HYDROCARBON EMISSIONS FROM VEGETATION FOUND IN CALIFORNIA'S CENTRAL VALLEY

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ABSTRACT

An essential database for modeling photochemical air pollution in California's Central Valley is a reliable gridded emission inventory for reactive organic gases (ROG). To date, however, there has been a lack of quantitative information concerning the amounts of organic gases emitted from natural sources, particularly vegetation, in the Sacramento Valley and San Joaquin Valley Air Basins. To address this need, we have measured the rates of emission of speciated hydrocarbons from more than thirty of the most important (based on acreage) agricultural and natural plant types relevant to California's Central Valley.

These measurements employed flow-through Teflon chambers, solid adsorbent/thermal desorption sample collection, and the close coupling of gas chromatography (GC) and GC-mass spectrometry (GC/MS) for compound identification and quantitation. Emission rate protocols were conducted in the summers of 1988 and 1989 on plant specimens grown at UC Riverside according to standard agricultural practices. Some four dozen individual compounds were identified as emissions from the agricultural and natural plant species studied. In addition to isoprene and the monoterpenes, sesquiterpenes, alcohols, acetates, aldehydes, ketones, ethers, esters, alkanes, alkenes and aromatics were all observed. Data obtained in this study demonstrated again that there can be large variations in emission rates from a single specimen of a given plant species, as well as from multiple specimens of a cultivar.

Mean emission rates for total monoterpenes ranged from none detected in the case of beans, grapes, rice and wheat, to as high as ~12-30 $\mu g\ hr^{-1}\ gm^{-1}$ for pistachio and tomato (normalized to dry leaf and total biomass, respectively). Other agricultural species exhibiting substantial rates of emission of monoterpenes included carrot, cotton, lemon, orange and walnut. All of the agricultural crops and natural plant species for which full sampling protocols were conducted showed total assigned plant emission (TAPE) rates above the detection limits in this study, with a range between 0.1 and 70 $\mu g\ hr^{-1}\ gm^{-1}$. Reliable measurements of biomass are required before the importance of these emission rates to the ROG inventory for California's Central Valley can be determined.

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DISCLAIMER

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

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GLOSSARY OF TERMS, ABBREVIATIONS AND SYMBOLS

a.m.u.	Atomic mass units
AQS	Air quality standard
CARB	California Air Resources Board
gm	Gram
GC	Gas chromatograph, gas chromatography, or gas chromatographic
GC-FID	Gas chromatography with flame ionization detection
GC/MS	Gas chromatography-mass spectrometry
H_2O	Water
hr	Hour
i.d.	Internal diameter
in.	Inch
K	Degrees Kelvin
kg	Kilogram
ℓ	Liter
m	Meter
mm	Millimeter (10^{-3} m)
m^3	Cubic meter
MID	Multiple ion detection technique, used together with GC-MS
min	Minute
m.w.	Molecular weight
m/z	Mass to charge ratio
NO_x	Oxides of nitrogen
O_3	Ozone
o.d.	Outer diameter
PDT	Pacific daylight time
PM-10	Particulate matter less than 10 μm in diameter
ppb	Parts per billion
ppbC	Parts per billion carbon
ppm	Parts per million
ROG	Reactive organic gases
SAPRC	Statewide Air Pollution Research Center
SoCAB	South Coast Air Basin
SS	Stainless steel
TAPE	Total assigned plant emissions

TC	Total carbon
TIC	Total ion current or total ion chromatogram
μE	Microeinstein
μg	Microgram (10^{-6} gram)
UCR	University of California, Riverside

I. EXECUTIVE SUMMARY

It is well established that vegetation emits a large number of organic compounds into the atmosphere and that on regional, continental and global scales, such emissions may be comparable to, or exceed, the emissions of non-methane hydrocarbons from anthropogenic sources. Moreover, laboratory and modeling studies have shown that vegetative emissions such as isoprene and the monoterpenes are highly reactive compounds under tropospheric conditions, and in the presence of NO_x and sunlight these biogenic emissions can contribute to the formation of ozone and other secondary air pollutants.

Although a number of studies have been conducted to determine the rates of emission of organic compounds from vegetation over the past two decades, the number of individual plant species for which data are available remains limited. In particular, essentially no experimentally-determined emission rate data exist for the agricultural crops grown in California's Central Valley. Yet this region, which includes the San Joaquin Valley in the south and the Sacramento Valley in the north, exhibits topographical and meterological conditions conducive to the formation of photochemical air pollution and has a persistent and, in some regions of the Valley, a growing secondary air pollutant problem due to dramatic growth in population and both mobile and stationary emission sources. Unless appropriate policies are pursued, in the coming decades air pollution could pose a serious threat to the continued productivity of agricultural operations in the Central Valley.

Among the most important resources for the development of such policies is an accurate and comprehensive inventory of emissions of organic compounds from both anthropogenic and natural sources (as well as an inventory of oxides of nitrogen emissions). However, prior to the present investigation there was an almost complete absence of experimentally-determined emission rates for even isoprene and the monoterpenes, let alone for other reactive gases which may be emitted from vegetation. To address this need, we have conducted a program to measure the rates of emission of speciated hydrocarbons from more than thirty of the most important (based on acreage) agricultural and natural plant types relevant to California's Central Valley using a flow-through Teflon enclosure technique previously employed in studies of this kind.

In conducting these emission rate measurements, we exploited advances which have been made during the past decade in solid adsorbent/thermal desorption techniques for the collection of low volatility, low concentration organic compounds, and the close coupling of gas chromatography with flame ionization detection (GC-FID) and GC-mass spectrometry (GC/MS) for unambiguous compound identification and quantitation. Therefore, our present approach has provided a significant improvement in the quantitative, speciated characterization of emission rates relative to approaches employed earlier in this and other laboratories.

The compounds identified as emissions from the agricultural and natural plant species investigated are listed in Table I-1 by compound class. Isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$), sesquiterpenes ($C_{15}H_{24}$), alcohols, acetates, aldehydes, ketones, ethers, esters, alkanes, alkenes and aromatics were all observed as emissions from one or more of the plant species studied. Consistent with the literature, we found isoprene to be emitted from the species of oak (Valley oak) chosen as representative of the natural foothill hardwood plant community in the Central Valley. Significantly, no other plant species studied emitted detectable levels of isoprene.

For a few of the species studied, one or two terpenes were the major emissions (as has been reported for many conifers). Far more common, however, was the presence of several terpenes at comparable concentrations, together with additional compound classes, as emissions from a single plant species. Oxygenated compounds were observed from virtually every plant species studied, with cis-3-hexenylacetate, cis-3-hexen-1-ol, n-hexanal and trans-2-hexenal being the most often observed oxygenates. Alkenes were also common emissions, and generally in higher concentrations than the n-alkanes.

Following GC/MS survey experiments to determine the speciated organics emitted from each plant type, and to permit subsequent identification by GC-FID based on retention time, systematic five-sample protocols were conducted between approximately 0900 hr and 1500 hr (PDT) for each plant species, with up to three different specimens sampled for each species. These measurements were conducted on the UCR campus during the summers of 1988 and 1989 on plant specimens grown according to standard agricultural practices and representing primarily cultivars

Table I-1. List of Organic Compounds Observed from Vegetation[a]

Isoprene

MONOTERPENES
Camphene
2-Carene
Δ^3-Carene
d-Limonene
Myrcene
cis-Ocimene
trans-Ocimene
α-Phellandrene
β-Phellandrene
α-Pinene
β-Pinene
Sabinene
α-Terpinene
γ-Terpinene
Terpinolene
Tricyclene
or α-Thujene (tentative)[b]

SESQUITERPENES
β-Caryophyllene
Cyperene
α-Humulene

ALCOHOLS
p-Cymen-8-ol (tentative)[b]
cis-3-Hexen-1-ol
Linalool

ACETATES
Bornylacetate
Butylacetate (tentative)[b]
cis-3-Hexenylacetate

ALDEHYDES
n-Hexanal
trans-2-Hexenal

KETONES
2-Heptanone
2-Methyl-6-methylene-1,7-octadien-3-one (tentative)[b]
Pinocarvone (tentative)[b]
Verbenone (tentative)[b]

ETHERS
1,8-Cineole
p-Dimethoxybenzene (tentative)[b]
Estragole (tentative)[b]
p-Methylanisole (tentative)[b]

ESTERS
Methylsalicylate (tentative)[b]

n-ALKANES
n-Hexane
C_{10}-C_{17}

ALKENES
1-Decene
1-Dodecene
1-Hexadecene (tentative)[b]
Menthatriene (tentative)[b]
1-Pentadecene (tentative)[b]
1-Tetradecene

AROMATICS
p-Cymene

[a]Unless labeled "Tentative", identifications were made on the basis of matching full mass spectra and retention times with authentic standards. The structures and electron impact mass spectra of the authentic standards are given in Appendix C.
[b]Tentative identifications were made on the basis of matching the mass spectra (and retention order when available) with published spectra (EPA/NIH Mass Spectral Data Base and/or Adams, 1989). The literature spectra and those of the plant emissions are given in Appendix D.

which are widely grown in the Central Valley. The native plant species studied were located in the UCR Botanic Garden.

The mean emission rates of isoprene (for the Valley Oak only), the monoterpenes, the sesquiterpenes and the total assigned plant emissions (TAPE) for each of the plant species for which full sampling protocols were conducted are summarized in Table I-2, along with the corresponding mean temperatures. Also included in Table I-2 is a column for total carbon (TC) which is an upper limit for the emission rates since it is calculated from the sum of all the carbon in the sample, i.e., it includes the TAPE and any additional GC peaks. 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 $\gtrsim 30$ $\mu g\ hr^{-1}\ gm^{-1}$ of monoterpene emissions from the two cultivars of tomato investigated. The Kerman pistachio also fell in the high emitter category with a rate of about 12 $\mu g\ hr^{-1}\ gm^{-1}$. 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 of the analytical methods employed. A second group, consisting of alfalfa, cotton, and olive displayed emission rates below 0.1 $\mu g\ hr^{-1}\ gm^{-1}$ 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 0.8 $\mu g\ hr^{-1}\ gm^{-1}$.

All of the agricultural crops for which full protocols were done exhibited total assigned plant emission (TAPE) rates above the detection limits in this study. Crops with TAPE emission rates above 10 $\mu g\ hr^{-1}\ gm^{-1}$ included pistachio and tomato. Although rice also exhibited a mean TAPE emission rate above 10 $\mu g\ hr^{-1}\ gm^{-1}$, this result must be used with caution since two of the five protocol samples had dry leaf weights of only 6-8 gm, 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

Table I-2. Summary of Mean Emission Rates by Compound Class for Agricultural and Natural Plant Species for which Complete Protocols were Conducted

Plant Species	Mean Emission Rates ($\mu g\ hr^{-1}\ gm^{-1}$)[c]				Mean Temperature (°C)
	Σ Monoterpenes	Σ Sesquiterpenes	TAPE	TC	
Agricultural					
Alfalfa (Pierce)[d]	0.4	<0.03	1.5	2.3	36.7
Almond (Nonpareil)	0.01	a	2.1	9.3	29.1
Apricot (Blenheim)	<0.12	a	1.4	5.3	29.8
Bean (Top Crop)[d]	b	b	0.19	2.2	33.8
Carrot (Imperator Long)	1.4	a	1.4	2.4	34.8
Cherry (Bing)	<0.07	0.53	1.1	3.2	28.0
Cotton (Pima)	1.1	0.05	1.9	3.1	36.2
Cotton (Pima)[d]	0.69	0.03	1.2	2.0	36.1
Grape (Thompson seedless)	b	b	2.0	8.2	33.8
Grape (French Columbard)	b	0.13	2.2	5.0	34.9
Lemon (Lisbon)	3.6	a	4.0	8.4	31.2
Nectarine (Armking)	<0.06	a	0.86	6.0	30.7
Olive (Manzanillo)	0.05	0.06	0.96	2.9	29.3
Orange (Washington Navel)	0.83	a	0.88	1.2	21.4
Orange (Valencia)	1.7	a	3.1	7.0	36.7
Pasture, Irrigated[d]	e	e	0.52	3.2	37.8
Peach (Halford)	0.27	0.85	5.9	7.6	32.1
Pistachio (Kerman)	12.5	b	16.2	19.1	33.6
Plum (Santa Rosa)	<0.06	b	3.9	6.0	36.3
Rice	b	b	11.3[f]	20.7[f]	37.0
Safflower[g]	0.09	0.79	2.7	5.4	40.6
Sorghum	0.07	b	2.2	5.0	38.8
Tomato[d] (Sunny)	26.7	0.10	27.5	29.5	38.0
Tomato (Sunny)	58.1	0.21	59.9	64.1	38.0
Tomato[d] (Canning)	33.8	0.17	35.5	39.1	35.4
Tomato (Canning)	66.7	0.33	70.2	77.2	35.4
Walnut (Hartley)	3.3	0.13	5.9	8.4	36.8
Wheat[d]	b	b	0.13	1.1	37.8

(continued)

Table I-2 (continued) - 2

Plant Species	Mean Emission Rates ($\mu g\ hr^{-1}\ gm^{-1}$)[c]				Mean Temperature (°C)
	Σ Monoterpenes	Σ Sesquiterpenes	TAPE	TC	
Natural					
Chamise	0.32	b	1.3	2.5	28.5
Grasslands, Annual[d]	<0.02	b	0.13	1.1	32.7
Manzanita (Big Berry)	e	e	0.22	1.3	27.4
Valley Oak[h]	<0.01	b	2.8	3.8	26.9
Whitethorn	4.5	0.32	10.2	14.8	28.0

[a]No data.
[b]None detected.
[c]Normalized to dry leaf weight, unless noted.
[d]Normalized to total dry weight (excluding fruit).
[e]No data; no survey conducted.
[f]Use with caution; see text.
[g]Normalized to dry weight of leaves and bracts.
[h]Isoprene = 2.3 $\mu g\ hr^{-1}\ gm^{-1}$.

TAPE from rice would be 3 $\mu g\ hr^{-1}\ gm^{-1}$ vs. the reported value of 11 $\mu g\ hr^{-1}\ gm^{-1}$. The natural plant species whitethorn also had a TAPE emission rate above 10 $\mu g\ hr^{-1}\ gm^{-1}$.

Crops with TAPE emission rates between 1 and 10 $\mu g\ hr^{-1}\ gm^{-1}$ 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 $\mu g\ hr^{-1}\ gm^{-1}$ 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 beans, nectarine, olive, Washington Navel orange, and wheat displayed TAPE emission rates below 1 $\mu g\ hr^{-1}\ gm^{-1}$.

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, in general, 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 I-3, and a corresponding grouping by order of magnitude ranges in the sum of total monoterpene and sesquiterpene emission rates is shown in Table I-4.

As seen in Table I-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 $\mu g\ hr^{-1}\ gm^{-1}$ for grasslands and manzanita to a high value of 10 $\mu g\ hr^{-1}\ gm^{-1}$ for whitethorn. Chamise and whitethorn were significant monoterpene emitters, while Valley oak was the only confirmed isoprene emitter found among either the agricultural or natural plant species investigated.

Table I-3. Qualitative Grouping of Agricultural Crops by Rates ($\mu g\ hr^{-1}\ gm^{-1}$) of Total Assigned Plant Emissions

Low <1	Middle 1-10	High >10
Bean	Alfalfa	Pistachio
Nectarine	Almond	Rice[d]
Olive	Apricot	Tomato[e]
Orange[a]	Carrot	
Pasture	Cherry	
Wheat	Cotton	
	Grape[b]	
	Lemon	
	Orange[c]	
	Peach	
	Plum	
	Safflower	
	Sorghum	
	Walnut	

[a]Washington navel.
[b]Thompson seedless and French columbard.
[c]Valencia.
[d]See text.
[e]Sunny and canning.

Table I-4. Qualitative Grouping of Agricultural Crops by Rates ($\mu g\ hr^{-1}\ gm^{-1}$) of Total Monoterpene plus Sesquiterpene Emissions

<0.1	0.1-1	1-10	>10
Almond	Alfalfa	Carrot	Pistachio
Bean[a]	Apricot	Cotton[f]	Tomato[h]
Grape[a,b]	Cherry	Lemon	
Nectarine	Cotton[c]	Orange[g]	
Plum	Grape[d]	Peach	
Rice[a]	Olive	Walnut	
Sorghum	Orange[e]		
Wheat[a]	Safflower		

[a]None detected.
[b]Thompson seedless.
[c]Normalized to total dry weight.
[d]French columbard.
[e]Washington navel.
[f]Normalized to dry leaf weight.
[g]Valencia.
[h]Sunny and canning.

The emission sampling protocol, which called for five measurements for a given plant species over the course of a six hour period from mid-morning to mid-afternoon, was designed in part to characterize, if possible, the temperature dependence of the emissions. However, in practice only in a few cases did the individual emission rates within a protocol vary with temperature in a correlated way, and we have reported mean emissions rates. Generally, the mean sampling temperatures 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 regards to their emissions at various temperatures.

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. These considerations should 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.

Another major conclusion of the present work is the clear 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. These findings suggest that ambient measurements should be conducted in vegetation canopies to establish whether some or all of the compounds identified here as emissions from vegetation can also be identified in ambient air.

Since the emission rates obtained in this study are normalized to dry biomass weight, quantitative application of these data requires biomass assessments for California's Central Valley which are being conducted under separate ARB sponsorship.

Although the data obtained in the present study for the rates of 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 rates 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 appropriate vegetation canopies.

- 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. from anthropogenic sources in California's airsheds.

II. INTRODUCTION

A. Background and Statement of the Problem

The highly complex series of reactions arising from the interaction of organic compounds and oxides of nitrogen (NO_x) under the influence of sunlight in the lower troposphere leads to photochemical air pollution, with its attendant manifestations of ozone formation, gas-to-particle conversion and visibility impairment (Seinfeld, 1989). While the emissions of NO_x ($NO + NO_2$) into the troposphere are largely due to anthropogenic sources (Logan, 1983) [especially in urban areas], nonmethane organic compounds are emitted from both anthropogenic and biogenic sources (Logan et al., 1981). To date, a wide spectrum of nonmethane organic compounds have been identified as being emitted from vegetation (see, for example, Table II-1 and Graedel, 1979; Zimmerman, 1979a; Roberts et al., 1983, 1985; Hov et al., 1983; Isidorov et al., 1985; Zimmerman et al., 1988; Jüttner, 1988; Yokouchi and Ambe, 1988; Petersson, 1988; Juuti et al., 1989), with isoprene ($CH_2{=}C(CH_3)CH{=}CH_2$) and the monoterpene isomers ($C_{10}H_{16}$) being the most commonly identified and measured.

Numerous studies have shown that isoprene is the major biogenic emission from certain deciduous trees (Rasmussen, 1972; Zimmerman, 1979a; Tingey et al., 1979; Isidorov et al., 1985; Lamb et al., 1985, 1986; Zimmerman et al., 1988; Rasmussen and Khalil, 1988) and that α- and β-pinene are either the major, or are among the major, emissions from coniferous trees (Rasmussen, 1972; Zimmerman, 1979a; Holdren et al., 1979; Tingey et al., 1980; Hov et al., 1983; Roberts et al., 1983, 1985; Isidorov et al., 1985; Lamb et al., 1985; Riba et al., 1987; Jüttner, 1988; Petersson, 1988; Juuti et al., 1989), and these compounds have generally been the only biogenic compounds considered in formulating biogenic emission inventories. Consistent with these previous studies, the total ion chromatogram (TIC) we obtained from the gas chromatography/mass spectrometry (GC/MS) analysis of the emissions of a Monterey pine is shown in Figure II-1, showing α- and β-pinene to be the major biogenic compounds emitted.

Table II-1. Organics Observed in Volatile Emissions of Vegetation (from Isidorov et al. [1985] except as indicated)

Compound	Compound
Propene	Chloroform
Butene	Dimethyl sulphide
Isoprene	Dimethyl disulphide
2-Methylbutane	Santene
1,3-Pentadiene	Cyclofenchene
2,3-Dimethylbutadiene	Bornilene
Methanol	Tricyclene
Ethanol	α-Thujene
Diethyl ether	α-Pinene
3-Hexen-1-ol	δ-Fenchene
Propanal	ε-Fenchene
Isobutanal	α-Fenchene
Crotonal	β-Fenchene
Isobutenal	Camphene
Butanal	Sabinene
n-Hexanal	β-Pinene
Acetone	Mycene
2-Butanone	3-Carene
Methyl vinyl ketone	α-Phellandrene
2-Pentanone	β-Phellandrene
3-Pentanone	α-Terpinene
Methyl isopropyl ketone	β-Terpinene
Furan	γ-Terpinene
2-Methylfuran	Limonene
3-Methylfuran	Ocimene[a]
Ethylfuran	Terpinolene
Vinyl furan	Alloocimene
Hexenyl furan	1,8-Cineole
Ethyl acetate	Fenchone
3-Octanone	Thujone
Diethylcyclopentenone	Camphor
3-Hexenylacetate	p-Cymene
Methylbutyrate	Menthane
Methylcapronalate	Anethole
Isobutenal	Perillene
Methyl chloride	

[a]From Evans et al. (1982).

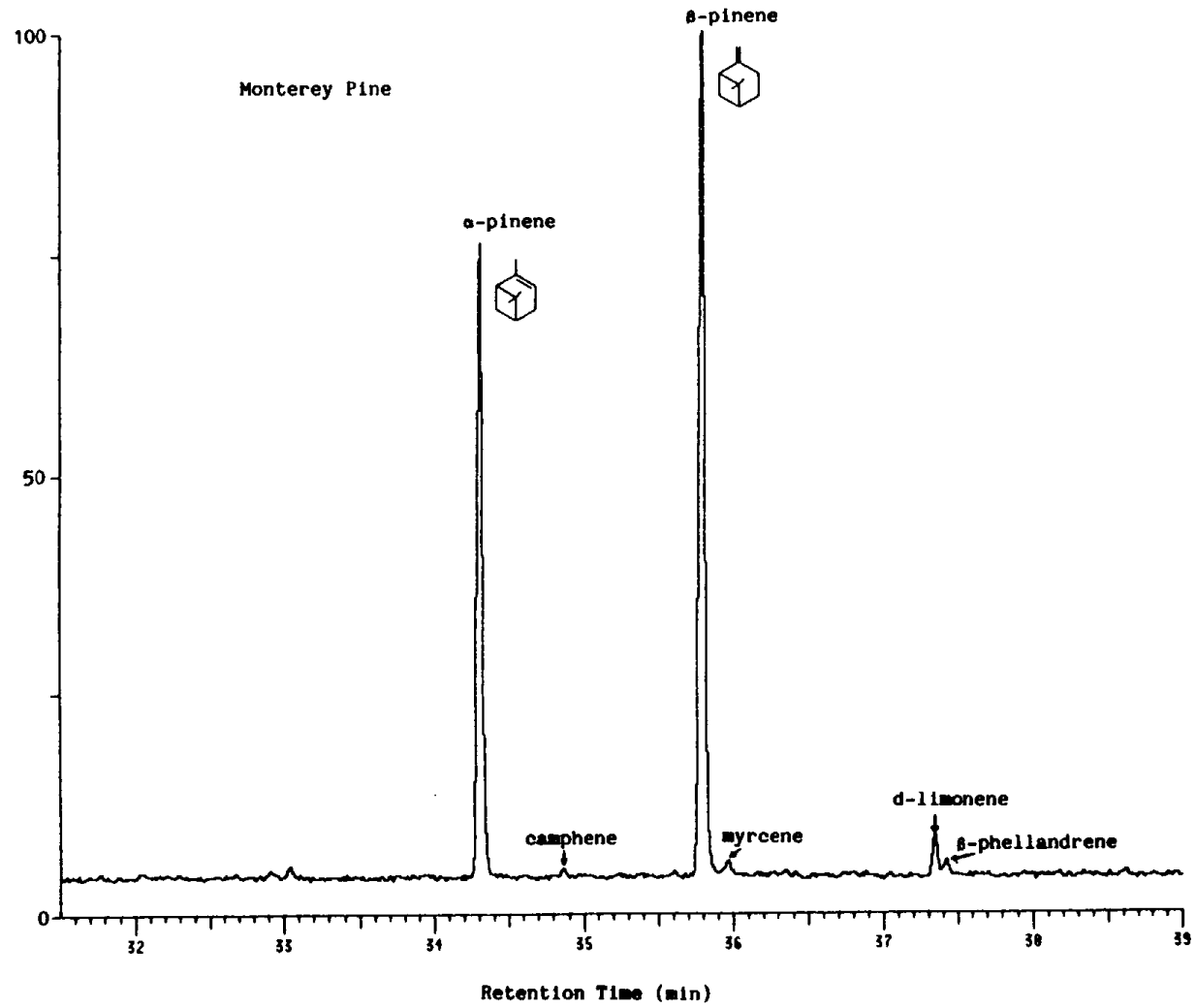


Figure II-1. Total ion chromatogram from the gas chromatography/mass spectrometry analysis of the emissions of a Monterey pine. The emissions were sampled from a Teflon enclosure onto a Tenax-GC adsorbent cartridge which was then thermally desorbed onto a 50 m HP-5 capillary colum.

On a regional and global scale the emissions of these compounds of vegetative origin appear to be comparable to, or exceed, the emissions of organic compounds from anthropogenic sources (Zimmerman et al., 1978, 1988; Lamb et al., 1987). Laboratory data have shown that isoprene and the monoterpenes are highly reactive compounds under tropospheric conditions (Lloyd et al., 1983; Killus and Whitten, 1984; Atkinson and Carter, 1984; Atkinson et al., 1986, 1988), and in the presence of NO_x and sunlight these biogenic emissions can contribute to ozone formation. Thus, recent computer modeling studies, using isoprene as a surrogate for biogenic nonmethane hydrocarbons, 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).

While a number of studies have been carried out to determine the organic compounds emitted and the corresponding emission rates from a variety of vegetation types (see, for example, Zimmerman, 1979a; Tingey et al., 1979, 1980; Evans et al., 1982; Winer et al., 1983; Lamb et al., 1985, 1986, 1987; Zimmerman et al., 1988), the number of plant species for which data are available is still small. In particular, and of especial importance with regards to the present study, essentially no biogenic emission rate data exist for the agricultural crops grown in California.

