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EXECUTIVE SUMMARY

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

Final Report

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EXECUTIVE 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 Francisco 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 Dimitriadis (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 λ 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 chaparral 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

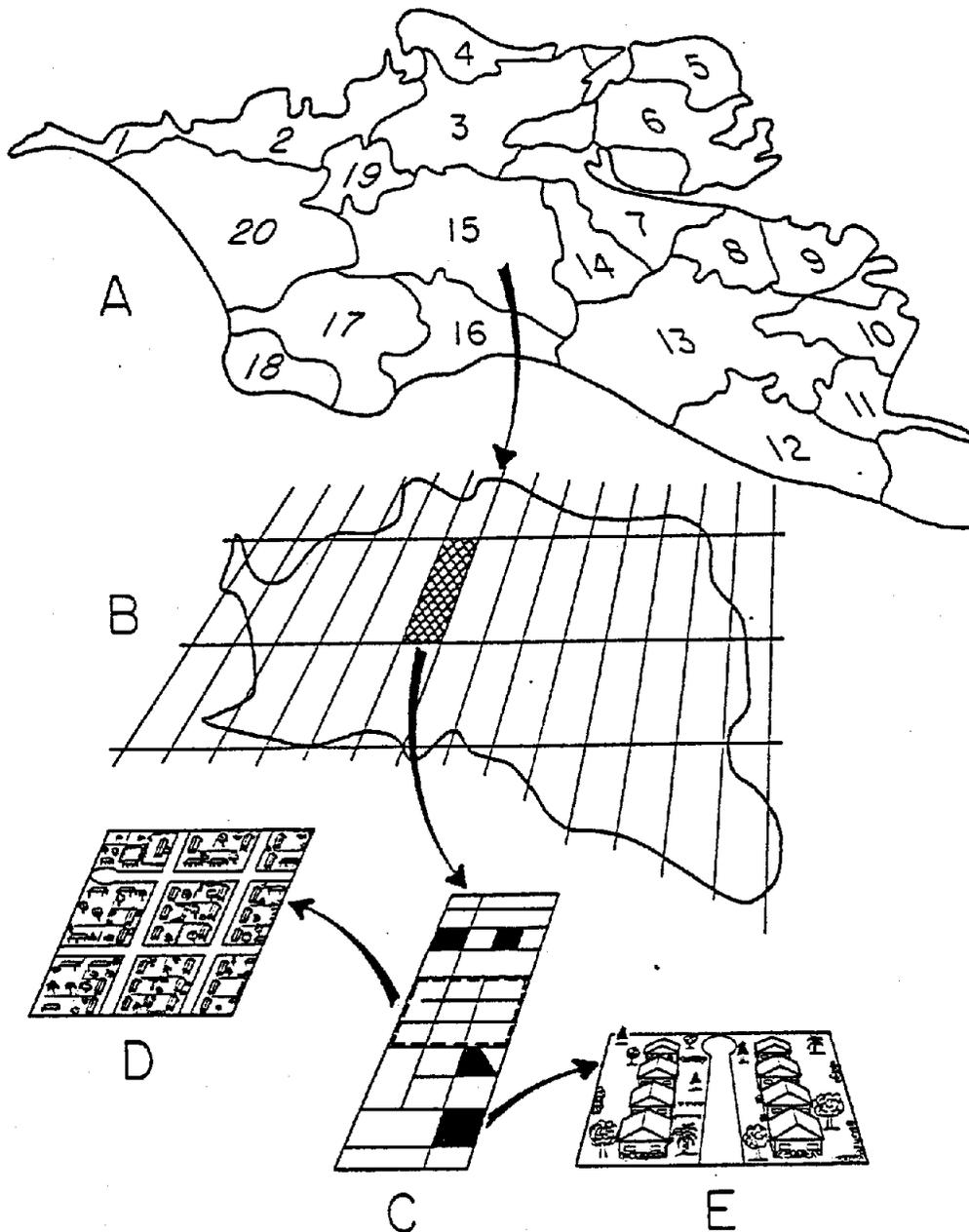


Figure I-1. Depiction of the three-stage, stratified, random sampling design used in this study. A. Twenty stratified polygons covering urban portion of study area; B. Polygon with sample cell grid and randomly selected cell; C. Randomly selected sample cell showing center frame of color infrared imagery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

