓ volume. The trapping step was followed by flushing the sample, at boiling water temperature, directly into the capillary column which was held at the -50°C starting temperature of the program. The loop sample, which was 10 times smaller than the trap sample, was transferred using carrier gas while the column was held at

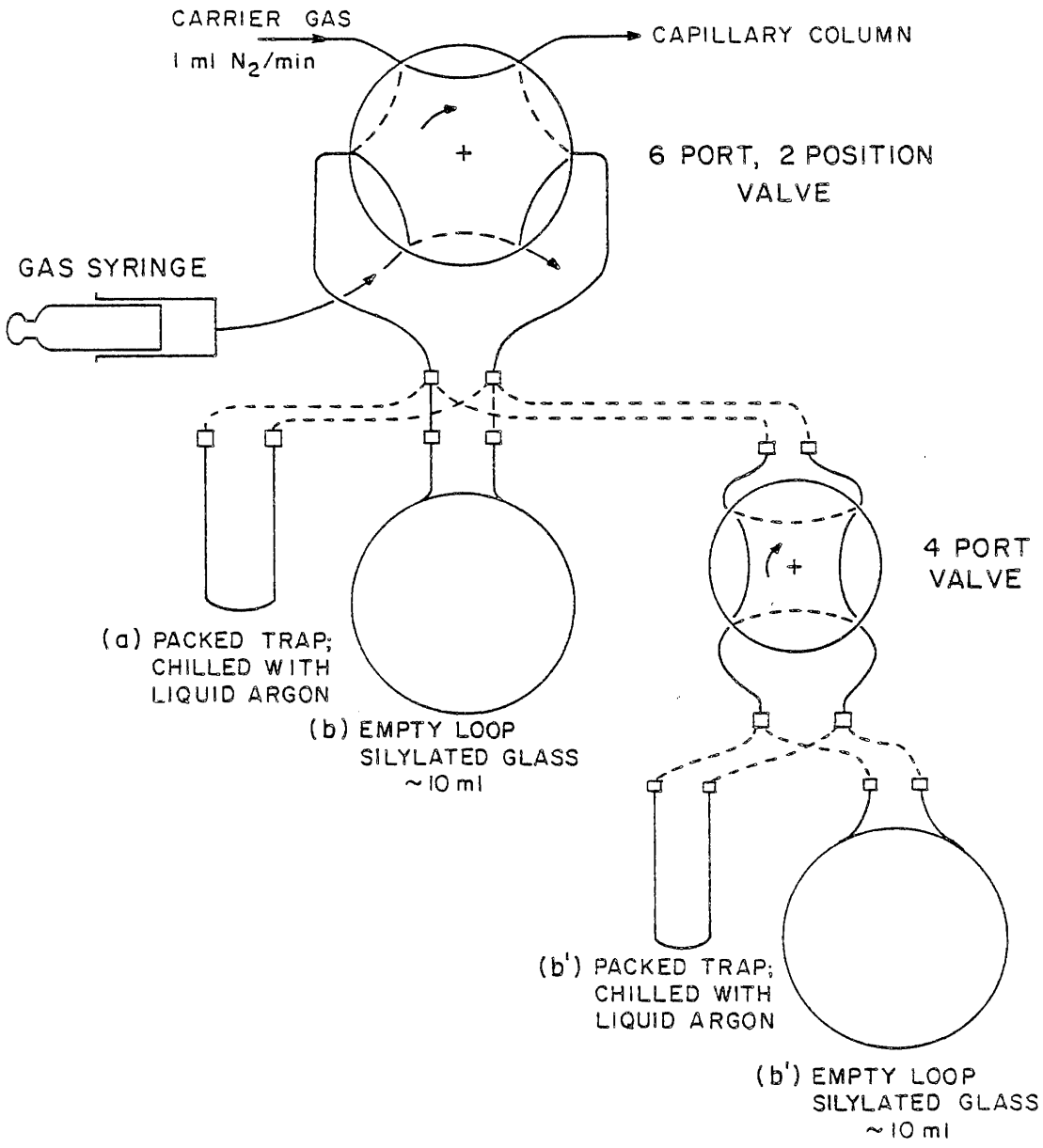


Figure III-12. Alternative sampling schemes tried during this study. Sample is brought to the instrument either with the gas syringe or attached to the four-port valve.

-90°C. This low temperature transfer from loop to column results in sharp peaks even for the five-carbon hydrocarbons (e.g., isoprene).

Glass Loop or Trap. Using a loop or trap in conjunction with a four-port valve for ease in handling, as shown in Figure III-12, was one method of sample storage considered. It was felt that trap samples would be stable for long periods of time provided they were maintained at liquid argon temperatures. Unfortunately, problems with reproducibility were encountered when removing the higher hydrocarbons from the trap to the column. For this reason and the fact that sufficient sensitivity was obtained from the loop method, the use of trap samples was abandoned.

Use of a 10 mℓ silylated glass loop reduced the problem of irreproducible losses of heavier hydrocarbons but the high surface-to-volume ratio of the loop lead to a loss of reactive hydrocarbons to the walls during storage. Thus, the use of a four-port valve, a possible problem area in itself in terms of contamination and hydrocarbon loss was not implemented.

Silylated Glass Bulbs. The use of 5 ℓ silylated glass bulbs was thought to be an improvement over the small 10 mℓ sampling loop. Samples could be taken directly by syringe and introduced into the sampling loop of a Carle six-port valve.

A thorough study of the stability of hydrocarbons in five liter silylated glass bulbs was conducted. After dosing the bulbs with about 1 ppmC of each of 19 hydrocarbons, chromatographic analyses employing a 9 mℓ silylated glass loop and a 150°C sampling valve showed less than 1% variation up to nC-12. Adding similar amounts of α-pinene, β-pinene and d-limonene resulted in about a 5% loss of the original hydrocarbon mixture after 17 hours, with the terpenes gaining or losing ~15%.

The next series of tests involved taping the flasks to exclude light and decreasing the monoterpene concentrations to a more realistic 75 ppbC of each component. This was done by a standard double dilution procedure, dosing a 46 ℓ bulb with liquid injection and then adding an aliquot of this gas mixture to the 5 ℓ sampling bulb. [Stability of the high concentration monoterpene mixture (5 ppmC) in the 46 ℓ bulb was shown to be quite good.] For the lower concentration samples the β-pinene in the silylated bulb dropped to 10% of the original value after 16 hours while the stability of the α-pinene and d-limonene was quite good (~90%). In

contrast, when an unsilylated acid-washed bulb was used the hydrocarbon stability was found to be very poor.

Another silylated bulb was dosed with a high concentration (several ppmC) of stock hydrocarbon mixture containing the three monoterpenes and allowed to stand overnight. After purging with ultra-zero air very little carryover was observed. Stability tests were then made using six monoterpenes at the ~25 ppbC level. The variability as determined by loop chromatographic analysis was less than 20% after 20 hours.

The three silylated bulbs were then given a similar treatment of purging, dosing at the ppm level with terpenes and repurging. Only one bulb showed good long term stability for all six hydrocarbons tested. β-pinene appeared to be the least stable followed by myrcene. Apparently, the hydrocarbons, particularly the monoterpenes, were irreversibly adsorbed on the walls of most of the treated bulbs. The results of a 24 hour bulb stability test are shown in Table III-4 for the best sampling bulb. Because only a single bulb appeared to be suitable for field sampling this approach was abandoned.

Stainless Steel Cannisters. Upon the recommendation of the Washington State University analytical group headed by Dr. Dagmar Cronn, several Summa-Polished PPT cannisters were purchased from D & S Instruments (DSI), Limited. The results of dosing these vessels and monitoring terpene stability at the 50 ppbC levels are discussed in more detail in Section VII. However, upon evaluation, these cannisters as received were not judged suitable for this application although they were subsequently used for ambient air analyses (see Section VII).

Although with sufficient treatment and testing it may have proven possible to develop a suitable storage container, it was decided instead to equip an available mobile laboratory (see below) with a capillary column gas chromatographic system which would permit on-site measurements of hydrocarbon emission rates. This eliminated the need for lengthy storage of organic samples in bulbs, traps, or cannisters.

3. Instruments and Columns

A fused-silica capillary column was employed to obtain a higher resolution than had been obtained in an earlier phase of the program with packed columns. The 30 m x 0.25 mm, SE-52 coated column, manufactured by J & W Scientific, Inc., was installed in a Hewlett-Packard 5710A gas

Table III-4 Stability of a Hydrocarbon Mixture in Silylated Bulb B (Area Units; Time in Hours)

Compound	Retention Time, min	Blank	$A_{t=0}$	$A_{t=1}$	$\frac{A_{t=1}}{A_{t=0}} \times 10^2$	$A_{t=3.5}$	$\frac{A_{t=3.5}}{A_{t=0}} \times 10^2$	$A_{t=23}$	$\frac{A_{t=23}}{A_{t=0}} \times 10^2$
isoprene	5.7	--	168	160	95.3	168	100.0	170	101.2
nC_6	8.7	136	377	338	89.7	319	84.6	377	100.0
nC_7	11.9	22	281	277	98.6	274	97.5	284	101.0
nC_8	14.7	0	283	297	104.9	282	99.6	294	103.9
nC_9	17.3	0	317	335	105.7	339	106.9	306	96.5
α-pinene	18.3	0	299	314	105.0	320	107.0	303	101.3
β-pinene	19.3	0	317	325	102.5	324	102.2	325	102.5
myrcene	19.6	0	256	260	101.6	243	94.9	240	93.8
nC_{10}	19.8	0	402	405	100.7	457	113.7	389	96.8
Δ^3carene	20.1	6	205	215	104.9	278	135.6	222	108.3
p-cymene	20.4	--	414	425	102.7	421	101.7	423	102.1
d-limonene	20.5	0	469	486	103.6	463	98.7	534	113.9

chromatograph equipped with a flame ionization detector (FID) and modified to accept gaseous samples. Samples were introduced to the column through a 6 port Carle valve and a passivated 9.0 mℓ glass loop. The passivation process consisted of rinsing the loop first with a 10% dichlorodimethylsilane in toluene solution, then with toluene and finally with methanol. The valve was encased in a 150°C thermostatically controlled oven to minimize adsorption/desorption problems with higher molecular weight hydrocarbons.

Samples were transfered onto the -90°C liquid nitrogen-chilled column over a 12 minute period by the 1 mℓ min^{-1} pressure-controlled nitrogen carrier gas. After raising the -90°C column to -50°C in 1.25 minutes, temperature programming from -50°C to 200°C at a rate of 8°C min^{-1} was begun. A peak integrator (Hewlett-Packard Model 3390A) was used to automate data collection. After 36 minutes the chromatogram was complete and the glass loop was heated and purged to eliminate any carry-over to the next injection.

4. Calibrations and Peak Identifications

The gas chromatograph was calibrated approximately once a month or whenever any changes were made. Calibrations consisted of injecting a known amount (~50 ppbC each) of 26 compounds from a calibration mixture. Factors relating ppbC to peak area were calculated and averaged over three or more samples. The response was approximately 100 ppbC mv^{-1} with a sensitivity of 1-5 ppbC. The retention times for many of the components (20 hydrocarbons and 6 monoterpenes) in the calibration mixture were plotted against the corresponding boiling points (as shown in Figure III-13) over the temperature range 0-250°C, and over the range 155-185°C, which encompasses the boiling points of the monoterpenes (Figure III-14). The excellent correlations obtained were useful in identifying individual peaks in complex gas chromatograms obtained for both emission rate measurements and ambient air samples.