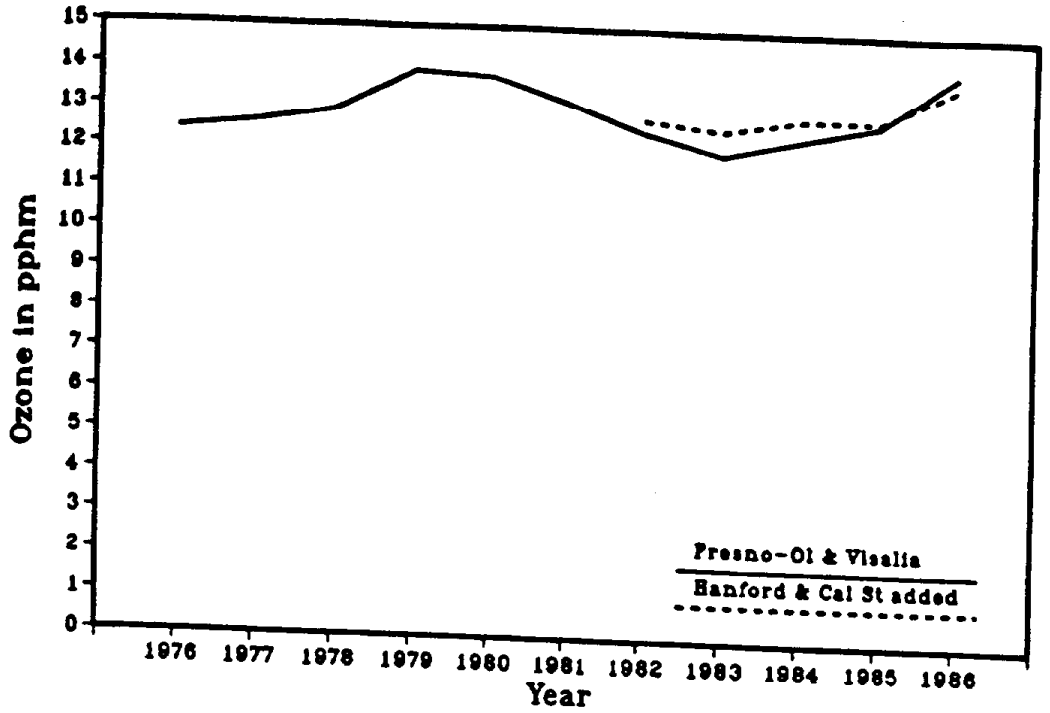
California continues to have the most serious photochemical air pollution problem in the United States, including the highest ozone levels. The two major areas in California affected by adverse air quality are the Los Angeles air basin in Southern California (South Coast Air Basin) and the Central Valley, which also receives polluted airmasses transported from the San Francisco Bay area (Figure II-2). The Central Valley, which includes the San Joaquin Valley in the south and the Sacramento Valley in the north (Figure II-2), has the highest concentration of agricultural production in California, and also exhibits the topographical and meteorological characteristics conducive to the formation of photochemical air pollution. Indeed, the California Air Resources Board (ARB) estimates that if emission densities similar to those in the Southern California Air Basin were placed in the Central Valley, air quality could become worse than in the Los Angeles Air Basin (ARB, 1988).

Figure II-2. Map of California showing the major air basins.

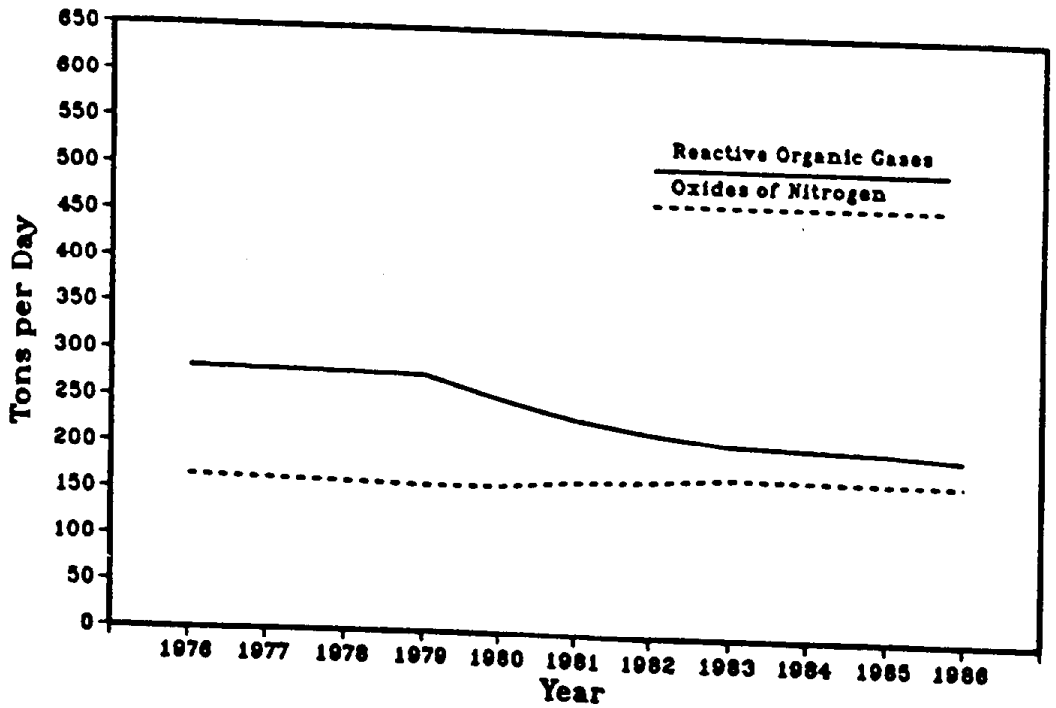
At the present time, the economy of the Central Valley is growing rapidly, at a rate greater than for the state as a whole. Unless appropriate policies concerning urbanization and air quality are pursued, in the coming two decades air pollution will pose a great threat to the continued productivity of agricultural operations in the Central Valley, particularly in the San Joaquin Valley Air Basin. Moreover, by measures such as the number of days above the federal ozone standard, portions of the Central Valley (e.g., Fresno and Kings counties) already experience worse air quality than such major cities as New York, Houston, Philadelphia, and Chicago (ARB, 1988).

One of the most critical impacts of these adverse pollutant levels is the reduction in yields of many of the state's important crops (ARB, 1987; Olszyk et al., 1988a,b; Winer et al., 1990). At the present time, the economic losses corresponding to these reduced yields in California are estimated to range up to several hundred million dollars (Howitt et al., 1984; ARB, 1987; Winer et al., 1989), with the most serious economic impacts occurring in the Central Valley.

Although many of the control strategies adopted for mobile and stationary sources are clearly effective in reducing primary pollutant emissions from individual sources, the increasing urbanization and industrialization of the Central Valley continues to limit the overall effectiveness of these gains. In fact, with the exception of carbon monoxide levels, the Central Valley has largely failed to participate in such improvements. Specifically, over the past 10 years ozone levels in the San Joaquin Valley Air Basin (Figure II-3A) have remained essentially constant despite significant reductions in hydrocarbon emissions (Figure II-3B). In addition, particulate matter and visibility have actually worsened in the southern portion of the Basin (ARB, 1988). Indeed, the fine particulate (PM-10) problem in the Central Valley is among the most complex and difficult in California (ARB, 1988). The trends evident in Figure II-3 reflect the complex relationship between secondary air pollutant levels and primary emissions of reactive organic gases (ROG) and oxides of nitrogen (NO_x) precursors (Finlayson-Pitts and Pitts, 1986), and suggest that achieving improvements in air quality in the Central Valley over the next two decades will be a challenging task.



(A)



(B)

Figure II-3. (A) San Joaquin Valley ozone trends analysis. Ozone trends for central portion, 1975-1987. 3 year mean of top 2% of maximum hourly concentration. (B) ROG and NO_x emissions for central portion of the valley, 1975-1987. Emission estimates for an average annual day.

This challenge will be made more difficult by the growth in population and industrial activity predicted to occur in the Central Valley over the next two decades, and the resulting increase in primary pollutant emissions which will occur if no further control programs are adopted. (See the example for the San Joaquin Valley in Figure II-4). Thus, it is essential to continue to improve the data bases upon which planning and computer modeling studies are based in order to develop and implement the most cost-effective control strategies in the future.

Among the most important tools for this purpose is an accurate and comprehensive inventory of emissions of organic gases of anthropogenic and biogenic origin and oxides of nitrogen. However, a major gap in the ROG emission inventory for most of the airsheds in California, including the Central Valley, has been the lack of quantitative information concerning the amounts of organic gases emitted from natural sources, particularly vegetation. More specifically, while reasonably complete and reliable data are available on the acreages of natural and agriculturally-important vegetation in the Central Valley, there is almost a complete absence of experimentally determined emission rates for even isoprene and the monoterpenes, let alone for other reactive gases which may be emitted from vegetation.

In order to provide a data base for the elucidation of the sources and sinks of ozone and PM-10 in the San Joaquin Valley and the San Francisco Bay Area, two large and comprehensive field studies will be conducted in the summer of 1990, these being the San Joaquin Valley Air Quality Study (SJVAQS) and the Atmospheric Utility Signatures, Predictions and Experiments (AUSPEX) study. The goals of the SJVAQS are to obtain an improved understanding of the causes of the ozone concentrations in the San Joaquin Valley and to provide the data required to assess the impacts of alternative emission control strategies for the reduction of ozone in this air basin. In order to more fully understand the potential role of biogenic emissions from agricultural crops and natural vegetation in the Central Valley prior to the SJVAQS and AUSPEX studies (for example, to optimize the ambient air sampling and measurement networks), the California Air Resources Board contracted the Statewide Air Pollution Research Center at the University of California, Riverside, to experimentally measure the emission rates of biogenic organic compounds

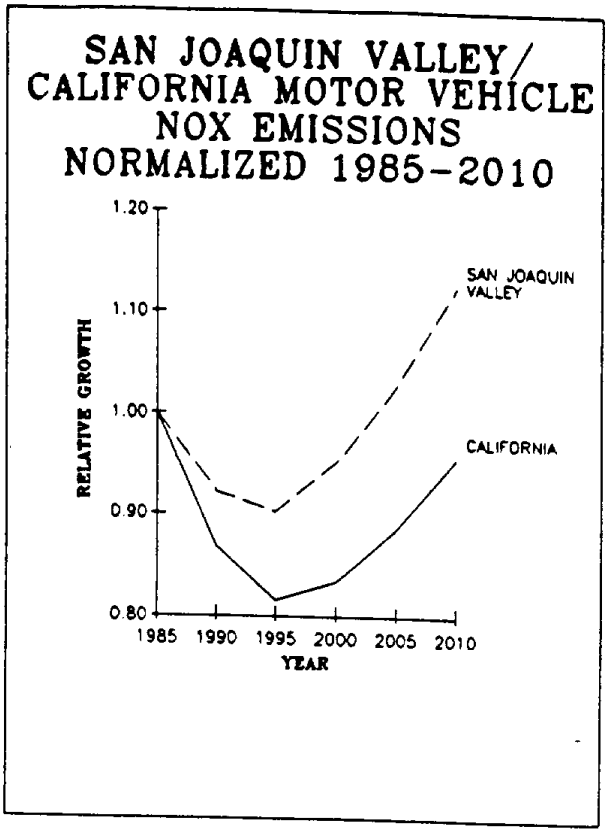


Figure II-4. San Joaquin Valley and California motor vehicle NO_x emissions for 1985-2010; normalized to 1985 (from ARB, 1988).

from the most important agricultural crops and natural vegetation in the Central Valley.

To obtain a gridded emission inventory for biogenic compounds, it is essential to experimentally measure the emission rates of organic compounds from the dominant vegetation species and to combine these data with plant species distribution or biomass assessments. The overall objective of this project was to experimentally determine the emission rates and chemical composition of organic gases from prominent vegetation sources that are likely to affect photochemical oxidant formation in California's Central Valley. These data will then be employed by ARB staff, in combination with available data on land use and biomass density, to develop a spatially-gridded hydrocarbon emission inventory for agriculturally-important and naturally-occurring vegetation sources.

B. Brief Description of Related Studies

Although it is well established that many species of vegetation emit significant amounts of hydrocarbons (Rasmussen and Went, 1965; Rasmussen, 1970; Holdren et al., 1979; Graedel, 1979; Zimmerman, 1979a,b; Tingey et al., 1979, 1980; Winer et al., 1983; Isidorov et al., 1985; Lamb et al., 1985, 1986; Jüttner, 1988; Petersson, 1988; Yokouchi and Ambe, 1988), because of the complexity, cost and magnitude of effort required to assemble detailed emission inventories for naturally-emitted organics, there have been relatively few previous attempts to obtain such data. However, Zimmerman (1979a,b,c) developed a vegetation enclosure procedure and made measurements of biogenic hydrocarbon emissions in Tampa Bay, Florida and Houston, Texas.

Subsequently, Winer and co-workers (Winer et al., 1982, 1983; Miller and Winer, 1984; Brown and Winer, 1986) conducted a similar, detailed investigation of hydrocarbon emissions from both ornamental and natural vegetation in California's South Coast Air Basin (SoCAB). In this project, sponsored by the ARB, enclosure samples were collected from indigenous plant species in 5 vegetation categories (Miller and Winer, 1984) and analyzed for isoprene and selected monoterpenes.

A limited number of other studies employing related methodologies have been reported (Flyckt, 1979; Schulting et al., 1980; Hunsaker, 1981; Hunsaker and Moreland, 1981; Lamb et al., 1985), and recently Lamb et al. (1987) compiled a national inventory of biogenic hydrocarbon emissions, relying on data from these previous studies. Most of these previous studies emphasized emissions of isoprene and monoterpenes, rather than other non-methane hydrocarbons (NMHC), since isoprene and monoterpenes such as α- and β-pinene, camphene, limonene and myrcene were among the major compounds emitted by the vegetation for which data then existed.

Although there have been isolated reports of detection of low molecular weight alkanes and alkenes, as well as certain oxygenates and aromatic compounds from vegetation (Rasmussen, 1972; Holzer et al., 1977; Shulting et al., 1980; Evans et al., 1982; Kimmirer and Kozlowski, 1982; Isidorov et al., 1985), to date no quantitative determinations of the emissions of such organic compounds from vegetation have been reported. Moreover, as indicated in Table II-2, because of a heavy emphasis on emissions from forests, scrublands, and grasslands, and on vegetation

categories found in urban airsheds, prior to this study there remained almost a complete lack of emissions data of any kind for agriculturally important crops.

1. Previous Experimental Approaches

As discussed recently by Lamb et al. (1987), the previous studies of hydrocarbon emissions from vegetation listed in Table II-2 involved a total of four basic approaches: one laboratory-based method and three field methods. The most common of these is the so-called enclosure method. For example, semi-quantitative estimates of hydrocarbon emissions were made by Rasmussen (1970, 1972) and by Sanadze and Kalandze (1966) using static gas exchange chambers containing either detached leaves or twigs, or whole plants. Zimmerman (1979a,b,c) enclosed tree branches or small plants in a large Teflon bag which was sealed, evacuated and refilled with hydrocarbon-free air. After a period of time the head space of this static system was analyzed by gas chromatography to determine the gas phase concentrations of organics.

Dynamic mass-balance, gas-exchange chambers which attempted to simulate the gaseous environment of plants in the field have also been employed (Tyson et al., 1974; Kamiyama et al., 1978; Tingey et al., 1978, 1979) in emission rate measurements, as well as in determining the influence of environmental factors on these rates. Winer et al., (1982, 1983) used a similar approach which is discussed in more detail below.

The advantages of such enclosure methods over the ambient techniques described below are their relative simplicity and the ability to sample different plant species individually, thereby obtaining species-specific emissions data. When combined with land-use data or biomass distribution maps, data from the enclosure techniques permit calculation of an explicit gridded emissions inventory. The disadvantages of this approach are the needs to minimize enclosure effects and to conduct a biomass survey, and the requirement to extrapolate from a small number of plant specimens.

The so-called micrometeorological approach, based on surface layer theory, involves measurement of hydrocarbon concentration gradients above a large, uniform, plane source (e.g., certain vegetation canopies). In this method, temperature and wind speed, or water vapor concentration gradients, must be measured in order to determine the eddy diffusivity, which in turn permits calculation of the hydrocarbon flux from the

Table II-2. Examples of Previous Experimental Measurements of Hydrocarbon Emissions from Vegetation

Investigator	Location	Measurement Technique	Predominant Plant Species Studied
Rasmussen and Went (1965)		enclosure	ornamental
Rasmussen (1972)		enclosure	deciduous and conifers
Tyson et al. (1974)		enclosure	coastal chaparral
Flyckt (1979)	Pullman, WA	enclosure	red oak
Zimmerman (1979b)	Tampa Bay, FL	enclosure	variety
Knoerr and Mowry (1981)	Raleigh, NC	micrometeorological	loblolly pine
Tingey et al. (1979,1980)	-	laboratory chamber	live oak, slash pine
Arnts et al. (1982)	Raleigh, NC	tracer model	loblolly pine
Winer et al. (1983)	Los Angeles, CA	enclosure	urban ornamentals and coastal chaparral
Lamb et al. (1985)	Lancaster, PA Atlanta, GA Seattle, WA	enclosure and micrometeorological	deciduous and Douglas fir
Lamb et al. (1986)	Goldendale, WA	tracer flux and enclosure	Oregon white oak

concentration gradient. Such gradient methods have extremely stringent sensor and site requirements (i.e., large areas of similar vegetation with long fetch) and are difficult to set up, and therefore their use has been confined primarily to making comparisons with enclosure measurements (Knoerr and Mowry, 1981; Lamb et al., 1985).

Lamb et al. (1986) have employed a third technique, also to test enclosure methods, in which they released an SF_6 tracer and measured the downwind concentration profiles of the SF_6 and the hydrocarbons. They found excellent agreement between results from this method, when applied to an isolated white oak grove in Oregon, with enclosure measurements of isoprene emission rates. Subsequently, Lamb and co-workers (Lamb et al., 1987) conducted several other comparisons of the micrometeorological techniques with enclosure measurements and found reasonable to good agreement.

A fourth approach, a special case of enclosure measurements, involved the studies conducted by Tingey and co-workers (Tingey et al., 1978, 1979, 1980) in environmental growth chambers under controlled conditions that permitted the determination of the independent effects of light and temperature on emissions of isoprene and the monoterpenes. These factors, and other influences on hydrocarbon emissions from vegetation, are discussed in the next section.

2. Factors Influencing Hydrocarbon Emissions from Vegetation

Several researchers have recorded large seasonal variations in rates of emission of hydrocarbons from vegetation. Rasmussen and Went (1965) measured volatile hydrocarbons at a sample location in the summer to be 10-20 parts-per-billion (ppb) compared with 2 ppb for the winter period. Holzer et al. (1977) also observed a large difference in emissions depending on seasons. Rasmussen and Went (1965) suggested that emissions are low in the spring from young foliage. They also observed two peaks in hydrocarbon emission in the vicinity of a mixed hardwood forest in autumn; these peaks were associated with leaf drop from two species of trees. It is possible that the fallen leaves were the major source of the observed peaks. Tyson et al. (1974) also suggested that the period of leaf fall from the coastal black sage (*Salvia mellifera*) may be a time of increased camphor emission as a result of high summer temperatures which are coincident.

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

Time of Day (Influences of Light and Temperature). There is an important difference between the diurnal concentration profiles of isoprene and the monoterpenes. Isoprene emission appears to be light dependent (Rasmussen and Jones, 1973; Sanadze and Kalandze, 1966; Tingey et al., 1978, 1979). The influence of varying light intensity on isoprene emission rate at various leaf temperatures is shown in Figure II-5 (Tingey et al., 1978, 1979). In contrast, monoterpenes from slash pine and black sage are emitted at similar rates in the light and dark (Rasmussen, 1972; Dement et al., 1975; Tingey et al., 1980).

There is general agreement among several investigators observing many plant species that isoprene and monoterpene (see Appendix B) emissions increase with increasing temperature (Figure II-6). These reports include Rasmussen (1972) with several conifer species; Dement et al. (1975) and Tyson et al. (1974) with *Salvia mellifera*; Kamiyama et al. (1978) with cryptomeria; Arnts et al. (1978) with loblolly pine; and Juuti et al. (1989) with Monterey pine (Appendix B). Above 43°C isoprene emissions drop dramatically (Tingey et al., 1978, 1979). Generally, isoprene emissions increase sigmoidally with temperature while monoterpene emissions increase exponentially.

Tingey and co-workers (Tingey et al., 1978, 1979, 1980) estimated that for average summer days in Tampa, Florida, the net influence of light and temperature would result in more than 80% of the isoprene emissions occurring after mid-morning and ceasing at night (Figure II-7), while approximately 55% of the total daily monoterpene emissions were expected to occur during daylight hours between 0600 and 1800 hr with an additional 25% emitted between sunset (1800 hr) and midnight. Thus, as shown in Figure II-8, monoterpene emissions are expected to follow a diurnal profile which closely mirrors that of the ambient temperature.

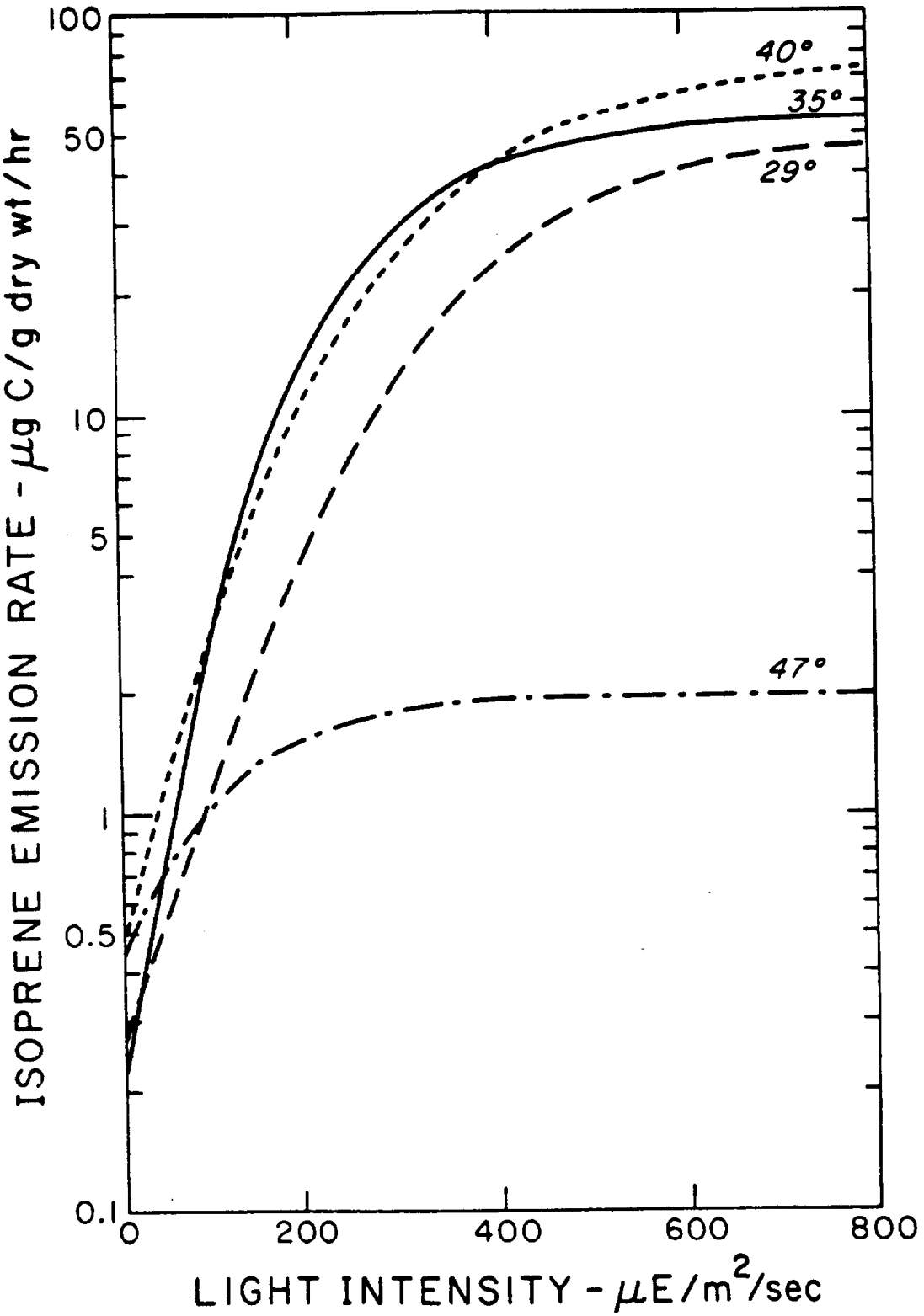


Figure II-5. The influence of varying light intensity on isoprene emission rate at various leaf temperatures (Tingey et al., 1978).

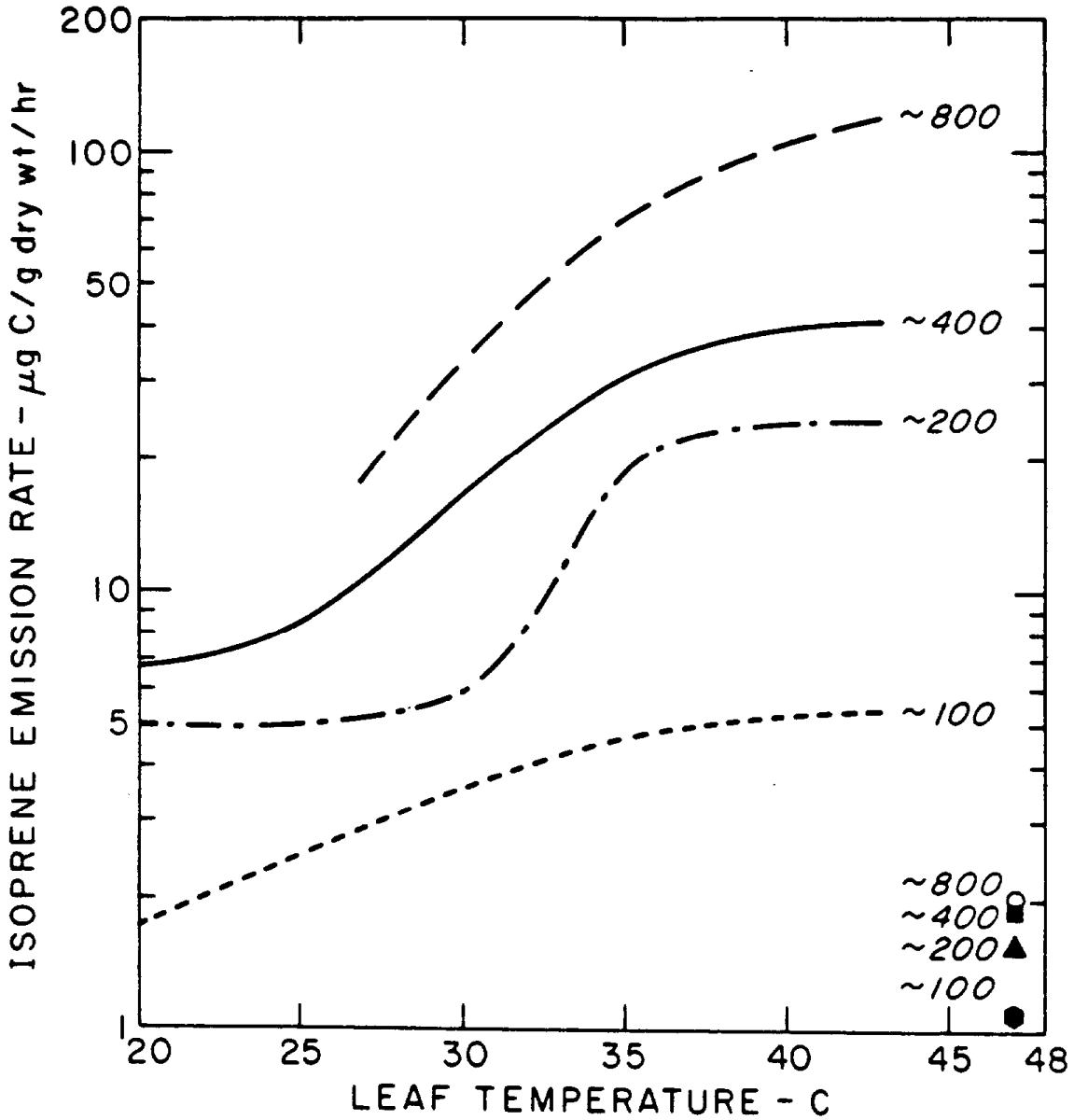


Figure II-6. The influence of varying temperature on isoprene emission rate at various light levels (given in $\mu E\ m^{-2}\ sec^{-1}$) [Tingey et al., 1978].