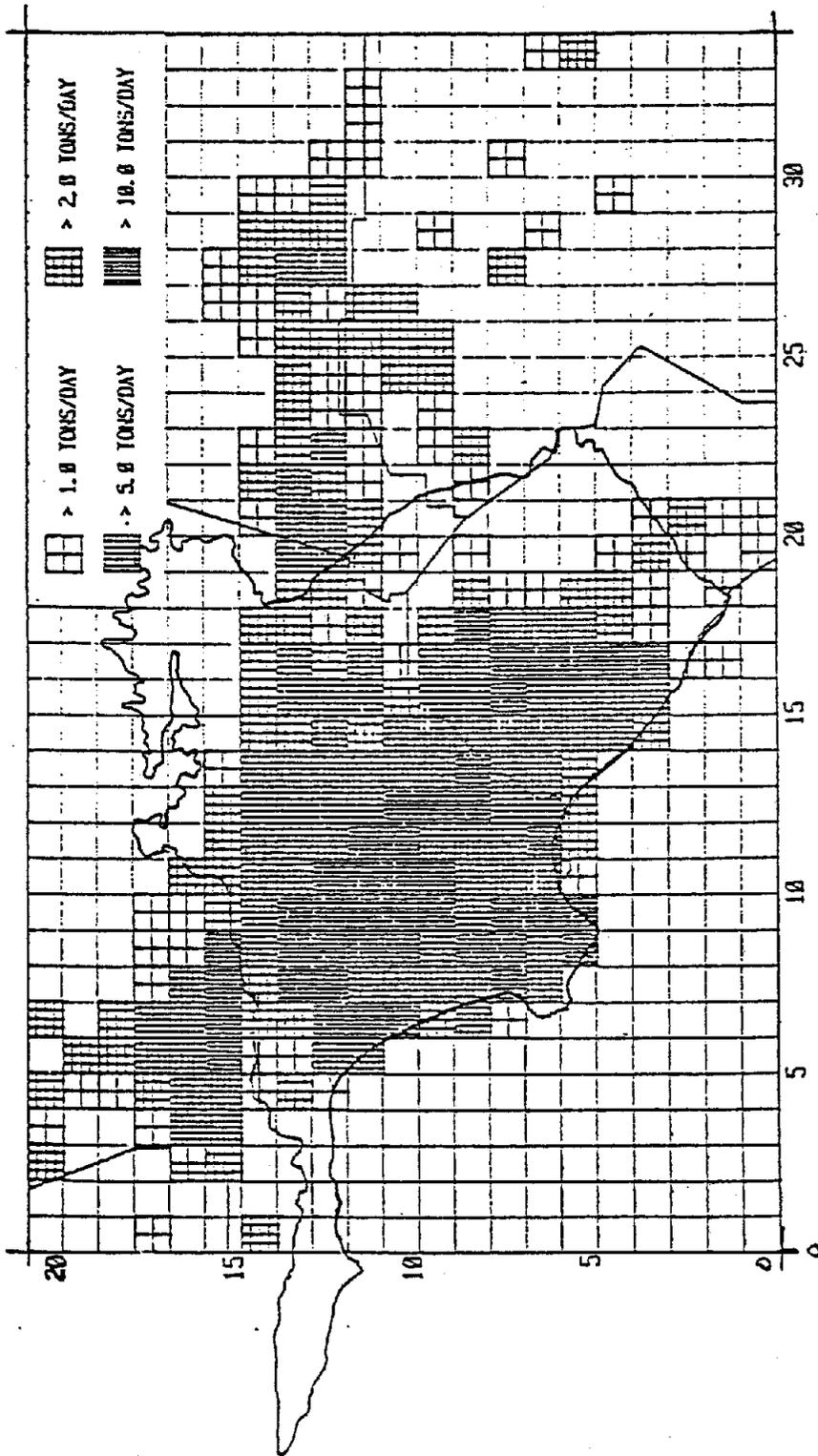


Figure I-2. Spatial distribution of reactive organic gas emissions from anthropogenic sources; 1979 average summer weekday. Each grid element is 5 km on a side (from SCAQMD/SCAG 1982a). The boundary of the study area used in this program is shown.