The calibration mixture was prepared by dosing a clean 49.95 ℓ Pyrex carboy with 0.2 μℓ isoprene and 1 μℓ each from four stock solutions. The stock solutions contained 50 μℓ aliquots of 6 or 7 compounds, as shown in Table III-5, and the concentration of these compounds in the solution was calculated from their mass. Since the approximate concentration of each

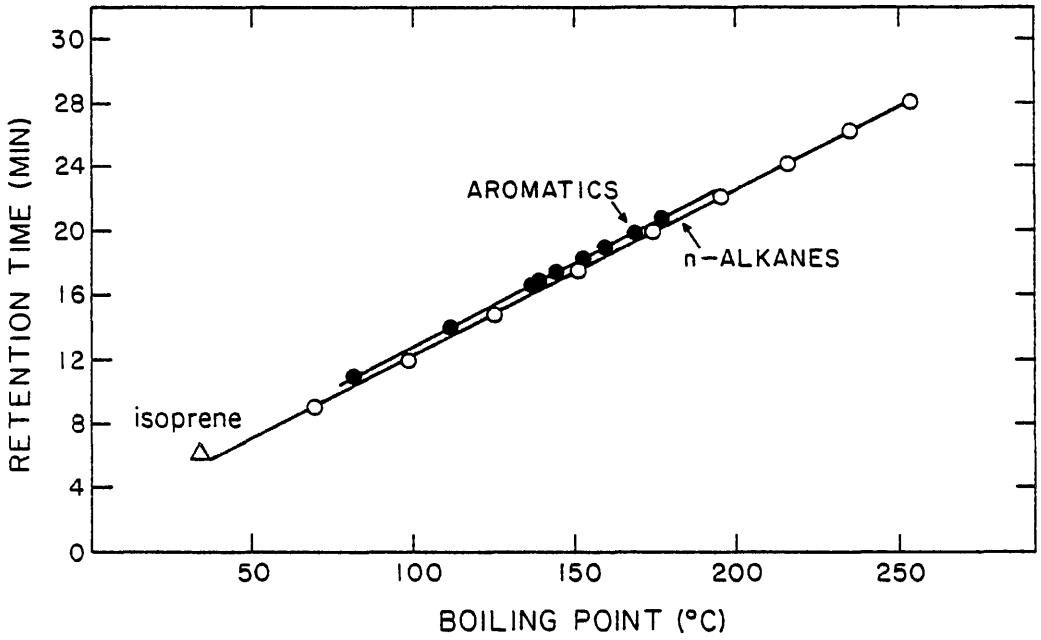


Figure III-13. Plots of retention time vs boiling point form excellent straight lines for each homologous series. Different series have nearly identical slopes but different intercepts.

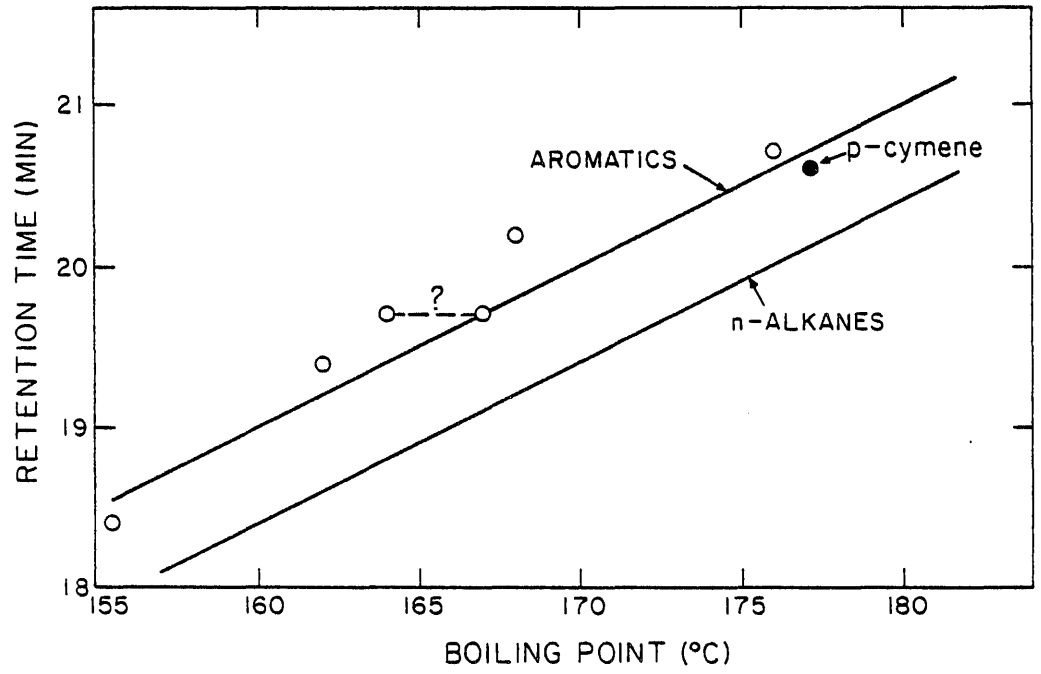


Figure III-14. A portion of Figure III-13 expanded (x 10) to include five common monoterpenes (open circles + p-cymene). Literature data on monoterpene boiling points is much less precise than for the hydrocarbons (hence in one case two boiling points are shown for the same compound).

Table III-5. Stock Solutions for Gas Chromatographic Calibrations

Solution 1	Solution 2	Solution 3	Solution 4
n-Hexane	Benzene	Methylcyclohexane	α-Pinene
n-Heptane	Toluene	m-Xylene	β-Pinene
n-Octane	Ethylbenzene	o-Xylene	Myrcene[a]
n-Nonane	Dodecane	Isopropylbenzene	Δ^3-Carene[a]
n-Decane	Tridecane	n-Propylbenzene	p-Cymene
n-Undecane	Tetradecane	1,2,4-Trimethylbenzene	d-Limonene
	Pentadecane		

[a]Vapor distilled to ensure purity.

compound in the carboy was 5 ppmC, 1:100 syringe dilutions were made so that the calibration could be done at a realistic level.

The candidate monoterpenes were selected on the basis of a large body of literature concerning experimentally observed emissions of hydrocarbons from vegetation. This literature was reviewed earlier in this Section and will not be redocumented here. Although there have been a few reports of significant vegetative emissions of higher terpenes (Bonner and Varner 1965) and of oxygenated compounds (Meigh 1955, Rasmussen 1972, Zimmerman 1979a), we proceeded on the basis that only if unknown peaks appeared in chromatograms obtained in emission rate measurements would additional analytical effort be expended to identify the corresponding compounds. In fact, with the exception of only one species (Brazilian pepper), no such peaks were observed in a reproducible manner for the species and conditions involved in this study.

Generally, peaks were identified from retention times obtained from the integrator. This was programmed to calculate concentrations of the 26 peaks present in the calibration mixture. If water present in the sample resulted in shifted retention times, pattern recognition was the primary method of identification. This was easily accomplished due to presence of certain contamination peaks (described below) which gave a consistent and recognizable pattern. When peaks were not recognized by the integrator, concentration calculations on a ppbC basis were made manually, using the appropriate factors obtained from the calibration.

While performing maintenance checks on the gas chromatograph in September 1981, the SE-52 capillary column was broken. It was replaced by a 30 m x 0.25 mm (ID) SE-54 capillary column. This resulted in no major changes in response. It was also necessary to replace the 9.0 mℓ Pyrex loop because of a worsening contamination problem. A 10.2 mℓ passivated Pyrex loop replacement resulted in much lower contaminant levels.

Because of shifts in retention time caused by water in the syringe samples, isoprene sometimes could not be unambiguously identified. For this reason, a separate Varian 1400 chromatograph was set up with a packed OV-101 column which was not affected by the presence of water. Since this column was useful over the entire monoterpene region, the chromatograms also provided validation of some of the more well-resolved peaks observed by the capillary system. Although much larger samples (generally 100 mℓ) could be taken with the freeze-out trap, the resolution was sufficiently lower than the capillary system that the sensitivity of the two instruments was about the same. Samples were run using this GC in parallel with the capillary column system system described above.

A Varian 1400 was installed on shock mounts in the mobile laboratory. It was equipped with a flame ionization detector, a standard Valco six-port valve, and an associated freeze-out trap. The column was 9.2 m x 3.2 mm OD stainless steel commercially packed OV-101 "Hi-Plate" and was used with a nitrogen carrier flow of 39 mℓ min^{-1}. Gas samples were injected using a 100 mℓ glass syringe and frozen in the trap at liquid argon temperature. Injection was accomplished by removing the liquid argon and immersing the trap in boiling water while simultaneously switching the sample valve. The column remained at 55°C for the first eight minutes, then was programmed at 20°C min^{-1} to 120°C where it remained until the chromatogram was complete, generally about 40 minutes.

This chromatograph was calibrated in parallel with the capillary column system using the same freshly prepared hydrocarbon mixtures. At the lowest practical attenuation of 4 the chromatogram showed significant drift and required nearly constant attention. The sensitivity at this attenuation was about 1 ppbC using 100 mℓ samples.

Problems. The two primary difficulties encountered with the capillary column GC system described above were contamination and excess water. Toluene was the most significant contaminent, but n-hexane, n-

heptane, n-octane, ethylbenzene, and m-xylene were also present. Blanks were obtained by purging the plant enclosure chamber as it normally operated, but without a plant present. These checks were executed after every forth plant sample. For every blank, the concentration, in parts per billion carbon (ppbC), was calculated for each compound observed, and the average concentration was obtained from the blank before and after a series of four emission rate measurements. These average concentrations were then subtracted from the concentrations present in the plant sample. Early in the field sampling program the contaminant concentrations were quite variable, but later, particularly after the capillary column was changed, these concentrations became more consistent and finally were virtually eliminated.

Although the contamination problem was eventually solved, water introduced to the GC samples from the plants themselves was a problem not easily overcome. Varying amounts of water in the samples produced minor (0.5 min) to major (3 min) shifts in retention times and on occasion broadening of peaks over the entire chromatogram. These problems were thought to be due to blockage of the column by ice. The water content was reduced when necessary by purging the chamber with non-humidified air, or, for plants which emitted a great deal of water (corresponding to dewpoint $>10^{o}C$), by increasing the flow of the dry purified air to 80 ℓ min^{-1}, thus diluting the water vapor.

This method worked well with shrubs and trees, but the amount of water emitted from the plants and soil while sampling ground covers and lawns could not be reduced to a reasonable level without seriously reducing sensitivity. Drying the samples with potassium carbonate was tried without success; samples were either contaminated or the water content was still too high. Instead, a 30 m capillary column with a larger bore, 0.32 mm ID, was installed. This new column was also fused silica, but employed a non-extractable bonded phase (DB-5) which was equivalent to the liquid phase SE-54. After installation of this column, shifts in retention times were noted with samples containing water, but no smearing of peaks was observed. As noted above, the installation of this column also minimized the contamination problem.

Correlation of Capillary GC Results with Capillary GC/Mass Spectrometer Results. To test compound assignments made on the capillary column

GC system in the mobile laboratory, selected results were compared with those obtained from a capillary column-equipped chromatograph which was coupled to a Finnigan 3200 mass spectrometer employing similar but slightly different sampling and analysis conditions. Hydrocarbon samples taken from Encelia farinosa in the enclosure chamber gave slightly shorter retention times with the GC/MS system. However, they produced an excellent correlation with the retention times. Using just the three pairs of numbers for retention times for α-pinene, β-pinene and d-limonene, least squares analysis gave a slope of 0.97, an intercept of -1.073 and a correlation coefficient of R = 0.99. Thus the two instruments were well correlated and identifications made by mass spectrometry could be transferred to the field instrument.

The GC-MS was used in several instances to verify peak identification and to determine the compounds responsible for unknown peaks. For example, the GC-MS confirmed that a peak of varying retention times, and which appeared to sometimes split into two peaks when sampling scrub oak, was actually isoprene. The problem was later shown to be caused by water vapor in the sample freezing at the column head, thereby shutting off the carrier flow. Because the melting did not occur at a consistent time the retention time varied. The second transient peak was identified as dichloromethane, a solvent used in cleaning the humidifier. Its source was later found and eliminated.

The GC-MS was also used to identify a major unknown peak in the emission of Brazilian pepper. In this case a high-concentration sample was taken of Brazilian pepper at the UCR campus. A similar chromatogram was obtained by the GC-MS and the unknown was identified as a monoterpene.

5. Direct, Valveless Injection of Air Samples for Capillary Gas Chromatographic Analysis

Although in many respects the GC techniques developed for this program were highly successful [i.e., small sample size (10 mℓ) with sensitivity of a few tenths ppb and good resolution of hydrocarbons across a broad molecular weight range], the major limitation of this technique proved to be the blanks. At least early in the program they not only showed numerous false peaks but peaks which were not reproducible and whose origin was difficult to define. It seemed clear that the full potential for this technique would only be reached if these artifacts

could be eliminated and the repeatability of both samples and blanks demonstrated. For this reason a parallel effort to develop an alternative method was initiated. Although this effort was not completely successful until the emission rate measurements were completed, we briefly describe this sub-program because we believe the technique used will have important future applications.

The basic approach focussed on eliminating the six-port valve altogether. In earlier programs, successful sampling had been done by direct injection from a syringe onto the chilled column. In this approach a short section of stainless steel capillary tubing (0.5 mm ID) was chilled with liquid argon while a sample was drawn through (see Figure III-15). At least 35 mℓ could be sampled without blocking the trap with ice. This trap could then be connected directly into the carrier gas line with the column, thawed with hot (or cold) water and the contents flushed directly into the column.

The advantage of using the capillary column was that stability of the flame detector was not upset by stoppage of carrier gas flow (about 1 mℓ min^{-1}) since it used 30 mℓ min^{-1} of auxilliary nitrogen along with hydrogen for the flame detector. Neither temperature programming nor shutoff of column flow caused any significant change of flame detector current even at full sensitivity. This can be seen in the chromatogram shown in Figure III-16, which was run at x 2 attenuation (i.e., nearly full sensitivity) as a "full" blank. That is, the trap was removed (carrier gas off), chilled with liquid argon, uncapped, and the 50 mℓ syringe attached but not pulled (for the blank). The trap was then capped, brought to the lab still chilled, attached to column and carrier supply, thawed, and the record of Figure III-16 obtained by temperature programming.