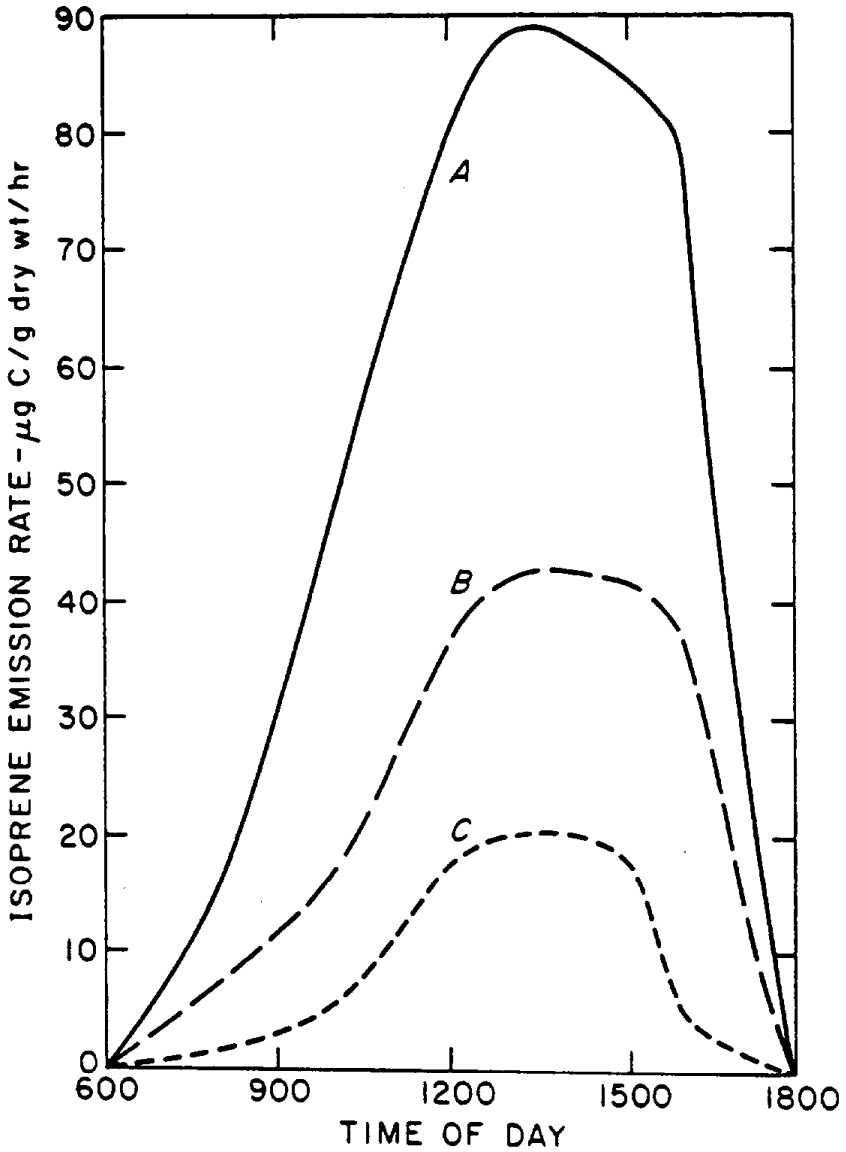


Figure II-7. Estimated isoprene emission rate for oak leaves in Tampa, Florida, for an average of summer days (Tingey et al., 1978). A - sunlit leaves; B - shaded leaves (one-half ambient sunlight); C - shaded leaves (one-fourth ambient sunlight).

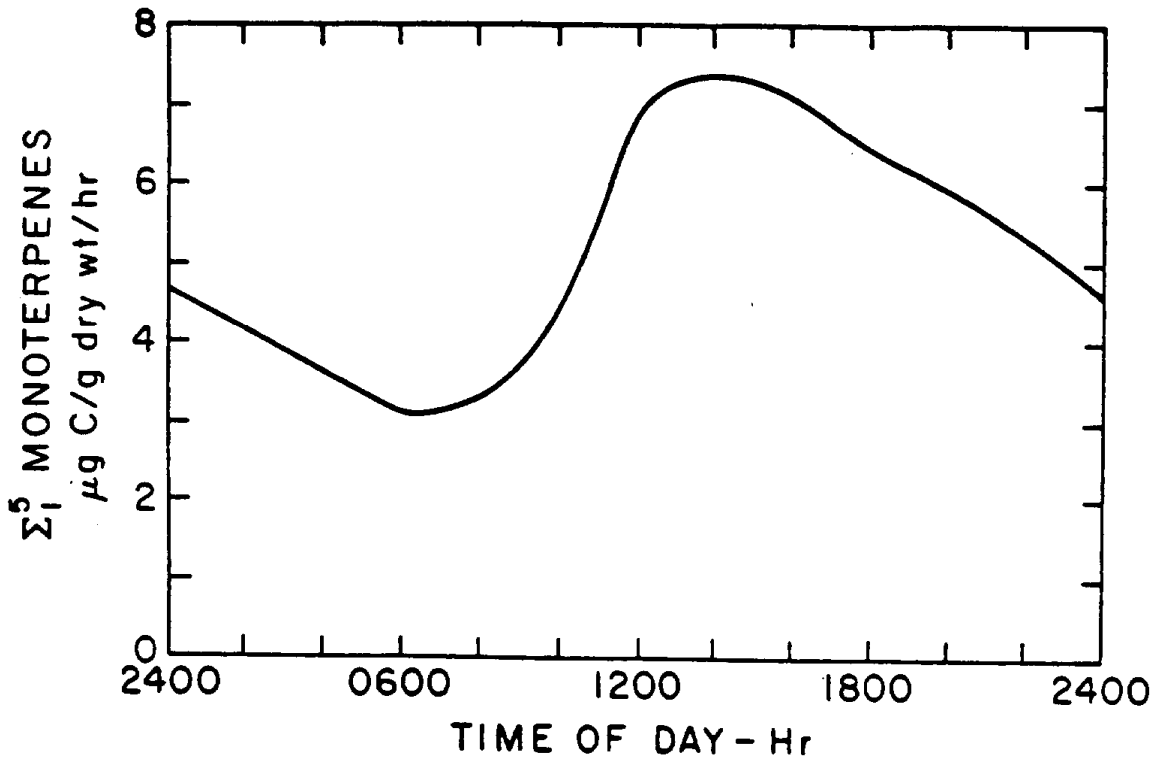


Figure II-8. Estimated diurnal emissions of five monoterpenes for slash pine in Tampa, Florida, for an average of summer days (Tingey et al., 1980).

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

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

3. Hydrocarbon Emission Rates Determined in Previous Experimental Studies

Based on their determinations of temperature algorithms for hydrocarbon emissions, Tingey and Burns (1980) placed many of the previous experimentally-measured emission rates on a common basis, and the resulting data for a variety of species are shown in Table II-3. It should be noted from this table that for the one common species studied by two investigators (live oak), the isoprene emission rates reported differed by more than a factor of four. It is also clear from this table, and from Table II-4, that very few experimental measurements have been made for agricultural species of importance in the California Central Valley.

Using a similar approach, and results from Zimmerman (1979a) along with Tingey's temperature algorithm (Tingey, 1981), Lamb et al. (1987) obtained the emission rate measurements (normalized to 30°C) shown in Table II-4. These were classified into three classes of deciduous isoprene emissions (high, low and none), coniferous emissions, agricultural crops, and water. Under agricultural emissions they provide values for four specific crops, one of which is tobacco, and a category called "other." No data are provided for isoprene and monoterpene emissions from those agricultural crops, only for "other NMHC."

As noted earlier, in 1979 the ARB supported a two year study by SAPRC researchers to address the lack of data concerning emissions of reactive hydrocarbons from vegetation in the South Coast Air Basin (Winer et al., 1983). A key component of this project was the experimental determination of the rates of emission of isoprene and selected monoterpenes from

Table II-3. Biogenic Hydrocarbon Emission Rates Estimated at 30°C (from Tingey and Burns [1980])

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

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

Table II-4. Emission Rate Estimates (30°C) ($\mu g\ gm^{-1}\ hr^{-1}$) (from Lamb et al. [1987])

Type	Examples	Isoprene	α-Pinene	Other NMHC
High isoprene	oak	22.9	0	1.8
Low isoprene	sycamore	8.4	0	2.3
Deciduous, no isoprene	maple	0	1.4	4.3
Coniferous	loblolly pine	0	2.8	8.0
Agriculture	alfalfa, wheat	---	---	0.015
	tobacco	---	---	0.35
	corn	---	---	2.0
	other	---	---	0.015
Water	---	---	---	145 $\mu g\ m^{-2}\ hr^{-1}$

approximately sixty ornamental and natural plant species which are found in Southern California. The specific monoterpenes of interest in that study were those which had been observed in ambient air above vegetation canopies, or in enclosure experiments, by previous researchers, and included α- and β-pinene, Δ^3-carene, d-limonene, myrcene and p-cymene.

Our initial emissions experiments involved the use of Teflon bag enclosures and static matrix air conditions. However, the use of a static-mode of operation did not prove satisfactory and subsequently we developed a series of rigid-frame, flow-through chambers and a sampling protocol which minimized the deviation of the plant environment from ambient conditions (Winer et al., 1983). No significant attempt was made in this study to obtain detailed and quantitative data for hydrocarbons other than isoprene and selected monoterpenes.

Approximately half the plant species studied exhibited measurable rates of emission of either isoprene or monoterpenes (Winer et al., 1983). However, with the possible exception of several of the naturally

occurring plant species, the data obtained were of no direct relevance to the present study of agricultural crops, although many of the experimental methodologies were directly applicable and these are discussed in detail in Section IV.

In addition to our previous experience with measuring hydrocarbon emissions from vegetation, in the intervening eight years we have conducted a large number of experimental research programs, involving both environmental chamber and ambient air studies, in which our sampling and analytical capabilities have been greatly advanced over those available circa 1979. In particular, as discussed in Section IV, we have developed substantial experience with solid adsorbent collection of volatile organics, thermal desorption of such samples, and subsequent analysis by gas chromatography (GC) and combined gas chromatography-mass spectrometry (GC/MS) techniques (Atkinson et al., 1987; Arey et al., 1987, 1989).

C. Rationale and Approach for Present Investigation

The overall goal of the present study was to obtain speciated hydrocarbon emissions data for at least thirty of the most important vegetation types relevant to California's Central Valley (which for the purposes of this project was defined as the area encompassing both the Sacramento and San Joaquin Valleys). Emphasis was given to obtaining data for a full range of organic emissions, rather than just isoprene and the monoterpenes, so that total nonmethane hydrocarbon assessments would be possible. The corresponding dry weight of the biomass of the plant specimens whose hydrocarbon emission fluxes are measured were also determined. These data were obtained in a form directly applicable to efforts by the ARB staff to assemble a detailed and comprehensive reactive organic gases emissions inventory for the Central Valley.

To accomplish the overall research objectives of this program, the following specific tasks were conducted:

- Selection of the thirty most important agricultural and natural plant species in California's Central Valley, with respect to anticipated hydrocarbon fluxes, based primarily on acreage.
- Fabrication of appropriate enclosure chambers designed to ensure the least perturbation of the plant specimens being sampled and the most reliable characterization of hydrocarbon emission rates.

- Refinement and testing of techniques for collecting gas-phase organics on solid adsorbents such as Tenax and activated carbon, with subsequent thermal desorption of the collected hydrocarbons onto GC and GC/MS systems for quantitative, speciated analysis.
- Design of sampling protocols which, within the limits of this program optimized the information obtained for each plant species concerning the individual and total hydrocarbon emissions as a function of light intensity and temperature.
- Utilizing all of the above methodologies, measurement of the individual hydrocarbon emissions from at least thirty of the most important vegetation types found in the California Central Valley for which data are not presently available. These measurements were conducted on the UCR campus for the reasons detailed below.
- Determination of the dry weights of the plant specimens whose hydrocarbon emission rates were measured.

III. SELECTION OF AGRICULTURAL AND NATURAL PLANT SPECIES STUDIED

A. Agricultural Species and Natural Plant Communities Found in California's Central Valley

A detailed tabulation of those agricultural and natural plant species which have large acreages in the Central Valley was developed by the ARB staff prior to this study. These data, which apply to six counties in the San Joaquin Valley (Fresno, San Joaquin and Tulare) and Sacramento Valley (Colusa, Sacramento and Yolo) airsheds, are shown in Table III-1. To create an initial candidate list of plant species for possible emission rate measurements, the list in Table III-1 was expanded to include data (California Agricultural Statistics Service, 1985) on the acreages, by county, of crops produced in California. The resulting initial candidate list is shown in Table III-2.

B. Criteria for Selection of Plant Species

In order to rank the agricultural and native species in terms of estimated relative importance, it would be necessary to assume an emission rate for each species. We considered adopting the emission rates assigned by Oliver et al. (1984) in a report to the ARB entitled "Biogenic Hydrocarbon Emissions in the Southern San Joaquin Valley Air Basin." In this "paper" study, Oliver et al. (1984) relied primarily on emissions factor data from four previous investigations (Zimmerman, 1979a; ABAG, 1981; Winer et al., 1983; Lamb et al., 1984) to assign overall total organic gas (TOG) emissions in grams per hour per square meter to individual plant species.

In principal, such data could be used to attempt to rank order the agricultural and natural plant species found in the Central Valley by hydrocarbon emission strength, using the numerical value of the product of the acreage times the TOG emission factor.

$$\text{Ranking Value} = \text{Acreage } (m^2) \times \text{TOG Emissions } (gm\ hr^{-1}\ m^{-2})$$

However, in the analysis by Oliver et al. (1984), many different agricultural crops were assigned identical emission rates for lack of any

Table III-1. Agricultural Species and Natural Plant Communities Most Abundant in Six Counties in San Joaquin Valley and Sacramento Valley Air Basins[a] Ranked by Approximate Acreage

	Agricultural Species or Natural Plant Community	Approximate Acreage (million acres)
1.	Pasture and range[b,c]	2.0
2.	Valley-foothill hardwood[d,e]	1.3
3.	Annual grassland[b,d,e]	1.2
4.	Cotton, lint[c]	0.6
5.	Mixed conifer[d,e,f] (focus is below 4000 feet elevation)	<<0.5
6.	Red fir[d,e,f] (focus is below 4000 feet elevation)	<<0.4
7.	Chamise-redshank chaparral[d,e]	0.3
8.	Grape, all types[c]	0.3
9.	Wheat[c]	0.3
10.	Hay, alfalfa[c]	0.3
11.	Lodgepole pine[d,e,f] (focus is below 4000 feet elevation)	<<0.2
12.	Ponderosa pine[d,e,f] (focus is below 4000 feet elevation)	<<0.2
13.	Corn[c]	0.2
14.	Mixed chaparral[d,e]	0.2
15.	Pasture and range[c] Irrigated & other	0.2
16.	Tomato[c]	0.2
17.	Rice[c]	0.1
18.	Fresh emergent wetland[d,e]	0.1
19.	Corn silage & forage[c]	0.1
20.	Montane chaparral[d,e,f] (focus is below 4000 feet elevation)	<<0.1
21.	Pinyon-juniper[d,e,f] (focus is below 4000 feet elevation)	<<0.01
22.	Almond[c]	0.1
23.	Barley[c]	0.1
24.	Oranges, navel & valencia[c]	0.1

Table III-1 (continued) - 2

Agricultural Species or Natural Plant Community	Approximate Acreage (million acres)
25. Jeffrey pine[d,e,f] (focus is below 4000 feet elevation)	<<0.1
26. Sugar beet[c]	0.09
27. Sagebrush[d,e]	0.08
28. Walnut[c]	0.07
29. Beans, dry[c]	0.07
30. Hay, grain & other[c]	0.06

[a]San Joaquin Valley Air Basin Counties: Fresno, San Joaquin, Tulare. Sacramento Valley Air Basin Counties: Colusa, Sacramento, Yolo.
[b]Considerable overlap is likely between the agricultural category Pasture and Range and the natural plant community Annual Grassland. (Some overlap is possible between the categories Pasture and Range and Valley-Foothill Hardwood as well.)
[c]Harvested acreage for agricultural crops is taken from the 1985 Crop Report for each county.
[d]Acreage for natural plant communities is adapted from draft information from the California Department of Forestry.
[e]For natural plant communities, a few abundant and significant species were to be selected from those typically associated with the plant community.
[f]Because the focus of this study was vegetation at lower elevations (generally below 4000 feet), the relevant acreage is presumably much less that the total listed. These plant communities were therefore of lower priority than the numeric order would imply.

Table III-2. Agricultural Species and Natural Plant Communities Found in California's Sacramento and San Joaquin Valleys[a]

Agricultural Species	
Alfalfa (Hay & Seed)	Pears
Almonds	Pistachios
Apples	Plums
Apricots	Potatoes
Artichokes	Prunes
Asparagus	Rice
Avocados	Safflower
Barley	Silage (All)
Beans (Dry)	Sorghum (Grain)
Broccoli	Strawberries
Cantaloupes	Sugar Beets
Carrots	Sunflower
Cauliflower	Sweet Potatoes
Celery	Tomatoes (Fresh Market & Processing)
Cherries	Walnuts
Corn (Grain & Sweet)	Wheat
Cotton (Lint)	
Garlic	**Natural Plant Communities**
Grapefruit	
Grapes (All, Raisin, Table & Wine)	Annual Grassland
Hay (Grain & Other)	Chamise (Redshank Chaparral)
Honey	Fresh Emergent Wetland
Kiwifruit	Jeffrey Pine
Lemons	Lodgepole Pine
Lettuce	Mixed Chaparral
Nectarines	Mixed Conifer
Oats	Montane Chaparral
Olives	Pinyon-Juniper
Onions	Ponderosa Pine
Oranges (Navel & Valencia)	Red Fir
Pasture (Irrigated)	Sagebrush
Pasture and Range	Valley (Foothill Hardwood)
Peaches	

[a]Sources: California Agricultural Statistics Service-1986 DOT Maps. California Department of Forestry.

information which would allow differentiation between them. For example, plant species as disparate as apple, almond, walnut, apricot, fig, pear, and prune, as well as all other deciduous trees, were all assigned a TOG emission rate of 0.006 gm hr^{-1} m^{-2}. Because, in the great majority of cases, there was no basis for assuming that the specific values assigned by Oliver et al. (1984) are valid, we had reservations about using a ranking value approach as a basis for eliminating plant species known to occur in substantial acreages in the Central Valley. We therefore used acreage, and the availability in the literature of emission rates for certain members of the natural plant communities, as the basis for eliminating certain plant types from the overall list of approximately sixty agricultural and natural species shown in Table III-2. For example, twelve agricultural species which appear on the California Agricultural Statistics Service maps for California, but which clearly have negligible acreages in the Central Valley, are shown in Table III-3. These species were not considered as candidate crops for emissions measurements in this program.

Similarly, the emissions contributions of natural plant communities which are relevant to the formation of photochemical air pollution in the Central Valley are those which occur below approximately four thousand feet elevation, i.e., below the generally prevailing temperature inversion. Thus, the acreages used in estimating the relative importance of the emissions from these plant communities, particularly for the conifer communities, are expected to be much lower than the total acreages provided by the Department of Forestry for these vegetation categories.

Fortunately, a significant amount of information was available concerning the prevalence of the various natural plant communities as a function of altitude (see Appendix A). As an example, it is well documented that the red fir plant community occurs only above approximately 6000 feet elevation, and therefore members of this community would not be relevant to the present study. Furthermore, there are substantial data already in the literature (Bufalini and Arnts, 1981; Lamb et al., 1985, 1986) concerning the hydrocarbon emissions from a variety of pine and oak species, as well as for several types of sage.

For this reason, relatively little emphasis was given to the natural plant communities. On the basis of the foregoing considerations, the number of such plant species to be studied was reduced to a working list of approximately 40 species.

Table III-3. Agricultural Crops Which Have Negligible or Unimportant Acreages in the California Central Valley

Apples	Sweet Corn
Artichokes	Grapefruit
Avocado	Pears
Broccoli	Strawberries
Cauliflower	Sunflower
Celery	Sweet Potato

C. Location of Measurements and Availability of Plant Specimens

The decision concerning where to conduct the emissions measurements, and the associated GC-FID and GC/MS analyses which are central to this project, was a crucial one. We considered conducting those measurements in the Central Valley itself, on agricultural crops and natural vegetation specimens located there. However, there were significant problems, and important tradeoffs, in attempting to carry out such a field study in the Central Valley.

First, conditions for making careful measurements would not be ideal under the circumstances encountered in actual agricultural fields in the Central Valley. Moreover, the logistical problems of locating suitable plots, gaining access to them, providing electrical power and other needed amenities, removing biomass samples, etc., would be formidable. In addition, the problems associated with carrying out in-field GC analyses under these conditions would probably be prohibitive, and any GC/MS supporting analyses would still have to be conducted at UCR. An additional factor was that the meteorlogical conditions which normally prevail in Riverside during the summer months are not greatly different from those in the Central Valley. Finally, the much greater costs of a remote site study, and the problem of separation of species by relatively large geographical distances, necessitating moving the measurement systems repeatedly, would have greatly reduced the number of species which could be studied.

For these reasons, we believed a more appropriate and cost-effective approach was to conduct the proposed study on the UCR campus, obtaining

and evaluating the emissions data in ways which would permit them to be applied directly to the Central Valley. In addition to eliminating or minimizing the problems cited above for a Central Valley field study, the advantages of this approach were many. First, the great majority of the approximately forty candidate agricultural crops or natural plant communities were already grown at UCR, either in the Agricultural Experiment Station, at the University Arboretum, or in connection with the on-going research projects of the SAPRC plant scientists collaborating on this program. For any plant specimens which were not available on the UCR campus, the lead time built into this project allowed the growth of appropriate specimens, or the transplanting of mature plants. All such species were grown in the ground using the same soil type. Cultural practices were standardized across species and reflected normal agricultural practices as modified for research purposes. Thus, essentially all of the required species were in close proximity to each other, and to our analytical laboratory. Without the high costs of supporting a remote location study, a larger number (>30) of species could be studied, increasing the opportunity to identify the important, high-emitting agricultural species.

A UCR-based study also permitted a much higher percentage of the resources provided by this contract to be devoted to the analysis phase of the program. As described below (in Sections IV and V), we were able to conduct detailed hydrocarbon analyses for each plant species studied, with a degree of compound identification and quantification not achieved in our previous (Winer et al., 1983) study.

For these and other reasons we conducted the emissions measurements and associated analyses on the UCR campus during the summers of 1988 and 1989.

D. Agricultural and Natural Plant Species Investigated

1. Agricultural Crops

The agricultural crop species for which emission rate measurements were made are listed in Table III-4. All of the herbaceous crops and a few of the wood trees (walnut, peach, almond) were located in an experimental plot in Field 8C on the Experiment Station at the University of California, Riverside.

Table III-4. Agricultural Crop Species for which Emission Rate Measurements were Conducted[a]

Species	Common Name	Cultivar	Planting Date	Row Spacing (m)	Plant Spacing (m)
Allium cepa	Onion	South Port White Globe	7/19/88	1.0	0.1
Beta vulgaris	Sugar Beets	UC H12	3/14/89	0.6-0.09	0.4-0.5
Carthamus tinctorius	Safflower		3/8/89	0.9	~ 1
Citrus limon	Lemon	Lisbon	1969-74	~ 6	~ 7.3
Citrus sinensis	Orange	Valencia	1983	~ 8.6	~ 8.6
Citrus sinensis	Orange	Washington Navel	ca. 1920	7.3	6.1
Daucus carota	Carrot	Imperator	7/19/88	1	0.03
Gossypium hirsutum	Cotton	SJ2	4/14/89	0.9-1	0.3-0.4
Irrigated pasture	Multiple[b]	Multiple[c]	3/9/89	Broadcast over 4 x 3 m plot	
Juglans regia	Walnut, English	Hartley	3/9/89	~ 6.1	~ 7.3
Lactuca sativa	Lettuce	Empire	7/19/88	1.0	0.03
Lycopersicon lycopersicum	Tomato	6203	3/8/89[f]	1.2-1.5	0.4
Lycopersicon lycopersicum	Tomato	Sunny	3/8/89[f]	1.2-1.5	0.4
Medicago sativa	Alfalfa	Pierce	3/23/89	Broadcast over 4 x 3 m plot	
Olea europea	Olive	Manzanillo			
Oryza sativa	Rice	M202	5/26/89[f]	Dense stand in pots	
Phaseolus vulgaris	Bean, Fresh	Top crop	3/8/89	0.6	0.2
Pistacia vera	Pistachio	Kerman	1978	~ 6.1	~ 7.3

Table III-4 (continued) - 2

Species	Common Name	Cultivar	Planting Date	Row Spacing (m)	Plant Spacing (m)
Prunus armeniaca	Apricot	Blenheim[d]	1978	~ 6.1	~ 7.3
Prunus armeniaca	Apricot	Royal[e]	1978	~ 6.1	~ 7.3
Prunus avium	Cherry, sweet	Bing	1978	~ 6.1	~ 7.3
Prunus domestica	Plum	Santa Rosa	1978	~ 6.1	~ 7.3
Prunus domestica	French Prune	Marriana	3/9/89	~ 7.6	~ 7.6
Prunus dulcis var. dulcis	Almond	Nonpareil	1978	~ 6.1	~ 7.3
Prunus persica	Peach	Halford	3/9/89	~ 6.1	~ 7.3
Prunus persica	Nectarine	Armking[d]	1978	~ 6.1	~ 7.3
Prunus persica	Nectarine	Silver Lode[e]	1978	~ 6.1	~ 7.3
Sorgum bicolor	Sorgum	DK 42Y	3/14/89	0.6-0.9	f 0.2
Triticum aestivum	Wheat	Yecorro Rojo	2/23/89	Broadcast over 4 x 3 m plot	
Vitis vinifera	Grape	Thompson Seedless	1983	3.7	2.4
Vitis vinifera	Grape	French Columbard	1983	3.7	2.4
Zea mays	Field Corn	Pioneer 3183	3/14/89	0.9	f 0.1

[a]Species according to Hortus Third (Bailey and Bailey, 1976).
[b]Orchard grass, perennial ryegrass, annual ryegrass, strawberry clover, birdsfoot trefoil.
[c]Unknown
[d]Formal sampling protocol.
[e]Survey.
[f]Started in greenhouse, than transplanted to pots in the field.