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

	km ²	Area 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

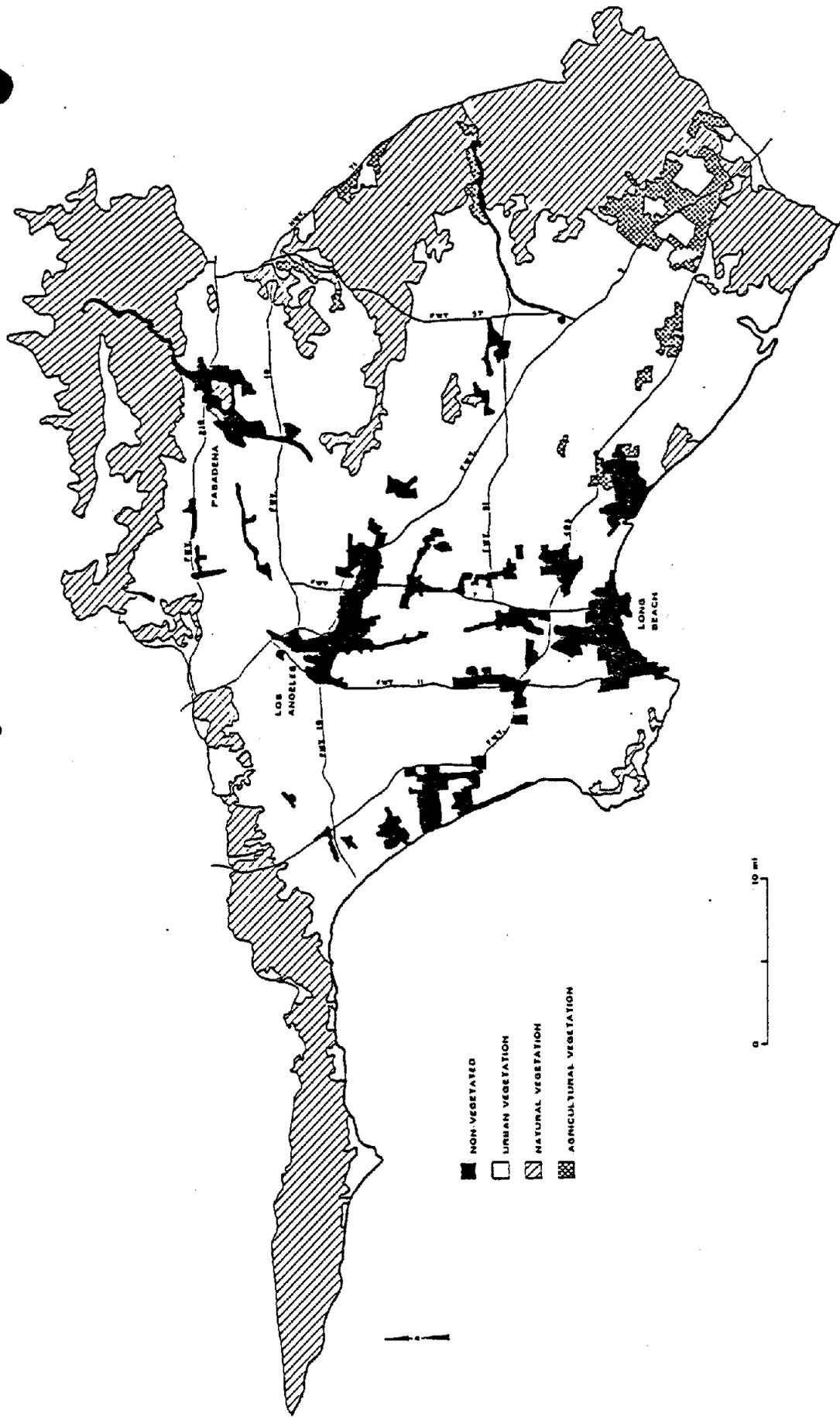


Figure I-3. Urban, natural and agricultural vegetation areas of the CSCAB as determined from a mosaic of 15 NASA U-2 color infrared images.