Transfer occurred during a four minute isothermal period at $-50^{o}C$. The column was then heated at $8^{o}C$ min^{-1} to $200^{o}C$ (35.25 minutes). This blank showed seven very small peaks (1 to 2 ppbC of organic compound each). As discussed above, it proved difficult in the early part of this program to achieve a blank with such small peaks using the standard approach. Not only were there usually 5 or 10 peaks, but they were usually larger than 1 ppbC and never of consistent size or even consistent relative size. The artifacts persisting in this valveless technique were

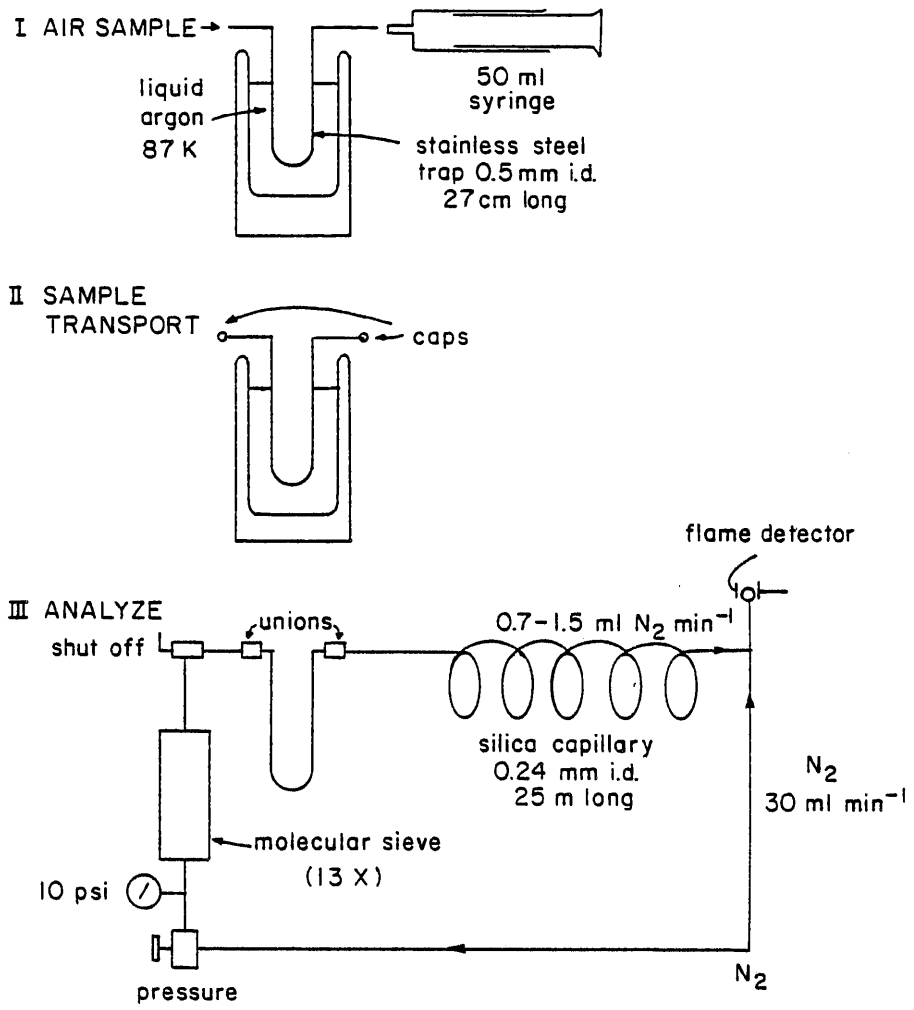


Figure III-15. System for valveless sampling and analysis.

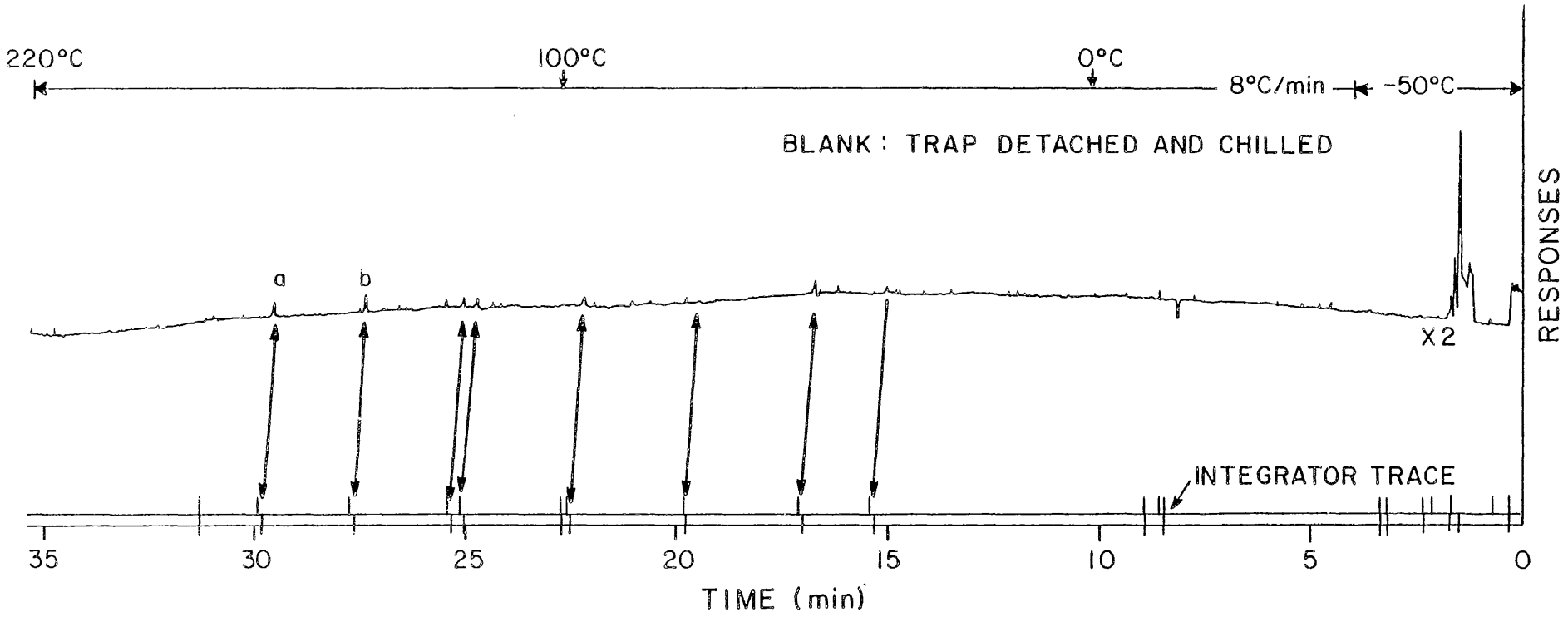


Figure III-16. Full sensitivity blank chromatogram using the valveless injection technique. The peaks marked a and b are very persistent and correspond to the two peaks marked a and b in Figure III-17.

of higher boiling point (retention time at the end of the gasoline boiling range).

This valveless injection temperature program method yielded excellent chromatograms. The peaks were very narrow. Even compounds with retention times of 20 or 30 minutes had widths (full width at half height) of only about 3 seconds. The ratio of area to peak height, as calculated by the electronic integrator, was nearly constant over the entire range. This means that (a) there was little loss of resolution as retention time increased; (b) peak height was a fair measure of concentration; and (c) there was little loss of sensitivity (peak height/per carbon) with increasing retention time. This was probably due to the fact that the less volatile compounds were immobilized by the low temperature at the beginning of the chromatogram and their actual "time in motion" was no longer than that for more volatile compounds.

An additional advantage of this procedure is that no sampling vessels, syringes or other surfaces are in contact with the sample as potential adsorbing surfaces. The sample is kept frozen at liquid argon temperature until it goes directly into the carrier gas stream. It is not necessary to risk loss of reactive components in a drying agent or on the wall of a sample vessel. The small amount of water present in 35 mℓ of air freezes in the trap and is swept into and through the column along with the organics. Although water does not give an ionization signal it sometimes causes the detector flame to go out. Water does not harm the column because it is gone by the time the column reaches room temperature.

An ambient air chromatogram obtained by the direct injection technique is shown in Figure III-17. This 50 mℓ sample was taken in heavy haze at 4 p.m. on December 9, 1981. This sample and the one discussed below were run without the initial four minute isothermal period at $-50^{\circ}C$. The retention times were therefore correspondingly shorter. The integrator recognized 129 peaks in this chromatogram with a total area of 33,217 units. A 56 area unit peak at 26.4 minutes is marked on Figure III-17. The retention times of isoprene and α-pinene are indicated by arrows on the chromatogram, however it is not certain that the corresponding small peaks are in fact isoprene and α-pinene. β-pinene falls among the nine carbon aromatics and would be difficult to identify in small concentrations. The two peaks with question marks at 22.3 minutes and

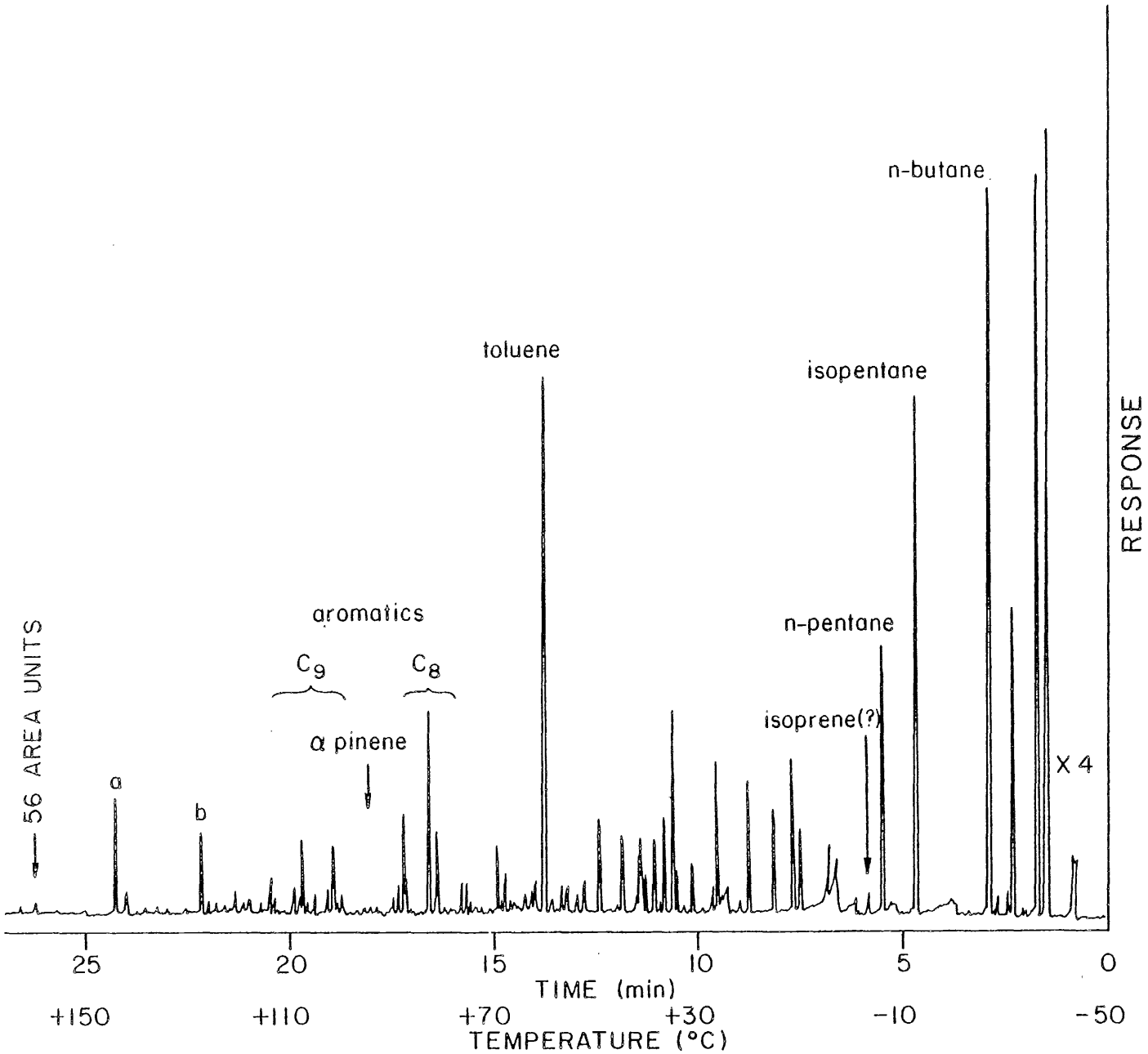


Figure III-17. Chromatogram of 50 mℓ of ambient air (UCR campus) at 4:00 p.m. on December 9, 1981, in heavy haze using valveless injection. The peaks labeled a and b are artifacts labeled in the blank (Figure III-16). The retention times for α-pinene and isoprene are shown. Note similarity to gasoline (Figure III-18).

