VI. EMISSION RATES

A. Introduction

The data required for the calculation and use of emission rates for the individual compounds, or classes of compounds, observed in this study consist of the following: (a) the steady state concentrations determined by gas chromatography; (b) the dry weights of the biomass specimens for which emission measurements were made; and (c) the temperatures recorded in the field during sampling from the plant enclosures.

The individual concentration data are **given** for each plant species in the appropriate tables in Section V. These tables list measured concentrations for the five enclosure samples obtained during the normal six hour sampling protocol described in Section IV (see Table IV-1).

Biomass data are reported below either as dry leaf weights or as total dry biomass, depending on the nature of the plant species. In a few cases where it was believed appropriate, emission rates are calculated and reported normalized to both dry leaf weight and total dry **weight.**

The temperatures reported below are the mean values calculated from the temperatures within the enclosure which were recorded every minute during each of the five sampling periods in a protocol. An overall mean, of the temperatures of the five individual sampling periods during a protocol is also reported.

B. Calculation of Emission Rates

For the plant enclosure method employed in this program, the concentration of an organic emission from a plant specimen rises to an asymptotic "steady state" value, [organic emission] $_{SS}$, determined by the rate of that emission (R) and the rate of removal (k_d) of the compound due to the flow (F) of the matrix air through the chamber.

$$
[organic emission]_{SS} = \frac{R}{Vk_d}
$$
 (1)

where k_d = Flow rate (F)/chamber volume (V). Hence,

 $\left[\text{organic emission} \right]_{\text{ss}} = R/F$ (2)

The approach to steady state is given by

$$
[organic emission]_t = \frac{R}{F} (1 - e^{-k}d^t)
$$
 (3)

where k_d and t are in the same time units.

Under the sampling conditions utilized in this study, $k_d t = 3$, and hence the concentrations of the organic emissions were approximately 5% below the steady state values. Taking into account the small variations in the flow rate, chamber volume and chamber flush times, the concentrations of the organic emissions were in all cases within 10% of their steady state values.

By rearranging expression (2) ,

$$
R = F[organic emission]_{SS}
$$
 (4)

the emission rate is calculated from the product of the observed close-tosteady state concentration and the flow rate, and is independent of the volume of the plant enclosure chamber.

If the steady state concentration is reported in ppbC and the flow rate in liters per minute, then from the perfect gas law the conversion factor to obtain emission rates in units of μ g hr⁻¹ at 30°C and 740 torr is 0.032 times the matrix air flow rate (which in this study was either 41.9 $\text{\textsterling min}^{-1}$ or 45.3 $\text{\textsterling min}^{-1}$). Division by the appropriate dry biomass weight yields the emission rate factor in units of μ g hr⁻¹ gm⁻¹ dry biomass weight. This conversion factor will change by up to 3.5% over the range of ambient temperatures (\sim 20°C to \sim 42°C) encountered during the measurement protocols. However, this correction in the conversion factor was considered negligible when compared with the inter-specimen variability observed in the emission rates.

A second possible correction for temperature was to account for the known exponential behavior of monoterpene emission rates with temperature (Tingey et al., 1980; Rasmussen, 1972; Juuti et al., 1990). Such corrections could be as large as a factor of 3 over the range of temperature encountered in this study, relative to a mean protocol temperature or a canonical temperature (e.g. 30°C). However, the plant-

VI-2

to-plant variability observed in the emission rates for a given species were generally so large that it was not deemed meaningful to make such a temperature correction. This is particularly true for categories of emissions other than monoterpenes (e.g. sesquiterpenes) for which no published quantitative information is available concerning the temperature dependence of such emissions.

C. Presentation of Data

In this section, the observed, close-to-steady state, concentration data required to calculate the emission rates for isoprene, monoterpenes, sesquiterpenes, total assigned plant emissions (TAPE), and total carbon emissions (TC) are summarized in an odd-numbered table for each plant species. These tables also include the mean temperatures measured during each sampling period, an overall average temperature, and the dry biomass weights corresponding to each of the five sampling protocol measurements.

The corresponding even-numbered tables then report the calculated emission rates, normalized to the appropriate dry biomass weight, for each of the five sampling protocol measurements, and the mean value of those five emission rate determinations. For cotton and tomato, emission rates are reported normalized to both dry leaf weight and dry total (leaves and \ stems) weight.

Although the emission factors are reported in this section for the sums of the compounds within a class (i.e. monoterpenes), the emission rates for individual organic compounds can be calculated from the data provided in Section V and the conversion factor and flow rates given in Section B above.

Tables VI-1 to VI-50 contain data for the agricultural plant species for which full, five-sample protocol measurements were made. Tables VI-51 to VI-60 contain data for members of the natural plant community for which complete sampling protocols were conducted. Tables VI-61 and VI-62 report single values of data and emission rates, respectively, for the four compound classes for those plant species for which only a single survey measurement of steady state concentrations were made, and for which dry leaf weight data are also available.

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Table VI-1. Data Required^a to Calculate Emission Rates for Alfalfa (Pierce)

 $_{\rm A}^{\rm A}$ All flow rates during protocol = b_{Dry} weight of leaves and stems. cTotal assigned plant emissions. ^dTotal carbon. 41.9 1.

^eNone detected.

 $\hat{\mathbf{r}}$

aNormalized to total dry weight of leaves and stems. bNone detected.

^cAverage does not include none detected values.

 $\bar{\alpha}$

 \overline{a}

 A
All flow rates during protocol = 45.3 1.
bDry weight of leaves.
Crotal assigned plant emissions.
drotal carbon.
eNone detected.
 $f_{\text{No data}}$.

 $\sim 10^{11}$ m $^{-1}$

 $\mathcal{A}^{\mathcal{A}}$

 $\sum_{k=1}^{n}$ Normalized to total dry weight of leaves.

bNone detected.

c~Jo data.

^dDoes not include none detected values.

 $\tilde{}$

Table VI-5. Data Required^a to Calculate Emission Rates for Apricot (Blenheim)

a

a all flow rates during protocol = 45.3 l.

bDry weight of leaves.

CTotal assigned plant emissions.

dTotal carbon.

eNone detected.

fNo data.

 \mathcal{A}

 $_{L}^{a}$ Normalized to total dry weight of leaves. bNone detected. $\rm _{\rm s}^{\rm c}$ No data. ^dAverage does not include none detected value.

 Δ

 A All flow rates during protocol = 41.9 1.
bDry weight of leaves and stems.
CTotal assigned plant emissions.
dTotal carbon.
eNone detected.

 $\hat{\mathbf{v}}$

Table VI-8. Emission Rates (μ g hr $^{-1}$ gm $^{-1}$) for Hydrocarbons Observed from Beans (Top Crop)^a at Indicated Temperatures

 $^{a}_{b}$ Normalized to total dry weight of leaves and stems. None detected.

 Δ

Table VI-9. Data Required^a to Calculate Emission Rates for Carrot (Imperator Long)

 A
All flow rates during protocol = 45.3 l.
b_{Dry} weight of leaves.
C_{Total} assigned plant emissions.
d_{Total} carbon.
e_{No} data.

 \sim

 \mathcal{A}^{max}

aNormalized to total dry weight of leaves. b_{None} detected. ^cNo data.

 \sim

Table VI-11. Data Required^a to Calculate Emission Rates for Cherry (Bing)

a

and flow rates during protocol = 41.9 l.

bDry weight of leaves.

Crotal assigned plant emissions.

dTotal carbon.

eNone detected.

 Δ

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 $\mathbf{t} = \mathbf{0}$

a Normalized to total dry weight of leaves.

None detected.

^CAverage does not include none detected value.

 $\overline{}$

Table VI-13. Data Required^a to Calculate Emission Rates for Cotton (Pima)

a
All flow rates during protocol = 41.9 l.
b_{Dry} weight.
C_{Total} assigned plant emissions.
d_{Total} carbon.

 $\hat{\mathbf{v}}$

a
Normalized to dry leaf weight. ^bNone detected.

T le VI-14b. Emission Rates (µg hr $^{-1}$ gm $^{-1}$) for Hydrocarbons Observed from Cotton^a (Pima) at Indicated Temperatures - Normalized to Total Dry Weight

	Rates From Protocol Emission					Mean Emission
Compounds	NH-89A	NH-89B	NH-89C	NH-89D	$NH-89E$	Rates
Isoprene	b	b	b	ъ	b	b
Monoterpenes	0.289	0.635	0.457	1.37	0.714	0.69
Sesquiterpenes	0.008	0.030	0.016	0.081	0.016	0.03
Total Assigned Plant Emissions	0.546	1.20	1.07	1.99	1.31	1.2
Total Carbon	1.26	2.14	1.89	2.84	1.97	2.0
Temperature (°C)	26.0	32.7	37.8	42.8	41.0	36.1

aNormalized to total dry weight. ^bNone detected.

	Mean Temperature	Biomass ^b	Steady State Concentration (ppbC)				
Run No.	(°C)	(gm)	Σ Monoterpenes	Σ Sesquiterpenes	TAPE ^C	TC ^d	
NH-92A	26.0	54.1	e	е	47	247	
NH-92B	31.3	48.7	е	e	115	365	
NH-92C	33.7	54.1	$\mathbf e$	e	42	236	
NH-92D	39.2	31.5	е	$\mathbf e$	65	268	
NH-92E	38.7	54.1	e	e	79	301	
Average	33.8						

Table VI-15. Data Required^a to Calculate Emission Rates for Grape (Thompson Seedless)

 \blacksquare

a
All flow rates during protocol = 41.9 l.
bDry weight of leaves.
CTotal assigned plant emissions.
dTotal carbon.
eNone detected.

 $\bar{}$

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 $\hat{\mathbf{r}}$

Table VI-16. Emission Rates (μ g hr⁻¹ gm⁻¹) for Hydrocarbons Observed from Grape (Thompson Seedless) at Indicated Temperatures

aNormalized to total dry weight of leaves and stems. b_{None} detected.

 $\label{eq:2.1} \frac{1}{\sqrt{2}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2.$

 \blacksquare

Table VI-17. Data Required^a to Calculate Emission Rates for Grape (French Colombard)

a_{All} flow rates during protocol = 41.9 l.
b_{Dry} weight of leaves.
C_{Total} assigned plant emissions.
d_{Total} carbon.
e_{None} detected.

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 \mathcal{A}^{max}

aNormalized to total dry weight of leaves. b_{None} detected.

 ω

 A
All flow rates during protocol = 45.3 l.
b_{Dry} weight of leaves.
C_{Total} assigned plant emissions.
d_{Total} carbon.
e_{No} data.

 $\hat{\mathbf{v}}$

 $\mathbf{u} \in \mathbb{R}^{d \times d}$

 $_{\text{a}}^{\text{a}}$ Normalized to total dry weight of leaves. bNone detected. ^cNo data.

 Δ

Table VI-21. Data Required^a to Calculate Emission Rates for Nectarine (Armking)

 $_{\rm A}^{\rm A}$ All flow rates during protocol = 45.3 l. $_{\circ}$ Dry weight of leaves. ^CTotal assigned plant emissions. ^dTotal carbon. ^eNo data.

 \mathbf{v}

 $\hat{\mathbf{v}}$

Table VI-22. Emission Rates (µg hr $^{-1}$ gm $^{-1}$) for Hydrocarbons Observed from Nectarine^a (Armking) at Indicated Temperatures

 $_{\rm c}^{\rm a}$ Normalized to total dry weight of leaves. D_{None} detected. **CHO data.**

 $\tilde{}$

Table VI-23. Data Required^a to Calculate Emission Rates for Olive (Mazanillo)

 $_{c}^{a}$ All flow rates during protocol = 41.9 l.

 \mathbf{v}

b_p weight of leaves.

 $\frac{c}{\sqrt{2}}$ Total assigned plant emissions.

^dTotal carbon.