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

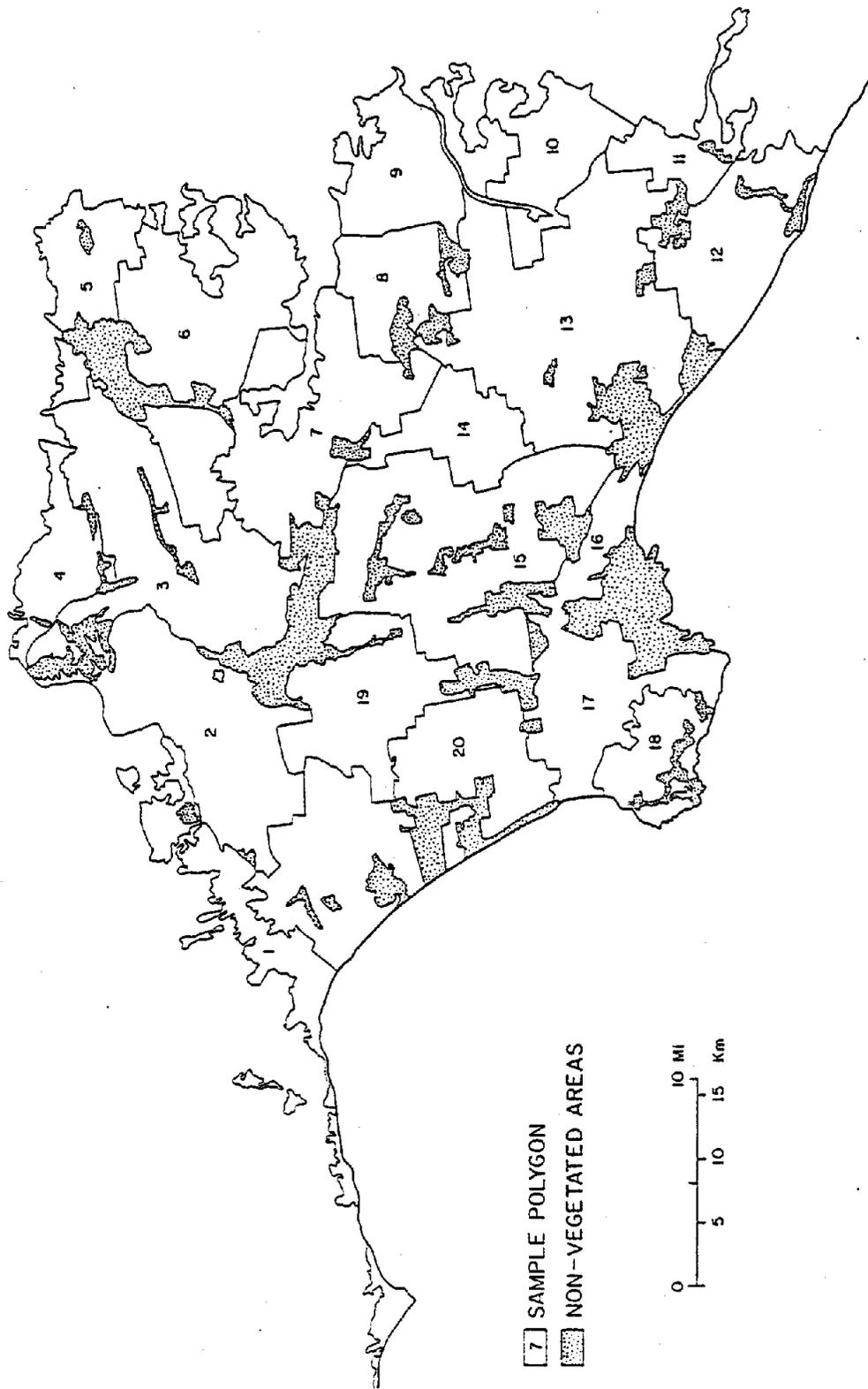


Figure I-4. Polygons for stratified sampling of urban vegetation.