24.4 minutes are very persistent even in blank samples. They are probably the same compounds which give the two larger peaks in the blank (Figure III-16) at 26.3 and 28.5 minutes (with four minutes longer retention time because of the four minute initial isothermal period at -50°C used for this blank).

For comparison, Figure III-18 shows a chromatogram of a sample of vaporized gasoline (at much higher concentration). The similarity to the ambient air sample is striking. The ambient air sample shows several large peaks with retention times of less than two minutes. These are probably unresolved two- and three-carbon hydrocarbons. The isoprene retention time is nearly identical to that of 1-pentene, but it should be possible to resolve isoprene from the six five-carbon mono-olefins.

6. Mobile Laboratory

This facility was based on a 27 foot 1967 Dodge Motor Home custom built on a 1 ton truck chassis by Travco Corporation (Model H7047C). The vehicle had a 178 in wheel base and was equipped with a 318 cu in V-8 engine, three speed automatic transmission, power steering and power brakes. A 50 gallon fuel tank was fitted to give the mobile laboratory a range of approximately 500 miles.

The interior was substantially modified from the standard motor home floor plan by Travco during manufacture to facilitate laboratory usage. Benches were added to the basic shell on each side of the rear section and storage cabinets were built on the right side. Provisions were made for sufficient electrical circuits of both 220 and 110 V AC. Two 6.5 KW Kohler (Model 5-RM21) electrical generators were mounted under the rear benches. A selection could be made at the electrical distribution unit between generator and line power. A pair of Duo Therm 10,000 BTU 110 V AC air conditioners (Model S72C) were mounted on the roof.

The mobile laboratory was further outfitted by SAPRC as shown in Figure III-19. The rear benches were used to shock-mount both of the gas chromatographs. An additional bench was added to the extreme rear. A workbench was mounted to the floor on the right side ahead of the storage cabinets. A two burner range was installed on the workbench in order to boil water for chromatographic injections. Ahead of this bench was a refrigerator was located which was used for the storage of calibration standards. Next to the entrance an additional seat was mounted to the

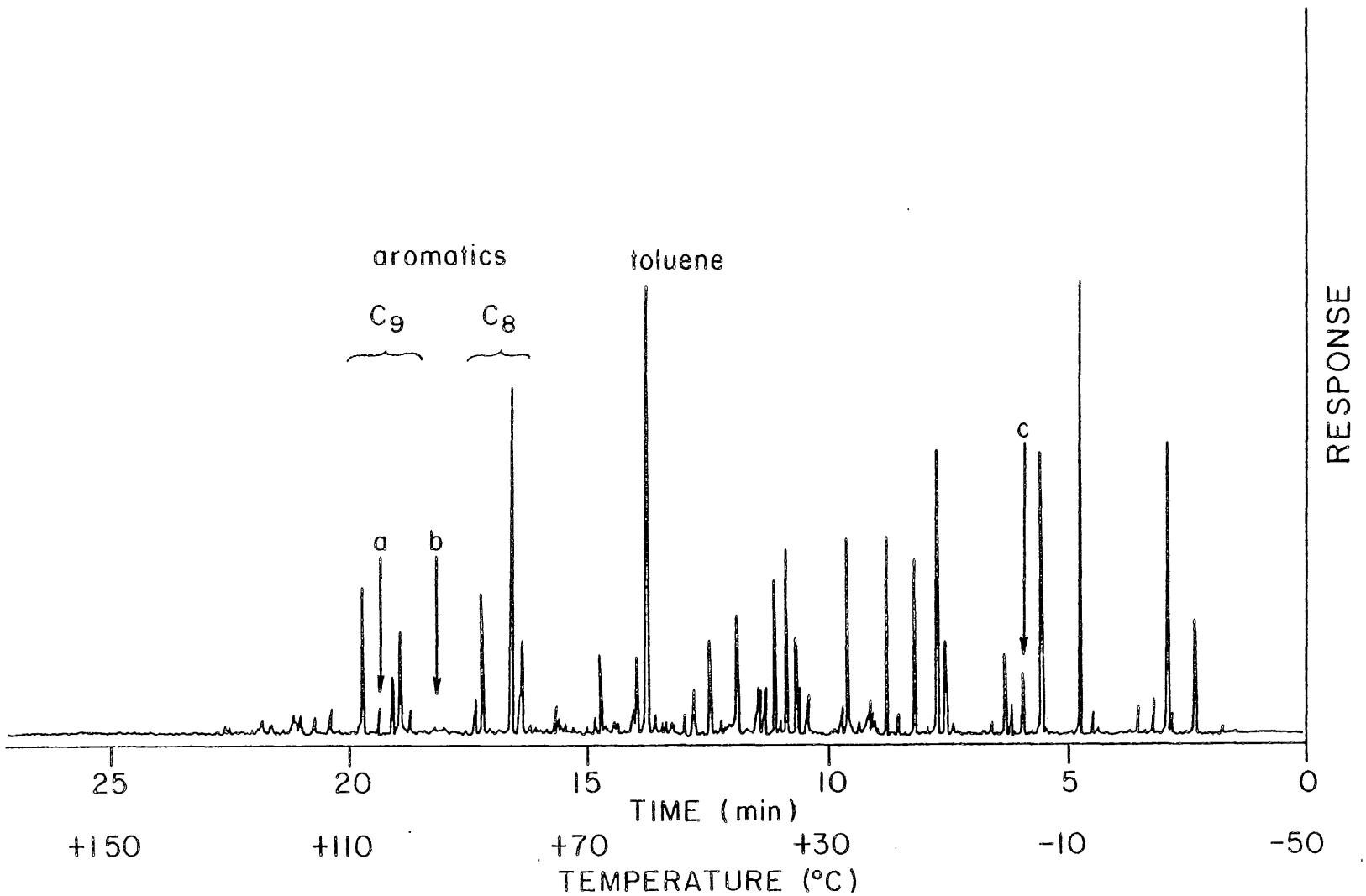


Figure III-18. Chromatogram of regular grade gasoline by the valveless injection system used to obtain Figure III-16 and III-17. Isoprene would appear ahead of an overlapping peak c which is due to 1-pentene. Letters a and b mark the retention times of β- and α-pinene, respectively.

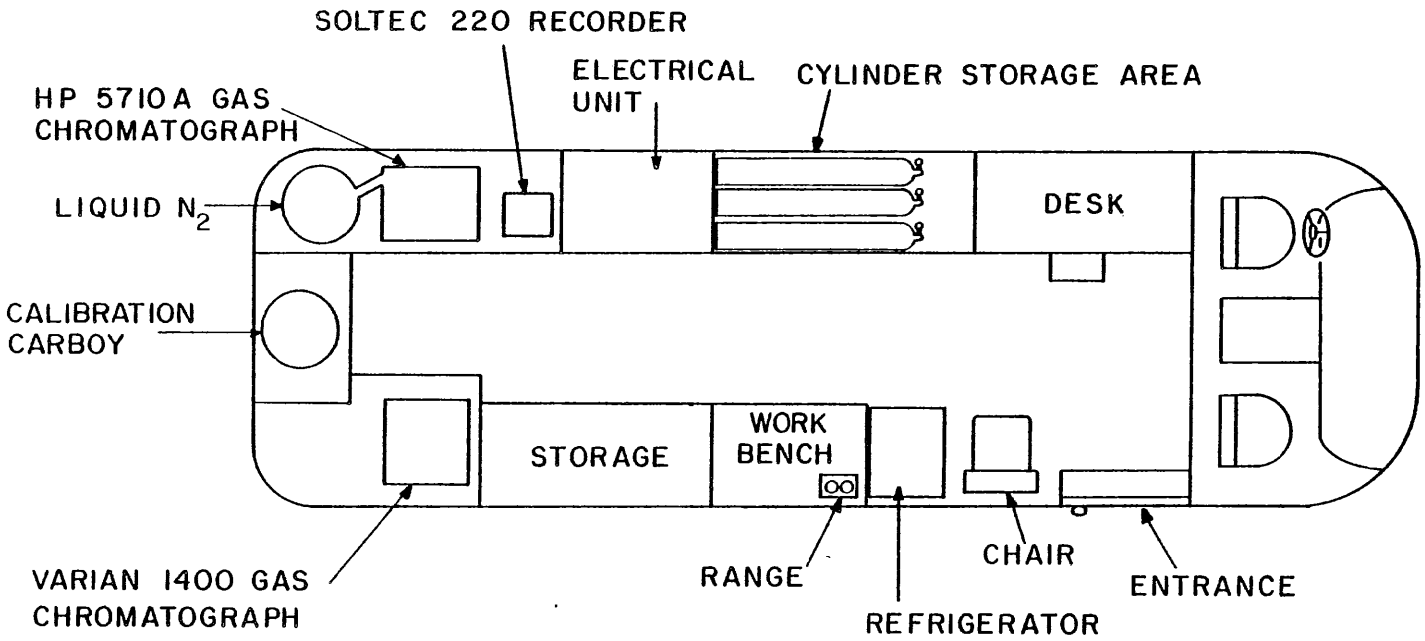


Figure III-19. Mobile laboratory equipped for measuring rates of emission of natural hydrocarbons from vegetation.

floor. On the left side a horizontal storage area was built to safely contain the compressed gas cylinders during transportation. A desk was added behind the driver's seat for the chromatographer. The center section of the mobile laboratory was maintained clear for the transportation of chambers and other hardware unloaded at the sampling site.

C. Selection of Plant Species and Measurement Locations

1. Urban Plant Species Studied

In parallel with the development of the plant enclosure methods and GC sampling and analysis techniques, lists of candidate plant species to be studied were assembled. Because of the laborious and time-consuming nature of the measurements it was recognized at the outset that emission rates could be obtained only for a limited number of the total species present in the natural, urban and agricultural portions of the study area. An attempt was therefore made to rank species in order of their abundance in the study area. This proved to be more difficult than anticipated for the urban region due to the lack of comprehensive and definitive data concerning the abundance of ornamental species in the study area (Pacific Coast Nurserymen and Gardener's Journal-private communication).

Initial tabulations of urban ornamental plant types were assembled with the assistance of several plant scientists on the UCR campus. The targeted plants were ranked according to presumed abundance in six groups which could be distinguished in the low altitude, high resolution photography obtained and analyzed as described in Section IV. The resulting list, which was employed at the beginning of the emission rate measurement program, is shown in Table III-6.

The list of ornamentals was expanded and modified in the course of the program as information was received from the botanists conducting the simultaneous study of species composition and green leaf mass in the field (see Section V). Based on this information a number of additional broad-leaf trees and shrubs were considered to be important and emissions rate measurements were made for these species. On the other hand, the relatively small green-leaf mass found for the palms led us to delete two palm species originally proposed for emission measurements. Two other species were also not investigated: rosemary because it was not found to be abundant during the field surveys, and pyracantha because it could not be

Table III-6. Preliminary List of Urban Ornamental Plants to be Sampled for Hydrocarbon Emission Rates[a]

Broad-Leaf Trees	Conifers	Flower and Ground Cover	Grasses	Palms	Shrubs
Ribbon gum	Monterey pine	Geranium	Bermuda (hybrids)	California fan palm	Oleander
Meyer lemon	Aleppo pine	African daisy		Canary Island palm	Chinese juniper
Magnolia	Italian cypress	Cape weed	Kentucky bluegrass	Mexican fan palm	Pyracantha
Ash	Deodar cedar	Gazania		Cocos palm	India-hawthorn
Jacaranda	Canary Island pine	Common periwinkle	Perennial ryegrass		Bottlebrush
Elm	Italian stone pine				Rose
Oak		Algerian ivy	Tall fescue		Rosemary
		Ice plant			Cotoneaster
					Cape-honeysuckle
					Common myrtle

[a]Ranked by common name in order of estimated abundance in the California South Coast Air Basin.

located in or near the Los Angeles Arboretum. The field data concerning species composition was generally consistent with the originial species selected in the conifer, grass, and flower and ground cover categories and hence these were not changed. The final set of urban ornamental species for which emission rate measurements were made is given in Table III-7. Thus, experimental measurements were made for 56 different ornamental plants, about 60% more species than had originally been selected for study. The 56 ornamentals sampled represented approximately 30% of the total of 193 distinct species found in the CSCAB study area by the field botanists in this program (see Section V).