 \mathcal{A}^{c} and

a
Normalized to total dry weight of leaves. b_{None} detected.

 $\mathcal{L}^{\text{max}}_{\text{max}}$ and $\mathcal{L}^{\text{max}}_{\text{max}}$

		Mean Temperature	Biomass ^b	Steady State Concentration (ppbC)				
	Run No.	(°C)	(gm)	Σ Monoterpenes	<i>E</i> Sesquiterpenes	TAPE ^C	TC ^d	
	NH-37A	14.3	98.3	10	e	11	27	
	NH-37B	14.7	95.2	46	е	47	72	
	NH-37C	20.2	98.3	11	e	11	36	
\leq	NH-37D	29.2	98.3	210	e	222	256	
လ	NH-37E	28.4	98.3	3	e	5	29	
	Average	21.4						

Table VI-25. Data Required^a to Calculate Emission Rates for Orange (Washington Navel)

 \blacksquare

 $_{c}^{a}$ All flow rates during protocol = 45.3 l. $^{D}_{Dry}$ weight of leaves.

 \mathbf{v}

 $^{\text{c}}$ Total assigned plant emissions.

Total carbon.

^eNo data.

 \pm

 ~ 0.01

 $_{\rm L}^{\rm a}$ Normalized to total dry weight of leaves. ^DNone detected. ^cNo data.

 $\label{eq:2.1} \frac{1}{\sqrt{2}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}$

 $\label{eq:2.1} \mathcal{L} = \mathcal{L} \left(\mathcal{L} \right) \left(\mathcal{L} \right) \left(\mathcal{L} \right) \left(\mathcal{L} \right)$

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Table VI-27. Data Required^a to Calculate Emission Rates for Orange (Valencia)

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 $^{a}_{c}$ All flow rates during protocol = 45.3 l. b_p weight of leaves. ^CTotal assigned plant emissions. d_{Total} carbon.

 \mathbf{v}

^eNo data.

 \mathcal{A}^{max}

aNormalized to total dry weight of leaves. b
None detected. **cNo data.**

	Mean Temperature	Biomass ^b		Steady State Concentration (ppbC)		
Run No.	(°C)	(gm)	Σ Monoterpenes	Σ Sesquiterpenes	TAPE ^C	TC ^d
NH-48A	30.0	497.6	е	e	80	572
NH-48B	36.4	602.1	e	e	73	877
NH-48C	41.4	425.5	е	e	161	1256
NH-48D	39.7	392.5	е	e	422	1349
NH-48E	41.7	425.5	e	e	92	1229
Average	37.8					

Table VI-29. Data Required^a to Calculate Emission Factors for Irrigated Pasture

a

a all flow rates during protocol = 41.9 l.

b Total dry weight.

C Total assigned plant emissions.

d Total carbon.

e No data (no survey GC/MS analysis conducted for irrigated pasture).

 \bullet

 $\ddot{}$

a
Normalized to total dry weight.

b_{None} detected.

^cNo data (no survey GC/MS analysis conducted for irrigated pasture).

 \mathbf{r}^{\top}

 \rightarrow

Table VI-31. Data Required^a to Calculate Emission Rates for Peach (Halford)

 $_{\sim}^{\alpha}$ All flow rates during protocol = 41.9 l.

 $\hat{\mathbf{v}}$

Dry weight of leaves.

 $^{\text{c}}$ Total assigned plant emissions.

Total carbon.

 $\sim 10^{-10}$

a
Normalized to total dry weight of leaves. ^bNone detected.

 $\ddot{}$

Table VI-33. Data Required^a to Calculate Emission Rates for Pistachio (Kerman)

a

All flow rates during protocol = 41.9 l.

bDry leaf weight.

CTotal assigned plant emissions.

dTotal carbon.

eNone detected.

fTree limb improperly handled, data suspect.

 $\bar{\mathbf{r}}$

 $^{a}_{b}$ Normalized to dry leaf weight. None detected.

 $\frac{c}{d}$ Value suspected to be high due to rough handling of tree limb. ^dDoes not include values for NH-76A.

 \bullet

Table VI-35. Data Required^a to Calculate Emission Rates for Plum (Santa Rosa)

a

All flow rates during protocol = 41.9 l.

bDry weight of leaves.

CTotal assigned plant emissions.

dTotal carbon.

eNone detected.

 \sim

 $\mathbf{A}^{(n)}$

 a Normalized to total dry weight of leaves.

b_{None} detected.

cAverage does not include none detected value.

 \blacksquare

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Table VI-37. Data Required^a to Calculate Emission Rates for Rice

aAll flow rates during protocol = 41.9 l.
bDry weight of leaves.
CTotal assigned plant emissions.
dTotal carbon.
eNone detected.

 \sim

 $\sim 10^{-10}$

 n_e ^aNormalized to total dry weight of leaves. ^DNone detected.

 $\Delta \sim 10^{11}$

	Mean Temperature	Biomass ^b	Steady State Concentration (ppbC)				
Run No.	(°C)	(gm)	Σ Monoterpenes	<i>I</i> Sesquiterpenes	TAPE ^C	TC ^d	
NH-75A	35.7	173.9	10	50	212	574	
NH-75B	40.3	254.0	19	207	610	996	
NH-75C	41.8	173.9	19	80	302	538	
NH-75D	43.1	170.4	e	143	430	1025	
NH-75E	42.1	173.9	5	94	389	672	
Average	40.6						

Table VI-39. Data Required^a to Calculate Emission Rates for Safflower

 \sim

a_{All} flow rates during protocol = 41.9 1.

b_{Dry} weight of leaves and heads with developing seeds and bracts; leaves ~7% of total biomass, leaves and heads ~84% of total biomass.

crotal assigned plant emissions.

drot

٠

aNormalized to total dry weight of leaves and heads with developing seeds and bracts. ^DNone detected.

 $\hat{\mathbf{v}}$

^CNot available.

	Mean Temperature	Biomass ^b	Steady State Concentration (ppbC)				
Run No.	(°C)	(gm)	<i>E</i> Monoterpenes	Σ Sesquiterpenes	TAPE ^C	TC ^d	
NH-81A	37.3	117.3	6	e	100	246	
NH-81B	37.5	42.7	4	е	128	270	
NH-81C	40.0	117.3	3	e	127	265	
NH-81D	39.7	68.5	4	e	164	405	
NH-81E	39.5	117.3	5	e	103	261	
Average	38.8						

Table VI-41. Data Required^a to Calculate Emission Rates for Sorghum

 $\hat{\mathbf{v}}$

^aAll flow rates during protocol = 41.9 1.

b_{Dry} weight of leaves; leaves were ~28% of the total dry weight from leaves, stems and heads.

cTotal assigned plant emissions.

^dNone detected.

eNone detected.

 \blacksquare

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Table VI-42. Emission Rates (µg hr⁻¹ gm⁻¹) for Hydrocarbons Observed from Sorghum^a at Indicated Temperatures

aNormalized to total dry weight of leaves. ^bNone detected.

 \mathcal{L}

 \blacksquare

 $_{c}^{a}$ All flow rates during protocol = 41.9 l. Dry weight (excluding fruit). cTotal assigned plant emissions.

 $\hat{\mathbf{v}}$

^dTotal carbon.

 $\sim 10^{-1}$

 $_{h}^{a}$ Normalized to total dry weight. ^DNone detected.

a
Normalized to dry leaf weight.

^bNone detected.

 $\overline{}$

Table VI-45. Data Required^a to Calculate Emission Rates for Processing Tomato (#6203 Canning)

aAll flow rates during protocol = 41.9 1.
b_{Dry} weight (excluding fruit).
cTotal assigned plant emissions.
dTotal carbon.

Table VI-46a. Emission Rates (μ g hr⁻¹ gm⁻¹) For Hydrocarbons Observed from Processing Tomato^d (#6203 Canning) at Indicated Temperatures

aNormalized to total dry weight. ^DNone detected.

Table VI-46b. Emission Rates (μ g hr $^{-1}$ gm $^{-1}$) For Hydrocarbons Observed from Processing Tomato⁸ (#6203 Canning) at Indicated Temperatures

			Emission Rates From Protocol			Mean Emission
Compounds	$NH-82A$	$NH-82B$	NH-82C	$NH-82D$	$NH-82E$	Rates
Isoprene	b	b	b	b	b	b
Monoterpenes	189	65.0	23.4	31.1	25.0	66.7
Sesquiterpenes	0.497	0.489	0.237	0.166	0.237	0.33
Total Assigned Plant Emissions	198	68.5	24.9	32.9	26.5	70.2
Total Carbon	206.2	74.0	30.3	40.7	34.8	77.2
Temperature (°C)	27.9	33.8	37.3	-39	39.2	35.4

^aNormalized to dry leaf weight.

^bNone detected.

 \bullet

Table VI-47. Data Required^a to Calculate Emission Rates for English Walnut (Hartley)

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 $^{a}_{b}$ All flow rates during protocol = 41.9 l. Dry weight of leaves. $\frac{c}{\sqrt{2}}$ Total assigned plant emissions.

 $\tilde{}$

^dTotal carbon.

 $\sim 10^{-11}$

aNormalized to total dry weight of leaves. ^bNone detected.

 \bullet

Table VI-49. Data Required^a to Calculate Emission Factors for Wheat

a

all flow rates during protocol = 41.9 l.

bTotal dry weight.

CTotal assigned plant emissions.

dTotal carbon.

eNone detected.

 $\hat{\mathbf{v}}$

 $\sim 10^{11}$ km $^{-1}$

aNormalized to total dry weight.

^bNone detected.

 $\bar{\omega}$

Table VI-51. Data Required^a to Calculate Emission Factors for Chamise

a

a all flow rates during protocol = 41.9 l.

b_{Dry} leaf weight.

cTotal assigned plant emissions.

dTotal carbon.

e None detected.

 $\ddot{}$

 $\hat{\mathbf{r}}$

 $^{\text{a}}_{\text{a}}$ Normalized to dry leaf weight. None detected.

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 $\sim 10^7$

 \sim

Table VI-53. Data Required^a to Calculate Emission Factors for Annual Grasslands

a

a all flow rates during protocol = 41.9 1.

b Total dry weight.

C Total assigned plant emissions.

d Total carbon.

e None detected.

 $\tilde{}$

 $\sim 10^{-1}$

 $\mathbf{v}^{(i)}$.

 μ Normalized to dry weight of leaves and stems.

^DNone detected.

 $\label{eq:2.1} \frac{1}{\sqrt{2}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}$

 $\sim 10^7$

0 Average does not include none detected values.

 $\tilde{}$

 $\mathcal{L}^{\text{max}}_{\text{max}}$

 $_{c}^{a}$ All flow rates during protocol = 41.9 l. b Dry weight of leaves. $\frac{c}{\sqrt{2}}$ Total assigned plant emissions. ^dTotal carbon. ^eNo data (no survey GC/MS analysis conducted for Manzanita)

 $\ddot{}$

 $\mathcal{L}^{\text{max}}_{\text{max}}$ and $\mathcal{L}^{\text{max}}_{\text{max}}$

^aNormalized to dry weight of leaves.

^DNone detected. ^CNo data.

 \sim

Table VI-57. Data Required^a to Calculate Emission Factors for Valley Oak

 $_{\rm L}^{\rm a}$ All flow rates during protocol = 41.9 l. $^{D}_{Dry}$ weight of leaves. $\frac{c}{c}$ Total assigned plant emissions. $\frac{q}{q}$ Total carbon.

 \mathbf{v}

^eNone detected.

 $\sim 10^{-10}$

aNormalized to dry weight of leaves. ^bNone detected.

 \sim

Table VI-59. Data Required^a to Calculate Emission Factors for Whitethorn

a

and flow rates during protocol = 41.9 l.

bDry weight of leaves.

Crotal assigned plant emissions.

dTotal carbon.

eNone detected.