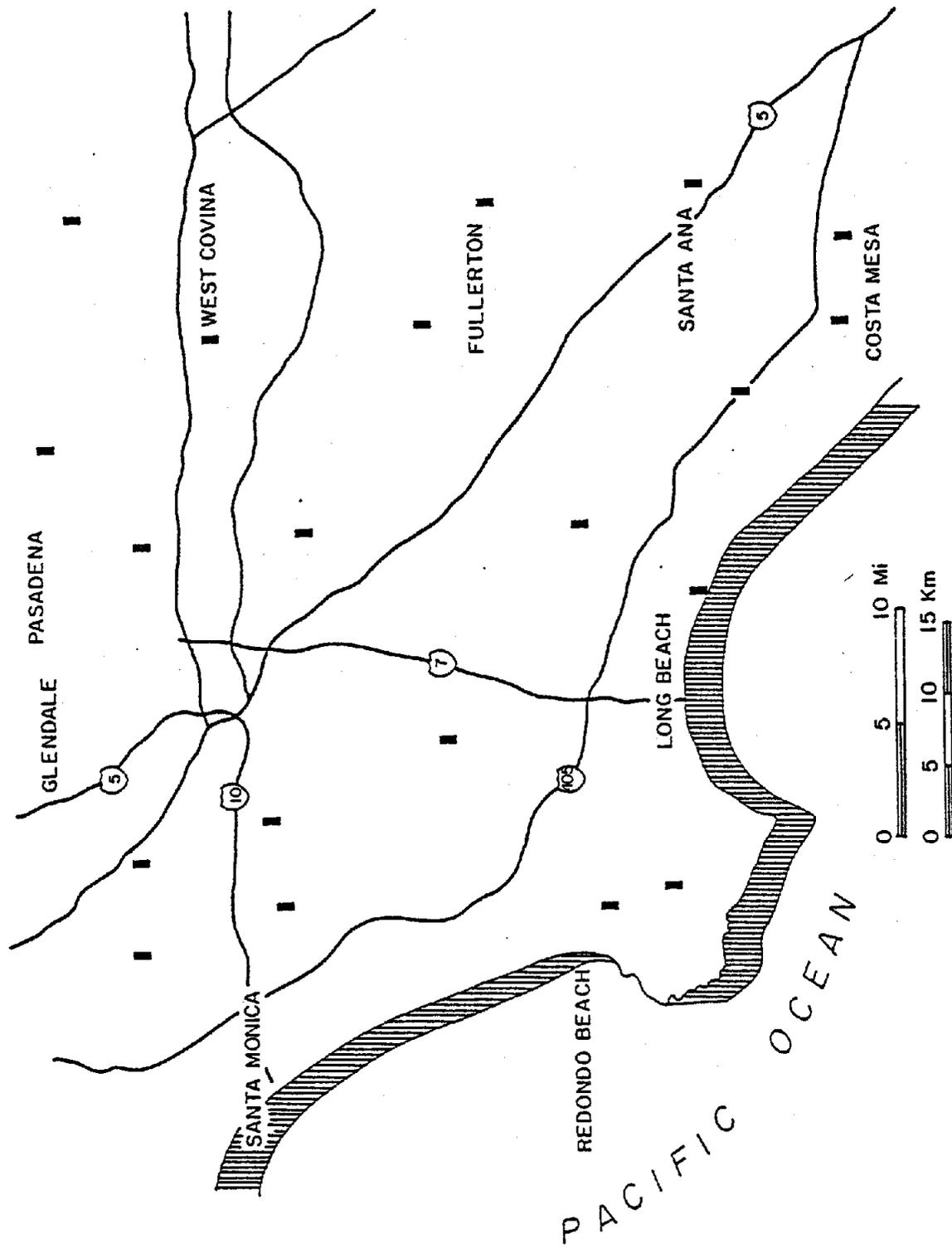


Figure I-5. Randomly selected sample areas.

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 km². 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 km² of chamise, 92 km² sage, 22 km² chaparral and 15 km² 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 $\mu\text{g g}^{-1}$ of dry leaf weight per hour ($\mu\text{g g}^{-1} \text{ hr}^{-1}$), except for ground cover which is in units of $\mu\text{g m}^{-2} \text{ hr}^{-1}$.