2. Natural Plant Species Studied

The Santa Monica mountains and the San Gabriel mountains form the western and northern perimeters of the South Coast Air Basin. Slopes below 3600 ft elevation are covered by either the coastal sage scrub or the chaparral vegetation types. Coastal sage predominates on the lower slopes of the mountains facing the ocean, interrupted by chaparral on the higher more mesic slopes. Sage predominates again on the hotter, drier lower slopes of the mountain interior. Coastal sage species often occupy sites where community succession leads back to the chaparral type. Generally, the chaparral is by far the most extensive of the two vegetation types within the South Coast Air Basin. Together they occupy almost 600 mi^2 (1500 km^2) in the study area (see Section IV).

The species comprising the coastal sage scrub vary according to site factors and the time since the last fire. According to Mooney (1977), the coastal sage scrub at Camp Pendleton is typical of much of the coastal region of Southern California. Here Salvia mellifera, Artemesia californica, Rhus laurina and Eriogonum fasciculatum are the dominant species. Salvia mellifera often comprises up to 50% of the total plant cover.

The chaparral can be characterized by three distinct species mixtures according to increasing elevation. The dominant species in the lowest zone is chamise (Adenostoma fasciculatum) which is between 50-100 percent of a vegetation mixture that occupies 50-90 percent of the ground. The intermediate zone has a 50-100 percent cover composed of several Ceanothus species which usually comprise 80-100 percent of the total cover. The next zone which is found on north facing slopes below 3000 ft and on all slopes above 3000 ft is scrub oak (Quercus dumosa) which comprises 20-50

Table III-7. Final List of Urban Ornamental Plants Sampled for Hydrocarbon Emission Rates[a]

Broad-Leaf Trees	Conifers	Flower and Ground Cover	Grasses	Palms	Shrubs
American elm	Aleppo pine	African daisy	Bermuda hybrid	California fan palm	Bottlebrush
Avocado[b]	Canary Island pine	Common periwinkle	Kentucky bluegrass	Date palm	Camellia[b]
Black locust[b]	Deodar cedar	English ivy[b]	Perennial ryegrass		Cape-honeysuckle
Brazilian pepper[b]	Italian cypress	Geranium	Tall fescue		Chinese juniper
California live oak	Italian stone pine	Ice plant			Common myrtle
California sycamore[b]	Monterey pine				Cotoneaster
Camphor[b]					Glossy privet[b]
Chinese elm					Heavenly bamboo[b]
Crape myrtle[b]					Hibiscus[b]
Evergreen ash					India-hawthorn
Evergreen pear[b]					Japanese pittosporum[b]
Fern pine[b]					Natal plum[b]
Jacaranda					Oleander
Magnolia					Rose
Meyer lemon					Shiny xylosma[b]
Olive					Sydney golden wattle[b]
Peruvian pepper[b]					
Ribbon gum					
Silver maple[b]					
Victorian box[b]					
Weeping willow[b]					

[a]Listed by common name in alphabetical order.
[b]Added to preliminary list.

percent of the total cover where total ground cover ranges from 90-100 percent (Hanes 1977). The associated species in each chaparral type are listed in Table III-8, based on Hanes (1977).

Because of the extreme complexity of species composition and areal distribution of the coastal sage and chaparral vegetation types it was necessary to restrict emission rate measurements to only the most dominant species in each type. Eight of the most frequently occurring species and one relatively rare species in the chaparral and coastal sage were sampled and these are shown in Table III-9.

Table III-8. Associated Species of Shrubs in the Chamise Ceanothus and Scrub Oak Chapparal Types

Type	Associated Species
Chamise chaparral (*Adenostoma fasciculatum*)	*Arctostaphylos* spp. *Ceanothus* spp. *Elymus condensatus* *Quercus dumosa* *Rhus ovata* *Rhus laurina* *Yucca whipplei*
Ceanothus chaparral (*Ceanothus* species)	*Adenostoma fasciculatum* *Quercus dumosa* *Heteromeles arbutifolia* *Rhus ovata*
Scrub oak chaparral (*Quercus dumosa*)	*Ceanothus leucodermis* *Cerococarpus betuloides* *Franxinus dipletela* *Garrya* spp. *Heteromeles arbutifolia* *Onicera* spp. *Prunus illicifolia* *Rhamnus crocea* ssp. (*ilicifolia*) *R. californica* *Rhus ovata* *Ribes* spp. *Sambucus* spp.

Table III-9. Natural Vegetation for which Emission Rate Measurements were Made

Common Name	Genus and Species
Black sage[a]	Salvia mellifera
Buckwheat	Eriogonum fasciculatum
Ceanothus	Ceanothus crassifolius
Chamise	Adenostoma fasciculatum
Encelia	Encelia farinosa
Manzanita	Arctostaphylos glandulosa
Rhamnus ceanothus[a]	Rhamnus crocea
Scrub oak	Quercus dumosa
Woolly blue curls[a]	Trichostema lanatum

[a]Added to preliminary list.

3. Agricultural Species Studied

Only one citrus species, the Meyer lemon, was studied and this is an ornamental. For reasons discussed elsewhere in this report, the few agricultural areas remaining in the CSCAB study area were excluded from this program.

Locations of Emission Rate Measurements. It was necessary to sample at only three locations in the study area of the California South Coast Air Basin to include all of the most abundant species identified for study. Tanbark Flats in the San Gabriel mountains and the Paramount Ranch in Agoura were chosen for the inland and coastal varieties of natural species, while the Los Angeles State and County Arboretum in Arcadia provided all of the necessary urban ornamental species (with the exception of pyracantha). The use of the Arboretum made it possible to avoid the time-consuming process of moving and re-establishing the instrumented mobile laboratory at a variety of urban sites.

Tanbark Flats. This site is approximately eight miles due north of LaVerne and is operated by the U. S. Department of Agriculture, Forest Service's Pacific Southwest Forest Range Experiment Station at San Dimas. It is in an isolated area in the San Gabriel mountains and had provisions for the necessary electrical power. It contains most of the inland-type varieties of natural vegetation found in the mountains and

foothills surrounding the CSCAB. The mobile laboratory was used here during the months of June and July, 1981 (which coincides with a major part of the smog season). Although this was also the dry season the vegetation did not appear to be totally dormant because of availability of subsurface water in this richly vegetated area. All but one of the emission rate values given for natural vegetation were from measurements conducted at the lysimeter area of the Tanbark Flats site.

Paramount Ranch. This site, near Agoura in the Santa Monica mountains, contains most of the natural coastal species, but a brush fire two years earlier had removed many of the species from the immediate area accessible to the mobile laboratory. For this reason, and due to time limitations, only one species was sampled here [Trichostema lanatum (woolly blue curls)], before the sampling program for urban ornamentals was begun.

Los Angeles State and County Arboretum, Arcadia. This site was centrally located in the CSCAB study area and offered convenient access to essentially all of the ornamental plant species deemed to be sufficiently abundant to warrant emission rate measurements. Moreover, the Arboretum staff, under the direction of Dr. Paul Cheo were most cooperative and helpful in making this study possible. By contrast the prospect of obtaining a similar high degree of cooperation and support at many individual residences or facilities within the study area seemed unlikely. Several species not found in the Arboretum were located on nearby streets. An electric cart was used to move sampling equipment and made it possible to return a sample taken by syringe to the instrumented laboratory within ten minutes or less. All of the species listed in Table III-7 were studied at the Arboretum.

University of California, Riverside. As previously noted ground cover and grass could be more accurately analyzed by enclosing an entire planted flat. Because these species were tested last, in the winter, it was most convenient to make measurements at UCR, using a greenhouse which provided temperatures more characteristic of spring or summer. Since these plants could be cared for under controlled conditions, it was felt that there was no reason not to conduct the emission rate measurements outside of the study area.

D. Results Obtained from Emission Rate Measurements

The plants for which hydrocarbon emission rates were determined by the chamber enclosure method are listed by genus and species, as well as by common name, in Tables III-10 through III-16. Also included in these tables are the date and time each sample was taken and the conditions of temperature, relative humidity and sunlight exposure under which the measurements were made. For each separate sample the steady state concentration obtained for each detected compound is given along with the dry weight of the leaf mass within the enclosure. The emission rates of isoprene and the monoterpenes per weight of leaf mass ($\mu g\ g^{-1}\ hr^{-1}$) are given in the final two columns.

The monoterpene rates for a given species were summed together, since only a single correction was necessary to normalize the data to a standard temperature. The algorithm used for this correction is discussed in Section VI. The individual monoterpene emission rates can be calculated from the individual steady-state concentrations which are given in Tables III-10 through III-16. Since multiple measurements for a given species were made in the great majority of cases, average emission rate values are given in the tables below the final experimental determination listed in each case. No compounds are shown for those cases where no measurable emissions of either isoprene or the monoterpenes were observed.

A summary of the emission rates given in these tables, including the pertinent corrected and averaged emission rates, is shown in Table III-17 and III-18 for native and urban species, respectively. The urban species are grouped into the six ornamental types discussed previously. All species investigated are shown in Tables III-17 and III-18, including those for which no measurable emissions were observed. Table III-19 summarizes the mean emission rates and standard deviations for those urban and natural species exhibiting measurable emissions of either isoprene or monoterpenes. The standard deviations obtained in the present study were generally substantially lower than those in similar, previous investigations. Again all emission rates are on a dry leaf weight basis.

Detection limits for isoprene and the monoterpenes ranged from ~1 to 5 ppbC. However, in units of $\mu g\ g^{-1}\ hr^{-1}$, those were highly variable as a result of the great variation in leaf tissue density. Thus while for most species detection limits ranged from ~0.1-2 $\mu g\ g^{-1}\ hr^{-1}$, for certain other

Table III-10. Conditions and Results for Emission Rate Measurements for Broad-Leaf Trees

Genus and Species	Common Name	Date	Sample Time, PST	Chamber Temp. °C	Sample RH, %	Sunlight Exposure	Compounds	Conc. ppbC	Dry Leaf Weight g	Isoprene Rate $\mu g\ g^{-1}\ hr^{-1}$	Sum of Monoterpene Rates $\mu g\ g^{-1}\ hr^{-1}$
Acer floridanum	Silver maple	10/7/81	1236	29.2	17%	partial	α-pinene	4.4	8.1		1.5
							Δ^3 carene	0.7			
							d-limonene	1.0			
"	"	"	1443	30.2	19%	full	α-pinene	8.9	7.1		2.6
							d-limone	0.6			
"	"	"	1543	25.4	28%	full	α-pinene	4.1	8.1		1.3
							d-limonene	0.3			
Acer floridanum	Silver maple	(average)								0	1.8
Cinnamonum camphora	Camphor	11/5/81	1121	25.6	35%	none			19.3		
"	"	"	1224	28.3	25%	none			16.6		
"	"	"	1432	24.0	31%	none			17.7		
Cinnamonum camphora	Camphor	(average)								0	0
Citrus limonia burm.	Meyer lemon	10/14/81	1028	27.1	18%	full			15.2		
"	"	"	1153	28.4	10%	full			6.9		
"	"	"	1319	29.9	<10%	full			16.4		
Citrus limonia burm.	Meyer lemon	(average)								0	0
Eucalyptus viminalis	Ribbon gum	8/20/81	0834	34.4	18%	full	isoprene	85.5	15.2	12	
"	"	"	0936	36.4	19%	full	isoprene	145.9	24.3	13	
"	"	9/1/81	0933	31.9	16%	full	isoprene	78.7	13.8	11	
Eucalyptus viminalis	Ribbon gum	(average)								12	0
Fraxinus uhdei	Evergreen ash	9/1/81	1058	31.4	17%	full			5.3		
"	"	"	1233	32.8	17%	full			4.1		
"	"	"	1344	35.4	s	full			9.9		
Fraxinus uhdei	Evergreen ash	(average)								0	0