 \sim

 \sim α

. Table VI-60. Emission Rates (µg hr⁻¹ gm⁻¹) for Hydrocarbons Observed from Whitethorn^a at Indicated Temperatures

 a Normalized to dry weight of leaves.

b_{None} detected.

caverage does not include none detected value.

aDry weight of leaves. $\frac{\text{b}}{\text{2}}$ Flow rate during survey - 45.3 l. c_{None} detected. $d_{\text{Flow rate}^{directed}}$ survey - 41.9 1.

Table VI-62. Emission Rates (μ g hr⁻¹ gm⁻¹) for Hydrocarbons Observed from Plant Species for Which Only Surveys were Conducted^a

Plant Species	$Iso-$ prene	Mono- terpenes	Sesqui- terpenes	TAPE ^C	TC^C	Tempera- ture $(0C)$
Lettuce Empire	b	b	b	0.02	0.41	28.6
Onion South Port White Globe	b	b	þ	2.9	7.1	32.5
Mountain Mahogany	b	0.06	b	0.90	4.0	41.9

 $_{\textrm{\tiny{h}}}^{\textrm{\tiny{a}}}$ Normalized to dry leaf weight.

b_{None} detected.

cvalues may be high if during these survey samples, the plants were not treated with the same caution exercised during protocol samples.

In presenting these data, the emphasis is on isoprene (in all but one case not detected above background), the monoterpenes (which have received the greatest attention in previous studies), total assigned plant emissions (TAPE) which comprise many individual compounds and classes of compounds for which definite assignments could be made (as discussed in Section V), and total carbon (TC) which represents an upper limit to all plant emissions.

A discussion of the data in these tables and their interpretation and implications is given in Section VII which follows.

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 $\mathcal{L}^{\text{max}}_{\text{max}}$ and $\mathcal{L}^{\text{max}}_{\text{max}}$ $\label{eq:2.1} \frac{1}{\sqrt{2}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2.$

VII. CONCLUSIONS AND FUTURE WORK

A. Summary of Emission Rates

Based on the data calculated in the preceding section, the mean **emission rates cf isoprene (for the Valley Oak only), the monoterpenes,** the sesquiterpenes and the total assigned plant emissions (TAPE) for each of the agricultural plant species for which full protocols were conducted in this program are summarized in Table **VII-1,** and for each of the natural plant species in Table VII-2, along with the corresponding mean temperatures. Also included in Tables VII-1 and VII-2 is a column for total carbon (TC) which is an upper limit for the emission rates since it is essentially calculated from the sum of all the carbon observed in the sample, i.e., it includes the TAPE and any additional GC peaks (as detailed in Section V).

Mean emission rates for the monoterpenes ranged from none detected in the case of beans, grapes (both Thompson seedless and French Columbard), rice and wheat, to as high as ≥ 30 µg hr⁻¹ gm⁻¹ of monoterpene emissions **from the two cultivars of tomato investigated (normalized to total dry** biomass, excluding fruit). The Kerman pistachio also fell in the high emitter category with a rate of about $12 \mu g h r^{-1} gm^{-1}$. Other species exhibiting substantial rates of emission of monoterpenes included the agricultural crops carrot, cotton, lemon, orange and walnut and the natural plant species whitethorn. Crops which fell into a low monoterpene emitter category included alfalfa, almond, apricot, cherry, nectarine, olive, peach, plum, safflower and sorghum.

For about a third of the agricultural crops studied, the sum of sesquiterpene emissions fell below the detection limits (see Section V) of the analytical methods employed (sesquiterpenes were not quantified for the seven samples taken in the summer of 1988). A second group, consisting of alfalfa, cotton, and olive displayed emission rates below **O. 1 µg hr- 1 gm- 1 while the remainder of the agricultural plant species** exhibited total sesquiterpene emission rates which fell into a relatively narrow range compared with monoterpene emissions, ranging between 0.1 and 1 μ g hr⁻¹ gm⁻¹. Note that the sesquiterpene emissions from the cherry, French columbard grape, olive, peach and, in particular the safflower, exceeded the monoterpene emissions from these species.

Table VII-1. Summary of Mean Emission Rates by Compound Class for Agricul- tural Plant Species for which Complete Protocols were Conducted

aNo data. $\frac{e}{e}$ No data; no survey conducted.

No data; no survey conducted.
 $\frac{e}{e}$ No data; no survey conducted. bne detected. $\begin{array}{ccc} \text{b} & \text{f} \\ \text{b} & \text{g} \end{array}$ with caution; see text. c Normalized to dry leaf weight, unless noted. $\qquad \qquad \texttt{S}$ Normalized to dry weight of

dNormalized to total dry weight (excluding fruit). leaves and bracts.

a_{Normalized} to dry leaf weight, unless noted. b_{None} detected. c_n Normalized to total dry weight. $\frac{d}{dx}$ No data; no survey conducted.

 $e_{\text{Isoprene}} = 2.3 \text{ µg} \text{ hr}^{-1} \text{ gm}^{-1}.$

All of the agricultural crops for which full protocols were carried out exhibited total assigned plant emission (TAPE) rates above the detection limits of this study. Crops with TAPE emission rates above 10 **¹** µg hr- 1 **gm-** included pistachio and tomato. Although rice also exhibited a mean TAPE emission rate above 10 μ g hr⁻¹ gm⁻¹, this result must be used with caution since, as seen in Table VI-37, two of the five protocol samples had dry leaf weights of only 6-8 gm with no corresponding reduction in the measured TAPE, resulting in calculated emission rates approximately an order of magnitude larger than the average of the remaining three emission rates. If these two high values are removed, the mean emission rate for TAPE from rice would be 3 μ g hr⁻¹ gm⁻¹ vs. the reported value of $11 \text{ µg hr}^{-1} \text{ gm}^{-1}$. The natural plant species whitethorn also had a TAPE emission rate above 10 μ g hr⁻¹ gm⁻¹.

Crops with TAPE emission rates between 1 and 10 μ g hr⁻¹ gm⁻¹ included alfalfa, almond, apricot, carrot, cherry, cotton, grape, lemon, Valencia orange, peach, plum, safflower, sorghum and walnut. Also having a TAPE emission rate above 1 μ g hr⁻¹ gm⁻¹ was the abundant natural plant species,

chamise, which had been reported to be a nonemitter in previous work (Winer et al., 1983). The remaining crops, i.e. beans, nectarine, olive, Washington Navel orange and wheat, displayed TAPE emission rates below $1 \mu g$ hr⁻¹ gm^{-1} .

1,. Grouping of Emitters and Comparison with Previous Studies

Agricultural Plant Species. From the data tables in Section V it is possible to calculate an upper limit to the isoprene emissions from the agricultural species studied. As discussed in Section V, pentane and isoprene co-eluted on the GS-Q column. If we assume that all of the observed C_F concentrations measured in the protocols was due to isoprene, then the upper limits to isoprene emissions from the agricultural crops were in the range 0.008 to 0.09 μ g hr⁻¹ gm⁻¹. The absence of significant isoprene emissions from the agricultural crops is consistent with the previous work of Evans et al. (1982) who screened beans, alfalfa, field corn, wheat, sugar beets and cotton for isoprene emissions and found nondetectable levels in the sugar beets and cotton and "low" isoprene emissions for the remaining crops.

The TAPE includes organic compounds that were obviously plant emissions, although the specific compound could not always be identified. The TC includes, in addition to the TAPE, any background peaks from the residual ambient air in the plant enclosure and/or contaminants in the medical air blanks (generally with the exception of acetone) and is, therefore, most likely to overestimate the plant emissions, especially if the plant is a very low emitter and/or a sample of small biomass was measured. Therefore, as discussed at the end of Section V, with the exception of wheat, irrigated pasture and possibly safflower, the total assigned plant emissions are good estimates of the total emissions from the particular plant specimen at the time of sampling.

A qualitative grouping of the agricultural crops studied by their rates of total assigned plant emissions is given in Table VII-3 and a **corresponding grouping by order of magnitude ranges in the sum of total** monoterpene and sesquiterpene emissions rates is shown in Table VII-4. Only the citrus (lemon and orange) and nut trees (pistachio and walnut) and the two tomato varieties emitted monoterpenes at levels comparable to, or greater than, the predicted a-pinene emission rates from coniferous trees of $-3.5 \text{ µg hr}^{-1} \text{ gm}^{-1}$ at 29-30 °C (Lamb et al., 1987).

Natural Plant Species. As seen in Table VII-2, mean emission rates for total assigned plant emissions from the natural plant communities studied ranged over two orders of magnitude, from a low value near 0.1 μ g hr⁻¹ gm⁻¹ for grasslands and manzanita to a high value of 10 ug hr⁻¹ gm⁻¹ for whitethorn. The Valley oak was the only confirmed isoprene emitter found among either the agricultural or natural plant species investigated. The isoprene emission rate of 2.3 μ g hr⁻¹ gm⁻¹ determined in the present study for Valley oak is at the low end of the range of emission rates reported for other oaks by previous workers (Zimmerman, 1979a; Flyckt et al. , 1980; Tingey et al., 1980). Calculating, as discussed above for the agricultural plant species, an upper limit to the isoprene emissions for the natural plant species other than the Valley oak, gives a range of 0.008 to 0.05 μ g hr⁻¹ gm⁻¹ for maximum isoprene emission rates.

Chamise and whitethorn were found to be significant monoterpene emitters. As mentioned above, previous work had suggested that chamise did not emit monoterpenes (Winer et al., 1983).

In **utilizing the data from the present study, it is important to** recognize that emphasis was placed on agricultural plant species, in part because considerable previous research has been conducted for natural, plant communities found in California's Central Valley, or for related plant communities. Thus, a significant literature is available concerning organic emissions from conifer species (Arnts et al., 1978; Zimmerman, 1979a; Roberts et al. , 1983, 1985; Hov et al., 1983; Isidorov et al., 1985; Lamb et al., 1985, 1986; JUttner, 1988; Petersson, 1988) and from sage and chaparral communities (Went, 1960; Tyson et al., 1974; Winer et al., 1983).

2. Estimates of Uncertainty and Variation in Emission Rates

Enclosure Effects. As discussed in Sections II and IV, there were early concerns that emission measurements made using the enclosure **technique were overestimating actual plant emissions** (Dimitriades, 1981), but recent comparisons of enclosure emission measurements with atmospheric tracer and micrometeorological gradient techniques have shown reasonable to excellent agreement (Lamb et al., 1987). It is clear, however, that reliable emission measurements require that considerable care be taken in using the enclosure technique. We noted during our
preliminary measurements made in 1988 that "rough handling" of a plant species when placing it within the enclosure enhanced emissions. Increased emissions both of monoterpenes and of the oxygenated species commonly observed from the agricultural crops were noted. An extreme **Proxample of this is shown in Table V-28 where no cis-3-hexen-1-ol (leaf** alcohol) and only 5 ppbC of cis-3-hexenylacetate were observed for survey sample NH-31, but for sample NH-27 in which the lettuce was disturbed to encourage emissions, -670 and -1100 ppbC of the alcohol and the acetate, respectively, were measured. It should be noted that both the alcohol and the acetate were often observed from plants during the protocol samples when every effort was made to gently place the plant or plant limb within the enclosure and these emissions were considered to be true representative plant emissions. Consistent with these findings, Isidorov et al. (1985) in a study in which efforts were made to minimize disturbances to the plant specimens reported cis-3-hexenylacetate to be one of the major emissions from bilberry shrubs.

Realizing that many replicate samples would be required to understand **the important variables associated with the enclosure sampling technique,** a student visitor (Soile Juuti) at SAPRC was encouraged to undertake a detailed study of the emissions from a Monterey Pine over a four week period. The publication resulting from this work has been included as Appendix B. Neither the absence of added $CO₂$ to the synthetic air flow stream, nor increased air movement within the enclosure (from the addition of a variable speed fan capable of operating at higher speeds) had an observable effect of the monoterpene emission rates from the Monterey Pine studied. In contrast, rough handling of the pine during the sampling protocol, i.e., manually compressing, and then releasing, the enclosure around the tree in a repetitive manner during the 15 min flush of the chamber preceeding sampling, increased the monoterpene emission rate by factors of 10-50.