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 (m²) 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
GRAPE 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	12000	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 $\mu\text{g g}^{-1} \text{hr}^{-1}$	Mean Monoterpene Emission Rate $\mu\text{g g}^{-1} \text{hr}^{-1}$
<u>Urban</u>			
<u>Broad-Leaf Trees</u>			
Black locust	<u>Robinia pseudoacacia</u>	11 ± 7	
Brazilian pepper	<u>Schinus terebinthifolius</u>		9 ± 9
California live oak	<u>Quercus agrifolia</u>	49 ± 37	
California sycamore	<u>Platanus racemosa</u>	11 ± 3	
Magnolia	<u>Magnolia grandiflora</u>		6 ± 3
Olive	<u>Olea europaea</u>		0.4 ± 0.3
Ribbon gum	<u>Eucalyptus viminalis</u>	7 ± 1	
Silver maple	<u>Acer floridanum</u>		2 ± 0.5
Weeping willow	<u>Salix babylonica</u>	233 ± 46	
<u>Conifers</u>			
Aleppo pine	<u>Pinus halepensis</u>		0.6 ± 0.4
Canary Island pine	<u>Pinus canariensis</u>		2 ± 2
Deodar cedar	<u>Cedrus deodara</u>		1 ± 1
Italian cypress	<u>Cupressus sempervirens</u>		0.1 ± 0.0
Monterey pine	<u>Pinus radiata</u>		0.6 ± 0.2
<u>Flower and Ground Cover</u>			
African daisy	<u>Osteospermum fruticosum</u>		350 ^b ± 28
<u>Palms</u>			
California fan palm	<u>Washingtonia filifera</u>	11 ± 12	
Date palm	<u>Phoenix dactylifera</u>	15 ± 1	
<u>Shrubs</u>			
Bottlebrush	<u>Callistemon citrinus</u>	15 ± 6	
Chinese juniper	<u>Juniperus chinensis</u>		0.7 ± 0.7
Common myrtle	<u>Myrtus communis</u>	44 ± 39	
Heavenly bamboo	<u>Nandina domestica</u>	20 ± 5	
Shiny xylosma	<u>Xylosma congestum</u>	8 ± 3	
<u>Natural</u>			
Black sage	<u>Salvia mellifera</u>		12 ^c
California sage brush	<u>Artemesia californica</u>		8 ± 9
Encelia	<u>Encelia farinosa</u>		6 ± 3
Rhamnus ceanothus	<u>Rhamnus crocea</u>	37 ± 12	
Scrub oak	<u>Quercus dumosa</u>	35 ± 10	
Woolly blue curls	<u>Trichostema lanatum</u>		21 ^c

^aCorrected to 30°C.

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

^cValues 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 $\mu\text{g g}^{-1} \text{hr}^{-1}$.

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
<u>Based on Aerial Imagery and Ground Survey Data</u>			
1	8.2	3.6	11.8
2	7.5	3.8	11.3
3	8.4	2.9	11.3
<u>Based on Ground Survey Data Only</u>			
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
<u>Naturals</u>	4.8	9.3	14.1

^aSpecies with emission rates below the detection limit were considered to be non-emitters.

^b15 hour daylight at 30°C, 9 hour dark at 25°C.

^cSum 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
<u>Based on Aerial Imagery and Ground Survey Data</u>			
1	14.5	7.7	22.2
2	13.6	7.3	20.9
3	14.4	6.9	21.3
<u>Based on Ground Survey Data Only</u>			
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
<u>Naturals</u>	20.8	31.3	52.1

^aSpecies with emission rates below the detection limit were considered to emit at the detection limit.

^b15 hour daylight at 30°C, 9 hour dark at 25°C.

^cSum 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 O₃ formation is the "EKMA" technique. This involves analyses of O₃ 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, Dimitriadis 1977, Whitten and Hogo 1978).