Table III-10 (continued) - 2

Genus and Species	Common Name	Date	Sample Time, PST	Chamber Temp. °C	Sample RH, %	Sunlight Exposure	Compounds	Conc. ppbC	Dry Leaf Weight g	Isoprene Rate μg g^{-1} hr^{-1}	Sum of Monoterpene Rates μg g^{-1} hr^{-1}
Jacaranda ovalifolia	Jacaranda	9/11/81	0936	31.4	22%	partial			11.4		
"	"	"	1040	32.2	22%	partial			7.0		
"	"	"	1142	34.6	23%	partial			10.8		
Jacaranda ovalifolia	Jacaranda	(average)								0	0
Lagerstroemia indica	Crape myrtle	9/1/81	1550	34.0	17%	full			10.9	0	0
Magnolia grandiflora	Magnolia	9/3/81	1305	32.4	18%	full	α-pinene	152	43.4		10
							β-pinene	42.0			
							myrcene	7.4			
							d-limonene	9.1			
"	"	10/13/81	1211	23.4	27%	partial	α-pinene	25.5	32.6		2.2
							β-pinene	7.6			
"	"	"	1427	23.5	21%	none	α-pinene	33.6	34.0		3.2
							β-pinene	11.9			
Magnolia grandiflora	Magnolia	(average)								0	5.2
Olea europaea	Olive	11/20/81	1151	23.7	22%	partial	α-pinene	3.2	18.1		0.4
"	"	"	1256	27.5	38%	partial	α-pinene	5.9	30.5		0.4
"	"	"	1512	25.1	10%	partial	α-pinene	2.3	37.5		0.1
Olea europaea	Olive	(average)								0	0.3
Persea americana	Avocado	10/29/81	1305	22.8	19%	partial			15.4		
"	"	10/30/81	1011	30.8	13%	full			10.5		
"	"	"	1111	29.6	22%	full			28.3		
Persea americana	Avocado	(average)								0	0
Pittosporum undulatum	Victorian box	10/27/81	1427	22.4	19%	none			11.3		
"	"	"	1527	21.6	15%	none			21.7		
"	"	10/28/81	0936	23.5	16%	partial			13.1		
"	"	10/30/81	1514	27.2	20%	full			19.4		
Pittosporum undulatum	Victorian box	(average)								0	0

Table III-10 (continued) - 3

Genus and Species	Common Name	Date	Sample Time, PST	Chamber Temp. °C	Sample RH, %	Sunlight Exposure	Compounds	Conc. ppbC	Dry Leaf Weight g	Isoprene Rate $\mu g\ g^{-1}\ hr^{-1}$	Sum of Monoterpene Rates $\mu g\ g^{-1}\ hr^{-1}$
Platanus racemosa	Calif. sycamore	10/7/81	0858	26.6	34%	full	isoprene	37.9	20.9	3.8	
"	"	"	1006	29.9	25%	full	isoprene	58.4	10.7	12	
"	"	"	1113	33.3	26%	partial	isoprene	104	11.0	20	
Platanus racemosa	Calif. sycamore	(average)								12	0
Podocarpus gracilior	Fern pine	11/3/81	0952	30.8	34%	full			26.7		
"	"	"	1055	36.4	27%	full			47.2		
"	"	"	1156	37.4	12%	full			97.6		
Podocarpus gracilior	Fern pine	(average)								0	0
Pyrus kawakami	Evergreen pear	10/15/81	1410	22.5	29%	partial			29.8		
"	"	10/21/81	0820	22.5	28%	partial			48.8		
"	"	"	0920	26.6	24%	full			37.8		
Pyrus kawakami	Evergreen pear	(average)								0	0
Quercus agrifolia	Calif. live oak	9/30/81	1206	28.9	23%	partial	isoprene	175	19.5	18	
"	"	"	1307	29.8	32%	partial	isoprene	434	24.4	34	
"	"	10/14/81	0907	22.8	19%	full	isoprene	79.4	8.4	20	
Quercus agrifolia	Calif. live oak	(average)								24	0
Robinia pseudoacacia	Black locust	11/19/81	1102	29.5	15%	partial	isoprene	54.5	8.3	13	
"	"	"	1208	27.9	17%	partial	isoprene	29.0	5.7	10	
"	"	"	1314	27.7	16%	partial	isoprene	8.3	6.3	2	
Robinia pseudoacacia	Black locust	(average)								8	0
Salix babylonica	Weeping willow	11/25/81	0941	19.8	14%	partial	isoprene	15.1	1.7	24	
"	"	"	1043	22.6	11%	full	isoprene	19.8	0.9	60	
"	"	"	1148	21.3	16%	full	isoprene	22.3	1.7	36	
Salix babylonica	Weeping willow	(average)								40	0

Table III-10 (continued) - 4

Genus and Species	Common Name	Date	Sample Time, PST	Chamber Temp. °C	Sample RH, %	Sunlight Exposure	Compounds	Conc. ppbC	Dry Leaf Weight g	Isoprene Rate μg g^{-1} hr^{-1}	Sum of Monoterpene Rates μg g^{-1} hr^{-1}
Schinus molle	Peruvian pepper	10/28/81	1150	24.8	17%	partial			4.0		
"	"	"	1249	21.9	17%	none			3.3		
"	"	11/17/81	1240	21.1	24%	partial			10.3		
Schinus molle	Peruvian pepper	(average)								0	0
Schinus terebinthifolius	Brazilian pepper	10/29/81	0953	21.8	26%	partial	α-pinene	22.8	13.9		9.0
							β-pinene	1.3			
							p-cymene	1.4			
							d-limonene	5.6			
							unknown	28.1			
"	"	"	1056	21.0	47%	partial	α-pinene	72.2	24.6		9.2
							β-pinene	3.8			
							myrcene	7.5			
							Δ^3 carene	0.9			
							p-cymene	4.8			
							d-limonene	16.7			
							unknown	7.6			
"	"	"	1151	23.1	40%	partial	α-pinene	11.5	29.3		1.1
							p-cymene	1.3			
							d-limonene	1.8			
							unknown	1.4			
"	"	"	1316	30.8	20%	full	α-pinene	3.1	34.9		0.2
							d-limonene	0.1			
Schinus terebinthifolius	Brazilian pepper	(average)								0	4.9
Ulmus americana	American elm	10/8/81	0939	25.2	35%	partial			2.7		
"	"	"	1047	23.6	34%	partial			9.5		
"	"	"	1156	25.3	27%	partial			3.6		
Ulmus americana	American elm	(average)								0	0
Ulmus parvifolia	Chinese elm	10/9/81	1159	30.9	17%	partial			6.0		
"	"	"	1311	30.8	16%	partial			2.8		
"	"	"	1415	30.3	12%	partial			10.5		
Ulmus parvifolia	Chinese elm	(average)								0	0

[a]Insufficient data.

Table III-11. Conditions and Results for Emission Rate Measurements for Conifers

Genus and Species	Common Name	Date	Sample Time, PST	Chamber Temp. °C	Sample RH, %	Sunlight Exposure	Compounds	Conc. ppbC	Dry Leaf Weight g	Isoprene Rate $\mu g\ g^{-1}\ hr^{-1}$	Sum of Monoterpene Rates $\mu g\ g^{-1}\ hr^{-1}$
Cedrus deodara	Deodar cedar	9/16/81	0956	31.2	13%	partial	α-pinene	3.3	20.2		0.3
"	"	"	1103	36.3	15%	full	α-pinene	47.3	30.2		4.0
							myrcene	4.7			
							d-limonene	4.2			
"	"	"	1213	33.8	19%	full	α-pinene	6.2	28.7		0.5
							d-limonene	0.4			
"	"	"	1428	38.8	21%	full	α-pinene	35.1	48.4		2.0
							myrcene	3.4			
							Δ^3 carene	1.4			
							d-limonene	3.9			
Cedrus deodara	Deodar cedar	(average)								0	1.7
Cupressus sempervirens	Italian cypress	9/9/81	0912	36.8	16%	full	α-pinene	3.4	100.9		0.2
							myrcene	3.7			
							d-limonene	3.9			
"	"	"	1217	39.6	14%	full	α-pinene	3.9	146.8		0.1
							d-limonene	2.3			
"	"	"	1432	35.0	23%	partial	myrcene	7.9	162.8		0.2
							d-limonene	8.4			
Cupressus sempervirens	Italian cypress	(average)								0	0.2
Pinus canariensis	Canary Island pine	11/19/81	1431	26.8	12%	full	α-pinene	5.5	42.0		0.8
							d-limonene	1.2			
"	"	11/20/81	0933	18.9	10%	partial	α-pinene	12.8	17.1		1.5
Pinus canariensis	Canary Island pine	(average)								0	1.2

Table III-11 (continued) - 2

Genus and Species	Common Name	Date	Sample Time, PST	Chamber Temp. °C	Sample RH, %	Sunlight Exposure	Compounds	Conc. ppbC	Dry Leaf Weight g	Isoprene Rate $\mu g\ g^{-1}\ hr^{-1}$	Sum of Monoterpene Rates $\mu g\ g^{-1}\ hr^{-1}$
Pinus halepensis	Aleppo pine	8/28/81	0911	36.1	16%	full	α-pinene	2.3	10.9		1.4
							myrcene	3.2			
							d-limonene	1.5			
"	"	9/3/81	0831	26.9	22%	full	d-limonene	0.5	12.7		0.1
"	"	9/9/81	1112	33.3	23%	full	α-pinene	3.6	28.9		0.7
							myrcene	5.3			
							d-limonene	1.3			
Pinus halepensis	Aleppo pine	(average)								0	0.7
Pinus pinea	Italian stone pine	9/29/81	1250	23.6	13%	none			9.6		
"	"	"	1434	24.2	27%	none			27.9		
Pinus pinea	Italian stone pine	(average)								0	0
Pinus radiata	Monterey pine	9/29/81	0947	21.8	28%	none	α-pinene	5.3	92.4		0.3
							β-pinene	4.8			
							d-limonene	2.3			
"	"	"	1116	21.8	17%	none	α-pinene	1.1	45.0		0.3
							β-pinene	2.3			
							myrcene	1.7			
							d-limonene	1.4			
"	"	11/24/81	0939	17.4	<10%	none	α-pinene	1.6	22.1		0.3
							β-pinene	1.1			
Pinus radiata	Monterey pine	(average)								0	0.3

Table III-12. Conditions and Results for Emission Rate Measurements for Flowers and Ground Cover

Genus and Species	Common Name	Date	Sample Time, PST	Chamber Temp. °C	Sample RH, %	Sunlight Exposure	Compounds	Conc. ppbC	Area m^2	Isoprene Rate $\mu g\ m^{-2}\ hr^{-1}$	Sum of Monoterpene Rates $\mu g\ m^{-1}\ hr^{-1}$
Hedera helix Hahnii	English ivy	2/23/82	1407	32.7	56%	partial			0.2		
"	"	2/24/82	0922	20.1	63%	none			0.2		
"	"	"	1028	20.3	63%	none			0.2		
Hedera helix Hahnii	English ivy	(average)								0	0
Lampranthus aurantiacus	Ice plant	2/23/82	0928	26.8	75%	partial			0.2		
"	"	2/24/82	1325	25.4	77%	none			0.2		
Lampranthus aurantiacus	Ice plant	(average)								0	0
Osteospermum fruticosum	African daisy	2/24/82	1132	20.0	67%	none	α-pinene	7.2	0.2		160
							β-pinene/ myrcene	4.1	0.2		
"	"	2/25/82	1316	29.0	73%	partial	α-pinene	15.3	0.2		340
							β-pinene/ myrcene	9.7	0.2		
Osteospermum fruticosum	African daisy	(average)								0	250
Pelargonium spp.	Geranium	9/28/81	1341	30.2	12%	partial			2.4[a]		
"	"	9/30/81	0918	29.6	13%	partial			3.5[a]		
"	"	"	1024	30.9	15%	partial			5.4[a]		
Pelargonium spp.	Geranium	(average)								0	0
Vinca Minor	Common periwinkle	2/23/82	1034	28.9	49%	partial			0.2	0	0

[a]Dry leaf weight (g).