During our protocol samples every effort was made to avoid touching the plant or tree limb with the Teflon of the enclosure. Noting the high emission rate of monoterpenes in the pistachio sample NH-76A, which was a factor of -4-5 higher than those of the two replicate samples {NH-76C and NH-76E) taken during the day, a review of the data sheet indicated potential mishandling during this first sample and, therefore, NH-76A has not been included in calculating the average emission rate from the pistachio.

measurements for a given plant species over the course of a six hour Temperature Effects and Specimen Variation. As discussed in Section IV, the emission sampling protocol, which called for five period from mid-morning to mid-afternoon, was designed in part to characterize, if possible, the temperature dependence of the emissions. Thus, the emissions from the same specimen were measured at 0900 hr, noon and 1430 hr allowing a three point temperature versus emissions plot to be made with the temperature range controlled by the ambient conditions encountered. The second and third specimens measured at 1030 and 1330 hr would show the plant-to-plant variablility in the emissions. An exponential temperature dependence for the monoterpene emissions was expected based on the work of Tingey and co-workers (Tingey et al., 1980) on slash pine.

Consistent with the work of Tingey et al. (1980) on slash pine, the temperature dependence observed in the recent four-week enclosure study of a Monterey pine by Juuti et al. (1990; and Appendix B) also showed an order of magnitude increase in the α - and β -pinene emissions over a temperature range from 10 to 40° C. At any given temperature the variability in the α - + β -pinene emission rate for this single plant was \pm a factor of \sim two.

Since a temperature variation of 10-17°C was commonly observed for the daily sampling protocols in this study, a variation in the emission rate of between a factor of 2 to 4 throughout the course of a given sampling protocol could be explained on the basis of the temperature variation. Since our work with the Monterey pine suggests that at any given temperature the emission rate could be expected to vary by ± a factor of two, reliable temperature versus emission profiles with only three data points to define the curve are unlikely.

In the study of Tingey and co-workers (Tingey et al., i980) on slash pine, emission rate measurments were made for fourteen individual plants. Each plant showed a similar temperature dependence (parallel lines for each temperature vs. log emissions profile), but the absolute emission rates at a given temperature varied by an order of magnitude from plant-to-plant. Thus, the specimen-to-specimen variability is likely to be too great to improve the curve fit by adding the 1030 and 1330 hr samples to the temperature vs. log emissions curve. In practice, in a few cases the individual emission rates for monoterpenes within a protocol did vary with temperature in a correlated way. The whitethorn and cotton samples are two examples of this, where the log of the emission rates for the 0900 hr, noon and 1430 hr samples give a reasonable straight line when plotted against the sampling temperature. For the cotton sample the sesquiterpene emissions give a line parallel to the monoterpenes.

We have reported here mean emissions rates, but have included in the data tables in Sections V and VI all the data used to calculate these mean values. Generally, the mean sampling temperatures (Table VII-1 and VII-2) were above 30 °C and our data could be viewed almost as an upper limit to the expected emissions. Therefore, these mean emission rates, when combined with biomass data for the Central Valley, will be sufficient to determine which, if any, species should be evaluated in a more rigorous way in regard to their emissions at various temperatures.

Tingey et al. (1980) suggest that the monoterpene vapor pressure (which over ambient temperatures is an exponential function of the temperature) and monoterpene pool size control the emissions rates. For example, pine needles are known to contain a large pool of monoterpenes available for volatilization into the atmosphere. For the agricultural species reported on here, in some cases, i.e. the carrot, lemon, nectarine and canning tomato, the morning lowest temperature emission rate **was** the highest value of the day (this was also the case for the pistachio, but as noted above the first data point was suspect). In these instances one could speculate that the monoterpene pool size may have been limiting. Relevant to this, Dement et al. (1975) noted that the emission rate of camphor from California black sage was higher for samples pretreated at a low night temperature.

A further important qualification of the data obtained in the present **study is that these results must be viewed as a "snapshot" of the emission** rates from the various plant species investigated. In each case, data reported are for a single day, and involve at most three different plant specimens for the given species. In a number of cases only two or even one plant specimen was involved with emission rate measurements being obtained from different limbs or branches of this one specimen. These

considerations must be borne in mind when the emission rate data reported here are employed in the construction of an emission inventory for vegetative emissions of organic compounds.

In summary, taking into account the results obtained in the present **study** *1* **and the earlier work of Tingey et al. (1980) and Juuti et al** (1990), an uncertainty as large as \pm a factor of five may apply to some or all of the mean emission rates reported in this study. This potential uncertainty should be reflected in the uncertainty of the emission inventories constructed from these data. Clearly, to narrow these uncertainties further additional studies for multiple plant specimens of a given species and over an entire growing season are warranted.

3. Importance of Compound Classes Other than Monoterpenes

Another major conclusion of the present **work is** the need to be concerned with the emissions of compounds other than the commonly studied monoterpenes and isoprene. Not only did we identify more than two dozen individual organic compounds other than the monoterpenes, but these fell into several compound classes, most of which were oxygenated organics, including alcohols, acetates, aldehydes, ketones, ethers, and esters. Additionally, at the temperatures typical of the Central Valley in summer, sesquiterpene emissions were found to be significant from several plant. species.

Lamb et al. (1987) in compiling a national inventory of biogenic hydrocarbon emissions notes that the role of oxygenated hydrocarbon emissions has not been documented to any significant extent. The emission of cis-3-hexen-1-ol (leaf alcohol) from higher plants was reported by Ohta (1984) and both leaf alcohol and 3-hexenylacetate were reported by Isidorov et al. (1985) as among the volatile organic compounds produced by plants characteristic of Northern hemisphere forests. As mentioned above, Isidorov et al. (1985) reported 3-hexenylacetate as one of the major emissions from bilberry shrubs. Both Ohta (1984) and Isidorov et al. (**1985) used Tenax-GC adsorbent for collection of the volatile emissions.** It is possible that these and other oxygenated compounds were not observed in certain previous studies because of poor recovery from the stainless steel canisters often employed for sample collection.

We observed cis-3-hexen-1-ol and, particularly, 3-hexenylacetate in the emissions from many of the agricultural plant species studied here.

It is of interest to note that no leaf alcohol or hexenylacetate was observed from the Monterey pine, even under conditions which produced very enhanced emissions. For many plant species, 3-hexenylacetate was the single largest emission (note that since the same GC-FID response was $~$ assumed for all species measured on the DB-5 GC column, the actual

3-hexenylacetate concentration may be somewhat greater than the calculated values). Our findings suggest that cis-3-hexenylacetate and cis-3-hexen-1-ol may be significant plant emissions from nonconiferous plant species and measurements should be conducted in vegetation canopies to confirm the importance of these emissions.

B. Atmospheric Lifetimes of Biogenic Emissions and Potential for Formation of Photochemical Air Pollution

Organic compounds emitted into the troposphere from anthropogenic sources, such as stationary and mobile combustion sources, oil production facilities, landfills and waste disposal sites, interact with oxides of nitrogen (NO_x) under the influence of sunlight through a complex series of chemical reactions and physical processes, resulting in the formation of photochemical air pollution. These photochemical processes lead to a degradation in air quality manifested by the formation of ozone, acidic deposition, secondary particulate (PM-10), as well as other atmospheric species.

Biogenic compounds emitted into the atmosphere from vegetation can undergo analogous chemical and physical processes and hence also contribute to the formation of adverse air quality. The recent modeling studies of Trainer et al. (1987a) and Chameides et al. (1988) have shown that the emissions of biogenic organic compounds can play extremely important roles in the formation of ozone in both urban (Chameides et al., 1988) and rural (Trainer et al., 1987a) areas, and that the regulation of organic compounds of anthropogenic origin may not be effective in reducing ozone levels in either urban or rural regions.

1. Tropospheric Lifetimes

Organic compounds emitted into the troposphere are removed and/or transformed by a number of physical and chemical processes which include wet and dry deposition, photolysis and gas-phase reactions with OH and NO_3 radicals and O_3 (Atkinson, 1988; Bidleman, 1988). For organic compounds present in the troposphere in the gas phase, the reactions with

OH and NO_3 radicals and O_3 dominate in the vast majority of cases (see, for example, Atkinson, 1988). The tropospheric lifetimes, τ , of organic compounds (the time required for the concentration of an emitted compound to decrease to 0.368 of its intital concentration) are then given by

$$
\tau^{-1} = (\tau_{OH})^{-1} + (\tau_{NO_3})^{-1} + (\tau_{O_3})^{-1}
$$

where

$$
\tau_{OH} = (k_{OH} [OH])^{-1}
$$

with analogous expressions for the NO_3 and O_3 reactions. Thus, the tropospheric lifetimes of the biogenic or anthropogenic compounds can be calculated by combining the rate constants for the reactions of these compounds with OH and NO_3 radicals and O_3 with the ambient concentrations of OH and NO_3 radicals and O_3 . While the rate constants at room temperature for the gas-phase reactions of a large number of organic **compounds of biogenic and anthropogenic er igin have been determined, the** ambient tropospheric concentrations of OH and, especially, $NO₃$ radicals are not well known at the present time, and this leads to significant, uncertainties in the calculated lifetimes of organic compounds in the atmosphere and, especially, in the assessment of the dominant tropospheric loss process for a given chemical.

Table VII-5 gives the tropospheric lifetimes of those biogenic compounds identified as being emitted from agricultural and natural vegetation in this study for which rate constant data are available, while Table VII-6 gives the corresponding lifetimes for a series of organic compounds which are among the major species emitted from anthropogenic sources in urban areas (Grosjean and Fung, 1984). In order to calculate the tropospheric lifetimes of these organic compounds with respect to gasphase reactions with OH radicals, NO_3 radicals and O_3 , the following ambient tropospheric concentrations were used: OH radicals, a 12-hr daytime average of 1.5 x 10^6 molecule cm^{-3} obtained from comparison of the ambient atmospheric concentrations of methylchloroform (CH $_3$ CCl $_3$) with its emission inventory (with this global tropospheric concentration being consistent with the lower tropospheric concentrations obtained by recent

Table VII-5. Calculated Tropospheric Lifetimes of Organic Compounds Observed as Biogenic Emissions in the Present Study

{continued)

 $^{\sf a}$ For a 12-hr gaytime average OH radical concentration of 1.5 x 10 $^{\sf 6}$ molecule cm⁻³ (Prinn et al., 1987). Rate constant data from Atkinson (1989), Atkinson et al. (1989a) and Corchnoy and Atkinson (1989). ^DFor a 24-hr average 0^3 concentration of 7 x 10⁻¹ molecule cm⁻³ [30 ppb] (Logan, 1985). Rate constant data from Atkinson and Carter (1984), and Atkinson et al. (1989b). cFor a 24-hr average NO₂ radical concentration of 2.4 x 10⁷ molecule cm⁻³ [1 ppt] (Atkinson et al. 1986b and text). Rate constant data from Atkinson et al. (1988, 1989a) and Corchnoy and Atkinson (1989). ${}^{\text{d}}$ Estimated as discussed in Atkinson and Carter (1984) and Atkinson (1987). eExpected to be of negligible significance as a tropospheric loss process.