Most of the fruit and nut tree species shown in Table III-4 were grown in the University of California Teaching Plots and were planted and maintained following cultural practices as close as possible to those used in commercial orchards. The cultivars used were (and still are) widely grown in the San Joaquin Valley of California. The rootstocks are not known, but represent common rootstocks used at the time of planting. The trees generally were approximately 10-11 years old and planted 5.5 to 6.1 meters apart in rows 7.3 meters apart. Irrigation was via furrows, for 48 hours approximately every three weeks during summer. There was no irrigation during the winter beginning when the leaves fell off the trees until the buds began to swell and started active growth in the spring. The only fertilization was with nitrogen (56 kg hectare^{-1}), broadcast under the trees. No pesticides had been applied during the past year on the trees used for this study. Pruning occurred each winter (late January to mid-February), since earlier pruning would have stimulated vegetation growth. Fruit thinning was not used on these trees, so they tended to have large fruit sets. There was no unusual frost during the winter of 1988-89 which would affected the growth of these trees.

The herbaceous crops, walnuts, and Halford peaches were grown in an area of field 8C which was especially prepared for this study. As shown in Table III-4, the planting dates, spacing between rows, and spacing of plants within rows varied depending on the normal cultural practices for each species. All of the crops were started from seed, except for the Halford peaches and Hartley walnuts which were nursery stock planted bare root. Irrigation and fertilization was as needed depending on the species and weather conditions. These species did not require any applications of chemicals for pest control during this study.

The orange and grape cultivars shown in Table III-4 were grown in experimental plots originally prepared for air pollution research studies. However, the plant material used was growing in ambient air and had not been subjected to any unusual air pollution treatments. Both the oranges and grapes were irrigated, fertilized, and received routine applications of chemicals to control pests as necessary to maintain healthy plants.

2. Native Plants

The native plant species used in this study are listed in Table III-5. All of the species were located in the UCR Botanic Garden. The chaparral shrubs (whitethorn, mountain mahogany, and bigberry manzanita), as well as the valley oak, were grown from seed collected in the Sierra Nevada Mountains and were at least 20 years old. The chamise were grown from seed and were at least 10-12 years old.

The valley oak was irrigated approximately biweekly. The chaparral species, except for chamise, were irrigated approximately monthly during the summer months, but generally depended on rainfall for water. The chamise was not irrigated and its growth depended solely on rainfall. The shrubs and oak did not receive any type of artificial pest control.

The annual grassland occurred due to natural seeding and was not maintained artificially in any way except for mowing to remove excess dried material. All of the species were under general long-term water stress due to the below average rainfall conditions at Riverside over the past three years.

Table III-5. Native Plant Species For Which Emission Rate Measurements Were Conducted[a]

Species	Common Name
Adenostema fasciculatum H. & A.[b]	Chamise
Arctostaphylos glauca Lindl.	Bigberry Manzanita
Avena spp., Bromus spp.	Annual Grassland
Ceanothus leucodermis Greene	Whitethorn
Cercocarpus betuloides Nutt.[c]	Mountain Mahogany
Quercus lobata Nee.[d]	Valley Oak

[a]Species according to Munz and Keck, 1975.
[b][A. f. var. densifolium Eastw.].
[c]ex T & G [C. betulaefolius Nutt. ex Hook. C. parvifolius var glaber Wats. C. montanus var. g. F. L. Martin. C. b. var. minor C.K. Schneid. C. rotundifolius Rydb. C. Douglassi Rydb.]
[d][Q. Hindsii Benth.]

IV. EXPERIMENTAL METHODS

A. Introduction and Background

As noted in Section II, the principal field and laboratory methods which have been used to measure hydrocarbon emission rates from vegetation have been described by Lamb et al. (1987), who also discussed the trade-offs between the three different approaches taken to date for field measurements of hydrocarbon emission rates from vegetation (Lamb et al., 1987). In the past there was concern that emission measurements made using the enclosure technique were overestimating the actual plant hydrocarbon emissions (Dimitriades, 1981), but the most recent direct comparison studies have shown no evidence for this (Lamb et al., 1985; 1986). The isoprene emission for an oak forest determined from a series of branch enclosure samples was in excellent agreement with that determined using an SF_6 atmospheric tracer technique (Lamb et al., 1986). Furthermore, comparison of emissions measurements made using enclosures with those from the micrometeorological gradient technique were in reasonable agreement for both isoprene emissions from a deciduous forest and α-pinene emissions from a coniferous forest (Lamb et al., 1985).

Since there is little evidence to suggest that the "micrometeorological" approach, involving the measurement of hydrocarbon concentration gradients above vegetation canopies, is superior in practice to the enclosure technique developed by Zimmerman et al. (1979a,b) and applied by Winer et al. (1983), we elected to employ the enclosure method in the present study. As noted in Section III, an additional consideration in this choice was the logistical and cost implications of conducting canopy measurements in the Central Valley.

The enclosure system, described in more detail below, was that employed previously by Winer et al. (1983). This technique, like the laboratory chambers utilized by Tingey (Tingey et al., 1979; 1980), used a flow-through system to minimize the deviation of the plant environment from ambient conditions. A rigid-frame chamber was constructed from Teflon film, thereby allowing >90% transmission of light down to wavelengths well below the actinic region (W. P. L. Carter, private communication). Sufficient carbon dioxide was added to the air supplied to the plant enclosure to achieve ambient CO_2 levels. Increases in temperature and humidity within the enclosure were also minimized by this flow system.

The approach taken in the analytical sampling and measurement aspects of the present study differed significantly from our earlier (Winer et al., 1983) investigations, reflecting important advances made in recent years in this (Atkinson et al., 1987; Arey et al., 1989) and other laboratories in sampling and analysis using solid adsorbents (Roberts et al., 1983, 1985; Isidorov et al., 1985; Jüttner, 1988). Specifically, we describe in the sections which follow the use of a solid adsorbent/thermal desorption technique for sample collection and the close coupling of GC-FID and GC/MS for unambiguous compound identification and quantitation. Therefore, our present approach has provided a significant improvement in the quantitative, speciated characterization of emission rates in the current study relative to the approaches employed in the earlier study by Winer et al. (1983) for ornamental vegetation in the South Coast Air Basin.

B. Plant Enclosure Methods

The initial plant enclosure was designed for emission measurements from fruit and nut trees and large agricultural crop plants (e.g. tomato). The enclosure chamber was constructed from a 2 mil Teflon film suspended from an external PVC frame, measuring approximately 0.5 m x 0.5 m x 1 m, providing a chamber volume of ~150 ℓ. This chamber was equipped with a stirring motor, with a Teflon-coated blade, and inlet and outlet ports suitable for introduction of matrix air and withdrawal of analytical samples, respectively. The basic properties of the chamber are depicted in Figure IV-1.

Gas chromatographic analyses were conducted to determine the suitability of various matrix air gases. These tests showed that medical breathing air contained a low background of organic species which eluted in the relevant retention time ranges covering the C_5-C_{10} hydrocarbons. Therefore "Medical Breathing Air" (Liquid Air; 99.6% stated purity level) was chosen over the more expensive "Zero Air" (Liquid Carbonic; <5 ppm H_2O, <1 ppm hydrocarbons).

The air-flow monitoring and control component of the matrix air delivery system (Figure IV-2) was contained in a metal case 11 in. x 11 in. x 18 in. high. Medical breathing air from a cylinder with a two-stage regulator was fed via 0.25 inch o.d. polyethylene tubing to the flow

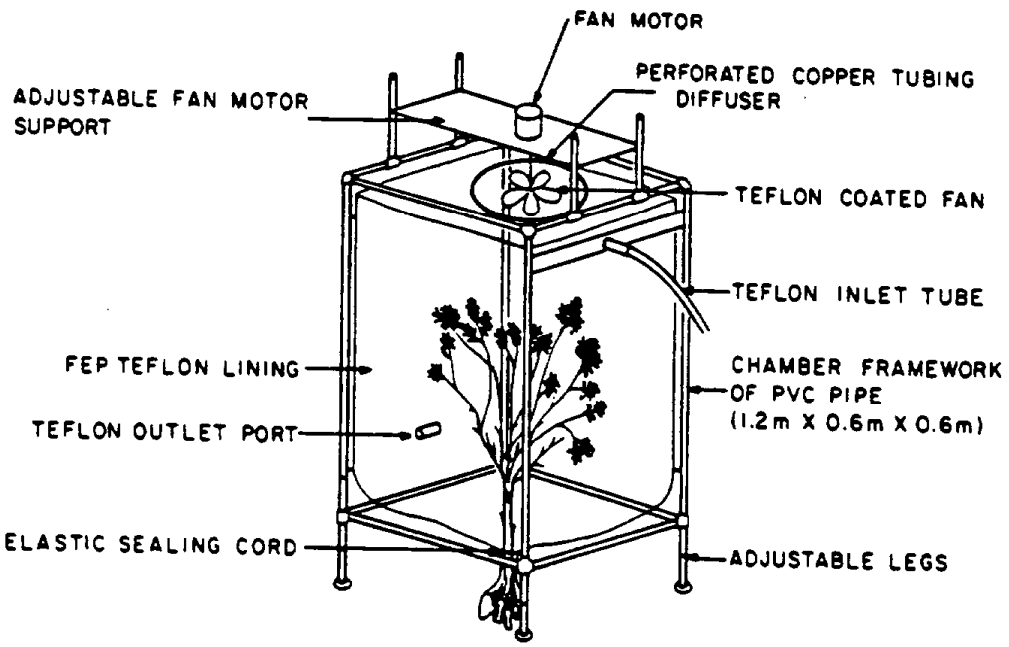


Figure IV-1. Plant enclosure chamber for measuring rates of emission of hydrocarbons from vegetation.

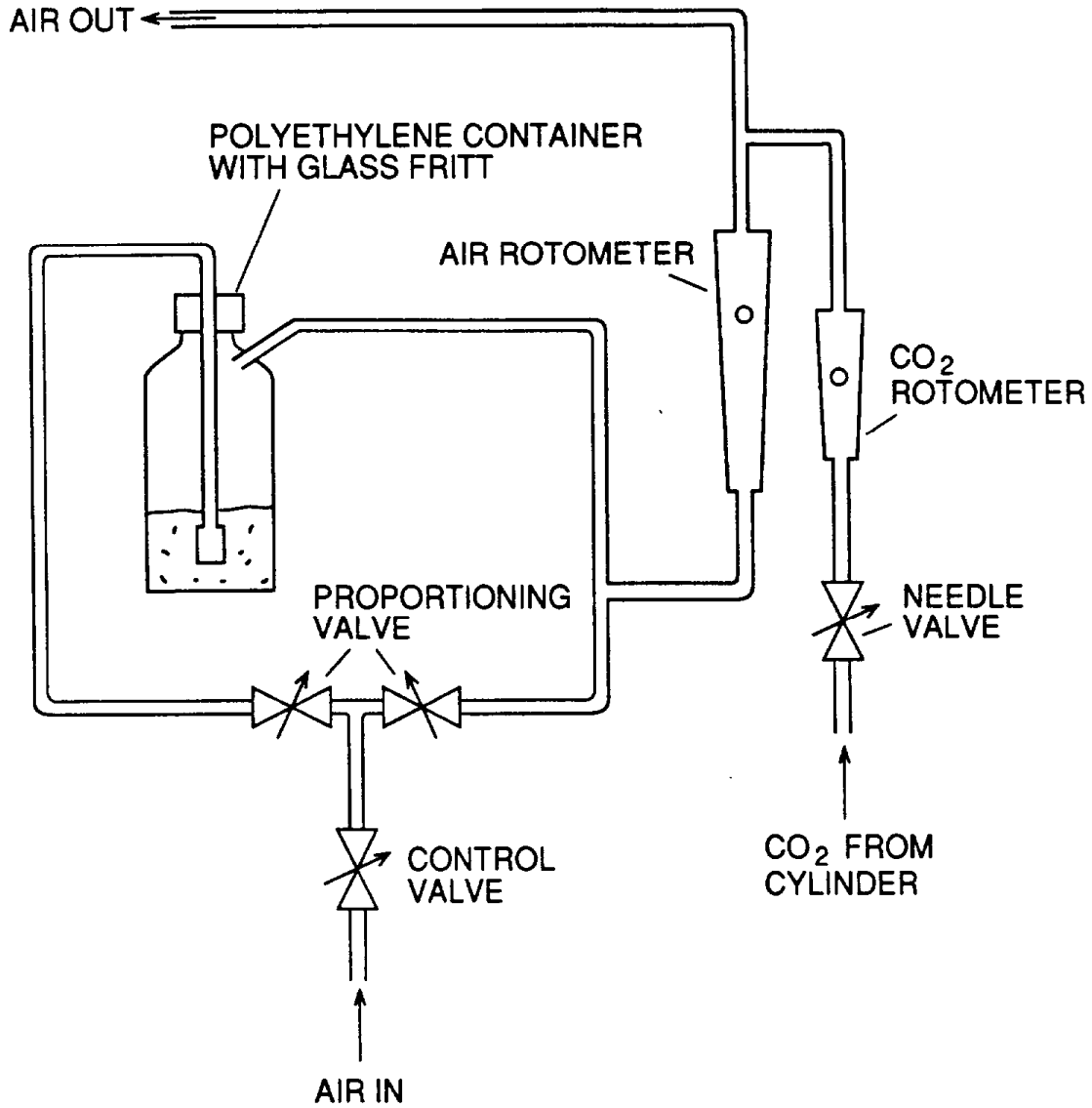


Figure IV-2. System for controlling CO_2 and humidity of matrix air used in plant enclosure experiments.

module. A flow control valve was used to set the flow rate to a proportioning valve which passed a fraction (from 0-100%) of the air through a humidifying chamber, which consisted of distilled water held in a 2.5-gal polyethylene container. Incoming dry air was bubbled through the water via a glass fritt. The proportioning valve allowed the ratio of dry to humidified air to be varied from zero to 100% depending on the measured humidity in the enclosure during actual field measurements (see below). A calibrated rotometer was used to monitor the air flow at this point.

Carbon dioxide was added to the matrix air before it left the control module. A cylinder of carbon dioxide was connected by 0.125 in. o.d. tubing to the flow module. A control valve and calibrated rotometer was utilized for flow monitoring. Typically, the carbon dioxide flow was set for a level of 360 ppm (i.e., the ambient atmospheric) concentration in the air supplied to the plant enclosure.

The output humidity was preset by adjusting the proportioning valve (see Figure IV-2) while monitoring the humidity in the chamber with a Vaisala Model HMI 32 humidity indicator. Once the flow rate and humidity level were set, the output air was connected to the plant enclosure chamber with 0.25 in. o.d. Teflon tubing. Both the air and carbon dioxide rotometers were monitored during the test period and maintained at the desired levels.

The plant enclosure chamber can be considered as a completely mixed flow reactor from which the concentration of the plant emissions should be sampled only after it has reached a steady state value. It can be calculated that after three air exchanges the concentration of the biogenic emissions should be within ~5% of the steady state value. Using carbon monoxide as a tracer, it was empirically demonstrated (Figure IV-3) that, as expected, a flow rate of ~45 liter min^{-1} through the Teflon exposure chamber (corresponding to ~20 air exchanges per hour) led to ~10% or less of the initially present carbon monoxide remaining in the chamber after 10 minutes. Thus, the flush time of 10 minutes at a flow rate of ~45 liter min^{-1} utilized before sampling the hydrocarbon emissions in the chamber resulted in near steady state concentrations of the biogenic emission and <10% of the original ambient concentration of anthropogenic and biogenic hydrocarbons remaining.

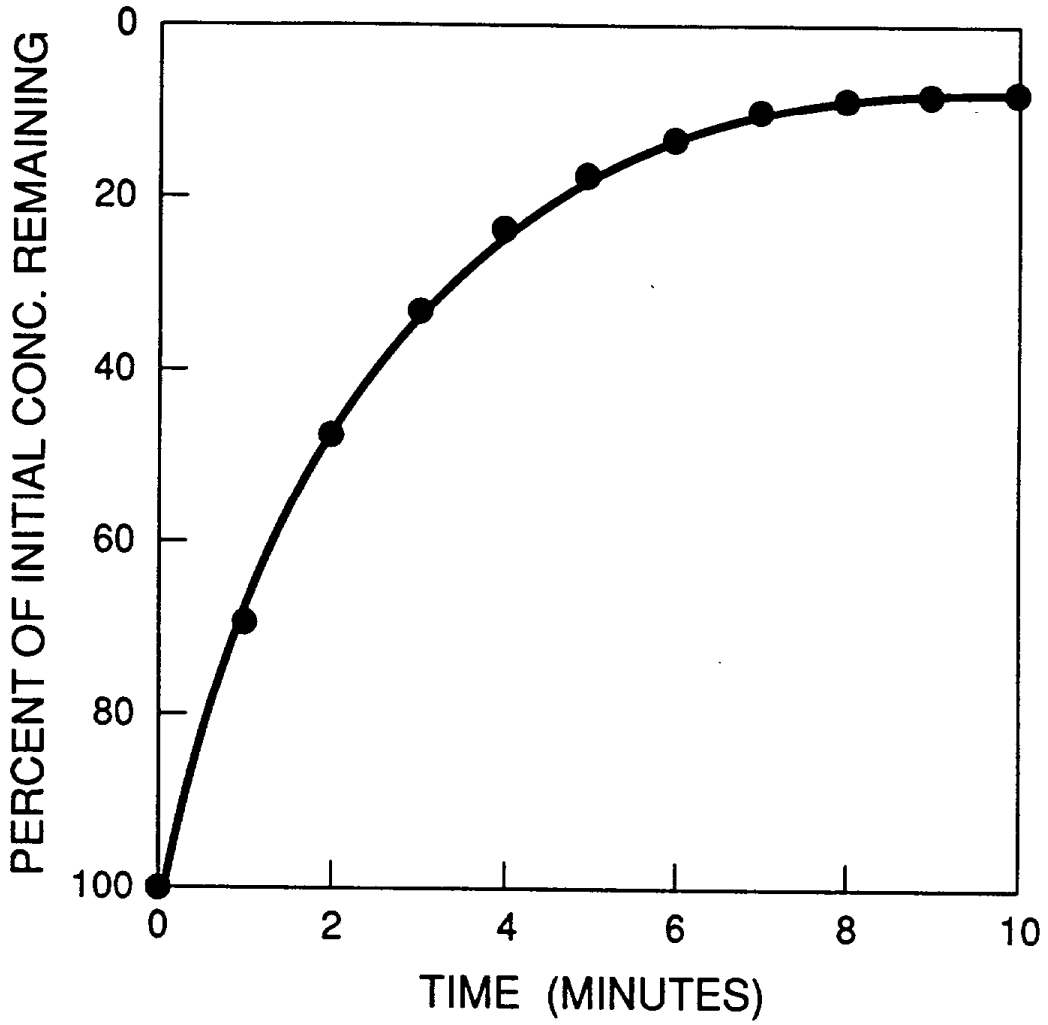


Figure IV-3. Demonstration of mixing time in flow-through chamber using carbon monoxide as a tracer.

The entire field sampling system was developed to be independent of AC power, permitting maximum flexibility as far as locating suitable plant specimens for study.

Enclosure for Ground Species. A second enclosure was constructed specifically to measure emissions from ground species such as vegetables. This consisted of a PVC framework, approximately 3 ft wide, 4 ft long and 1 ft high, enclosed by 2 mil Teflon film. The enclosure was fitted with inlet and outlet ports suitable for introduction of matrix air and withdrawal of analytical samples, respectively. The skirts of the enclosure could be fitted tightly to the ground to create a chamber which was operated in the same manner as described above.

Figure IV-4 shows a copy of the data sheet used in the field to record conditions associated with the emission measurement experiments, including those related to the matrix air and ambient conditions at the time the samples were withdrawn.

C. Emission Surveys and Sampling Protocols

Initial surveys, with samples for GC/MS and GC-FID analysis simultaneously collected, were conducted for each plant species of interest to determine qualitatively by GC/MS the speciated hydrocarbon emissions for that plant type. Every effort was made to identify emissions. For example, if the observed emissions were low and the survey had been conducted early in the day at lower temperatures, the species was surveyed again when the temperature was near to the maximum values typical of the Central Valley. The GC/MS results were used to establish peak identification for GC retention times used in the subsequent quantitative sampling protocol. In several instances additional samples were collected for GC/MS analysis during the protocol sampling. These samples were taken because it was felt that larger samples would allow identification of additional species emitted, or, in the case of the alfalfa sample, because the biomass had increased substantially between the survey and protocol samples.

As shown in Table IV-1, the standard sampling protocol consisted of a total of five measurements per species over a six-hour period, centered around noon, for three different plant specimens, including two replications for one of the specimens. This protocol was chosen after

SAPRC/ARB NATURAL HYDROCARBON EMISSIONS STUDY 1988-89

Sample No. NH-_____ Date 1988-_____

Species _____ Time _____

Site Location_____ Matrix Air I.D._____

Specimen Location_____ Added RH _____

_____ CO_2 Tank No._____

Ambient Conditions

Temp._____

% RH (WB/DB)_____

Sky/Cloud_____

Visibility_____

Test Flow Conditions

	Rotometer/Flow
Initial Air Flow	_____ / _____
Final Air Flow	_____ / _____
CO_2 Flow Rate	_____ / _____

Chamber Outlet

	Time (Hr:Min:Sec)	Temp (°C)	% RH
Start Purge	_____	_____	_____
	_____	_____	_____
	_____	_____	_____
	_____	_____	_____
	_____	_____	_____
Start Sample	_____	_____	_____
	_____	_____	_____
	_____	_____	_____
	_____	_____	_____
	_____	_____	_____
Stop Sample	_____	_____	_____
Remove Bag	_____		

Mean Temp. During Sampling _____ °C (°F)

Mean RH During Sampling _____ % RH

Comments _____

_____

Figure IV-4. Data sheet used in the field to record conditions associated with the emission measurement experiments.

Table IV-1. Emissions Sampling Protocol Including Replication and Testing of Three Plant Species

Time (PDT)	Plant Specimen 1	Plant Specimen 2	Plant Specimen 3
0900	Isoprene/ Monoterpenes		
1030		Isoprene/ Monoterpenes	
Noon	Isoprene/ Monoterpenes		
1330			Isoprene/ Monoterpenes
1430	Isoprene/ Monoterpenes		

consideration of the reported diurnal emission profiles of isoprene and the monoterpenes (see discussion in Section II and Figures II-7 and II-8) to try to optimize information concerning the time dependence of emissions from the plant species of interest. The 0900 hr (all times are PDT) sample was expected to be near the minima for isoprene and the monoterpene emissions and the noon and 1430 hr samples near their maxima. By taking emission measurements on the same specimen at these three times, a rough diurnal emission profile could be expected. The second and third specimens measured at 1030 and 1330 hr would then provide information on plant-to-plant variability in emissions for a given species.

D. Analytical Procedures

As discussed in Section II, the major expected plant emissions were isoprene and the monoterpenes. Therefore, identifications and GC-FID calibrations initially concentrated on these species. The goal of the program, however, was to identify and quantify all the emissions present. As additional compound types were tentatively identified by

GC/MS analysis, additional standards were obtained and, as can be seen from the final list of authentic standards acquired (Table IV-2), the compound classes identified as emissions in addition to isoprene and the monoterpenes included sesquiterpenes, alcohols, acetates, aldehydes, ketones, ethers, n-alkanes, alkenes and aromatics.

As noted earlier, the basic approach to sampling and analysis employed in this program was the collection of gas samples from the plant enclosure chamber onto Tenax and Carbosieve solid adsorbents either singly or in combination for the $C_5 \rightarrow C_{15}$ hydrocarbons, followed by thermal desorption and GC-FID or GC/MS analyses. The use of the solid adsorbent allowed the collection of 1-2 ℓ samples, in contrast with the 10 mℓ samples employed in the earlier study by Winer et al. (1983). The present larger sample sizes should result in an improvement in the limit of detection for hydrocarbon emissions of well over a factor of 10 in comparison with this previous study.

Compound identification in GC-FID analyses must be made solely on the basis of retention time matching. GC/MS analysis, of course, also gives spectral information in addition to the retention time, but since many of the spectra of the monoterpenes and sesquiterpenes are very similar (see Appendix C), adequate GC separation with reproducible retention time values is critical to accurate speciated identification. It should be noted, however, that different compound classes can generally be readily distinguished by GC/MS. Thus, early in the program a peak which co-eluted with Δ^3-carene in the GC-FID analysis was determined not to be a terpene by GC/MS analysis and was finally conclusively identified as 3-hexenyl-acetate, an emission commonly found from agricultural plant species. The addition of an internal retention time marker (1,2,4-trimethylbenzene or p-xylene) to each GC-FID and GC/MS sample allowed accurate identifications to be made on the basis of retention time differences from these markers.

1. Gas Chromatography/Mass Spectrometry

The identifications of the $\geq C_6$ organics emitted by the surveyed plant species (and of isoprene in the valley oak sample) were made by gas chromatography/mass spectrometry (GC/MS) utilizing a Hewlett/Packard 5890 GC equipped with a 50 m HP-5 (5% phenyl-methylsilicone) fused-silica capillary column and interfaced to a 5970 mass selective detector (MSD).