Table III-13. Conditions and Results for Emission Rate Measurements for Grasses

Genus and Species	Common Name	Date	Sample Time, PST	Chamber Temp. °C	Sample RH, %	Sunlight Exposure	Compounds	Conc. ppbC	Area m^2	Isoprene Rate $\mu g\ m^{-2}\ hr^{-1}$	Sum of Monoterpene Rates $\mu g\ m^{-1}\ hr^{-1}$
Cynodon dactylon	Bermuda hybrid	2/24/82	1537	23.6	63%	none			0.2		
"	"	2/25/82	1417	29.0	70%	partial			0.2		
Cynodon dactylon	Bermuda hybrid	(average)								0	0
Festuca elatior	Tall fescue	2/25/82	1008	25.9	71%	partial			0.2		
"	"	"	1621	25.3	73%	partial			0.2		
Festuca elatior	Tall fescue	(average)								0	0
Lolium perenne	Perennial ryegrass	2/25/82	1110	25.5	76%	none			0.2		
"	"	2/26/82	0847	25.2	80%	full			0.2		
Lolium perenne	Perennial ryegrass	(average)								0	0
Poa pratensis	Kentucky bluegrass	2/25/82	0904	22.3	68%	none			0.2		
"	"	"	1519	26.6	73%	none			0.2		
Poa pratensis	Kentucky bluegrass	(average)								0	0

Table III-14. Conditions and Results for Emission Rate Measurements for Palms

Genus and Species	Common Name	Date	Sample Time, PST	Chamber Temp. °C	Sample RH, %	Sunlight Exposure	Compounds	Conc. ppbC	Dry Leaf Weight g	Isoprene Rate $\mu g\ g^{-1}\ hr^{-1}$	Sum of Monoterpene Rates $\mu g\ g^{-1}\ hr^{-1}$
Phoenix dactylifera	Date palm	2/19/82	1557	31.5	27%	full	isoprene	725	134.1	18	
"	"	2/22/82	1008	27.1	32%	partial	isoprene	395	134.1	8.9	
"	"	"	1114	33.0	18%	partial	isoprene	1130	134.1	25	
Phoenix dactylifera	Date palm	(average)								17	0
Washingtonia filifera	Calif. fan palm	11/10/81	1038	28.8	28%	full	isoprene	89.9	7.1	26	
"	"	"	1137	31.3	29%	full	isoprene	58.8	7.1	17	
"	"	"	1238	31.4	27%	full	isoprene	18.9	7.1	6	
"	"	2/26/82	1155	26.2	51%	full	isoprene	69.1	52.7	3.8	
"	"	"	1310	23.9	54%	full	isoprene	22.2	50.0	1.3	
"	"	"	1432	22.4	54%	full	isoprene	3.8	52.5	0.2	
Washingtonia filifera	Calif. fan palm	(average)								9	0

Table III-15. Conditions and Results for Emission Rate Measurements for Shrubs

Genus and Species	Common Name	Date	Sample Time, PST	Chamber Temp. °C	Sample RH, %	Sunlight Exposure	Compounds	Conc. ppbC	Dry Leaf Weight g	Isoprene Rate μg g^{-1} hr^{-1}	Sum of Monoterpene Rates μg g^{-1} hr^{-1}
Acacia longifolia	Sydney golden wattle	10/27/81	1104	23.2	26%	partial			8.5		
"	"	"	1212	22.9	35%	partial			13.8		
"	"	"	1323	22.4	23%	none			7.5		
Acacia longifolia	Sydney golden wattle	(average)								0	0
Callistemon citrinus	Bottlebrush	11/11/81	1101	24.0	10%	partial	isoprene	8.7	7.5	2.8	
"	"	"	1201	32.3	12%	full	isoprene	92.1	5.7	32	
"	"	"	1259	33.5	14%	full	isoprene	127	11.1	24	
Callistemon citrinus	Bottlebrush	(average)								20	0
Camellia sasanqua	Camellia	10/14/81	1548	19.9	10%	partial			7.3		
"	"	10/15/81	0915	17.8	14%	partial			7.4		
"	"	"	1042	19.4	15%	partial			12.6		
Camellia sasanqua	Camellia	(average)								0	0
Carissa macrocarpa	Natal plum	11/3/81	1408	34.1	<10%	full			13.1		
"	"	"	1515	30.6	13%	full			8.8		
"	"	"	1618	23.4	-	full			6.3		
Carissa macrocarpa	Natal plum	(average)								0	0
Cotoneaster pannosa	Cotoneaster	10/29/81	1508	21.9	15%	partial			3.6		
"	"	"	1610	19.6	<10%	partial			0.9		
"	"	10/30/81	1212	33.3	16%	full			19.3		
Cotoneaster pannosa	Cotoneaster	(average)								0	0
Hibiscus spp.	Hibiscus	11/25/81	1448	20.5	24%	partial			10.0		
"	"	"	1547	20.2	<10%	full			22.3		
Hibiscus spp.	Hibiscus	(average)								0	0

Table III-15 (continued) - 2

Genus and Species	Common Name	Date	Sample Time, PST	Chamber Temp. °C	Sample RH, %	Sunlight Exposure	Compounds	Conc. ppbC	Dry Leaf Weight g	Isoprene Rate $\mu g\ g^{-1}\ hr^{-1}$	Sum of Monoterpene Rates $\mu g\ g^{-1}\ hr^{-1}$
Juniperus chinensis	Chinese juniper	9/11/81	1442	37.8	<10%	partial	d-limonene	0.5	31.4		0
"	"	9/15/81	0739	26.4	20%	full	myrcene	5.2	23.5		0.7
							d-limonene	2.6			
"	"	"	0848	29.0	16%	full	α-pinene	1.1	39.2		0.2
							myrcene	1.6			
							d-limonene	0.6			
"	"	"	1306	40.0	12%	partial	α-pinene	4.3	17.2		3.3
							myrcene	14.2			
							p-cymene	1.0			
							d-limonene	6.6			
Juniperus chinensis	Chinese juniper	(average)								0	1.1
Ligustrum lucidum	Glossy privet	11/4/81	1009	26.5	20%	full			15.3		
"	"	"	1116	27.5	19%	full			15.8		
"	"	"	1222	30.6	12%	partial			13.5		
Ligustrum lucidum	Glossy privet	(average)								0	0
Myrtus communis	Common myrtle	11/4/81	1331	30.4	19%	partial	isoprene	540	18.1	57	
"	"	"	1541	21.6	17%	partial	isoprene	12.8	15.9	1.4	
"	"	11/5/81	0955	19.0	42%	partial	isoprene	28.5	27.1	1.8	
"	"	11/6/81	1105	22.0	21%	partial	isoprene	110	10.4	21	
"	"	11/10/81	1337	34.7	<10%	full	isoprene	430	12.4	69	
Myrtus communis	Common myrtle	(average)								30	0
Nandina domestica	Heavenly bamboo	9/22/81	1332	37.0	15%	full	isoprene	457	15.2	60	
"	"	"	1440	31.5	17%	full	isoprene	114	11.6	20	
"	"	"	1541	32.1	14%	full	isoprene	113	7.0	32	
Nandina domestica	Heavenly bamboo	(average)								37	0

Table III-15 (continued) - 3

Genus and Species	Common Name	Date	Sample Time, PST	Chamber Temp. °C	Sample RH, %	Sunlight Exposure	Compounds	Conc. ppbC	Dry Leaf Weight g	Isoprene Rate µg g^{-1} hr^{-1}	Sum of Monoterpene Rates µg g^{-1} hr^{-1}
Nerium oleander	Oleander	9/10/81	1343	40.5	<10%	full			6.4		
"	"	9/10/81	1447	39.1	<10%	full			4.8		
"	"	9/11/81	0836	27.4	20%	partial			4.1		
Nerium oleander	Oleander	(average)								0	0
Pittosporum tobira	Japanese pittosporum	10/13/81	0854	20.5	29%	full			10.8		
"	"	"	1000	23.5	28%	partial			11.5		
"	"	"	1106	22.8	26%	partial			10.4		
Pittosporum tobira	Japanese pittosporum	(average)								0	0
Raphiolepis indica	India-hawthorn	9/15/81	1516	34.3	16%	partial			17.2		
"	"	9/16/81	1536	34.4	14%	partial			39.9		
"	"	9/18/81	1118	35.7	21%	partial			30.0		
"	"	"	1226	40.6	14%	partial			14.8		
Raphiolepis indica	India-hawthorn	(average)								0	0
Rosa spp.	Rose	9/28/81	1023	28.4	30%	partial			11.9		
"	"	"	1154	32.1	17%	partial			13.9		
"	"	"	1305	34.4	17%	partial			7.1		
Rosa spp.	Rose	(average)								0	0
Tecomaria capensis	Cape-honeysuckle	9/17/81	0914	33.1	11%	partial			3.1		
"	"	"	1019	38.1	12%	partial			2.8		
"	"	"	1120	39.8	14%	full			3.0		
Tecomaria capensis	Cape-honeysuckle	(average)								0	0
Xylosma congestum	Shiny xylosma	11/10/81	1536	25.6	11%	partial	isoprene	11.6	11.8	2.0	
"	"	11/11/81	1401	28.7	12%	partial	isoprene	28.7	7.2	7.6	
"	"	"	1500	27.6	14%	partial	isoprene	10.7	3.6	5.6	
Xylosma congestum	Shiny xylosma	(average)								5.0	0

Table III-16. Conditions and Results for Emission Rate Measurements for Naturally Occurring Vegetation

Genus and Species	Common Name	Date	Sample Time, PST	Chamber Temp. °C	Sample RH_b %	Sunlight Exposure	Compounds	Conc. ppbC	Dry Leaf Weight g	Isoprene Rate $\mu g\ g^{-1}\ hr^{-1}$	Sum of Monoterpene Rates $\mu g\ g^{-1}\ hr^{-1}$
Adenostoma fasciculatum	Chamise	7/2/81	0728	30.9	35%	full			8.8		
"	"	7/8/81	0950	30.1	44%	full			7.6		
"	"	"	1153	30.1	44%	full			7.6		
Adenostoma fasciculatum	Chamise	(average)								0	0
Adenostoma fasciculatum	Chamise	3/4/82	1052	19.4	27%	full			a		
"	"	"	1220	22.9	39%	full			a		
"	"	"	1341	23.4	25%	full			a		
Adenostoma fasciculatum	Chamise	(average)								0	0
Arctostaphylos glandulosa	Manzanita	7/9/81	0724	22.4	50%	full			23.9		
"	"	"	1219	45.7	33%	full			23.9		
Arctostaphylos glandulosa	Manzanita	(average)								0	0
Artemesia californica	Calif. sage brush	3/3/82	0911	18.2	64%	full	Unknown[b]	81.0	32.3		7.5
"	"	"	1020	17.7	85%	full	Unknown[b]	8.9	32.3		0.8
"	"	"	1134	24.2	80%	full	α-pinene	5.3	71.8		2.8
							Unknown[b]	64.5			
Artemesia californica	Calif. sage brush	(average)								0	3.7
Ceanothus crassifolius	Ceanothus	7/1/81	0951	28.9	30%	partial			6.3		
"	"	"	1050	31.3	33%	partial			6.3		
"	"	"	1359	33.3	29%	full			12.4		
Ceanothus crassifolius	Ceanothus	(average)								0	0
Encelia farinosa	Encelia	3/3/82	1327	19.8	91%	full	α-pinene	84.6	54.6		4.3
"	"	"	1603	14.5	58%	partial	α-pinene	33.8	49.9		1.8
"	"	3/4/82	0906	16.2	71%	full	α-pinene	21.3	49.8		1.2
Encelia farinosa	Encelia	(average)								0	2.4

Table III-16 (continued) - 2

Genus and Species	Common Name	Date	Sample Time, PST	Chamber Temp. °C	Sample RH, %	Sunlight Exposure	Compounds	Conc. ppbC	Dry Leaf Weight g	Isoprene Rate $\mu g\ g^{-1}\ hr^{-1}$	Sum of Monoterpene Rates $\mu g\ g^{-1}\ hr^{-1}$
Eriogonum fasciculatum	Buckwheat	6/30/81	0755	30.7	36%	full			20.9		
"	"	"	0900	34.4	30%	full			6.0		
"	"	"	1003	36.2	24%	full			6.0		
Eriogonum fasciculatum	Buckwheat	(average)								0	0
Quercus dumosa	Scrub oak	7/2/81	0827	37.8	36%	full	isoprene	432	9.7	100	
"	"	"	0933	38.8	24%	full	isoprene	460	9.7	100	
"	"	7/8/81	1251	42.0	33%	full	isoprene	425	5.8	160	
"	"	7/9/81	0920	32.7	44%	full	isoprene	91.0	5.9	33	
Quercus dumosa	Scrub oak	(average)								98	0
Rhamnus crocea	Rhamnus ceanothus	7/9/81	1319	40.4	26%	full	isoprene	1170	25.3	110	
"	"	7/14/81	0821	31.7	25%	partial	isoprene	62.9	4.3	35	
"	"	"	0921	38.2	16%	partial	isoprene	248	4.3	140	
Rhamnus crocea	Rhamnus ceanothus	(average)								95	0
Rhus ovata	Sugar bush	6/30/81	1224	41.9	19%	full			22.6		
"	"	7/1/81	0753	23.8	32%	full			22.6		
"	"	"	0853	31.3	34%	full			22.6		
"	"	"	1252	36.4	21%	partial			22.6		
Rhus ovata	Sugar bush	(average)								0	0
Salvia mellifera	Black sage	7/9/81	1424	30.6	29%	full	α-pinene	1.4	2.7		12.3
							myrcene	9.8			
							d-limonene	3.9			
Salvia mellifera	Black sage	(average)								0	
Trichostema lanatum	Woolly blue curls	7/16/81	1306	40.9	38%	full	α-pinene	29.3	3.7		47.2
							β-pinene	7.7			
							myrcene	29.7			
							d-limonene	8.4			
Trichostema lanatum	Woolly blue curls	(average)								0	47.2

[a]Dry leaf weight not obtained.
[b]Unknowns possibly terpenes.