	Lifetime with respect to reaction with		
Anthropogenic	OH ^a	0_3 _b	NO_2 ^C
Alkanes			
n-Butane n-Octane	6.1 days 1.8 days	>4500 yrs >4.5 yrs	20 yrs 7.3 yrs
Alkenes			
Ethene Propene	1.8 days 7.0 hrs	9.2 days 1.5 days	6.3 yrs 51 days
Aromatics			
Benzene Toluene o-, p-Xylene 1,2,4-Trimethylbenzene	13 days 2.6 days 1.1 days 5.6 hrs	>4.5 yrs >4.5 yrs $\frac{1}{4.5}$ yrs >4.5 yrs	>19 yrs 22 yrs 3.2 yrs 270 days
Oxygenates Formaldehyde ^d	1.6 days	>4.5 yrs	2.2 yrs

Table VII-6. Calculated Tropospheric Lifetimes of Representative Anthropogenic Emissions

 $^{\sf a}$ For a 12-hr average daytime OH radical concentration of 1.5 x 10⁶ mole-
cule cm⁻³ (Prinn et al., 1987). Rate cosntant data from Atkinson (1989 cule cm^{-3} (Prinn et al., 1987). Rate cosntant data from Atkinson (1989). bette cm (11 mm events, 1987). Mate constant data from Atkinson (1984).

1985). Rate constant data from Atkinson and Carter (1984).

^cFor a 24-hr average NO_3 radical concentration of 2.4 x 10⁷ molecule cm⁻³ (Atkinson et al., 19866 and text). Rate constant data from Atkinson et al. (1988).

dalso photolyzes with a lifetime of 10 hrs.

direct (Hubler et al., 1984; Perner et al., 1987; Platt et al., 1988) and indirect (Arey et al., 1989) studies; $0₃$, a 24-hr average of 7 x 10¹¹ molecule cm⁻³ (30 ppb) applicable to background air (Logan, 1985) which is also within a factor of 2-3 of the average $24-hr$ O₃ concentrations observed in urban areas; and NO_3 radicals, a 24-hr average of 2.4 x 10⁷ molecule cm^{-3} (1 ppt) arrived at from consideration of the daytime NO_3 radical concentrations expected from the formation reaction of $NO₂$ with $O₃$ and the photolysis of NO_3 radicals $[-2 \times 10^6$ molecule cm^{-3} for 7×10^{11} molecule cm⁻³ (30 ppb) of 0_3 and 2.4 x 10¹⁰ molecule cm⁻³ (1 ppb) of NO_2 , with this daytime concentration being approximately linearly dependent on the $NO₂$ concentration] and the observed nighttime concentrations which range from $\langle 2 \times 10^7 \text{ molecule cm}^{-3} \text{ to } 1 \times 10^{10} \text{ molecule cm}^{-3}$ (Atkinson et al., 1986b). While the OH radical and $0₃$ concentrations used are expected to be reasonably applicable to most tropospheric conditions, the actual tropospheric concentrations of the $NO₃$ radical are uncertain to at least an order of magnitude, although it should be noted that daytime NO_3 radical concentrations are likely to be generally similar to those of OH radicals, and this is extremely important for those organic compounds which react with OH and NO_3 radicals with similar rate constants (the monoterpenes and the hydroxy-substituted aromatics).

The lifetime data given in Table VII-5 shows that most of the biogenic emissions identified in this study are highly reactive, with many of them having calculated tropospheric lifetimes of a few hours or less. Comparison of the data in Table VII-5 for the biogenic compounds with those in Table VII-6 for organics emitted from anthropogenic sources further shows that, with the possible exceptions of the more highly alkylsubstituted aromatic hydrocarbons and alkenes, the organic compounds emitted from biogenic sources are significantly more reactive in the troposphere than are the anthropogenic emissions (the ozone forming potential of these biogenic compounds is discussed below). This observation indicates that these biogenic organics, including not only isoprene and the monoterpenes but also certain of the aldehydes, ethers, alkenes and aromatics, have the definite potential to play a major role in the chemistry of the air masses into which they are emitted.

2. Ozone Forming Potential

It is recognized that all organic compounds emitted into the troposphere are not equal with respect to the formation of ozone (see, for example, Carter and Atkinson, 1987, 1989). Clearly, as evident from Tables VII-5 and VII-6, there is a wide range of reactivities, and hence lifetimes, in the organic compounds emitted into the troposphere and these variations in reactivity are to a first approximation responsible for differences in ozone-forming potential. However, the reaction mechanisms of an organic compound subsequent to the initial OH radical, $NO₃$ radical and/or $0₃$ reactions in the atmosphere play an important role in the potential for an organic compound to form ozone.

Ozone is formed from the reaction sequence

$$
NO2 + hv + NO + O(3P)
$$
 (phot)

$$
O(^{3}P) + O_{2} + M + O_{3} + M \quad (M = air)
$$
 (fast)

$$
NO + O_3 \rightarrow NO_2 + O_2 \tag{2}
$$

and at steady state

$$
[03] = knhot[NO2]/k2[NO]
$$

In the presence of organic compounds, NO is converted to $NO₂$ during the degradation reaction scheme of the organic compounds and the $NO₂/NO$ concentration ratio increases, leading to increased $0₃$ formation.

The small $({\leq}C_{\mu})$ alkanes (RH) have fairly simple reaction schemes following their initial reaction with the OH radical (their only significant tropospheric removal process). For example

$$
OH + RH + H2O + R
$$
 (3)

$$
R + O_2 \rightarrow RO_2 \tag{4}
$$

$$
RO2 + NO + RO + NO2
$$
 (5)

$$
RO + O_2 \rightarrow \text{carbonyl} + HO_2 \tag{6}
$$

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$$
RO \rightarrow carbonyl + R'
$$
 (7)

$$
HO_2 + NO \rightarrow OH + NO_2 \tag{8}
$$

where R' is an alkyl radical with less carbon atoms than the parent RH alkane and which then undergoes the series of reactions (4) through (8) to lead to the formation of carbonyl compounds (which react further in the troposphere by photolysis and reaction with the OH radical), the conversion of NO to $NO₂$ and the regeneration of OH radicals.

In general, as seen from Tables VII-5 and VII-6, organic compounds may also be removed from the troposphere by photolysis and reactions with $NO₃$ radicals and $O₃$ in addition to the OH radical reaction. Thus, the general reaction scheme for the degradation of an organic compound can be written in a simplistic manner as

$$
\text{organic} + (\text{hv}, \text{OH}, \text{NO}_3, \text{O}_3) + \alpha \text{RO}_2 \tag{a}
$$
\n
$$
\text{RO}_2 + \beta \text{NO} + \gamma \text{NO}_2 + \delta \text{OH} \tag{b}
$$

where reaction (a) includes all loss process of the organic under atmospheric conditions, and α , β , γ and δ are coefficients (which may be, greater than or less than unity, including zero) which will generally **depend on the importance of the various loss processes and on the** organic/NO_x concentration ratio (Carter and Atkinson, 1987, 1989). The reaction process (a) determines the lifetime of the organic in the troposphere ($\tau = k_a^{-1}$) and can be viewed as being the "kinetic reactivity" of an organic compound (Carter and Atkinson, 1989; Carter, unpublished data, 1989). The subsequent reactions leading to conversion of NO to $NO₂$ and the (re)generation of OH radicals [reaction process (b)] are responsible for the "mechanistic reactivity" of the organic compound. Carter (Carter and Atkinson, 1989; Carter, unpublished data, 1989) has shown that to a first approximation the ozone forming potential of an organic compound ("ozone reactivity") is given by

ozone reactivity = (kinetic reactivity) x (mechanistic reactivity)

with the proviso that for rapidly reacting compounds (those reacting on a time scale less than a few hours) the kinetic reactivity levels off and becomes independent of the lifetime for the most reactive compounds. [Indeed, the "kinetic reactivity" can be quantified as the fraction of the organic emitted which has photolyzed or reacted {Carter, unpublished data, 1989)).

In contrast to the situation for many of the organic compounds emitted from anthropogenic sources, while the data are available to assess the "kinetic reactivities" of organic compounds of biogenic origin, there are essentially no data available, from either experimental or modeling studies, to allow the "mechanistic reactivities" of these biogenic compounds to be assessed or estimated. Thus at the present time, while it is clear that many of the organic compounds emitted from vegetation are highly reactive in the troposphere and hence have high "kinetic reactivities," the magnitudes of the "mechanistic reactivities" of these compounds are not known, and hence the overall reactivities of biogenic compounds, relative to anthropogenic organic emissions, with respect to ozone formation cannot be quantified.

C. Recommendations for Future Research

Although the data obtained in the present study for the rates *ot* emissions of organic compounds from agricultural plant species are by far the most detailed and comprehensive relative to any previous investigation of this type, additional research is needed to broaden and extend the utility of these results. In particular, the following research tasks are recommended for future investigations.

• Data obtained in the present study demonstrated again that there can be large variations in emission from a given plant species, not only between different specimens of the same cultivar, but even for replicate measurements from the same specimen. For those agricultural plant species which are found to dominate the vegetative emission inventory for the Central Valley, it would be prudent to conduct additional measurements of emission rates for a statistically robust sample of plant specimens, in order to reduce the uncertainty in the observed emission rates. This will be especially needed if meaningful estimates of the variation of emissions **with temperature are to be made.**

• For the most important plant species, it would also be important to conduct emission rate measurements over the entire spring, summer, fall smog season, in order to determine how emissions vary with time of year and stage of growth for a given plant.

• Additional emission rate measurements may be needed for various members of the natural plant communities found in the Central Valley which may be shown to have dominant biomass contributions below the generally prevailing temperature inversion heights.

• Additional studies are recommended of rice, irrigated pasture, and wheat if these are shown to constitute important components of the overall vegetative emission inventory assembled for the Central Valley.

• Efforts should be made to identify the compounds observed as emitted from vegetation in this study (in particular cis-3-hexen-1-ol and cis-3-hexenylacetate) in appropriate vegetation canopies.

• If recent proposals for massive tree-planting in the Central Valley (as well as in other airsheds in California) are to be implemented to address needs for windbreaks, sequestering carbon, and to reduce urban heat island effects, the emissions of organic compounds from the candidate tree species should be determined quantitatively as one basis for selecting the most appropriate trees for such planting programs.

 \bullet A longterm research program is needed to elucidate the atmospheric chemistry of many of the individual organic compounds identified in this **study (and earlier work) as arising from vegetation. Information on the** atmospheric transformations of such compounds is required in order to reliably assess their potential for contributing to the formation of ozone and other secondary air pollutants, and thereby understand the relative importance of organic emissions from vegetation vs. emissions from anthropogenic sources in California's airsheds.

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 $\mathcal{L}(\mathcal{L}^{\text{max}})$, where \mathcal{L}^{max}

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IX. APPENDICES

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APPENDIX A

Species Typically Associated with Natural Plant Communities in the Central Valley

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Valley Foothill Hardwood plant connunity: Includes such species as blue oak, valley oak, Englemann oak, interior live oak, coast live oak, **digger** pine, California buckeye, tanoak, lupine spp., several shrub species, etc.

Annual Grassland plant community: Includes such species as wild oats, soft chess, ripgut, red brome, wild barley, foxtail fescue, filaree spp., turkey mullein, true clovers, bur clover, popcorn flower, etc.

Mixed Conifer plant community: Includes such species as Ponderosa pine, Douglas fir, white fir, incense cedar, sugar pine, Jeffrey pine, California black oak, etc. This plant community can occur from approximately 2500 to 10,000 feet elevation.

Red Fir plant community: Includes largely red fir, with lodgepole pine. This plant community is expected only above about 6000 feet elevation.

Chamise-Redshank Chaparral plant community: Includes such species as chamise, redshank, toyon, sugar sumac, poison oak, California buckthorn, ceanothus spp., manzanita spp., California scrub oak, etc.

Lodgepole Pine plant community: Includes largely lodgepole pine, with red fir. This plant community is expected only above about 6000 feet eleva**tion.**

Ponderosa Pine plant community: Includes largely Ponderosa pine, along with such species as white fir, incense cedar, Coulter pine, Jeffrey pine, sugar pine, Douglas fir, canyon live oak, California black oak, etc: This plant community can occur from approximately 800 to 7000 feet elevation.