Table IV-2. Compounds for which Authentic Standards Were Available for Use in the Identification of Plant Emissions[a]

Isoprene

MONOTERPENES
Camphene
2-Carene
Δ^3-Carene
d-Limonene
Myrcene
cis-Ocimene
trans-Ocimene
α-Phellandrene
β-Phellandrene
α-Pinene
β-Pinene
Sabinene
α-Terpinene
γ-Terpinene
Terpinolene

SESQUITERPENES
β-Caryophyllene
Cyperene
α-Humulene
Longifolene

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

ACETATES
Bornylacetate
cis-3-Hexenylacetate
trans-2-Hexenylacetate

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

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

ETHERS
Anethole
1,8-Cineole

n-ALKANES
$C_6 \rightarrow C_{17}$

ALKENES
1-Decene
1-Dodecene
1-Tetradecene

AROMATICS
p-Cymene

[a]The structures and electron impact mass spectra of these compounds are given in Appendix C.

The HP-5 column used with the MSD and the 15 m megabore DB-5 capillary column used for GC-FID analyses are both 5% phenyl-methylsilicone phases and similar elution patterns were expected from the two columns, although the higher resolving power of the 50 m HP-5 column resulted in fewer co-eluting peaks. For the columns utilized the first summer data was collected, a similar elution order was observed for the twelve standard monoterpenes tested (see Figure IV-5) and quantification was accomplished by GC-FID analyses (as described in the following section).

The elution of myrcene and ocimene (both acyclic terpenes, see Appendix C.1. for structures) on the 50 m HP-5 column used for the second summer's analyses differed somewhat from the first HP-5 column used (see Figures IV-5 and IV-6; note different temperature programs, as detailed below). Thus, β-pinene and myrcene were not well resolved on the second HP-5 column. Fortunately β-pinene and myrcene were resolved on the megabore DB-5 column (although β-pinene and sabinene co-eluted on the DB-5 column). From the mass spectra obtained of the plant emissions, the major component at the retention time of β-pinene and myrcene could be identified as β-pinene or myrcene and the presence of a minor amount of the second terpene could be observed in the GC-FID analyses. Additionally, for the HP-5 column used the second summer, the cis-ocimene peak, the earlier eluting of the two ocimene peaks (see Figure IV-6), eluted just prior to limonene on the second HP-5 column, while previously it had eluted just after the limonene peak (see Figure IV-5) and eluted after limonene on the megabore DB-5 column. Since the relative retention times of all the standards were tested on each column used, no confusion resulted from these retention order differences, but this does point out the need to verify elution order on each individual column.

When unidentified terpenes were found in the emissions of pistachio and tomatoes, terpenes in addition to the twelve originally available standards were sought, and two were obtained. The elution of 2-carene and terpinolene from the HP-5 column is shown in Figure IV-7. Since these terpenes were found to be among the agricultural species' emissions, they were among the terpenes used for calibration of the GC-FID quantifications (as detailed below). Very recently a standard of β-phellandrene was obtained from Union Camp Corp. and its mass spectrum is included in Appendix C.

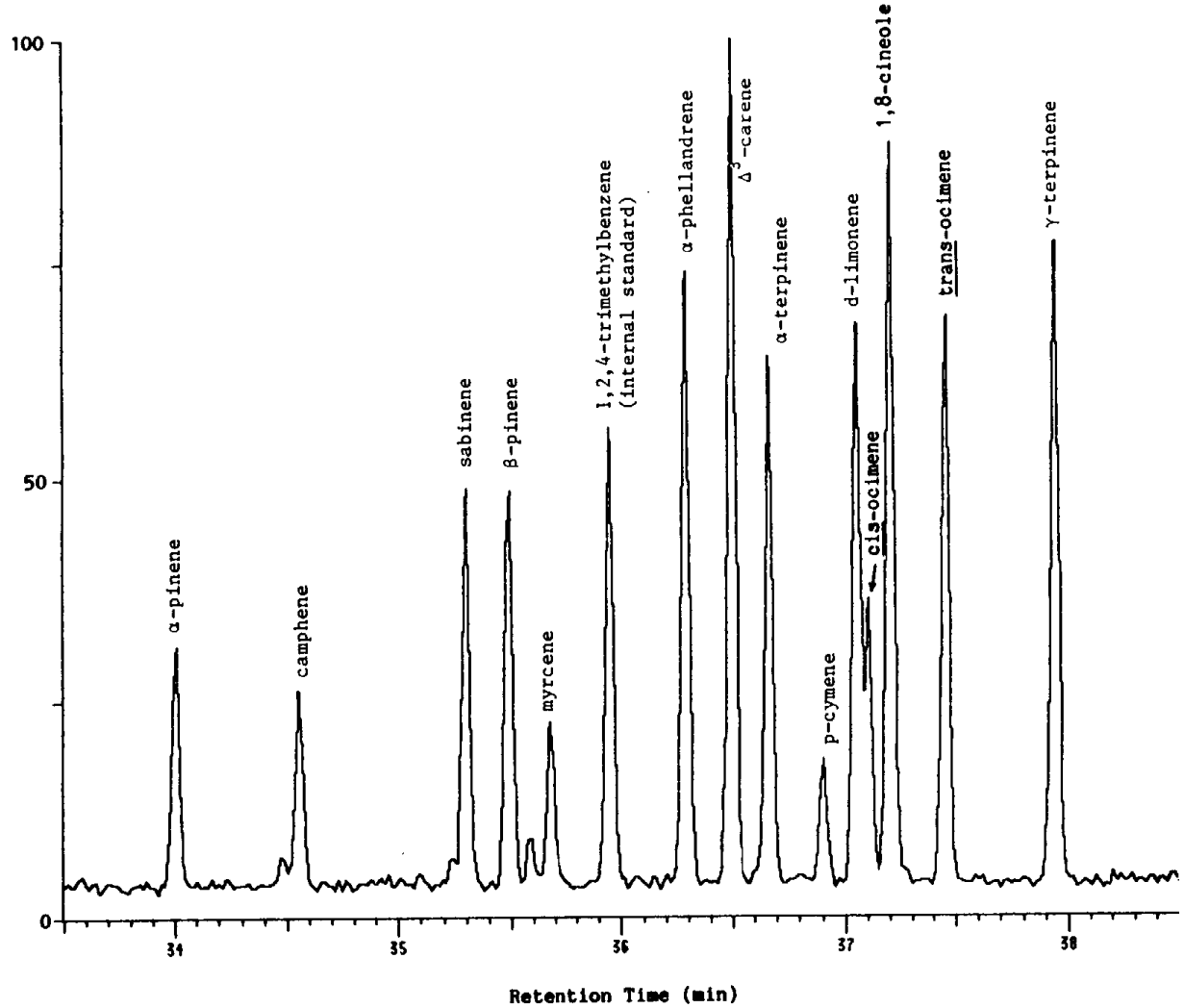


Figure IV-5. TIC from GC/MS analysis of standards using a 50 m HP-5 capillary column (No. 340-32-04, used summer 1988) for separation. The standards were applied in methanol solution (the methanol was removed by N_2 flush) to a Tenax-GC cartridge which was thermally desorbed in a 200 °C inlet onto the head of the HP-5 column held at -25 °C. After 10 min at -25 °C, the column was programmed at 6 °C min^{-1}.

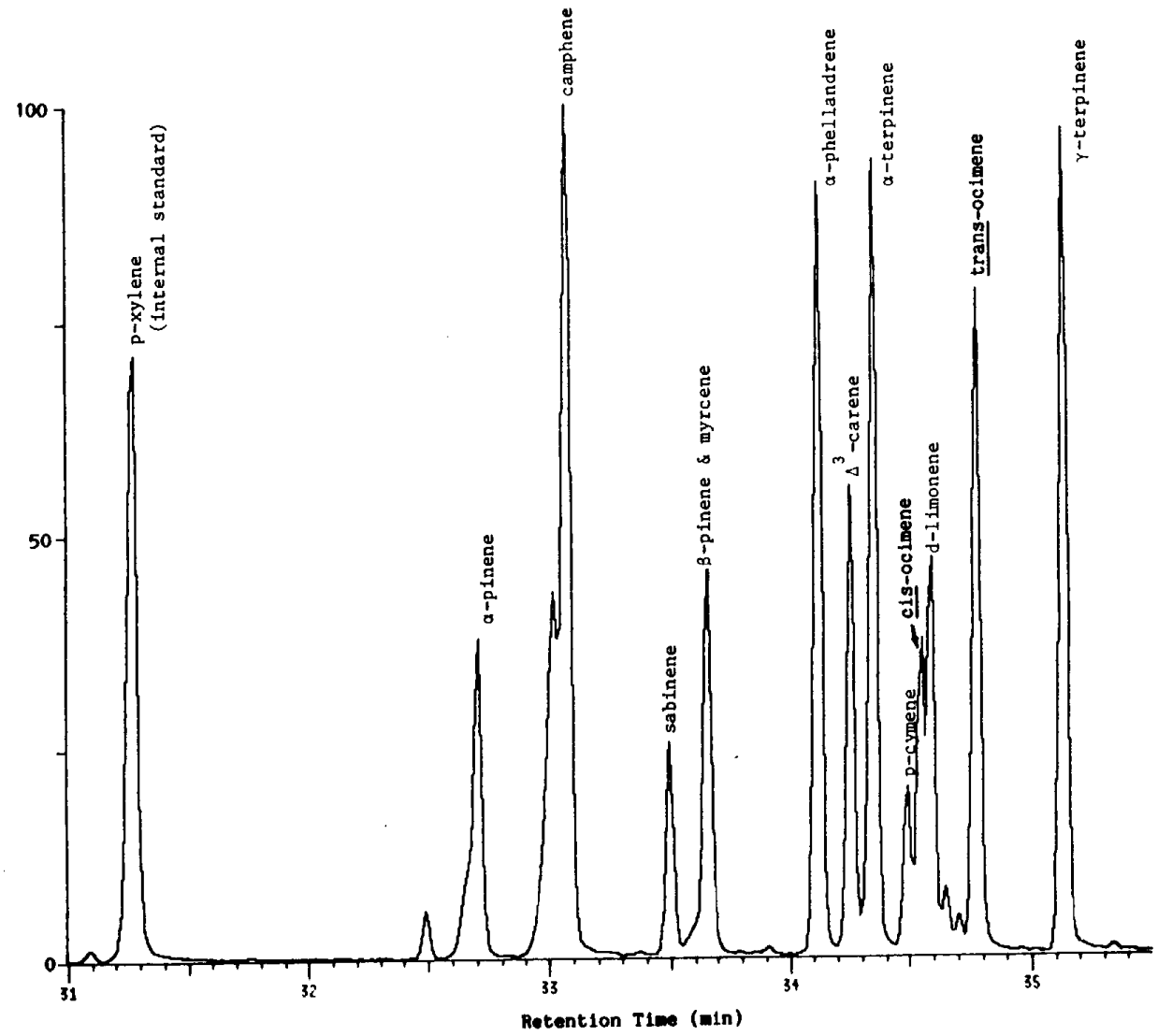


Figure IV-6. TIC from GC/MS analysis of standards using a 50 m HP-5 capillary column (No. 248-68-14, used summer 1989) for separation. The standards were applied as described in Figure IV-5. Desorption of the Tenax cartridge was at 250 °C, with the HP-5 column held at -80 °C for ten min followed by programming at 8 °C min^{-1}.

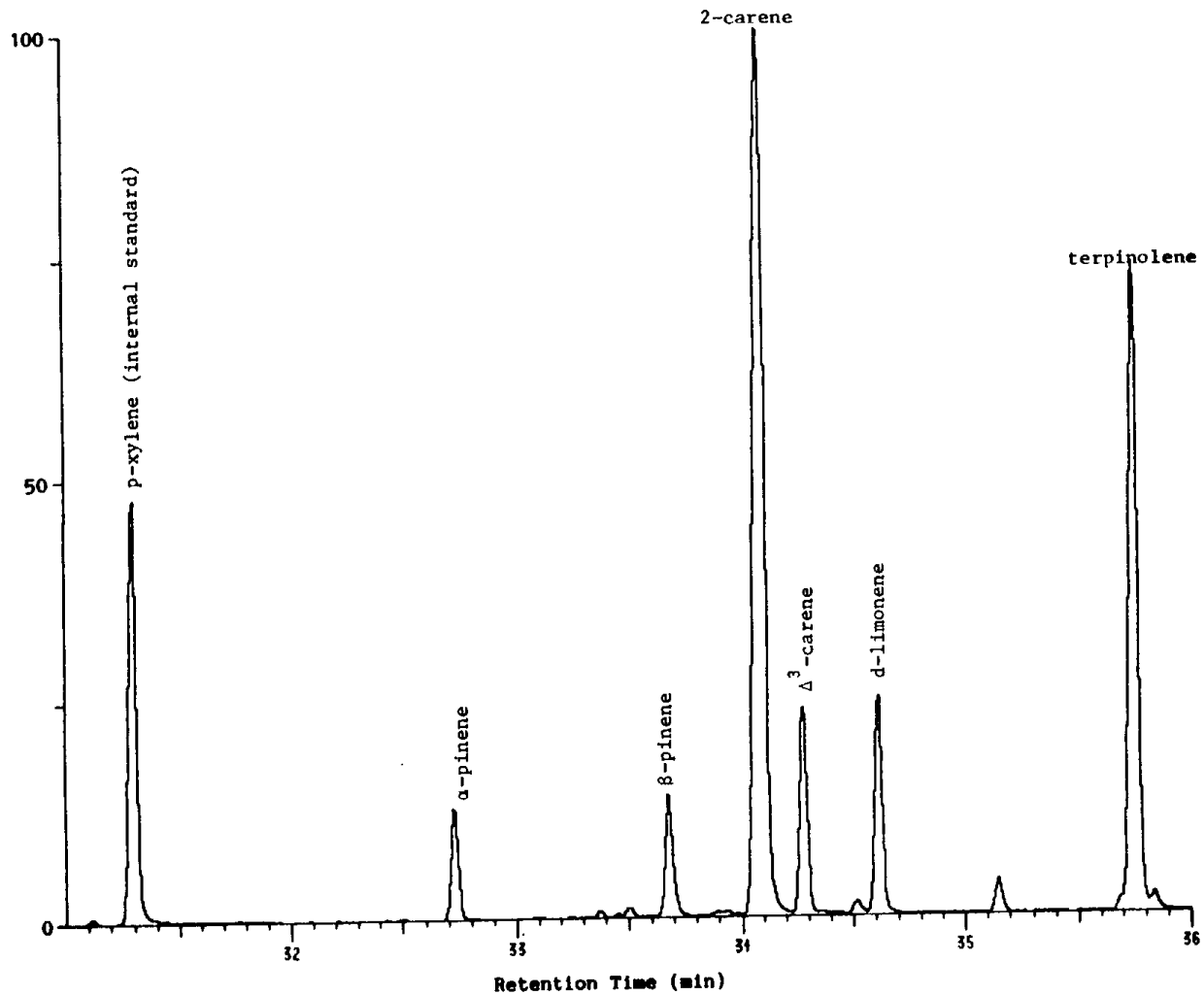


Figure IV-7. TIC from GC/MS analysis of terpinolene and 2-carene (also for comparison, p-xylene, α-pinene, β-pinene, Δ^3-carene and d-limonene). Column and conditions were as stated in Figure IV-6.

To survey the plant emissions by GC/MS, 1 to 10 ℓ samples from the plant enclosure chamber were pulled through cartridges containing Tenax-GC solid adsorbent which were immediately returned to the laboratory for analysis. The first summer, some rough handling of the plants was allowed to encourage emissions for GC/MS identification. Since this rough handling seemed to particularly enhance the release of 3-hexenylacetate (which was also observed from several plants when no rough handling was involved), during the second summer of survey sampling very large (i.e. often ~10 ℓ) Tenax samples were employed for GC/MS analysis and the plants were handled as during the protocol samples, i.e., minimizing leaf contact during placement of the chamber. While it was recognized that for samples >2 ℓ some breakthough could occur, the intent of the GC/MS samples was not to be quantitative, but rather to provide as much material as possible to allow unambiguous identification by obtaining full mass spectra. (It should be noted that quantification was by GC-FID analysis of ≤2.6 ℓ samples.)

The cartridges employed for GC/MS analysis were of 0.25 in. o.d. Pyrex tubing x 7.5 cm length to fit the HP 5890 GC inlet. Initially, thermal desorption and cold-trapping of the compounds collected on the Tenax was accomplished by placing the cartridge directly in the GC inlet, then turning off the GC septum purge flow for 10 minutes while heating the injection port to 225°C and maintaining the column oven at -25°C. After the 10-minute desorption, the compounds were chromatographed by programming the oven at 6°C min^{-1}. The MSD was operated in the full scanning mode (40-400 amu) for compound identification.

The desorption temperature was increased to 250 °C when it became apparent that species of higher molecular weight than the terpenes, i.e., terpene-derivatives and sesquiterpenes, were also present in some plant emissions. Additionally, for the second summer of analyses the initial column oven temperature was changed to -80 °C (with programming after ten minutes at 8 °C min^{-1}) in an attempt to identify very volatile, $\lesssim C_6$, emissions. Tenax-GC/Carbosieve cartridges were also occasionally used for GC/MS analyses for this purpose.

GC/MS identifications of compounds from among those listed in Table IV-2 as plant emissions were made based upon matching both the retention time and full mass spectrum of the plant emission with that of the

authentic standard. For example, the spectra upon which the identifications of limonene in a lemon sample, terpinolene in a pistachio sample, and 2-carene in a tomato sample were based are shown in Figures IV-8, IV-9 and IV-10, respectively. It is clear from these figures that the terpene assignments were made with a high degree of confidence. In addition to compounds from among those listed in Table IV-2, other compounds such as 2-methyl-6-methylene-1,7-octadien-3-one were tentatively identified as plant emissions by matching the mass spectra of the emission with reference spectra contained in the "EPA/NIH Mass Spectral Data Base" and/or by matching the spectra and reported elution order with those given in "Identification of Essential Oils by Ion Trap Mass Spectroscopy" (Adams, 1989). Several of the plant emissions remain unidentified, in part due to the lack of available standards. Compounds identified as "unknown" terpenes ($C_{10}H_{16}$) or "unknown" sesquiterpenes ($C_{15}H_{24}$) were judged from their mass spectra to have the indicated molecular formulas, but the specific isomer could not be determined.

2. Gas Chromatography Quantification

Gas samples were analyzed for isoprene, the monoterpenes and other plant emissions by GC-FID using a Hewlett Packard 5710A gas chromatograph coupled to a Hewlett Packard 3390 recording integrator. A 15 m DB-5 megabore column (J & W, Inc.), held at -80 °C for five minutes and then temperature programmed at 8 °C min^{-1} to 200 °C, was used to separate the compounds of interest.

0.5-Liter to 2.6-ℓ volume (the sample size depending on how strong an emitter the plant proved to be during the survey sampling) samples of the plant emissions were collected from the enclosure chamber onto cartridges containing Tenax-GC solid adsorbent backed up by Carbosieve S-II. After addition of the retention time marker compound the sample cartridge was attached to the carrier gas line and the column and the carrier flow started. A heat desorber set at 220 °C was placed around the cartridge for the duration of the analysis.

The Tenax-GC (60/80 mesh)/Carbosieve S-II (80/100 mesh) cartridges consisted of ~3 mm diameter glass tubes packed with a Tenax-GC and a small amount of Carbosieve, held in place with a glass wool plug at either end. The flow during sampling entered from the Tenax end of the cartridge, while the N_2 carrier flow during analysis entered from the Carbosieve

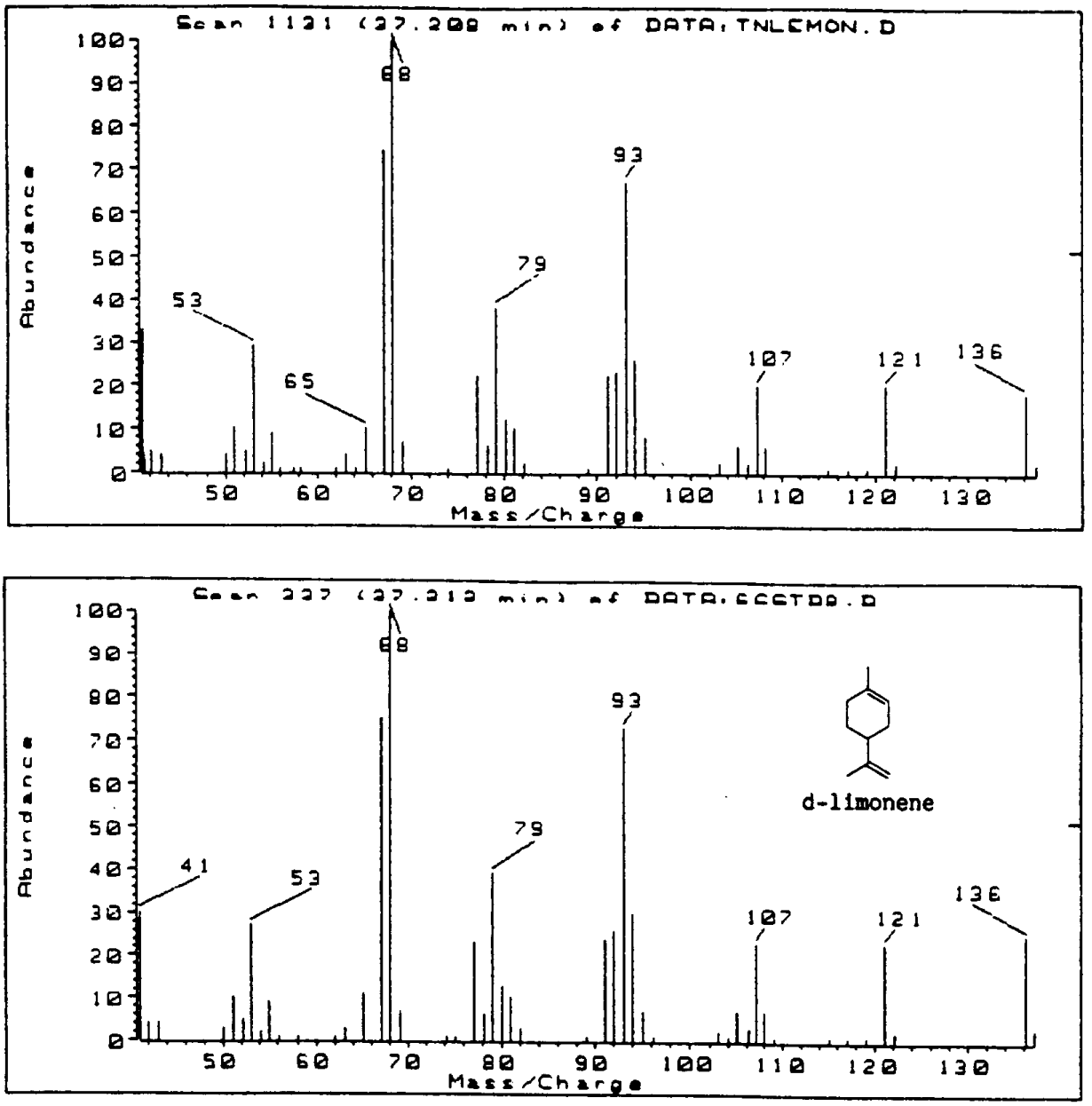
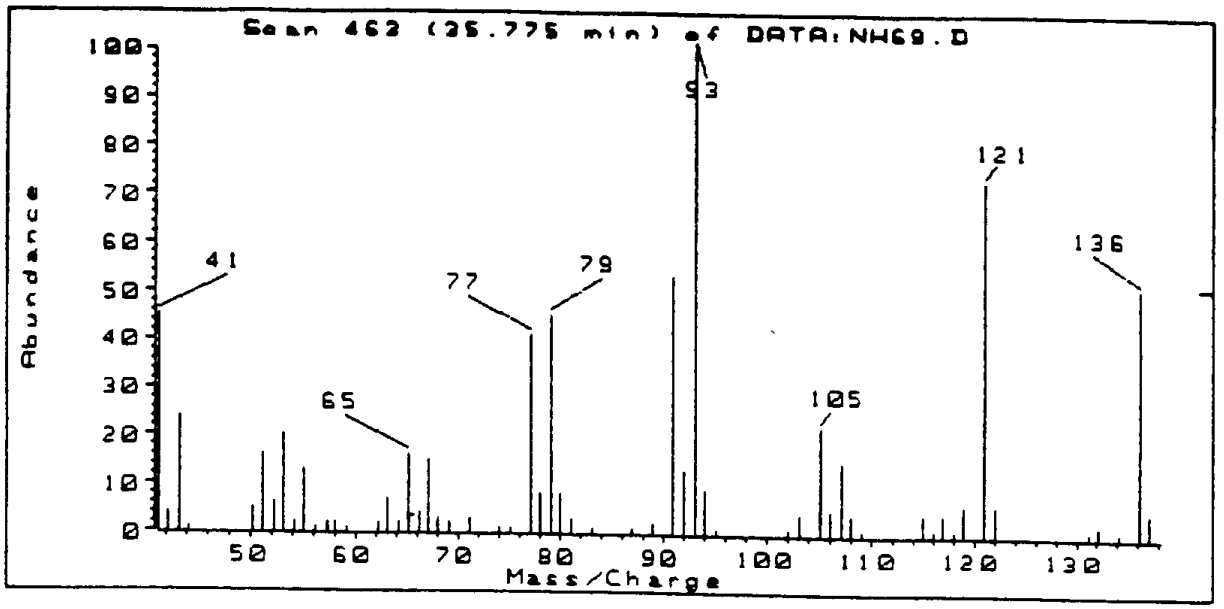


Figure IV-8. Mass spectra of the peak (37.2 min) identified as d-limonene in the lemon sample NH-5 (top) and of a standard sample of limonene (bottom). Note the characteristic fragment ion of limonene at m/z 68. Capillary column and conditions as given in Figure IV-5.