Table III-17. Emission Rates Measured for Naturally Occurring Vegetation [a]

Genus and Species	Emission Rate $\mu g\ g^{-1}\ hr^{-1}$	
	Isoprene	Monoterpenes
Adenostoma fasciculatum (c)	-	-
Arctostaphylos glandulosa (c)	-	-
Artemesia californica	-	8
Ceanothus crassifolius (c)	-	-
Encelia farinosa	-	6
Eriogonum fasciculatum (c and cs)	-	-
Quercus dumosa (c and cs)[b]	35	-
Rhamnus crocea (c)	37	-
Rhus ovata (c and cs)	-	-
Salvia mellifera (cs)	-	12
Trichostema lanatum[c] (cs)	-	21

[a]Corrected to 30°C.
[b]Member of chaparral (c) and/or coastal sage (cs).
[c]A relatively rare component of the coastal sage scrub.
(-) Not observed at detection limit.

species detection limits were in the range 5-15 $\mu g\ g^{-1}\ hr^{-1}$, with a few much higher (e.g., California live oak - 50 $\mu g\ g^{-1}\ hr^{-1}$). Finally, ground covers generally had detection limits in the range 70-80 $\mu g\ m^{-2}\ hr^{-1}$ (for comparison African daisy was observed to have an emission rate of 350 $\mu g\ m^{-2}\ hr^{-1}$).

1. Natural Vegetation

The following observations can be made for the natural species sampled and their emission rates for isoprene and monoterpenes as shown in Table III-17. A notable species in this list is scrub oak (Quercus dumosa) because it emits isoprene and because it is a component of both the coastal sage and chapparral types. A second notable species is black sage (Salvia mellifera) which emits monoterpenes and often makes up as much as 50 percent of the coastal sage cover.

Rhamnus ceanothus (Rhamnus crocea) also emits isoprene, but this species is usually a minor component of the scrub oak chaparral type. Woolly blue curls (Trichostema lanatum) emits monoterpenes but is a relatively rare species in the ccastal sage scrub.

Table III-18. Summary of Hydrocarbon Emission Rate Determinations for Urban Vegetation[a]

Common Name	Genus and Species	Average isoprene emission rate $\mu g\ g^{-1}\ hr^{-1}$	Average of sum of monoterpene emission rates $\mu g\ g^{-1}\ hr^{-1}$
Broad-Leaf Trees			
American elm	Ulmus americana	-	-
Avocado	Persea americana	-	-
Black locust	Robina pseudoacacia	11	-
Brazilian pepper	Schinus terebinthifolius	-	9
California live oak	Quercus agrifolia	49	-
California sycamore	Platanus racemosa	11	-
Camphor	Cinnamonum camphora	-	-
Chinese elm	Ulmus parvifolia	-	-
Crape myrtle	Lagerstroemia indica	-	-
Evergreen ash	Fraxinus uhdei	-	-
Evergreen pear	Pyrus kawakami	-	-
Fern pine	Podocarpus graciliar	-	-
Jacaranda	Jacaranda ovalifolia	-	-
Magnolia	Magnolia grandiflora	-	6
Meyer lemon	Citrus limonia burm.	-	-
Olive	Olea europaea	-	0.4
Peruvian pepper	Schinus molle	-	-
Ribbon gum	Eucalyptus viminalis	7	-
Silver maple	Acer floridanum	-	2
Victorian box	Pittosporum undulatum	-	-
Weeping willow	Salix babylonica	233	-
Conifers			
Aleppo pine	Pinus halepensis	-	0.5
Canary Island pine	Pinus canariensus	-	2
Deodar cedar	Cedrus deodara	-	1
Italian cypress	Cupressus sempervirens	-	0.1
Italian stone pine	Pinus pinea	-	-
Monterey pine	Pinus radiata	-	0.6
Flower and Ground Cover			
African daisy	Osteospermum fruticosum	-	350[b]
Common periwinkle	Vinca minor	-	-
English ivy	Hedera helix Hahnii	-	-
Geranium	Pelargonium spp.	-	-
Ice plant	Lampranthus auranticis	-	-

Table III-18 (continued) - 2

Common Name	Genus and Species	Average isoprene emission rate $\mu g\ g^{-1}\ hr^{-1}$	Average of sum of monoterpene emission rates $\mu g\ g^{-1}\ hr^{-1}$
Grasses			
Bermuda hybrid	Cynodon dactylon	-	-
Kentucky bluegrass	Poa pratensis	-	-
Perennial ryegrass	Lolium perenne	-	-
Tall fescue	Festuca elatior	-	-
Palms			
California fan palm	Washingtonia filifera	11	-
Date palm	Phoenix dactylifera	15	-
Shrubs			
Bottlebrush	Callistemon citrinus	15	-
Camellia	Camellia sasanqua	-	-
Cape-honeysuckle	Tecomaria capensis	-	-
Chinese juniper	Juniperus chinensis	-	0.7
Common myrtle	Myrtus communis	44	-
Cotoneaster	Cotoneaster pannosa	-	-
Glossy privet	Ligustrum lucidum	-	-
Heavenly bamboo	Nandina domestica	20	-
Hibiscus	Hibiscus spp.	-	-
India-hawthorn	Raphiolepis indica	-	-
Japanese pittosporum	Pittosporum tobira	-	-
Natal plum	Carissa macrocarpa	-	-
Oleander	Nerium oleander	-	-
Rose	Rosa spp.	-	-
Shiny xylosma	Xylosma congestum	8	-
Sydney golden wattle	Acacia longifolia	-	-

[a]Corrected to 30°C.
[b]$\mu g\ m^{-2}\ hr^{-1}$.
(-) Not observed at detection limit.

Several of the most common species (Table III-16) namely, sugar bush (Rhus ovata), buckwheat (Eriogonum fasciculatum), ceanothus (Ceanothus crassifolius), manzanita (Arctostaphylos glandulosa) and chamise (Adenostoma fasciculatum) did not emit measurable amounts of either isoprene or the monoterpenes. It is quite significant that chamise was a

Table III-19. Mean Emission Rates and Standard Deviations for Urban and Naturally Occurring Vegetation[a]

Common Name	Genus and Species	Mean Isoprene Emission Rate $\mu g\ g^{-1}\ hr^{-1}$	Mean Monoterpene Emission Rate $\mu g\ g^{-1}\ hr^{-1}$
Urban			
Broad-Leaf Trees			
Black locust	Robina pseudoacacia	11 ± 7	
Brazilian pepper	Schinus terebinthifolius		9 ± 9
California live oak	Quercus agrifolia	49 ± 37	
California sycamore	Platanus racemosa	11 ± 3	
Magnolia	Magnolia grandiflora		6 ± 3
Olive	Olea europaea		0.4 ± 0.3
Ribbon gum	Eucalyptus viminalis	7 ± 1	
Silver maple	Acer floridanum		2 ± 0.5
Weeping willow	Salix babylonica	233 ± 46	
Conifers			
Aleppo pine	Pinus halepensis		0.6 ± 0.4
Canary Island pine	Pinus canariensus		2 ± 2
Deodar cedar	Cedrus deodara		1 ± 1
Italian cypress	Cupressus sempervirens		0.1 ± 0.0
Monterey pine	Pinus radiata		0.6 ± 0.2
Flower and Ground Cover			
African daisy	Osteospermum fruticosum		350[b] ± 28
Palms			
California fan palm	Washingtonia filifera	11 ± 12	
Date palm	Phoenix dactylifera	15 ± 1	
Shrubs			
Bottlebrush	Callistemon citrinus	15 ± 6	
Chinese juniper	Juniperus chinensis		0.7 ± 0.7
Common myrtle	Myrtus communis	44 ± 39	
Heavenly bamboo	Nandina domestica	20 ± 5	
Shiny xylosma	Xylosma congestum	8 ± 3	
Natural			
Black sage	Salvia mellifera		12[c]
California sage brush	Artemesia californica		8 ± 9
Encelia	Encelia farinosa		6 ± 3
Rhamnus ceanothus	Rhamnus crocea	37 ± 12	
Scrub oak	Quercus dumosa	35 ± 10	
Woolly blue curls	Trichostema lanatum		21[c]

[a]Corrected to 30°C.

[b]$\mu g\ m^{-2}\ hr^{-1}$.

[c]Values from one measurement.

non-emitter because it occupies vast acreages and represents a very large proportion of the biomass in the chaparral regions.

2. Urban Vegetation

Several features are apparent from the values obtained for the emission rates for urban species. First, many of the plants did not produce detectable amounts of hydrocarbons (Table III-17 and III-18). Secondly, isoprene rates were either high or not detectable; there were no cases of emission just above the detection limit. Monoterpene emission rates were generally lower than isoprene and often near the detection limit. Finally, from the above data, isoprene appears to contribute more significantly to vegetative hydrocarbon emissions than all of the monoterpenes combined for the dominant species in the study area.

E. Comparison of Present Results with Other Work

Although many hydrocarbon emission rate studies on a variety of plant species have been performed in the past (see Tables III-1 and III-3), the preponderance of the data cannot be strictly intercompared. While inconsistencies in reported units, reported temperatures and methodologies were prevalent, the major problem was with discrepancies in the units used to report emission rates. For example, ppb, ppb in^{-2} min^{-1}, kg km^{-2} d^{-1}, and μg g^{-1} hr^{-1} are only some of the units that have been used. In the present study, the units μg g^{-1} hr^{-1} were adopted in order to be consistent with recently published data (Zimmerman 1979a, Tingey 1981, Evans et al. 1982) and to be most useful for further calculations.

Additionally emission rates have been reported over the range of temperatures from 9 to 32°C. Since it has been shown that isoprene and monoterpene emissions vary exponentially with temperature (Tingey et al. 1979), all emission measurements were corrected to 30°C using the formulae detailed in Section VI. This temperature was chosen because it was determined to be characteristic of mid-day summer temperatures throughout the study area.

Finally, methods used in measuring plant emissions differed widely, ranging from measuring emissions from individual plant leaves enclosed in chambers (Rasmussen 1972) to measuring emissions from unenclosed plants in a forest (Arnts et al. 1978, 1982).

Tables III-20 and III-21 compare the present work with two sources that most closely match the parameters used in the present study, namely Evans et al. (1982) and Zimmerman (1979a,b). Since neither of these investigators performed measurements in the Southern California locale, only one species, Ulmus americana, was measured in both studies. However, in all but one case, [Lagerstroemia indica (Crape myrtle) versus Myrtica cerifera (Wax myrtle)], the comparisons made in Tables III-20 and III-21 are between plants of the same genus.

Table III-20 also compares emission rates of different species within the same genus, Quercus, by one investigator, Zimmerman. He observed significant variability between species of the same genus. Therefore, it is not surprising that the emission rate data from the present study vary significantly in many cases from those of Zimmerman (1979a) and Evans et al. (1982). There is, however, excellent agreement between the present results and those of Zimmerman (1979a) and Evans et al. (1982) with respect to the type of hydrocarbon emitted by a given plant (i.e., whether the plant emits isoprene, monoterpenes, or neither).

Table III-20. Comparisons of Emission Rates for Isoprene and Selected Monoterpenes[a]

Plant Type	Isoprene Emission Rate $\mu g\ g^{-1}\ hr^{-1}$		Sum of Monoterpene Emission Rates $\mu g\ g^{-1}\ hr^{-1}$	
	Zimmerman 1979a	Present Work	Zimmerman 1979a	Present Work
Acacia longifolia		-		-
Sweet acacia[b]	-		4.5	
Acer floridanum		-		2
Acer rubrum	-		0.5	
Cupressus sempervirens		-		0.1
Cypress[b]	-		8.2	
Fraxinus caroliniana	-		-	
Fraxinus uhdei		-		-
Lagerstroemia indica		-		-
Myrtica cerifera	-		1	
Neruim oleander		-		-
Oleander[b]	-		-	
Quercus agrifolia		49		-
Quercus dumosa		35		-
Quercus laevis	23		0.6	
Quercus laurifolia	10		-	
Quercus myrtifolia	15		-	
Quercus nigra	24		<0.1	
Quercus virginiana	9.1		0.1	
Salix babylonica		233		-
Salix caroliniana	12		-	
Ulmus americana	-	-	-	-

[a]Emission rates corrected to 30°C.
[b]Genus and species not given.
(-) Below detection limit.

Table III-21. Comparisons of Emission Rates for Isoprene and Selected Monoterpenes[a]

Plant Type	Isoprene Emission Rate $\mu g\ g^{-1}\ hr^{-1}$		Sum of Monoterpene Emission Rates $\mu g\ g^{-1}\ hr^{-1}$	
	Evans et al. (1982)	Present Work	Evans et al. (1982)	Present Work
Acer sacharum	-		1.8	
Acer floridanum		-		1.7
Eucalyptus globulus	44		8.3	
Eucalyptus viminalis		4		-
Platanus occidentalis	21		-	
Platanus racemosa		7		-
Quercus borealis	15		-	
Quercus agrifolia		33		-
Rhamnus Californica	22		-	
Rhamnus crocea		25		-
Salix nigra	19		-	
Salix babylonica		157		-

[a]Corrected to 28°C.
(-) Below detection limit.