Mixed Chaparral plant community: Includes such species as California scrub oak, chaparral oak, manzanita spp., mountain mahogany, ceanothus spp., chamise, huckleberry oak, bush Chinquapin, tobacco brush, mountain misery, scotchbroom, etc.

Fresh Emergen Wetland plant community: Includes such species as bigleaf sedge, baltic rush, redroot nutgrass, common cattail, river and tule balrush, etc.

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 $\label{eq:2.1} \frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\sum_{i=1}^N\frac{1}{\sqrt{2\pi}}\int_{\mathbb{R}^N}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi$ $\label{eq:2} \mathcal{L}(\mathcal{L}) = \mathcal{L}(\mathcal{L}) \mathcal{L}(\mathcal{L})$ $\mathcal{L}^{\text{max}}_{\text{max}}$, $\mathcal{L}^{\text{max}}_{\text{max}}$

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APPENDIX B

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MONOTERPENE EMISSION RATE MEASUREMENTS FROM A MONTEREY PINE

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Montane Chaparral plant community: varies across the state, but includes such species as whitethorn and snowbrush ceanothus, greenleaf manzanita, other manzanita spp., bittercherry, mountain mahogany, etc. This plant community can occur from approximately 3000 to 10,000 feet elevation.

Pinyon-Juniper plant community: Includes such species as single leaf or Perry pinyon, western juniper, Utah juniper, California juniper, California scrub oak, canyon live oak, etc. This plant community can occur from approximately 3500 to 9000 feet elevation.

Jeffrey Pine plant community: Includes largely Jeffrey pine, along with such species as Ponderosa pine, Coulter pine, sugar pine, lodgepole pine, incense cedar, red fir, black cottonwood, aspen, California black oak, etc. This plant community can occur from approximately 500 to 9500 feet elevation.

Sagebrush plant community: Includes such species as big sagebrush and other sagebrush species, rabbitbrush, horsebrush, gooseberry, western chokecherry, curlleaf mountain mahogany, butterbrush, etc.

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ABSTRACT

The monoterpenes emitted from a Monterey pine (Pinus radiata) were investigated using a dynamic flow-through enclosure technique. The **monoterpenes identified and quantified were a= and S=pinene, d-limonene** + β -phellandrene, myrcene, camphene and Δ^3 -carene, with α - and β -pinene accounting for over **80J** of the total monoterpene emissions. The monoterpene emission rate increased with temperature, in good agreement with previous data for other coniferous species. The absence of added $CO₂$ to the synthetic air flow stream, exposure to elevated levels (300-500 parts-per-billion mixing ratio) of $0₃$ for 3-4 hr, and increased air movement within the enclosure had no observable effect on the monoterpene emission rate at a given temperature. In contrast, "rough handling" of the pine during the sampling protocol resulted in increases in the monoterpene emission rate by factors of 10-50. These results will be useful to those designing enclosure sampling protocols for the determination of the emission rates of biogenic organic compounds from **vegetation.**

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from handling and/or from the enclosure itself. In this work, we have carried out a study of the effects of several of these variables on the emission rates of monoterpenes from a Monterey pine (Pinus radiata).

EXPERIMENTAL

The emission rate measurements were performed with a Monterey pine over a 4 week period, using the dynamic flow-through enclosure technique described by Winer et al. (1983]. For the majority of the measurements, the pine tree (of height -1 m and planted in a plastic pot) was enclosed in a Teflon chamber of circular cross-section (diameter 1.1 m) and height -1 m. The chamber was fitted around the top of the plant pot, resulting in an approximately conical shape of volume -450 liters. Cylinder synthetic air (99.6% stated purity, with no organic compounds being observed in the region of monoterpene elution by the GC-FID analyses described below) was passed through a humidifier unit and premixed with $CO₂$ to yield a $CO₂$ mixing ratio of 360 parts-per-million (ppm), and was flowed through the enclosure at a flow rate of 45 liter min⁻¹. This flow was maintained for 15 min prior to sampling. All flows were monitored with calibrated rotameters, and the relative humidity and temperature in the enclosure were monitored by a Vaisala Hodel HHI 32 instrument. The enclosure was equipped with a stirring fan which caused a just noticeable **movement or the pine needles close to the fan. The tree was removed from** the chamber between measurements and stored outdoors. All measurements were made outdoors under ambient solar lighting conditions.

After flowing synthetic air through the chamber containing the tree for 15 min, gas samples of 1.3-1.4 liter volume were collected at a flow rate of $~0.8$ liter min⁻¹ onto Tenax-GC solid adsorbent for analyses by gas chromatography with flame ionization detection (GC-FID) and, in selected cases, combined gas chromatography-mass spectrometry (GC-HS). For the GC-FID analyses, the samples were thermally desorbed at 225 °C for 5 min onto the head of a 15 m megabore DB-5 fused silica column which was held at 0 $°C.$ and then temperature programmed at 8 $°C$ min⁻¹ to 200 $°C.$ The GC-MS analyses involved the thermal desorption of the samples at 250 °C onto the head of a 50 m HP-5 capillary column held at -25 °C for 10 min and then temperature programmed at 6° C min⁻¹. The identifications of the

B-4

INTRODUCTION

A variety of organic compounds, including isoprene {2-methyl-1,3 butadiene) and a series of monoterpenes, are emitted from vegetation [see, for example, Rasmussen, 1970, 1972; Graedel, 1979; Zimmerman, 1979a,b; Tingey et al., 1979, i980; Lamb et al., 1985, 1986; Isidorov et al., 1985] and on regional or global scales these biogenic emissions may dominate over anthropogenic nonmethane organic emissions [Zimmerman et al., 1978, 1988; Lamb et al., 1987]. Recent computer modeling studies, using isoprene as a surrogate for all biogenic emissions, have shown that vegetative emissions may play important roles in the production of ozone in urban [Chameides et al., 1988] and rural [Trainer et al., 1987a] areas and in the chemistry of the lower troposphere [Trainer et al., 1987b; Jacob and Wofsy, 1988].

The emission rate of isoprene from hardwood trees depends on light intensity [Rasmussen, 1972; Tingey et al., 1979) and temperature [Tingey et al., 1979; Lamb et al., 1985, 1986]. Tingey et al. [1979) showed that the isoprene emission rate from a live oak {Quercus Virginia) increased to an asymtotic value with increasing light intensity at a given temperature, and increased with temperature up to -44 °C. Monoterpene emission rates from coniferous species have also been reported to be temperature dependent, but independent of light intensity [Rasmussen, 1972; Tingey et al., 1980; Lamb et al., i985]. The emission rate from a slash pine {Pinus elliottii) increased exponentially with temperature [Tingey et al, 1980), showing an order of magnitude increase between 20 and 50 °C.

The extensive studies of Lamb and coworkers showed that the emissions of isoprene from a deciduous forest and of a-pinene from Douglas fir made using an enclosure method were in reasonable agreement with micrometeorological gradient profile measurements [Lamb et al., 1985) and that isoprene emission rates from oak {Quercus garryane) as measured by the enclosure method agreed very well with those derived from tracer measurements [Lamb et al., 1986]. Enclosure methods of measuring emission rates [Zimmerman, 1979a,b; Winer et al., 1983) have the obvious potential of disturbing the plant due to changing the microenvironment around the plant, through changes in humidity, temperature, $CO₂$ concentration, effective wind speed and mechanical motions, including damage to the plant

 $B-3$

All measurements in the CSTR chamber were carried out under conditions such that the steady state concentrations were achieved.

Measurements as a Function of Temperature in the Teflon Enclosure.

^Aseries of measurements of the monoterpene concentrations in the enclosure were made over the period April 21 through May 12, 1989 under "standard" conditions, in which the $CO₂$ concentration was maintained at 360 ppm and the tree was handled as gently as possible. Thirty such measurements were carried out during 13 daytime periods, covering the times 0420 hr to 1540 hr. The temperature within the enclosure varied from 12 °C to 39 °C and the relative humidity from 48-93%. The monoterpene concentrations showed no obvious dependence on the relative humidity, but increased with increasing temperature.

 α - and β -Pinene accounted for over 80% of the total monoterpene concentrations observed. The average percentage contributions of the individual monoterpenes to the total for these 30 measurements were: β -pinene, 48 ± 5%; a-pinene, 34 ± 5%; myrcene, $\leq 10\%$; d-limonene + β -phellandrene, $7 \pm 2\frac{7}{2}$; camphene, $0.6 \pm 0.4\frac{7}{2}$; and Δ^3 -carene, $0.4 \pm 0.6\frac{7}{2}$ (where the indicated errors are one standard deviation). Since there were indications that a small contribution of residual ambient air in the enclosure interferred with the myrcene measurements, the myrcene data are not discussed further. There was no evidence for any change in the monoterpene concentration distribution with temperature. Since α - and β pinene were the major monoterpenes observed, their sum was used to examine the effects of temperature and other variables, as discussed below.

The measured $a-+ \beta$ -pinene concentrations in the enclosure are plotted against the temperature in Figure 1 (open circles). There is a clear increase in the emission rate with increasing temperature, and a least-squares analysis of these data obtained over the temperature range **12-39 °C leads to an exponent Bin the assumed equation**

 $a-$ + β -pinene concentration = A e^{BT}

of $B = 0.085 \pm 0.027$, where the indicated error is two least-squares standard deviations. This temperature exponent is in excellent agreement with that of 0.074 determined by Tingey et al. [1980j for monoterpene emissions from slash pine over the temperature range of 20-46 °C.

The temperature dependence determined here for the emission of **a-+** s-pinene from a Monterey pine is very close to the temperature variation of the vapor pressures of these two monoterpenes, which yields $B = 0.060$ over the temperature range -0-40 °C [strictly, over extended temperature ranges the vapor pressures obey an equation of the form vapor pressure $=$ $ce^{-D/T}$]. Furthermore, the temperature dependencies of the vapor pressures of the monoterpenes are all very similar, and this is consistent with our observation that the monoterpene concentration distribution did not change with temperature and also with the data of Tingey et al. (1980] which showed esentially identical temperature dependencies of the emission rates from slash pine of the monoterpenes α - and β -pinene, myrcene, d-limonene and β -phellandrene.

The data shown in Figure 1 from this set of 30 experiments indicate that at any given temperature the scatter, or reproducibility, of the data for emissions from this one tree were \pm a factor of \sim 2 around the mean. While one or two of the higher emission values may have been caused by unavoidable handling effects and some uncertainty(< **±20J)** existed because of the non-attainment of steady state conditions (see above), it appears that the majority of this \pm 2 factor in the emissions rate is due to fluctuations in the plant's emissions.

Effect of $CO₂$.

Two experiments were carried out in which no CO_2 was added to the cylinder synthetic air. An identical, within the uncertainties, distribution of the monoterpenes was observed, and the measured **a-+ S**pinene concentrations are plotted in Figure 1 (filled triangles). These two data points are indistinguishable from the data obtained in the presence of tropospheric levels of CO_2 , showing that, at least for the time scales pertaining for each of these experiments (15 min), the absence of $CO₂$ has no obvious effect on the relative abundances of the monoterpenes emitted or on the monoterpene emission rate.

 $B-7$
Effect of Simulated Wind Speed.

As discussed above, for the "standard" set of measurements the enclosure was equipped with a small fan which led to a just observable needle movement close to the fan. In order to investigate the effect of air perturbation, a household 3-speed fan was installed in the enclosure and operated at medium speed for one experiment and then at high speed for a further experiment, both leading to pronounced needle movement. The data obtained (not differentiated for fan speed} are plotted as the filled circles in Figure 1. In addition to the monoterpenes, a series of other organic compounds were emitted from the fan lubrication system (as shown by an experiment without the tree present in the enclosure}, including 1,2,4-trimethylbenzene which co-eluted with myrcene on the DB-5 column. The relative abundances of α -pinene, β -pinene, Δ ³-carene, camphene and d-limonene (+ B-phellandrene} were unchanged from the "standard" experiments, and the α - + β -pinene concentrations were within the scatter of the "standard" data set (Figure 1). These observations imply that air movement has no marked effect on the monoterpene emission rates, at least under the experimental conditions used in this study.