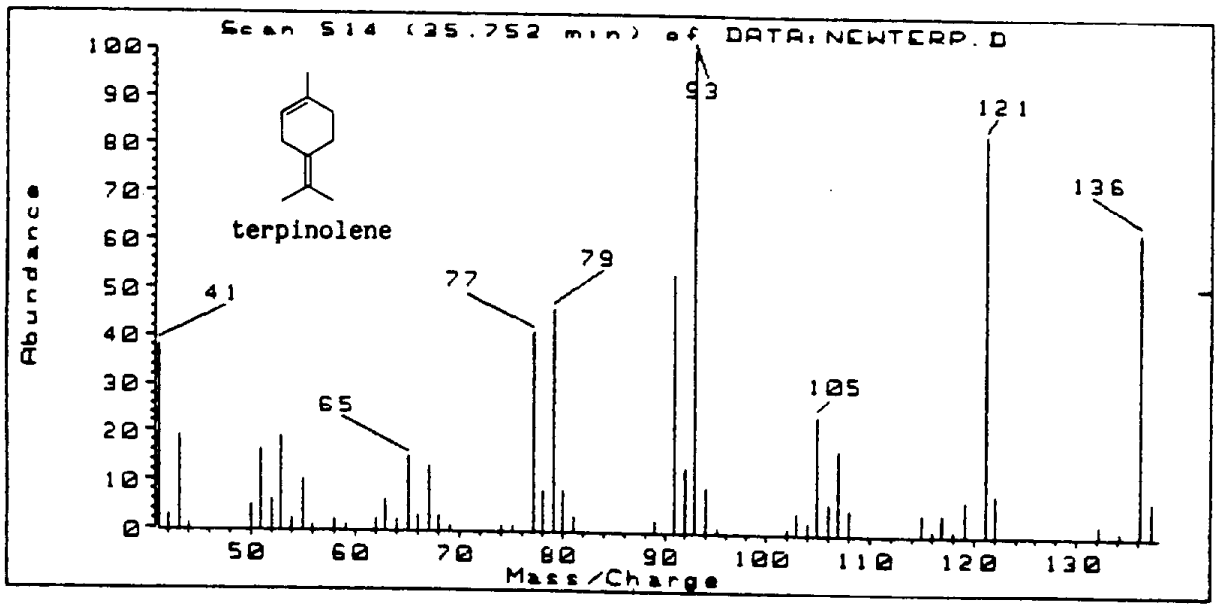
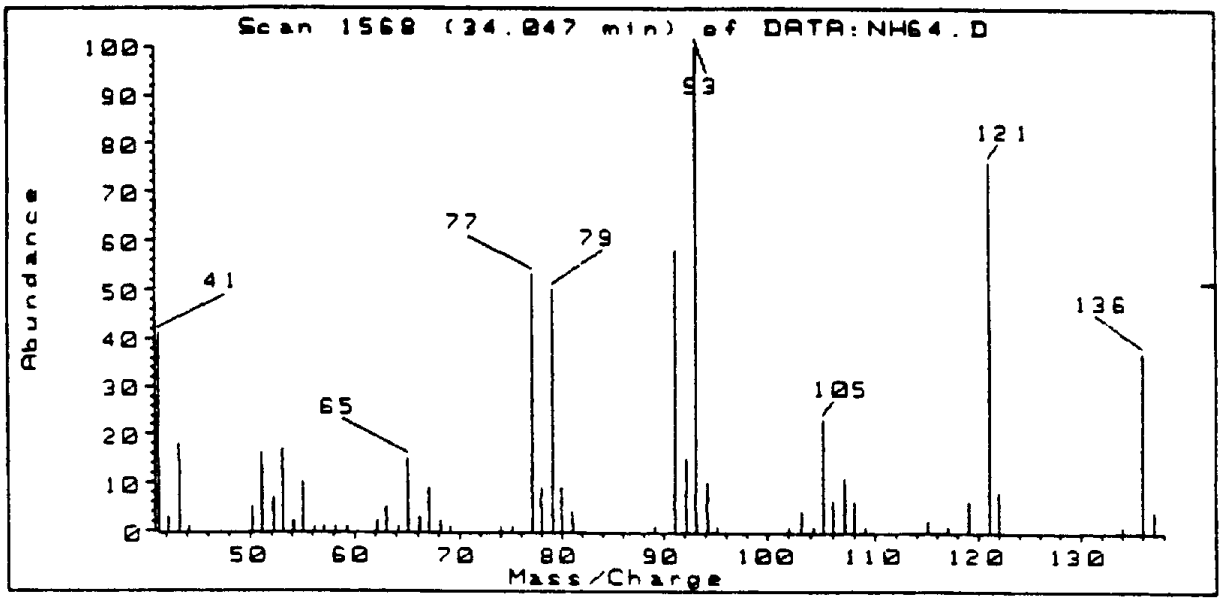


Figure IV-9. Mass spectra of the peak (35.8 min) identified as terpinolene in the pistachio sample NH-69 (top) and a standard sample of terpinolene (bottom). Capillary column and conditions as given in Figure IV-6.



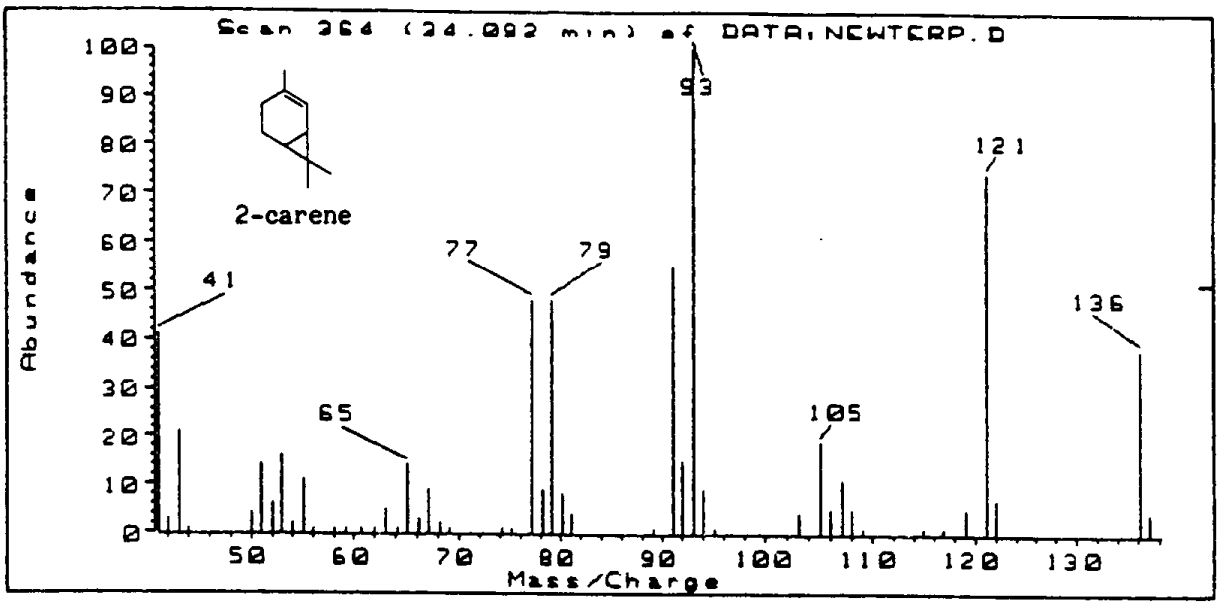


Figure IV-10. Mass spectra of the peak (34.05 min) identified as 2-carene in the canning tomato sample NH-64 (top) and a standard sample of 2-carene (bottom). Capillary column and conditions as given in Figure IV-6.

end. By this arrangement the monoterpenes were adsorbed onto the Tenax solid adsorbent, while more volatile organics such as isoprene were adsorbed on both adsorbents. While isoprene readily desorbs from the Carbosieve adsorbent, this is not the case for lower volatility organics such as the monoterpenes, and our arrangement avoided exposure of the Carbosieve to these lower volatility compounds, which are adsorbed onto the upstream Tenax adsorbent.

In preliminary gas chromatography experiments it was shown that peaks due to ambient hydrocarbons from anthropogenic sources would generally not interfere with detection of isoprene or the monoterpenes. However, using authentic standards it was also shown that the close spacing of the monoterpene retention times made peak identification difficult without the use of one or more retention time marker compounds. The compounds initially chosen were 2,2-dimethylbutane for the isoprene region of the chromatogram and 1,2,4-trimethylbenzene for the monoterpene region. One µl of 1,2,4-trimethylbenzene and 0.8 µl of 2,2-dimethylbutane were flushed into an ~160-ℓ volume Teflon bag filled with dry synthetic air. After the Tenax-GC /Carbosieve S-II cartridge samples were collected in the field, a 10-30 mℓ volume from the tracer bag was pulled through the cartridge. The volume of tracer was generally adjusted to give a marker peak reasonably similar in size to the biogenic emissions if possible. These markers were necessary because of small shifts in the retention times of the compounds of interest from analysis to analysis, making positive identification of the monoterpenes (which eluted in a narrow time interval) and, especially, isoprene extremely difficult in the absence of the retention time marker compounds.

When the emissions from carrots were measured at the end of the first summer of measurements, it was observed that myrcene co-eluted with 1,2,4-trimethylbenzene on the 15 m DB-5 column. Therefore, for the second summer of sampling p-xylene was utilized as the internal retention time marker for the "terpene region". Another analytical development utilized in the second summer of sampling was GC-FID analysis of the $C_3 \rightarrow C_5$ hydrocarbon species on a 30 m GS-Q Megabore fused silica column. A second Tenax-GC/Carbosieve S-II cartridge sample of each plant emission was collected for desorption onto the GS-Q column. This column allowed reliable isoprene identification and quantitation, as well as quantitation

of the total volatile ($C_3 \rightarrow C_5$) plant emissions. For several of the later species studied, a Tenax/Carbosieve cartridge was used for analysis of the volatile species on the GS-Q column and a cartridge containing only Tenax was used for the analysis of the monoterpenes and other emissions on the DB-5 column. This simplified the analysis somewhat since retention time shifts from sample to sample were reduced when using only the Tenax adsorbent which does not retain water.

The HP 5710A GC equipped with the 15 m DB-5 megabore column was calibrated either by introducing known quantities of the monoterpenes into the SAPRC 6400-liter indoor Teflon chamber and withdrawing known volumes through the Tenax-GC cartridge, or by spiking known quantities of the terpenes dissolved in methanol solution, onto the Tenax cartridge. Authentic samples of α-pinene, camphene, sabinene, β-pinene, myrcene, 2-carene, Δ^3-carene, α-phellandrene, p-cymene, d-limonene, ocimene, γ-terpinene and terpinolene were used to determine calibration factors (see Table IV-3). As expected for a flame ionization detector, similar factors were measured for all the monoterpenes, and based on the numerous calibrations carried out (Table IV-3), an average factor of 5×10^{-8} ppm (in 100 mℓ volume)/unit area was used for all monoterpenes.

The concentrations of the monoterpene emissions from the agricultural and natural species are expressed in ppbC which were calculated by multiplying the area of the GC peak by 5×10^{-5} and dividing by the volume of the sample taken in liters. This same calculation of concentration in ppbC was used for all the plant emissions measured on the DB-5 column. It should be recognized that for oxygenated species, this calculation may somewhat underestimate the concentration (since the response of the detector to, for example, one ppbC of acetone is less than the response to one ppbC of a monoterpene), but it should be completely appropriate for isoprene, the sesquiterpenes, and alkanes.

The calibration for isoprene on the HP 5710A GC equipped with the 30 m GS-Q column was very similar. The ppbC of isoprene emitted was calculated as the area of the GC peak multiplied by 4.69×10^{-5} divided by the sample size in liters. For the species other than isoprene observed on the GS-Q column, a factor which averaged the response of isoprene and of acetone was used, since it was thought that, in accord with the findings of Isidorov et al. (1985), many of the $C_3 \rightarrow C_5$ species observed on

Table IV-3. Terpene Calibration Factors in Units of:

10^{-8} ppm (in 100 mℓ Volume)/Area

Compounds	Date[a]							
	3/89	3/89	3/89	4/89	6/89	6/89	7/89	7/89
α-pinene	4.54[b]	4.70[b]	4.70				4.76	
camphene				4.18			5.15	
sabinene				4.48			5.36	5.61
β-pinene	5.35[b]	4.38[b]	4.23				4.84	
myrcene	7.43				10.4[b]		7.40	
2-carene					5.73		4.84	
Δ^3-carene	5.11[b]	5.11[b]	4.80				5.24	
α-phellandrene							5.37	
p-cymene							4.95	
d-limonene	6.35[b]	4.87[b]	4.53				4.92	
ocimene					5.38[b]		5.48	
γ-terpinene							5.39	
terpinolene					5.93[b]	7.06[b]	5.22	

[a]15 m DB-5 megabore column replaced May 1, 1989.
[b]Compound in methanol solution added to Tenax.

this column were likely to be oxygenated. Therefore the ppbC of emissions were calculated as the GC peak area multiplied by 6.56×10^{-5} divided by the sample volume in liters.

In addition to the samples collected on solid adsorbent for subsequent thermal desorption and GC-FID analysis, 100 mℓ gas samples were collected, generally at 0900 hr and noon during the protocol sampling, for analysis on three or four other GC columns with FID detection. These columns were packed columns previously used for volatile hydrocarbon analyses during smog chamber experiments. These columns were used since $<C_5$ species did not give reproducible retention times on the DB-5 column, and although we did not expect large emissions of $<C_5$ compounds, we wanted to have the ability to detect them if they were present. The columns and

the species which could be detected on each system were as follows: (1) a 36 ft x 0.125 in. stainless steel (SS) column of 10% 2,4-dimethylsulfolane on C-22 firebrick (60/80 mesh), operated at 0 °C for the analysis of C_3-C_5 alkanes; (2) a 10 ft x 0.125 in. SS column of 10% Carbowax E-600 on C-22 firebrick, operated at 75°C, primarily for analysis of volatile oxygenates; (3) a 5 ft x 0.125 in. SS column of Porapak N (100/120 mesh) operated at 60°C for analysis of ethane, ethene and acetylene; and (4) a 20 ft x 0.125 in. SS column of 5% DC703/C20M on AW, DMCS, Chromosorb G (100/120 mesh), operated at 60°C, with a 3 mℓ SS sample loop for analysis of isoprene in selected cases. For analyses on columns (1)-(3), the 100 mℓ gas samples were cold-trapped in ~2-3 mℓ SS loops with liquid argon. The traps used with columns (1) and (3) were thawed with ice water while the trap used with column (2) was thawed with boiling water. The information gained from the use of the GS-Q column described above essentially replaced that from analyses on columns (1) and (2) above.

E. Dry Biomass Determinations

Plants were harvested for dry weight measurements after all hydrocarbon emission samples had been taken for that sample. Woody plants were harvested by cutting off the entire branch that had been enclosed within the large Teflon bag. Herbaceous plants were cut off at ground level. The weight measurements focussed on dry leaf weights. Fruit, if present (for example on the tomatoes and certain citrus), was not included in the dry biomass weights.

For some herbaceous plants (alfalfa, beans, annual grassland, pasture, and wheat) leaves could not be separated from stems. As a result, only the total dry weight was obtained. For some woody plants (olive, chamise, mountain mahogany, and whitethorn) leaves and stems were not originally separated. Thus, five extra samples of each of these species were collected to determine representative leaf:stem weight ratios. These ratios were then applied to the original total dry weight data to obtain representative dry leaf weights. The emission rates of the cotton and the two tomato varieties were determined both for total dry weight (excluding tomato fruit) and dry leaf weight.

The plants were initially dried outside in closed fiberglass greenhouses where temperatures normally reached over 50°C during the day. This drying was necessary to reduce the amount of plant material. The reduced samples were then placed in controlled temperature ovens (Fisher Scientific Model 255G and Precision Scientific Model 18) at 50°C. The plants were weighed daily until constant weights were obtained (variation less than 5% between dates). Weights were obtained with a Fisher Scientific Model XT top-loading balance.

V. IDENTIFICATION OF EMISSIONS

A. Introduction

The agricultural and natural species chosen for study, alphabetized according to their common names, are listed in Table V-1 and this is the order in which the detailed GC/MS and GC-FID data identifying their emissions is presented. As noted in Section IV, our original focus on isoprene and the monoterpenes had to be enlarged as additional compound classes were found to be significant emissions from the plant species studied.

The compounds identified as emissions from the agricultural and natural plant species studied are listed in Table V-2 according to compound class. Isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$), sesquiterpenes ($C_{15}H_{24}$), alcohols, acetates, aldehydes, ketones, ethers, esters, alkanes, alkenes and aromatics were all observed as emissions from various plant species. Isoprene and the monoterpenes are listed separately from the other alkenes since the literature strongly suggests that these are the most important emissions from plants. As discussed in Section II, the high emission rates of isoprene, particularly from oak species and the pinenes from coniferous trees, has resulted in an emphasis on these species in formulating biogenic emissions inventories.

Consistent with the literature, we found isoprene to be emitted from the species of oak (Valley oak) chosen as a representative of the natural foothill hardwood plant community in the Central Valley. Significantly, no other plant species studied emitted detectable levels of isoprene.

For a few of the species studied, as has been reported for many conifers (see, for example, Figure II-1), one or two terpenes were the major emissions. For example, β-phellandrene and 2-carene were the largest emissions from the two tomato varieties examined, and terpinolene and d-limonene were the single largest emissions from the pistachio and the Valencia orange, respectively. Far more common, however, was the presence of several terpenes at similar concentrations, together with additional compound classes, as the emissions from a single plant species. This could have implications for previous work in which estimates of the upper limit of emissions from a plant species, for which no emissions were

Table V-1. Agricultural and Natural Plant Species Chosen for Study

Agricultural Species
Alfalfa
Almond
Apricot
Bean
Beet (Sugar)
Carrot
Cherry
Corn (Grain)
Cotton (Lint)
Grape (Table)
Grape (Wine)
Lemon
Lettuce
Nectarine
Olive
Onion
Orange (Navel)
Orange (Valencia)
Pasture (Irrigated)
Peach
Pistachio
Plum
Prune
Rice
Safflower
Sorghum (Grain)
Tomato (Fresh Market)
Tomato (Processing)
Walnut
Wheat
Natural Plant Species
Chamise
Grassland (Annual)
Manzanita (Big Berry)
Mountain Mahogany
Oak (Valley)
Whitethorn

Table V-2. Compounds Identified[a] as Emissions from the Agricultural and Natural Plant Species Studied

Isoprene

MONOTERPENES
Camphene
2-Carene
Δ^3-Carene
d-Limonene
Myrcene
cis-Ocimene
trans-Ocimene
α-Phellandrene
β-Phellandrene
α-Pinene
β-Pinene
Sabinene
α-Terpinene
γ-Terpinene
Terpinolene
Tricyclene
or α-Thujene (tentative)[b]

SESQUITERPENES
β-Caryophyllene
Cyperene
α-Humulene

ALCOHOLS
p-Cymen-8-ol (tentative)[b]
cis-3-Hexen-1-ol
Linalool

ACETATES
Bornylacetate
Butylacetate (tentative)[b]
cis-3-Hexenylacetate

ALDEHYDES
n-Hexanal
trans-2-Hexenal

KETONES[c]
2-Heptanone
2-Methyl-6-methylene-1,7-octadien-3-one (tentative)[b]
Pinocarvone (tentative)[b]
Verbenone (tentative)[b]

ETHERS
1,8-Cineole
p-Dimethoxybenzene (tentative)[b]
Estragole (tentative)[b]
p-Methylanisole (tentative)[b]

ESTERS
Methylsalicylate (tentative)[b]

n-ALKANES
n-Hexane
C_{10}→C_{17}

ALKENES
1-Decene
1-Dodecene
1-Hexadecene (tentative)[b]
p-Mentha-1,3,8-triene (tentative)[b]
1-Pentadecene (tentative)[b]
1-Tetradecene

AROMATICS
p-Cymene

[a]Unless labeled "Tentative", identifications were made on the basis of matching full mass spectra and retention times with authentic standards. The structures and electron impact mass spectra of the authentic standards are given in Appendix C.

[b]Tentative identifications were made on the basis of matching the mass spectra (and retention order when available) with published spectra (EPA/NIH Mass Spectral Data Base and/or Adams, 1989). The literature spectra and those of the plant emissions are given in Appendix D.

[c]Acetone was tentatively identified from the GC-FID analysis on the GS-Q column (see text for details).

detected, were based on the analytical limit of detection assuming emission of either a single or a very few dominant biogenic compounds.

Sesquiterpenes were observed from several plant species, generally in lower amounts than the terpene emissions from that particular plant, but the bing cherry, peach and safflower were notable exceptions, having higher sesquiterpene emissions.

Oxygenated compounds were observed from virtually every plant species studied. Cis-3-hexenylacetate, cis-3-hexen-1-ol, n-hexanal and trans-2-hexenal were the most often observed oxygenated hydrocarbons. A commonly observed, early eluting, unidentified emission (tentatively of m.w. 100), is probably also oxygenated and perhaps an acetate. One compound observed from several plant species has been tentatively identified as 2-methyl-6-methylene-1,7-octadien-3-one. Oxygenated terpene derivatives such as linalool, verbenone and 1,8-cineole were generally observed less often and in lower abundance than the monoterpenes. A number of the unidentified species eluting after the monoterpenes may well be terpene derivatives.

Alkenes, most often 1-decene, 1-dodecene and 1-tetradecene, were also common emissions. n-Alkanes were also observed, but generally in lower amounts than the alkenes.

B. Plant Emissions Identified and Quantified

As discussed in Section IV, a survey was to be made for each species during which samples were taken for analysis by GC/MS and GC-FID, and if significant emissions were observed, a full sampling protocol was to be conducted. For each of twenty-eight species a survey and full protocol sampling with quantification of emissions was made. Following survey sampling, the full protocol sampling was not conducted for the following species: sugar beet, grain corn, lettuce, onion, French prune, and mountain mahogany. The only monoterpenes observed as emissions from these plant species were very low levels of ocimene in the French prune and mountain mahogany (levels likely to be below the limit of detection for the sample sizes used during the protocol sampling); a small sesquiterpene peak was seen in the corn emissions. The emissions from the sugar beet, lettuce and onion were principally cis-3-hexen-1-ol and cis-3-hexenylacetate. As discussed in Sections VI and VII, the emission of this alcohol and acetate was affected by the handling of the plant specimens.

Additionally, GC-FID protocol samples of the irrigated pasture and big berry manzanita were taken while GC/MS analysis was unavailable. From the GC-FID analysis, it was evident that the big berry manzanita did not produce significant biogenic emissions and that the emissions from the irrigated pasture were largely very volatile ($C_3 \rightarrow C_5$) species not readily amenable to GC/MS identification.

For each species (with the two exceptions noted above) there is a table listing the emissions identified by GC/MS during the survey analysis and an accompanying figure showing the total ion chromatogram from the analysis of the Tenax sample of the plant emissions. A second table for each species gives the concentration data determined by GC-FID during the protocol sampling. The assigned peaks correspond to the compounds identified by GC/MS and are shown on the accompanying GC-FID chromatogram from a representative protocol sample. Since several mathematical operations are required before the emission factors are derived from the concentration data, extra significant figures have been retained in these concentration data tables.

A few comments should be made about the TIC and GC-FID chromatograms for those most familiar with this type of data. In some cases the identified monoterpene peaks are quite small in comparison to other peaks in the TIC. Constructing mass chromatograms (where the response of a single ion is extracted from the total ion current) for the molecular ion (m/z 136) and/or most abundant fragment ion (m/z 93) of the monoterpenes ensured that no detectable monoterpene peak was overlooked. The assignment of a corresponding GC-FID peak as the monoterpene required that the retention time difference of the peak from the marker match the value previously determined using the authentic monoterpene standard. For compounds other than the monoterpenes some reliance on pattern recognition was required, e.g. assuming that the largest GC-FID peak in a given retention window corresponded to the largest GC/MS peak in the corresponding retention time window.

All the major peaks, but not every peak visible on the TICs, have been labeled. In several instances small peaks were not labeled since from their mass spectra they were judged to be alkylbenzenes and, as with the toluene peak, were assumed to be of anthropogenic origin. Additionally if a given peak was small and the spectrum was weak and/or unlikely

to allow future identification of the compound, it was not numbered. The sometimes large, unlabeled peak present near the end of many of the GC-FID chromatograms is an artifact peak that appears in the blank from thermal desorption of the Tenax or Tenax/Carbosieve cartridges. Occasionally Tenax artifact peaks are also labeled on the TICs, particularly for samples taken in the summer of 1988. As discussed below, the summing of the areas of all the peaks in specified retention time windows on the GC-FID chromatogram ensured that a maximum upper limit could be put on the plant emissions.

To allow the maximum utility of the data in emission inventory calculations to be realized, a great deal of detail is provided in the concentration data tables. The ppbC data for each GC peak identified as a plant emission, with the specific emitted compound named where possible, are given. Individual totals are given for the monoterpenes and sesquiterpenes emitted, the total plant emissions (referred to as total assigned plant emissions [TAPE] in Section VI where the emission factors are presented) and total carbon. The total carbon was calculated to give an upper limit to the plant emissions and will include, in addition to the peaks assigned as plant emissions, some background peaks from the residual ambient air in the plant enclosure and/or contaminants in the medical air blanks (generally excluding 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.

As noted in Section IV, for the majority of the agricultural and natural species examined (all those studied during the second summer) two separate adsorbent cartridge samples were taken to allow optimum analysis of the volatile $\sim C_3 \rightarrow C_5$ compounds (analyzed on a GS-Q column) in addition to the $\sim C_{6,7} \rightarrow C_{15}$ compounds analyzed on the DB-5 and HP-5 columns by GC-FID and GC/MS, respectively. The first individual total given on the concentration data tables is Σ(Assigned Peaks) which is the total ppbC calculated from the areas of the peaks assigned as plant emissions, i.e., the numbered peaks from the GC/MS identifications for which corresponding peaks could be assigned in the GC-FID analyses on the DB-5 column. These assigned peaks include the monoterpenes and sesquiterpenes, and separate totals are given for these plant emissions. Also included in the Σ(Assigned Peaks) are the C_6-alcohol, <u>cis</u>-3-hexen-1-ol, and the C_6-aldehydes, n-hexanal and <u>trans</u>-2-hexenal, when these were present.

Another total given from the GC-FID analysis on the DB-5 column is designated as $\Sigma C_7 \rightarrow C_{15}$, i.e., the ppbC calculated from summing the areas of all the peaks present in a retention time window from just after the toluene peak through the sesquiterpene region of the chromatogram. This sum will include any peaks of anthropogenic origin present (as noted in Section IV, <10% of ambient air should remain in the enclosure chamber at the time of sampling), as well as any unidentified plant emissions.

Even with the use of 2,2-dimethylbutane as a retention time marker, identification of isoprene (or any compound eluting before toluene) on the DB-5 column was difficult due to retention time shifts caused by water vapor in the sample. Since isoprene has been found to be such an abundant plant emission from certain plant species (e.g., Evans et al., 1982) we felt it was very important to be able to analyze specifically for this compound. The retention time of isoprene on the GS-Q column was unaffected by water vapor and, therefore, in the summer of 1989 we used a GS-Q column for volatile species analysis. The next entry on the concentration data tables is designated as C_5. Since isoprene and n-pentane co-eluted on the GS-Q column, this entry may be viewed as an upper limit to the isoprene emitted. For two air blanks in which samples were taken by the normal procedure except that no plant was present in the enclosure chamber, the measured values for C_5 were 0.7 and 1.0 ppbC, most likely representing a small amount of n-pentane in the pure air. With the exception of the Valley oak, none of the plant species gave C_5 values significantly higher than the air blank samples. The contribution of n-pentane from the pure air to the C_5 given for the Valley oak sample is negligible. Additionally, isoprene was confirmed in the Valley oak sample by GC/MS analysis, and also was independently quantified by syringe sample measurements (see Table V-70).