If we restrict our consideration to relatively small percentage increases (<~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,

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

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 $\sim 6\%$ of the total ROG emissions. The "worst case" upper limit value obtained was 93 tons day^{-1} , or $\sim 7\%$ 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 $\sim 0.3-0.4$ 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" predicts 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 $\sim 2-3\%$ of

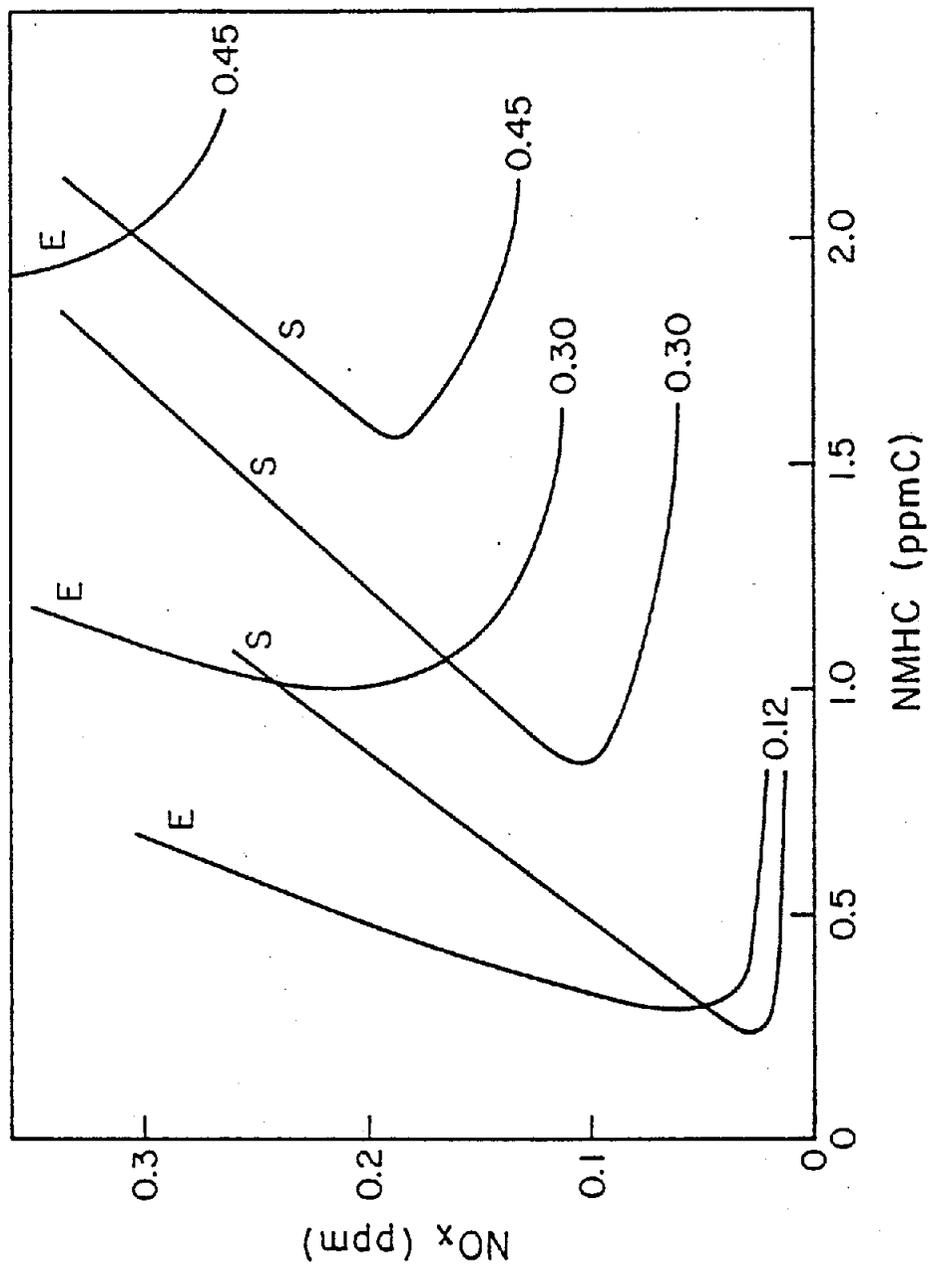


Figure I-6. Isopleth plots for $O_3 = 0.12, 0.3$ and 0.4 ppm calculated using the standard EPA EKMA model (E) and the SAPRC EKMA model (S). Note that axis labels refer to molar quantities.