Effect of Rough Handling.

Four experiments were carried out in which the pine tree was roughly handled while in the enclosure prior to sampling. This was achieved by manually compressing, and then releasing, the enclosure around the tree in a repetitive manner during the 15 min flush of the chamber preceeding sampling. The tree was hence in repeated contact with the Teflon enclosure, although no obvious damage (for example, broken needles} occurred. While the relative abundances of the individual monoterpenes were essentially identical to those in the "standard" measurements, the emissions were greatly increased. As shown in Figure 1, the α -+ β -pinene concentrations for the "roughed up" tree experiments (filled squares} were factors of 10-50 higher than those in the "standard" experiments conducted at the same temperature, far outside of the reproducibility of the individual experiments. These data show that rough handling markedly increases the monoterpene emission rates for this Monterey pine. Similar

effects have recently been observed for citrus and other broad-leaved plants (Arey et al., 1989).

For the rough handling experiment conducted at 16-17 °C, emission rate measurements were also made at intervals following the initial experiment to determine the time needed for the vastly increased emission rate to return to "normal". As shown in Figure 1 the measurement 1 hr after the rough handling **([I)** appears to have been within the normal emission range, as was the replicate *2* hrs after the rough handling (I]). Effects of Exposure to Elevated $0₃$ Concentrations.

As discussed above, these measurements were carried out in a CSTR chamber. Measurements of the concentrations of the monoterpenes were carried out prior to and immediately after the Monterey pine had been exposed to O_3 concentrations of 300 ppb for 3 hr and 500 ppb for 4 hrs. Because of the higher flow rate in the CSTR chamber than in the Teflon enclosure (-600 liter min⁻¹ versus 45 liter min⁻¹), the monoterpene concentrations in the CSTR chamber were significantly lower (by an average factor of 24 , which can be compared to the factor of $-10-11$ expected from the flow rates and residence times in the two chambers), and only $a-$ and s-pinene could be analyzed accurately. Two sets of experiments were carried out. In the first, three measurements were taken prior to the addition of $0₃$ at a mixing ratio of 300 ppb (for 3 hr) to the CSTR chamber, and measurements were taken immediately after the $0₃$ supply was turned off, and at 40 min and 80 min after. In the second experiment, measurements were taken prior to $0₃$ addition (500 ppb for a 4 hr period), immediately after turning off the $0₃$ supply and 65 min and 165 min later.

Since the temperatures within the CSTR chamber increased throughout each experiment, the temperature dependence of the α - + β -pinene emission rate determined in the all-Teflon chamber was assumed to allow comparison of the data taken before and after the exposures to 0_3 . The α -+ β -pinene concentrations measured during these experiments are plotted in Figure 2, with the dashed line being the temperature dependence obtained from the Teflon enclosure "standard" experiments shown in Figure 1. When the temperature dependence of the monoterpene emission rate is taken into account, the α - + β -pinene concentrations measured prior to and after exposure of the pine to 300 ppb of O_3 for 3 hr were indistinguishable.

For the exposure to $0₃$ at 500 ppb for 4 hr, the measured $a-+ \beta$ -pinene concentrations before and after the $0₃$ exposure were essentially constant. These concentrations were within a factor of 2 of those expected based on the temperature (see Figure 2), with the pre-exposure data point for this 500 ppb O₃ exposure appearing to be somewhat high. These data then indicate that, within the expected reproducibility of \pm a factor of -2, the monoterpene emissions were not affected to any significant extent by these $3-4$ hour exposures to elevated $0₃$ at levels which were at or above those observed in polluted urban areas in the U.S.

The small data set for these O_3 exposures require cautious interpretation of the data. The Monterey pine was growing in ambient Riverside air and, therefore, exposed to levels of $0₃$ occasionally reaching -200 ppb. The data do suggest, however, that sudden high levels of $0₃$ will not result in a marked increase (or decrease) of monoterpene emissions.

CONCLUSIONS

Our experimental data on the temperature dependence of α - + β -pinene emissions from a Monterey pine are in agreement with the earlier results of Tingey et al. [1980] for a slash pine, showing a monoterpene emission rate increase of an order of magnitude for an -30 °C temperature increase. As also discussed by Tingey et al. (1980], this temperature dependence of monoterpene emission rates is very similar to the temperature dependence of the monoterpene vapor pressures.

The experimental variables investigated in this study have implications for the design and use of enclosure methods for the direct determination under field conditions of biogenic emission rates from vegetation. The data obtained in this study indicate that the emission rates are not affected, outside of the \pm a factor of -2 repeatability, by neglecting to add $CO₂$ at ambient levels to the pure air flow or by use of a fan to ensure mixing within the enclosure. However, mechanical agitation of the plant through touching of the needles with the Teflon film markedly increased the emissions rates. Clearly, extreme care must be taken in fitting the enclosure over the plant or portion of the plant for which emissions are to be measured.

To date, two enclosure methods have primarily been used for direct field measurements, these being the semi-static enclosure technique developed and used by Zimmerman [1979a,b] and the dynamic flow technique of Winer et al. [1983] used in this study. The semi-static enclosure technique involves enclosing the branch in a Teflon chamber, partially evacuating this chamber and taking a background sample, and then filling the chamber with pure air and again sampling. While the semi-static enclosure method would appear to be prone to high emission rates caused by touching of the leaf surfaces with the enclosure during evacuation, the general agreement between the data reported from such studies and from micrometeorological and tracer flux measurements [Lamb et al., 1985,1986] suggests this is not the case, in part perhaps, due to correction from the background sample for excess emissions [Zimmerman, 1979b].

The micrometeorological and tracer flux approaches have stringent requirements involving large areas of similar vegetation with long fetch and cannot be readily used in many areas. Therefore, enclosure techniques for emission rate measurements under field conditions are necessary and it appears that if proper care is taken, reliable measurements can be obtained.

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FIGURE CAPTIONS

- Figure 1. Plot of the **a-+** B-pinene concentrations from a Monterey pine (Pinus radiata) measured in the Teflon enclosure as a function of temperature. 0- Standard experiments (see **text);A**carried out with no added CO_2 ; \bullet - carried out with increased air movement around the tree (see text); \blacksquare - immediately after rough handling (see text) of enclosed tree; **[I** - 1 hr and \Box - 2 hr after rough handling experiment at \sim 16 °C. (--) least-squares fit to "standard" experiments shown.
- Figure 2. Plot of the **a-+** B-pinene concentrations from a Monterey pine measured in the CSTR chamber as a function of temperature. o, Δ - prior to addition of O_3 to the CSTR chamber; \bullet - after cessation of $0₃$ exposure at 300 ppb for 3 hr; Δ - after **cessation of** $0₃$ **exposure at 500 ppb for** 4 **hr.** $(- - -)$ temperature dependence obtained from Teflon enclosure "standard" experiment measurements shown in Figure 1.

FIGURE 1.

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FIGURE 2.

APPENDII C

ELECTRON IMPACT MASS SPECTRA OF STANDARD COMPOUNDS UTILIZED TO IDENTIFY PLANT EMISSIONS

- 1. Electron Impact Mass Spectra of Isoprene, Selected Monoterpenes and Sesquiterpenes
- *2.* Electron Impact Mass Spectra of Alcohols

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- 3. Electron Impact Mass Spectra of Acetates
- 4. Electron Impact Mass Spectra of Aldehydes
- 5. Electron Impact Mass Spectra of Ketones
- 6. Electron Impact Mass Spectra of Ethers
- 7. Electron Impact Mass Spectra of n-Alkanes, Alkenes and Aromatics

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C.1. Electron Impact Mass Spectra of Isoprene. Selected Monoterpenes and Sesquiterpenes (Listed in order of their elution on an HP-5 capillary column):

Isoprene

Monoterpenes a -Pinene Camphene Sabinene **6-Pinene** Myrcene 2-Carene a-Phellandrene Λ^3 -Carene a -Terpinene cis-Ocimene^a d-Limonene **6-Phellandrene** trans-Ocimene^a Y -Terpinene Terpinolene Sesquiterpenes Cyperene Longifolene B-Caryophyllene a-Humulene

aour ocimene standard contained two well resolved terpene peaks and was specified to be a mixture of the cis and trans ocimene isomers. The peaks were assigned as the cis or trans isomer on the basis of their reported elution order (cis before trans) on a DB-5 column (Adams, 1989). It should be noted that on the DB-5 megabore column and the HP-5 column utilized the first summer, d-limonene eluted before both ocimene isomers.

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C.2. Electron Impact Hass Spectra of Alcohols {Listed in order of their elution on an HP-5 capillary column):

> cis-3-Hexen-1-ol trans-2-Hexen-1-ol Linalool Myrcenol a-Fenchol Isopulegol Menthol Terpinene-4-ol a-Terpineol Citronellol^a trans-Carveol^a Nerol^a cis-Carveol^a Geraniol

a_{trans}-Carveol and nerol when co-injected, were not resolved. The elution order for these compounds as reported by Adams (1989) on a DB-5 column **was:** trans-carveol, nerol, citronellol then cis-carveol.

 $\sim 10^{-11}$

 $\label{eq:2.1} \frac{1}{\sqrt{2}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2.$

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C.3. Electron Impact Mass Spectra of Acetates (Listed in order of their elution on an HP-5 capillary column):

> cis-3-Hexenylacetate trans-2-Hexenylacetate Bornylacetate

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 $\label{eq:2.1} \frac{1}{\sqrt{2}}\int_{0}^{\infty}\frac{1}{\sqrt{2\pi}}\left(\frac{1}{\sqrt{2\pi}}\right)^{2\alpha} \frac{1}{\sqrt{2\pi}}\int_{0}^{\infty}\frac{1}{\sqrt{2\pi}}\left(\frac{1}{\sqrt{2\pi}}\right)^{\alpha} \frac{1}{\sqrt{2\pi}}\int_{0}^{\infty}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}$ $\label{eq:2.1} \frac{1}{\sqrt{2}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2.$ $\mathcal{L}^{\mathcal{L}}(\mathcal{L}^{\mathcal{L}})$ and $\mathcal{L}^{\mathcal{L}}(\mathcal{L}^{\mathcal{L}})$ and $\mathcal{L}^{\mathcal{L}}(\mathcal{L}^{\mathcal{L}})$ $\label{eq:2.1} \frac{1}{\sqrt{2}}\int_{\mathbb{R}^3} \frac{d\mu}{\sqrt{2}} \left(\frac{d\mu}{\mu} \right)^2 \left(\frac{d$

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 $\label{eq:2.1} \mathcal{L}(\mathcal{L}^{\mathcal{L}}_{\mathcal{L}}(\mathcal{L}^{\mathcal{L}}_{\mathcal{L}})) \leq \mathcal{L}(\mathcal{L}^{\mathcal{L}}_{\mathcal{L}}(\mathcal{L}^{\mathcal{L}}_{\mathcal{L}})) \leq \mathcal{L}(\mathcal{L}^{\mathcal{L}}_{\mathcal{L}}(\mathcal{L}^{\mathcal{L}}_{\mathcal{L}}))$ $\label{eq:2.1} \mathcal{L}(\mathcal{L}^{\mathcal{L}}_{\mathcal{L}}(\mathcal{L}^{\mathcal{L}}_{\mathcal{L}})) \leq \mathcal{L}(\mathcal{L}^{\mathcal{L}}_{\mathcal{L}}(\mathcal{L}^{\mathcal{L}}_{\mathcal{L}})) \leq \mathcal{L}(\mathcal{L}^{\mathcal{L}}_{\mathcal{L}}(\mathcal{L}^{\mathcal{L}}_{\mathcal{L}}))$