For the samples measured the first summer (1988), the ppbC of the peaks eluting prior to toluene (i.e., $C_3 \rightarrow C_6$) on the DB-5 column were calculated to allow these very volatile species to be added to the total carbon observed, and thus to give a true upper limit to the plant emissions. As noted above, the retention times of compounds eluting before toluene were not reproducible on the DB-5 column used for GC-FID analysis, and the GC/MS system, in the majority of cases, did not allow identifications to be made of compounds more volatile than toluene. Thus,

volatile impurities in the pure air blanks (which included acetone as discussed further below) could not be corrected for, nor could corrections be made for the variable ambient contributions from the <10% of ambient air not flushed from the plant enclosure.

For the samples measured the summer of 1989, the ppbC of the volatile species from the GS-Q column were summed and are designated as $\Sigma C_3 \rightarrow C_5$. Acetone was found to be present in the pure air blanks and was not included in this sum, unless noted. The exceptions, where acetone was included since it was present at significantly higher levels than in the pure air blank, were the wheat and irrigated pasture samples. Generally the volatile emissions were small in comparison with the $\geq C_7$ compounds. The Valley oak, of course, was one exception and the wheat and irrigated pasture also contained volatiles (other than isoprene and acetone) which we were not able to identify.

It would appear that for the samples other than the first summer's (NH-24, NH-26 through NH-32 and NH-36 and NH-37) where $\Sigma C_3 \rightarrow C_6$ was calculated from the DB-5 column data, that the C_6 species have been overlooked. As noted above, the frequent plant emissions that are a C_6-alcohol and C_6-aldehydes elute after toluene on the DB-5 column and have, therefore, been included. Small benzene and n-hexane peaks (<2 ppb) were observed in one of the pure air blank samples. Additionally, benzene is present in ambient air (an ambient sample analyzed by the same method as the plant emissions showed a benzene peak of 16 ppbC) and, as with toluene and the alkylbenzenes, should be assumed to be of anthropogenic origin, unless present at high levels. To assure that no major emission was overlooked, for those samples taken with a Tenax/Carbosieve cartridge (NH-43, NH-45 through NH-51 and NH-54, NH-71 and NH-75), the ppbC for the $\Sigma C_3 \rightarrow C_6$ from the DB-5 column analyses has been calculated and is listed on the concentration data tables below the $\Sigma C_3 \rightarrow C_5$ calculated from the GS-Q column. These two sums are generally in reasonable agreement, with no indication that the $\Sigma C_3 \rightarrow C_5$ has underestimated the ppbC of the volatile species present.

Starting with sample NH-76, a Tenax-only cartridge was generally used to take the sample to be analyzed on the DB-5 column, and a Tenax/Carbosieve cartridge was used to take the sample for analysis of isoprene and the volatile species on the GS-Q column. Without the Carbosieve, which

retained water, the Tenax sample on the DB-5 column gave reproducible retention times and although the sample collected would not be quantitative for the full range of volatiles from C_3, it is expected to have been quantitative for n-hexane and benzene. Thus, for these remaining samples, the area of the chromatogram in which n-hexane and benzene would elute was surveyed and an upper limit for these C_6-species has been calculated and added to the concentration data tables under the notation ΣC_6.

The total plant emissions are the same as the Σ(Assigned Peaks) except for the Valley oak, where the isoprene was, of course, included. The final values given in the concentration data tables are Total Carbon (in ppbC). The Total Carbon is essentially the ppbC calculated for the summation of the areas of all the GC peaks, i.e., the $\Sigma C_7 \rightarrow C_{15}$ from the DB-5 columnn and ΣC_3-C_5 from the GS-Q column (toluene, certain C_6 compounds, markers, and acetone excluded, as noted) and represents an upper limit for the plant emissions. The differences between the Total Carbon and the Total Plant Emissions are either due to unrecognized or unidentified plant emissions, to contaminants present in the pure gases used during sampling, and/or to anthropogenic hydrocarbons not flushed from the plant enclosure chamber. The blank samples mentioned above gave values for $\Sigma C_7 \rightarrow C_{15}$ of 36 and 82 ppbC and for $\Sigma C_3 \rightarrow C_5$ of 28 and 32 ppbC, resulting in expected background values for (Total Carbon - Total Plant Emissions) of 64 and 114 ppbC, respectively.

For half of the thirty species for which complete protocols were conducted, the Total Plant Emissions represents 50% or more of the Total Carbon. The values for the (Total Carbon - Total Plant Emissions) for the 36 plant species reported here range from 25-890 ppbC and for all but five species this value is <250 ppbC. The five exceptions and their values of (Total Carbon - Total Plant Emissions) are: processing tomato (290 ppbC), safflower (370 ppbC), fresh market tomato (450 ppbC), wheat (570 ppbC) and irrigated pasture (890 ppbC). The tomatoes emitted high levels of monoterpenes and on a percentage basis >90% of the total carbon is assigned for both varieties examined. Fifty percent of the total carbon for the safflower has been assigned. For the irrigated pasture and wheat, the unassigned volatile emissions were high, with $C_3 \rightarrow C_5$ values of 550 and 440 ppbC, respectively. Although these $C_3 \rightarrow C_5$ compounds could not be identified by GC/MS, these volatiles are believed to be true plant

emissions and, therefore, for the irrigated pasture and the wheat the Total Carbon is more representative of the true emissions than the Total Plant Emissions.

For all species except the wheat, irrigated pasture and perhaps the safflower, the total assigned emissions (or the emission rates designated as TAPE in Section VI) are good estimates of the total emissions from the particular plant specimen at the moment of sampling. The Total Carbon may be used as an upper limit of the emissions, but will tend to overestimate the emissions. For example, the emission rate based on the average Total Plant Emissions for the almond is 2.1 $\mu g\ hr^{-1}\ gm^{-1}$ and that based on the average Total Carbon is 9.3 $\mu g\ hr^{-1}\ gm^{-1}$ (see Table VI-4). However, the almond sample had a relatively low biomass and the average value of (Total Carbon - Total Plant Emissions) in ppbC is 83, not above the expected background.

The remainder of this section is comprised of the tables giving identifications of the plant emissions (by GC/MS) and quantifications (by GC-FID) for each of the 36 species (including six for which only surveys were conducted) studied, together with the corresponding chromatograms. In Sections VI and VII the emission rate calculations are presented and discussed, including variations in emission rates from specimen to specimen of a given plant species and the other uncertainties involved in developing an emissions inventory for the Central Valley.

Table V-3. Emissions Identified from Alfalfa (Pierce) by GC/MS Analysis of Survey Sample NH-83C[a] (TIC Shown in Figure V-1)

Peak No.	Compound Identification[b]
1	unknown (m.w. 100)
2	n-hexanal
3	cis-3-hexen-1-ol
4	p-xylene (internal standard)
5	α-pinene
6	sabinene
7	1-decene
8	myrcene
9	3-hexenylacetate
10	cis-ocimene[c]
11	d-limonene
12	1,8-cineole
13	trans-ocimene[c]
14	unknown (m.w. 150)
15	2-methyl-6-methylene-1,7-octadien-3-one (tentative)
16	1-dodecene
17-20	unknown sesquiterpenes (m.w. 204)
21	β-caryophyllene
22-25	unknown sesquiterpenes (m.w. 204)

[a]Survey sample NH-59 showed alfalfa emitted compounds #3, 9 and 13 from the above list. NH-83C was a repeat of the survey conducted during the protocol, since the biomass of the alfalfa had increased substantially since survey sample NH-59.

[b]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.

[c]Our 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).

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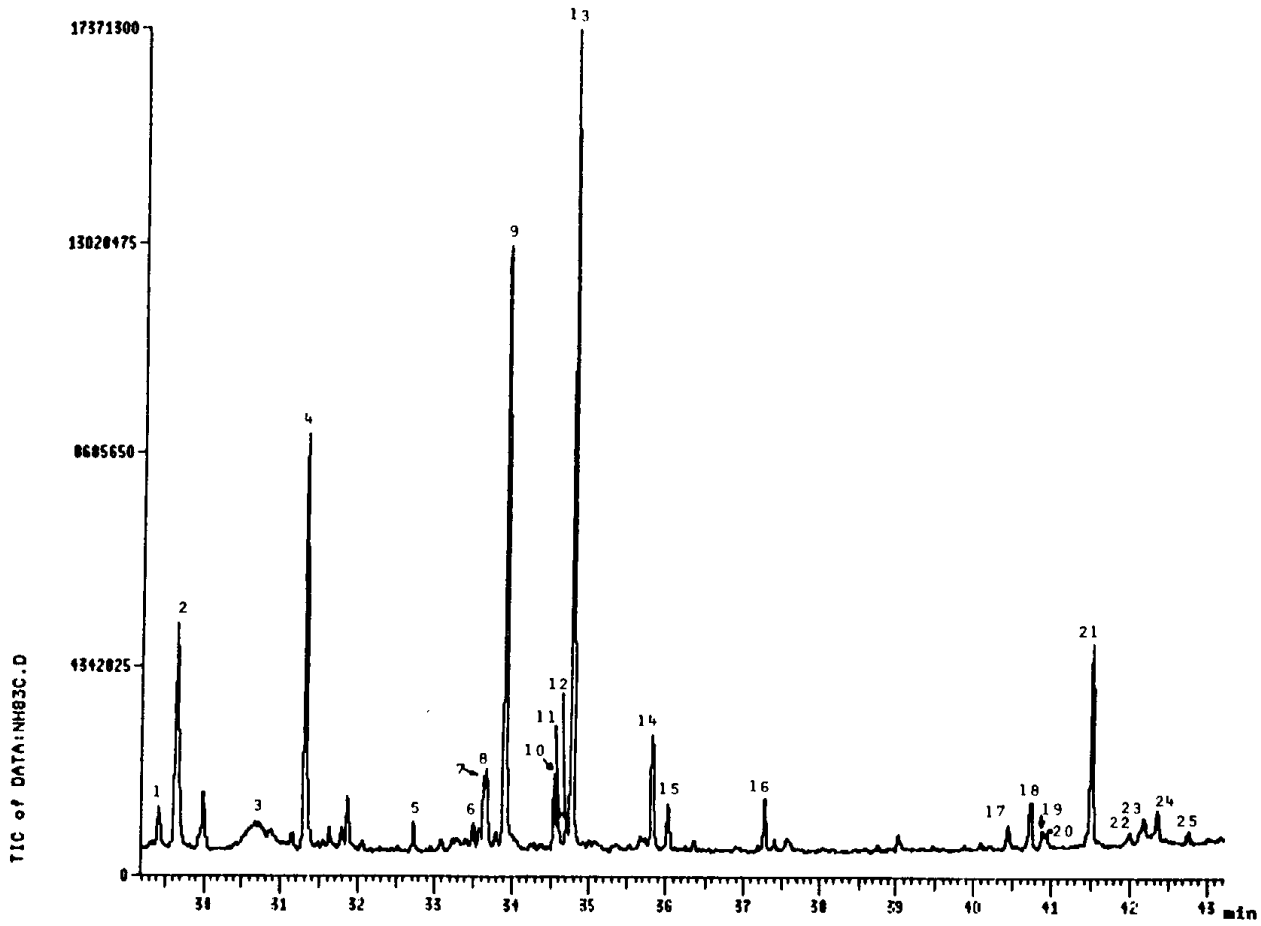

Figure V-1. TIC from GC/MS analysis of 3.7 ℓ Tenax sample of alfalfa (Pierce) emissions (sample NH-83C). Identities of numbered peaks given in Table V-3.

Table V-4. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Alfalfa (Pierce) - 1989 July 11

Assigned Peaks[a]	NH-83A 0900	NH-83B 1030	NH-83C 1200	NH-83D 1330	NH-83E 1445	Identification
2[b]	12	47	20	48	8	unknown
3	37	122	36	c	5	cis-3-hexen-1-ol
4	d	d	d	d	d	p-xylene
5	2	2	n.a.[e]	3	3	α-pinene
6	2	2	n.a.	2	n.a.	sabinene
7,8	9	10[b]	21	5	n.a.	1-decene and myrcene
9	91	309	78	351	28	3-hexenylacetate
10	n.d.[f]	2	10	n.d.	10	cis-ocimene
11,12	6	1	8	3	17	d-limonene and 1,8-cineole
13	13	32	101	158	76	trans-ocimene
15[b]	7	12	23	23	24	2-methyl-6-methylene-1,7-octadien-3-one (tentative)
16	4	11	17	28	13	1-dodecene
21	n.d.	3	10	14	n.d.	β-caryophyllene
toluene[g]	c	2	n.d.	n.d.	2	
ΣC_6[s]	c	c	11	c	c	
Σ(Assigned Peaks)[h]	183	553	324	635	184	
ΣMonoterpenes	32	49	140	171	106	
ΣSesquiterpenes	n.d.	3	10	14	n.d.	
$\Sigma C_7 \rightarrow C_{15}$[i]	227	664	475	823	358	
C_5[j]	3	4	5	4	5	
$\Sigma C_3 \rightarrow C_5$[k]	49	56	72	57	78	
Total Plant Emissions[l]	183	553	324	635	184	
Total Carbon[m]	276	720	547	880	436	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-2. The numbers correspond to the GC/MS identifications as given on Figure V-1 and in Table V-3.
[b-t]Footnotes given on Table V-73.

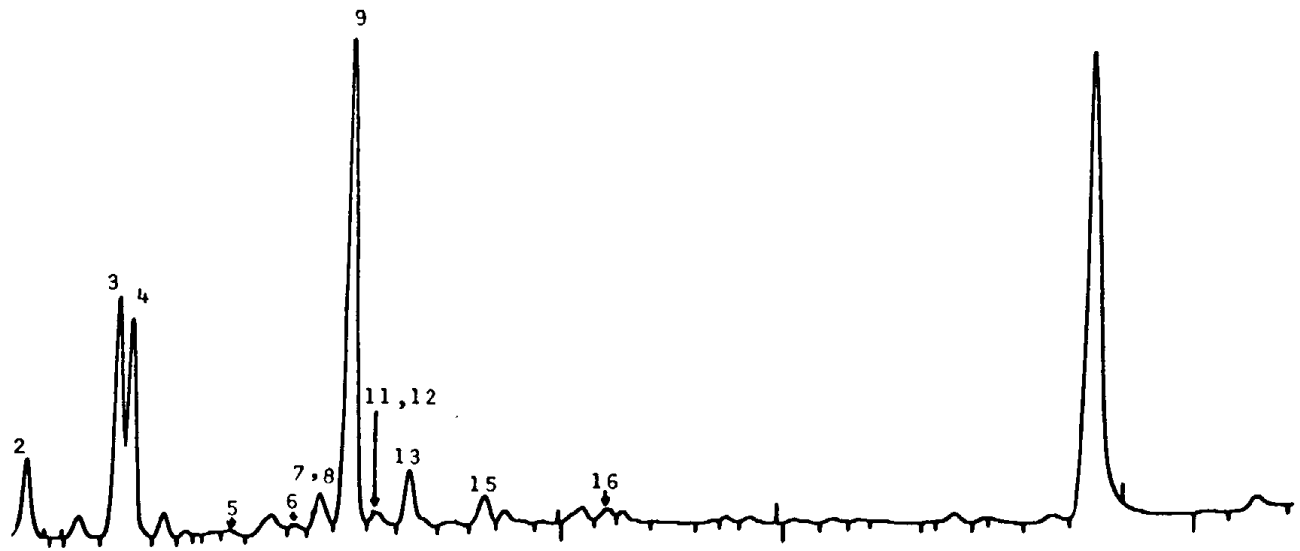

Figure V-2. GC-FID analysis of 1.2% Tenax sample of alfalfa (Pierce) emissions (NH-83A). The assigned peaks have been numbered to correspond the the GC/MS identifications given in Table V-3.

Table V-5. Emissions Identified from Almond (Nonpareil) by GC/MS Analysis of Survey Sample NH-17 (TIC Shown in Figure V-3)

Peak No.	Compound Identification[a]
1	*cis*-3-hexen-1-ol
2	1,2,4-trimethylbenzene (internal standard)
3	3-hexenylacetate
4	*trans*-ocimene[b]
5	unknown
6	unknown (m.w. 128)
7	unknown sesquiterpene[c]
8	β-caryophyllene
9,10	unknown sesquiterpenes[c]

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.
[b]No *trans*-ocimene was observed in survey sample NH-17, but it was observed in a second survey sample (NH-22). Also see footnote c on Table V-3.
[c]Although no m/z 204 ion was present in the spectra of these peaks, the observed fragment ion patterns, as well as the retention times, of these peaks strongly suggest that they are sesquiterpenes of m.w. 204.

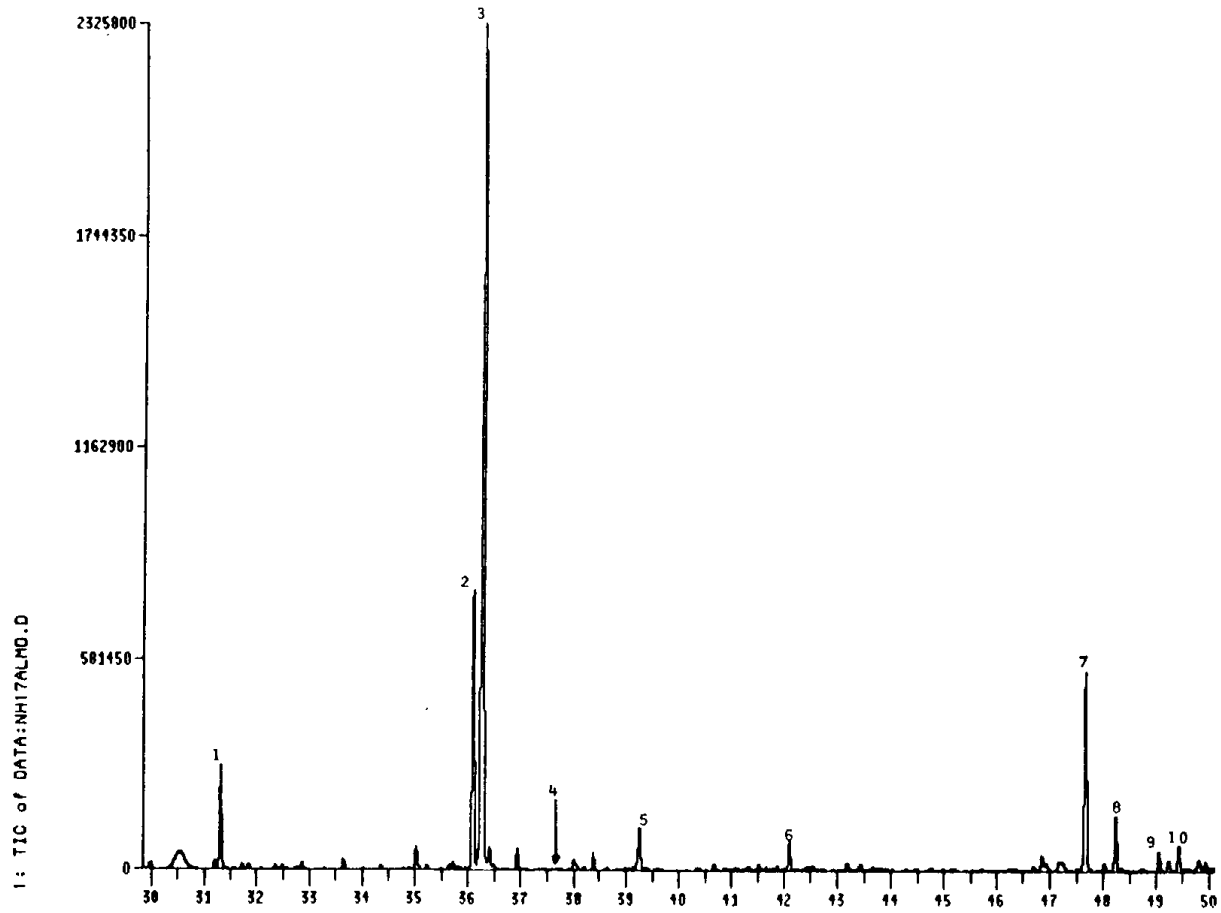

Figure V-3. TIC from GC/MS analysis of 1 ℓ Tenax sample of almond (Nonpareil) emissions (NH-17). Identities of numbered peaks given in Table V-5.

Table V-6. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Almond (Nonpareil) - 1988 September 13

Assigned Peaks[a]	NH-28A 0900	NH-28B 1030	NH-28C 1200	NH-28D 1330	NH-28E 1445	Identification
1	4	4	n.d.[f]	1	2	cis-3-hexen-1-ol
2	d	d	d	d	d	1,2,4-trimethylbenzene
3	9	22	34	18	24	3-hexenylacetate
4	n.d.	1	n.d.	n.d.	n.d.	trans-ocimene
toluene[g]	4	5	3	4	3	
Σ(Assigned Peaks)[h]	13	26	34	19	26	
ΣMonoterpenes	n.d.	1	n.d.	n.d.	n.d.	
ΣSesquiterpenes	c	c	c	c	c	
$\Sigma C_7 \rightarrow C_{15}$[i]	33	83	120	86	75	
C_5[j]	c	c	c	c	c	
$\Sigma C_3 \rightarrow C_6$[q]	20	40	23	28	23	
Total Plant Emissions[l]	13	26	34	19	26	
Total Carbon[m]	53	123	143	114	98	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-4. The numbers correspond to the GC/MS identifications as given on Figure V-3 and in Table V-5.
[b-t]Footnotes given on Table V-73.

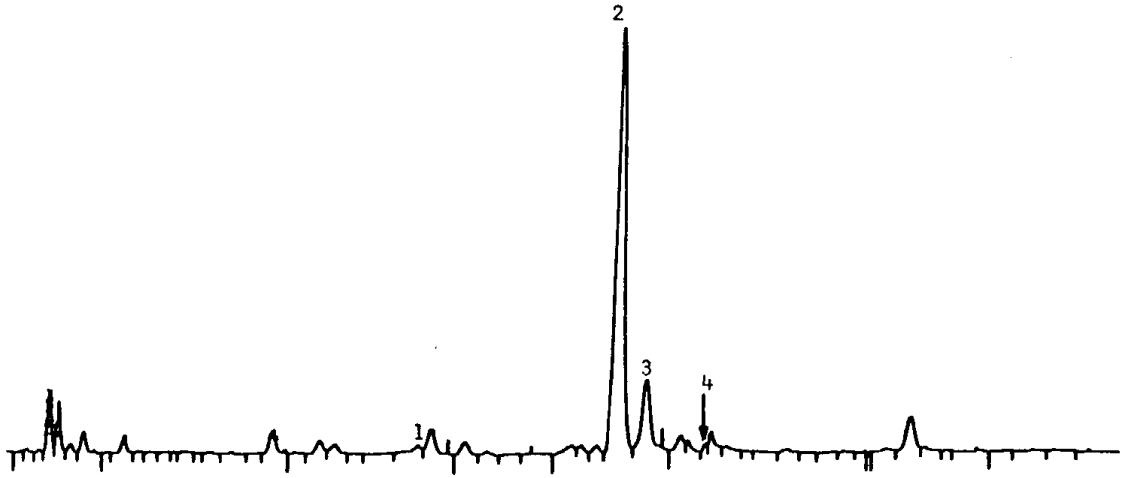

Figure V-4. GC-FID analysis of a 1.3 ℓ Tenax/Carbosieve sample of almond (Nonpareil) emissions (NH-28B). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-5.

Table V-7. Emissions Identified from Apricot (Royal) by GC/MS Analysis of Survey Sample NH-15 (TIC Shown in Figure V-5)

Peak No.	Compound Identification
1	cis-3-hexen-1-ol
2	myrcene
3	1,2,4-trimethylbenzene (internal standard)
4	3-hexenylacetate
5	cis-ocimene[a]
6	trans-ocimene[a]
7	linalool
8	2-methyl-6-methylene-1,7-octadien-3-one (tentative)
9	unknown
10	unknown

[a]See footnote c on Table V-3.

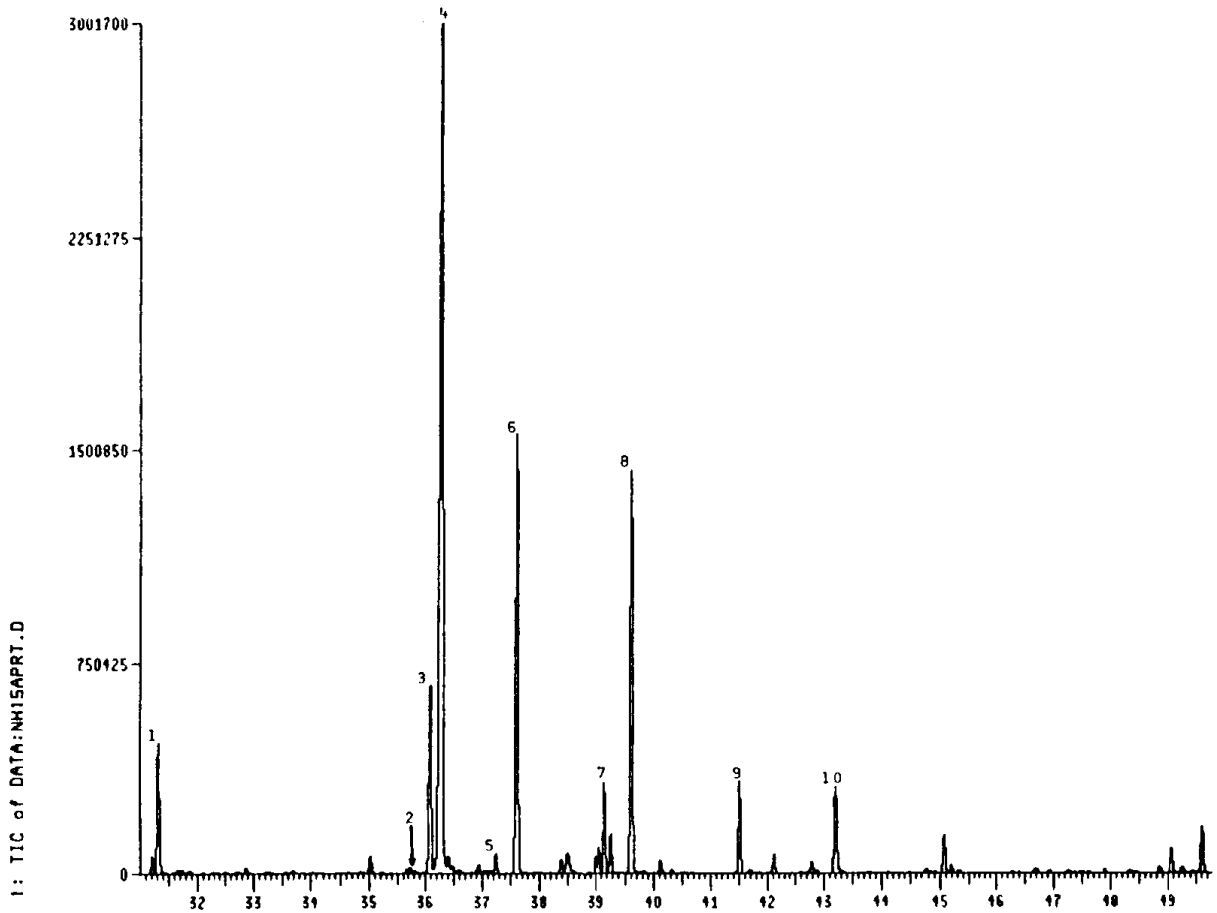

Figure V-5. TIC from GC/MS analysis of 1.4 ℓ Tenax sample of apricot (Royal) emissions (NH-15). Identities of numbered peaks given in Table V-7.