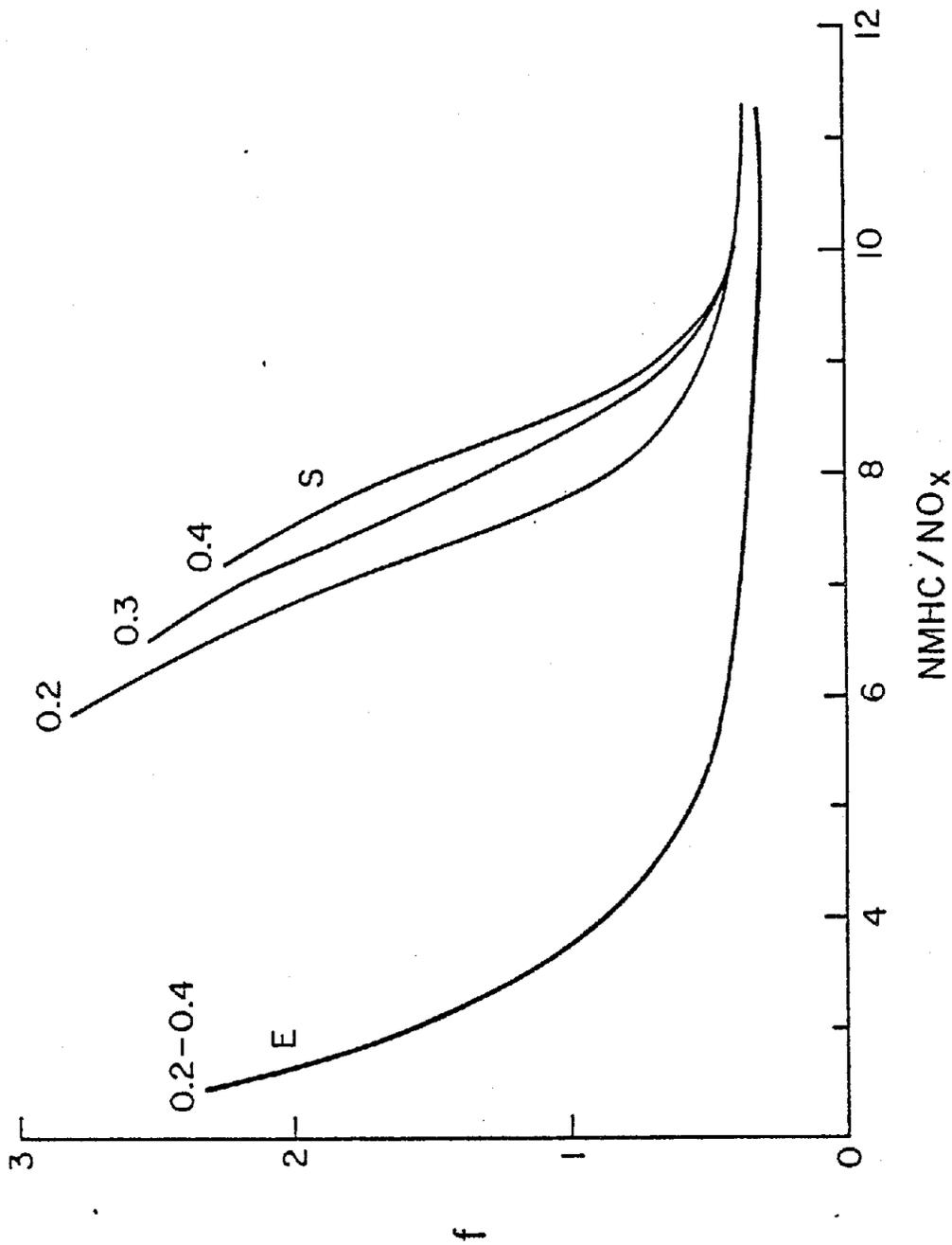


Figure I-7. Proportionality factor, f , for equation II plotted against HC/NO_x ratio for $O_3 = 0.2, 0.3$ and 0.4 ppm calculated using the standard EPA EKMA model (E) and the SAPRC EKMA model (S). Note that the abscissa units refer to mole ratios (ppmC/ppm) which must be divided by ~ 3.5 to give weight 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 O₃ 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 ~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 O₃ 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 O₃ 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 O₃ formation (Kamens 1981), and that isoprene is less reactive, in terms of O₃ 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 O₃ levels in localized areas, even if their effects on average O₃ 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.

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