 $\label{eq:2.1} \frac{1}{2} \sum_{i=1}^n \frac{1}{2} \sum_{j=1}^n \frac{$

 $\mathcal{L}(\mathcal{L}(\mathcal{L}))$ and $\mathcal{L}(\mathcal{L}(\mathcal{L}))$. The contribution of the contribution of $\mathcal{L}(\mathcal{L})$

 $\label{eq:2.1} \mathcal{L}(\mathcal{L}(\mathcal{L})) = \math$

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C.4. Electron Impact **Mass** Spectra of Aldehydes (Listed in order of their elution on an HP-5 capillary column):

 $\mathcal{L}^{\text{max}}_{\text{max}}$, where $\mathcal{L}^{\text{max}}_{\text{max}}$

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n-Hexanal trans-2-Hexenal Citronellal **Safranal** Neral Geranial Hydroxycitronellal

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 $\label{eq:2.1} \frac{1}{\sqrt{2}}\sum_{i=1}^n\frac{1}{\sqrt{2}}\sum_{i=1}^n\frac{1}{\sqrt{2}}\sum_{i=1}^n\frac{1}{\sqrt{2}}\sum_{i=1}^n\frac{1}{\sqrt{2}}\sum_{i=1}^n\frac{1}{\sqrt{2}}\sum_{i=1}^n\frac{1}{\sqrt{2}}\sum_{i=1}^n\frac{1}{\sqrt{2}}\sum_{i=1}^n\frac{1}{\sqrt{2}}\sum_{i=1}^n\frac{1}{\sqrt{2}}\sum_{i=1}^n\frac{1}{\sqrt{2}}\sum_{i=1}^n\frac$

 $\label{eq:2.1} \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^{2} \left(\frac{1}{\sqrt{2}}\right)^{2} \left(\$

 $\label{eq:2.1} \frac{1}{\sqrt{2}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2.$

 $\label{eq:2.1} \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^{2} \left(\frac{1}{\sqrt{2}}\right)^{2} \left(\$

 $\label{eq:2.1} \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^{2} \left(\frac{1}{\sqrt{2}}\right)^{2} \left(\$ $\label{eq:2.1} \frac{1}{\sqrt{2}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac$

 $\label{eq:2.1} \frac{1}{\sqrt{2\pi}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2\pi}}\left(\frac{1}{\sqrt{2\pi}}\right)^2\frac{1}{\sqrt{2\pi}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{$ $\langle \rangle$.

 $\mathcal{L}(\mathcal{L}(\mathcal{L}))$ and $\mathcal{L}(\mathcal{L}(\mathcal{L}))$. The contribution of the contribution of the contribution of $\mathcal{L}(\mathcal{L})$

 $CH_3CH_2)$ ₄CHO

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m.w. 152

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 $\label{eq:2.1} \frac{1}{\sqrt{2}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2.$ $\label{eq:2.1} \frac{1}{\sqrt{2}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2.$

 $\label{eq:2.1} \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^{2} \left(\frac{1}{\sqrt{2}}\right)^{2} \left(\$ $\label{eq:2.1} \frac{d\mathbf{y}}{d\mathbf{y}} = \frac{1}{2} \left(\frac{\partial \mathbf{y}}{\partial \mathbf{y}} + \frac{\partial \mathbf{y}}{\$

 $\label{eq:2.1} \mathcal{L}(\mathcal{L}(\mathcal{L})) = \mathcal{L}(\mathcal{L}(\mathcal{L})) = \mathcal{L}(\mathcal{L}(\mathcal{L})) = \mathcal{L}(\mathcal{L}(\mathcal{L}))$

 $\label{eq:2.1} \frac{1}{\sqrt{2\pi}}\sum_{i=1}^n\frac{1}{\sqrt{2\pi}}\sum_{i=1}^n\frac{1}{\sqrt{2\pi}}\sum_{i=1}^n\frac{1}{\sqrt{2\pi}}\sum_{i=1}^n\frac{1}{\sqrt{2\pi}}\sum_{i=1}^n\frac{1}{\sqrt{2\pi}}\sum_{i=1}^n\frac{1}{\sqrt{2\pi}}\sum_{i=1}^n\frac{1}{\sqrt{2\pi}}\sum_{i=1}^n\frac{1}{\sqrt{2\pi}}\sum_{i=1}^n\frac{1}{\sqrt{2\pi}}\sum_{i=1}^n\$

C.5. Electron Impact Mass Spectra of Ketones (Listed in order of their elution on an HP-5 capillary column):

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2-Heptanone Fenchone a-Thujone β -Thujone Camphor Menthone Isomenthone Pulegone Carvone Pipertone

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 $\sim 10^{11}$ km s $^{-1}$ $\label{eq:2.1} \begin{split} \mathcal{L}_{\text{max}}(\mathcal{L}_{\text{max}}) & = \mathcal{L}_{\text{max}}(\mathcal{L}_{\text{max}}) \mathcal{L}_{\text{max}}(\mathcal{L}_{\text{max}}) \,, \end{split}$

 $\label{eq:2.1} \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^{2} \left(\frac{1}{\sqrt{2}}\right)^{2} \left(\$ $\label{eq:2.1} \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^{2} \left(\frac{1}{\sqrt{2}}\right)^{2} \left(\$

 $\mathcal{L}(\mathcal{L}^{\text{max}})$ and $\mathcal{L}(\mathcal{L}^{\text{max}})$

 $CH_3CO(CH_2)_4CH_3$

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C.6. Electron Impact Mass Spectra of Ethers (Listed in order of their elution on an HP-5 capillary column):

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 $1,8$ -Cineole Anethole

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 $\mathcal{L}^{\text{max}}_{\text{max}}$, where $\mathcal{L}^{\text{max}}_{\text{max}}$ $\label{eq:2.1} \mathcal{L}(\mathcal{L}^{\mathcal{L}}_{\mathcal{L}}(\mathcal{L}^{\mathcal{L}}_{\mathcal{L}})) \leq \mathcal{L}(\mathcal{L}^{\mathcal{L}}_{\mathcal{L}}(\mathcal{L}^{\mathcal{L}}_{\mathcal{L}})) \leq \mathcal{L}(\mathcal{L}^{\mathcal{L}}_{\mathcal{L}}(\mathcal{L}^{\mathcal{L}}_{\mathcal{L}}))$ $\label{eq:2.1} \frac{1}{\sqrt{2}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2.$ $\label{eq:2.1} \mathcal{L}(\mathcal{L}^{\text{max}}_{\mathcal{L}}(\mathcal{L}^{\text{max}}_{\mathcal{L}})) \leq \mathcal{L}(\mathcal{L}^{\text{max}}_{\mathcal{L}}(\mathcal{L}^{\text{max}}_{\mathcal{L}}))$ $\label{eq:2.1} \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^{2} \left(\frac{1}{\sqrt{2}}\right)^{2} \left(\$ $\mathcal{L}^{\text{max}}_{\text{max}}$ and $\mathcal{L}^{\text{max}}_{\text{max}}$

 $1, 8$ -cineole $m.w. 154$

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C.7. Electron Impact Mass Spectra of n-Alkanes, Alkenes and Aromatics {Listed in order or their elution on an HP-5 capillary column):

> n-Hexane n-Heptane n-Octane p-Xylene n-Nonane 1-Decene n-Decane p-Cymene n-Undecane 1-Dodecene n-Dodecane n-Tridecane 1-Tetradecene n-Tetradecane n-Pentadecane n-Hexadecane n-Heptadecane

 $\left\langle \mathbf{v}\right\rangle$ $\mathcal{L}^{\mathcal{L}}(\mathcal{L}^{\mathcal{L}})$ and the contract of the contrac $\label{eq:2.1} \frac{1}{2} \sum_{i=1}^n \frac{1}{2} \sum_{j=1}^n \frac{$ $\mathcal{L}(\mathcal{L}(\mathcal{L}))$ and $\mathcal{L}(\mathcal{L}(\mathcal{L}))$. The contribution of the contribution of $\mathcal{L}(\mathcal{L})$ $\frac{1}{\sqrt{2}}$

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 $CH_3CH_2)$ ₆CH₃

p-xylene m.w. 106

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 $CH_3CH_2)$ ₈CH₃

m.w. 170

 $CH_3CH_2)_{10}CH_3$

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1-tetradecene m.w. 196

 $CH_2=CH(CH_2)_{11}CH_3$

 \bar{z}

 $CH_3(CH_2)_{12}CH_3$

 \mathbb{L}

 $m.w. 212$

 $CH_3CH_2)_{13}CH_3$

 $CH_3CH_2)_{14}CH_3$

 $CH_3(CH_2)_{15}CH_3$

 $\label{eq:2.1} \frac{1}{\sqrt{2}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac$

 $\label{eq:2.1} \frac{1}{\sqrt{2}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2.$

 $\label{eq:2.1} \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^{2} \left(\frac{1}{\sqrt{2}}\right)^{2} \left(\$

 $\mathcal{L}^{\text{max}}_{\text{max}}$ and $\mathcal{L}^{\text{max}}_{\text{max}}$

 $\label{eq:2.1} \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^{2} \left(\frac{1}{\sqrt{2}}\right)^{2} \left(\$

 $\label{eq:2.1} \mathcal{F}(\mathcal{F}) = \mathcal{F}(\mathcal{F}) \mathcal{F}(\mathcal{F}) = \mathcal{F}(\mathcal{F}) \mathcal{F}(\mathcal{F})$ $\mathcal{L}(\mathcal{L}(\mathcal{L}))$ and $\mathcal{L}(\mathcal{L}(\mathcal{L}))$. The contribution of $\mathcal{L}(\mathcal{L})$

APPENDIX D

ELECTRON IMPACT MASS SPECTRA OF TENTATIVELY IDENTIFIED COMPOUNDS AND LITERATURE REFERENCE SPECTRA

Spectra Are Given of the Following Tentatively Identified Compounds (Listed in order of their elution on an HP-5 capillary column):

> 1-Butylacetate^a Tricyclene^a or a-Thujene^a p-Methylanisole^a 2-Methyl-6-methylene-1,7-octadien-3-onea p-Mentha-1,3,8-trieneb p-Dimethoxybenzene^a Pinocarvone^b p-Cymen-8-olb Estragole^a Methylsalicylate^b Verbenone^a 1-Pentadecene^a 1-Hexadecene^a

aReference spectrum from EPA/NIH Mass Spectral Data Base, 1980. bReference spectrum from Adams, 1989.

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 $D-3$

p-methylanisole $m.w. 122$

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 $D-4$

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150

 110 120 $130 -$

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2-methyl-6-methylene-1,7-octadiene-3-one

p -mentha-1, 3, 8-triene m.w. 134

MENTHATRIENE <1,3,8-PARA-> CAS # 18368-95-1 MF C10 H14 FW 134 DB5-0661 CN 1,3-Cyclohexadiene, 1-methyl-4-(1-methylethenyl)- (9CI) \cdots SYNONYMS Mentha-1,3,8-triene, p-.

p-dimethoxybenzene

m.w. 138

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m.w. 150


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PINOCARVONE
CAS# 16812-40-1
                   MF C10 H14 O
                                      FW 150
                                                  DB5-0781
CN Bicyclo[3.1.1]heptan-3-one, 6,6-dimethyl-2-methylene-
   (9CI)SYNONYMS Nopinenone, 3-. Pinen-3-one, 2(10)-.
100%
           53
      41
                     79
                               107
                                          135
                 69
                          91
                                     122
                                                150
              60
                             100
      40
                      80
                                    120
                                                    160
                                            140
```
p-cymen-8-ol $m.w. 150$

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m.w. 148

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 \dot{a} 100 110 120 130 140 150

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m.w. 152

150 $C_{10}H_{14}O$
Bicyclo[3.1.1]hept-3-en-2-one, 4,6,6-trimethyl- $80 - 57 - 9$

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1-hexadecene

m.w. 224

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