Table V-8. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Apricot (Bleinheim) - 1988 September 15

Assigned Peaks[a]	NH-29A 0900	NH-29B 1030	NH-29C 1200	NH-29D 1330	NH-29E 1445	Identification
1	2	2	n.d.[f]	n.d.	<1	cis-3-hexen-1-ol
2	2	5	n.d.	n.d.	n.d.	myrcene (peaks 4 and 5 coeluted, area of marker subtracted to estimate myrcene)
3	d	d	d	d	d	1,2,4-trimethylbenzene
4	17	26	30	31	16	3-hexenylacetate
6	n.d.	2	<1	n.d.	3	trans-ocimene
8	<1	2	3	4	5	2-methyl-6-methylene-1,7-octadien-3-one (tentative)
toluene[g]	3	5	5	4	3	
Σ(Assigned Peaks)[h]	21	37	33	35	24	
ΣMonoterpenes	2	7	<1	n.d.	3	
ΣSesquiterpenes	c	c	c	c	c	
$\Sigma C_7 \rightarrow C_{15}$[i]	51	86	85	94	104	
C_5[j]	c	c	c	c	c	
$\Sigma C_3 \rightarrow C_6$[q]	12	27	31	33	31	
Total Plant Emissions[l]	21	37	33	35	24	
Total carbon[m]	67	113	116	127	135	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-6. The numbers correspond to the GC/MS identifications as given on Figure V-5 and in Table V-7.
[b-t]Footnotes given on Table V-73.

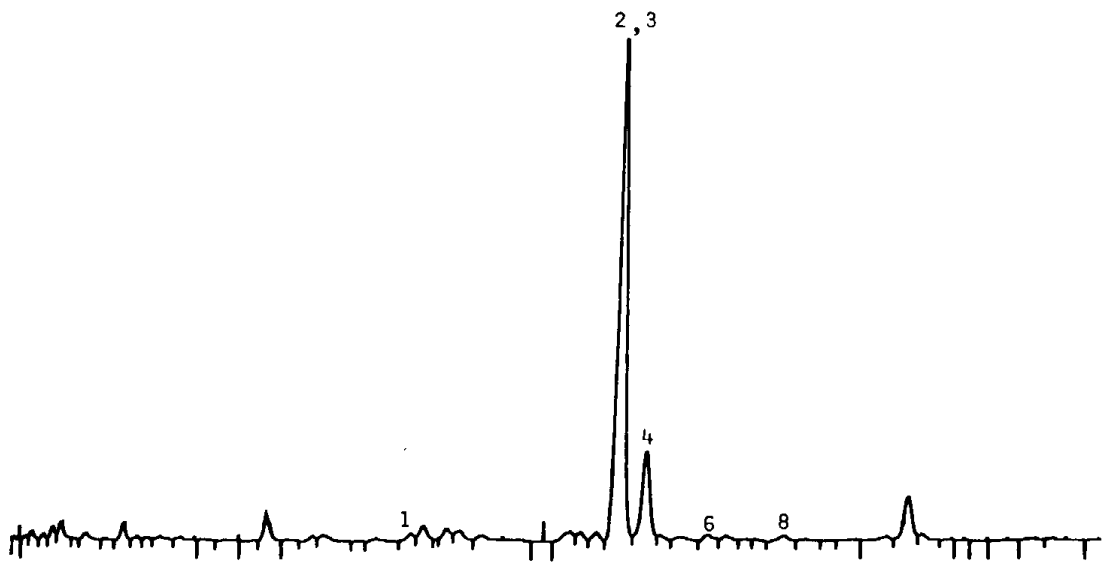

Figure V-6. GC-FID analysis of a 1.3 ℓ Tenax/Carbosieve sample of apricot (Bleinheim) emissions (NH-29B). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-7.

Table V-9. Emissions Identified from Beans (Top Crop, Fresh Bush Green Beans) by GC/MS Analysis of Survey Sample NH-68 (TIC Shown in Figure V-7)

Peak No.	Compound Identification
1	*cis*-3-hexen-1-ol
2	p-xylene (internal standard)
3	unknown (m.w. 128)
4	unknown
5	1-decene
6	n-decane
7	3-hexenylacetate[a]
8	1-dodecene
9	1-tetradecene

[a]No 3-hexenylacetate was observed in survey sample NH-68, but it was observed in a previous bean survey sample (NH-55).

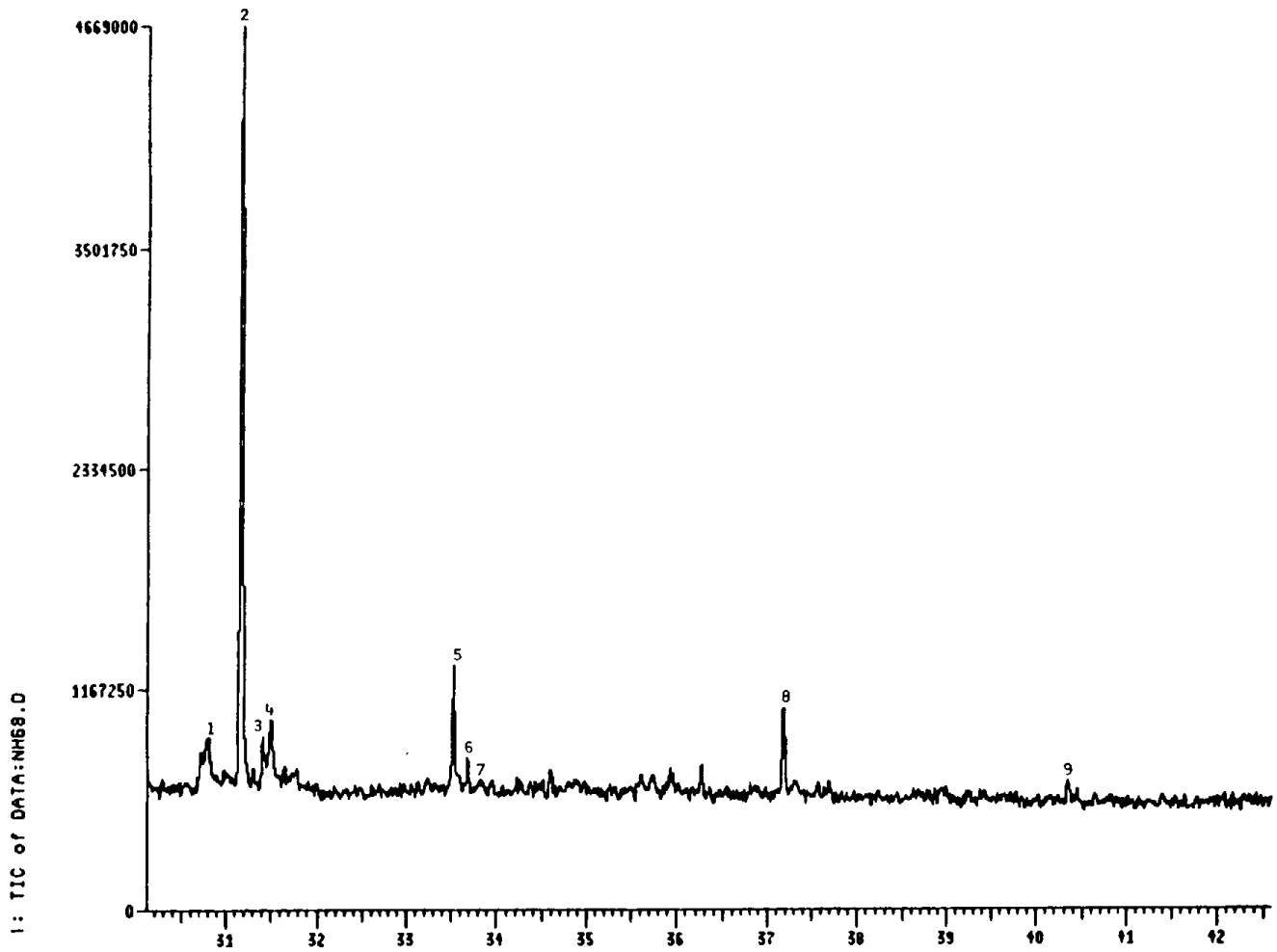

Figure V-7. TIC from GC/MS analysis of 6.3 ℓ Tenax sample of bean (Top Crop, fresh bush green beans) emissions (NH-68E). Identities of numbered peaks given in Table V-9.

Table V-10. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Bean (Top Crop) - 1989 May 23

Assigned Peaks[a]	NH-46A 0900	NH-46B 1030	NH-46C 1200	NH-46D 1330	NH-46E 1445	Identification
1	n.a.[e]	n.d.[f]	3	n.d.	4	cis-hexen-1-ol
2	d	d	d	d	d	p-xylene
5,6	n.d.	7	10	12	4	1-decene and n-decane
7	n.d.	n.d.	n.d.	n.d.	n.d.	3-hexenylacetate
8	2	7	11	11	7	1-dodecene
9	1	5	10	5	5	1-tetradecene
toluene[g]	2	<1	<1	<1	<1	
Σ(Assigned Peaks)[h]	3	19	34	28	20	
ΣMonoterpenes	n.d.	n.d.	n.d.	n.d.	n.d.	
ΣSesquiterpenes	n.d.	n.d.	n.d.	n.d.	n.d.	
$\Sigma C_7 \rightarrow C_{15}$[i]	122	107	146	148	121	
C_5[j]	6	2	2	n.d.	2	
$\Sigma C_3 \rightarrow C_5$[k]	118	67	102	128	176	
$\Sigma C_3 \rightarrow C_6$[t]	134	42	68	93	90	
Total Plant Emissions[l]	3	19	34	28	20	
Total Carbon[m]	240	174	248	276	297	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-8. The numbers correspond to the GC/MS identifications as given on Figure V-7 and in Table V-9.
[b-t]Footnotes given on Table V-73.

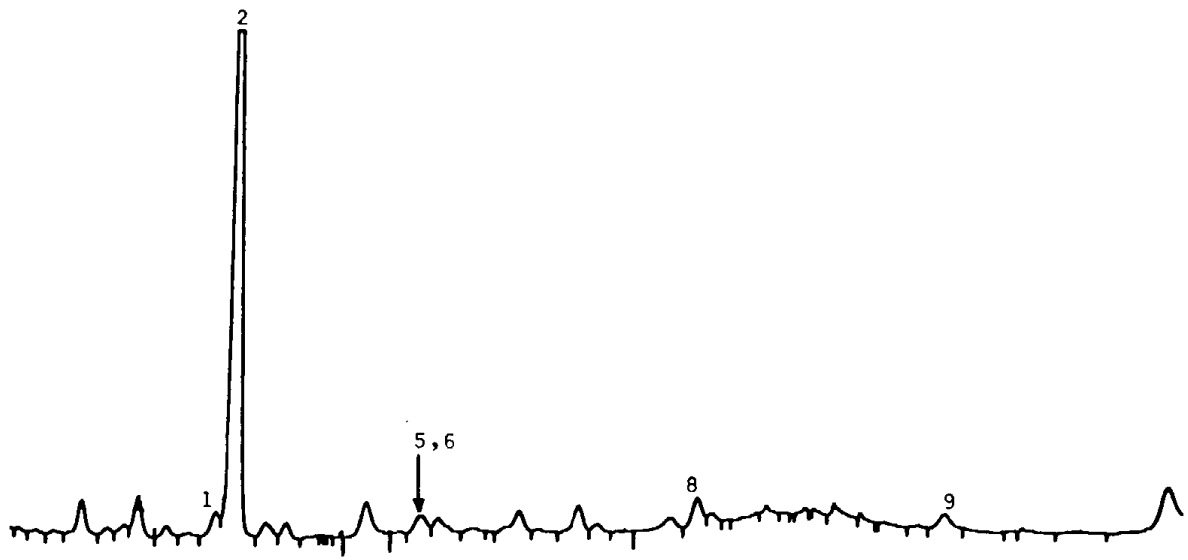

Figure V-8. GC-FID analysis of 1.3 ℓ Tenax/Carbosieve sample of bean (Top Crop, fresh bush green beans) emissions (NH-46E). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-9.

Table V-11. Emissions Identified from Sugar Beet (UC/H12) by GC/MS Analysis of Survey Sample NH-71 (TIC Shown in Figure V-9)

Peak No.	Compound Identification
1	*cis*-3-hexen-1-ol
2	p-xylene (internal standard)
3	3-hexenylacetate

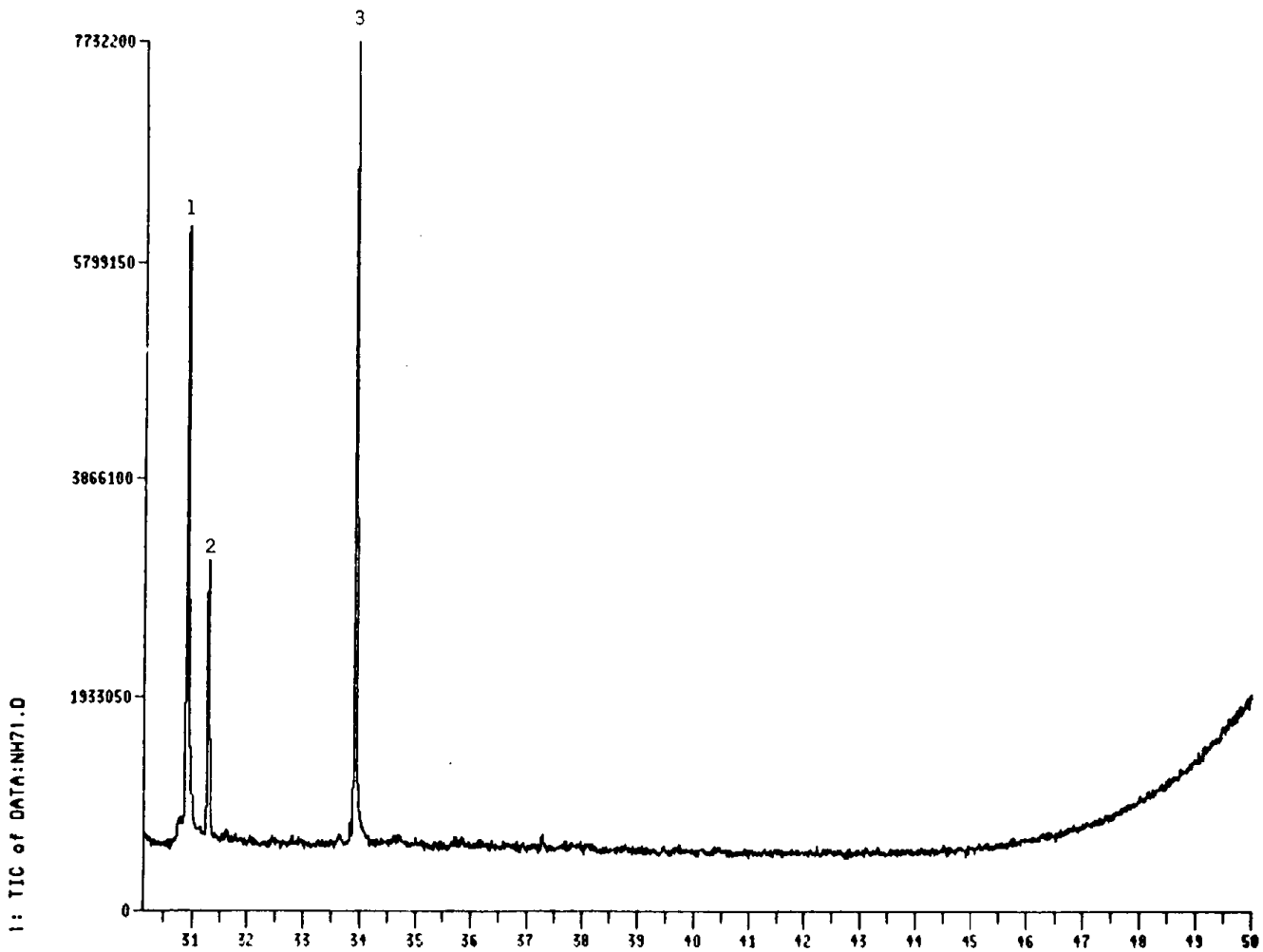

Figure V-9. TIC from GC/MS analysis of 5 ℓ Tenax sample of sugar beet (UC/H12) emissions (NH-71). Identities of numbered peaks given in Table V-11.

Table V-12. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Sugar Beet (UC/H12) - 1989 June 15

Assigned Peaks[a]	NH-71 1400	Identification
1	176	cis-3-hexen-1-ol (area of p-xylene marker subtracted to estimate alcohol concentration)
2	d	p-xylene
3	309	3-hexenylacetate
toluene[g]	1	
Σ(Assigned Peaks)[h]	485	
ΣMonoterpenes	n.d.[f]	
ΣSesquiterpenes	n.d.	
$\Sigma C_7 \rightarrow C_{15}$[i]	620	
C_5[j]	4	
$\Sigma C_3 \rightarrow C_5$[k]	49	
$\Sigma C_3 \rightarrow C_6$[t]	55	
Total Plant Emissions[l]	485	
Total Carbon[m]	649	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-10. The numbers correspond to the GC/MS identifications as given on Figure V-9 and in Table V-11.
[b-t]Footnotes given on Table V-73.

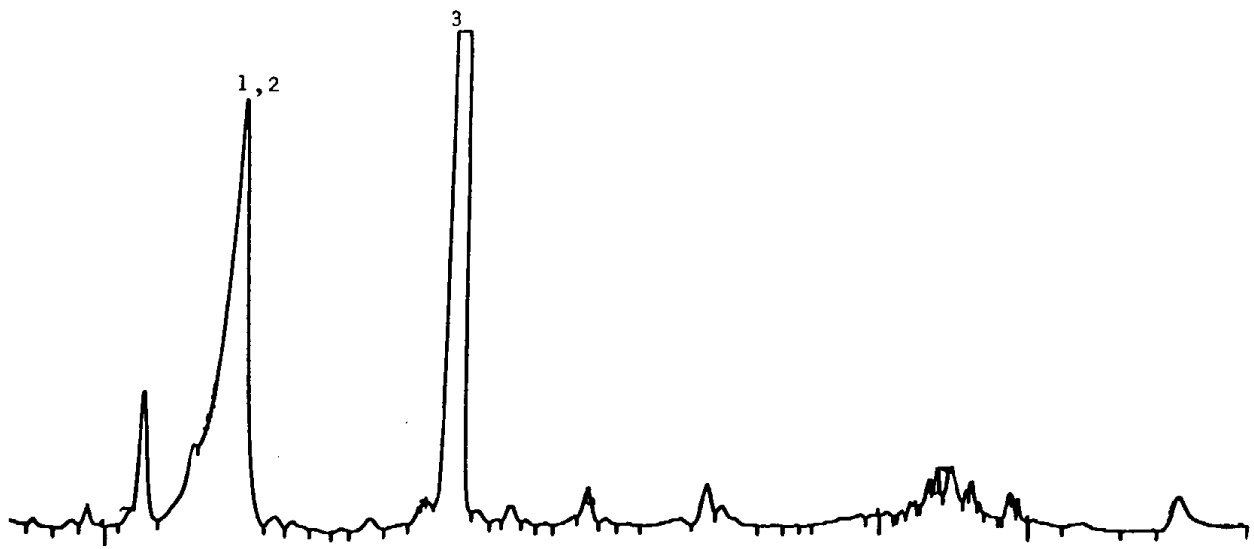

Figure V-10. GC-FID analysis of 1.3 ℓ Tenax/Carbosieve sample of sugar beet (UC/H12) emissions (NH-71). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-11.

Table V-13. Emissions Identified from Carrots (Imperator) by GC/MS Analysis of Survey Sample NH-33 (TIC Shown in Figure V-11.)

Peak No.	Compound Identification
1	α-pinene
2	sabinene
3	β-pinene
4	myrcene
5	1,2,4-trimethylbenzene (internal standard)
6	3-hexenylacetate
7	α-phellandrene
8	α-terpinene
9	p-cymene
10	d-limonene
11	β-phellandrene
12	γ-terpinene
13	terpinolene

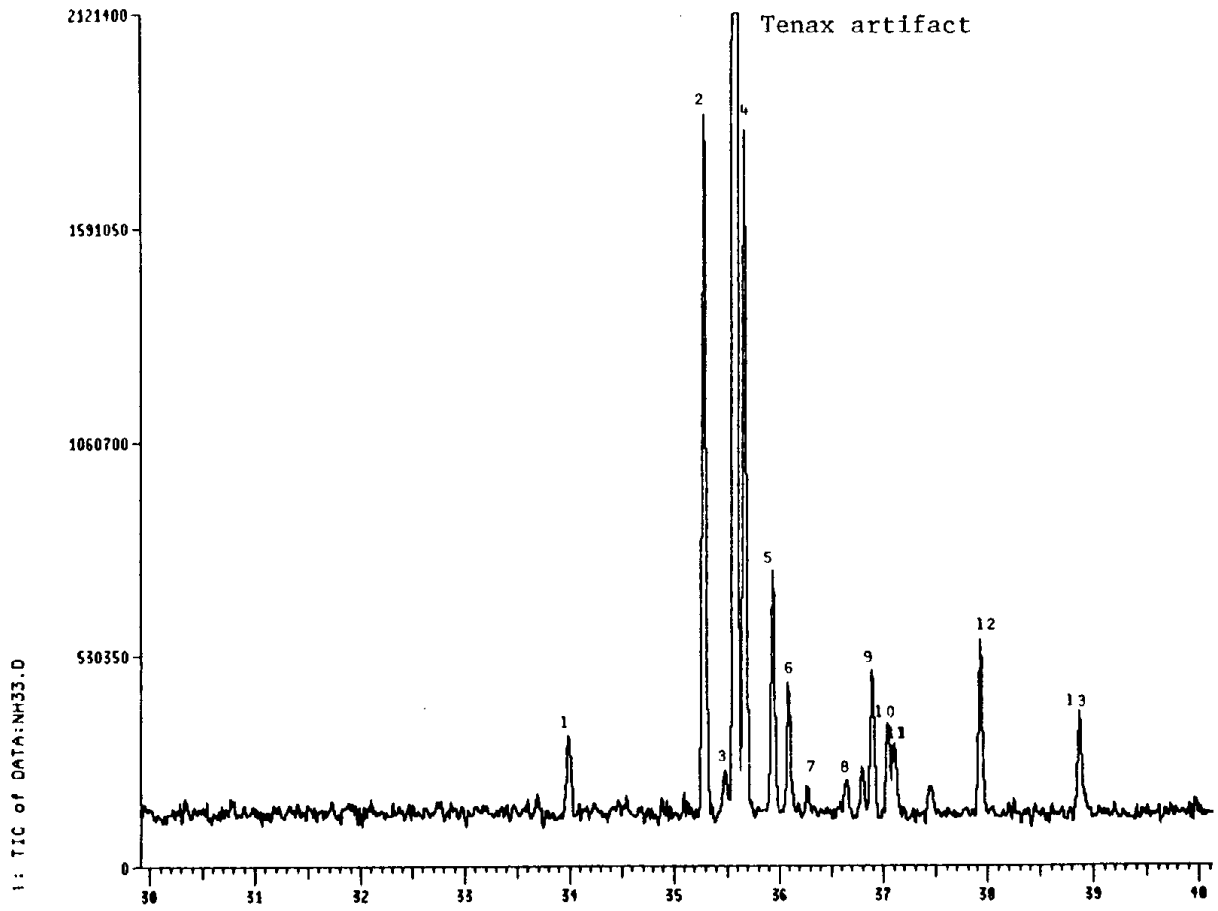

Figure V-11. TIC from GC/MS analysis of 1.4 ℓ Tenax sample of carrot (Imperator) emissions (NH-33). Identities of numbered peaks given in Table V-13.

Table V-14. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Carrot (Imperator) - 1988 October 11

Assigned Peaks[a]	NH-36A 0900	NH-36B 1030	NH-36C 1200	NH-36D 1330	NH-36E 1445	Identification
1	6	3	5	4	4	α-pinene
2,3	38	24	46	40	57	sabinene and β-pinene
4	52	45	68	64	55	myrcene (peaks 4 and 5 coeluted, area of marker subtracted to estimate myrcene)
5	d	d	d	d	d	1,2,4-trimethylbenzene
6,7	1	2	3	3	3	3-hexenylacetate and α-phellandrene
8,9,10,11	15	3	9	8	9	α-terpinene, p-cymene, d-limonene and β-phellandrene
12	18	3	5	4	6	γ-terpinene
13	63	2	n.a.[e]	1	6	terpinolene
toluene[g]	5	4	4	<1	<1	
Σ(Assigned Peaks)[h]	193	82	136	124	140	
ΣMonoterpenes	192	80	133	121	137	
ΣSesquiterpenes	c	c	c	c	c	
$\Sigma C_7 \rightarrow C_{15}$[i]	223	118	213	204	175	
C_5[j]	c	c	c	c	c	
$\Sigma C_3 \rightarrow C_6$[q]	27	23	65	58	39	
Total Plant Emissions[l]	193	82	136	124	140	
Total Carbon[m]	250	141	279	262	214	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-12. The numbers correspond to the GC/MS identifications as given on Figure V-11 and in Table V-13.
[b-t]Footnotes given on Table V-73.

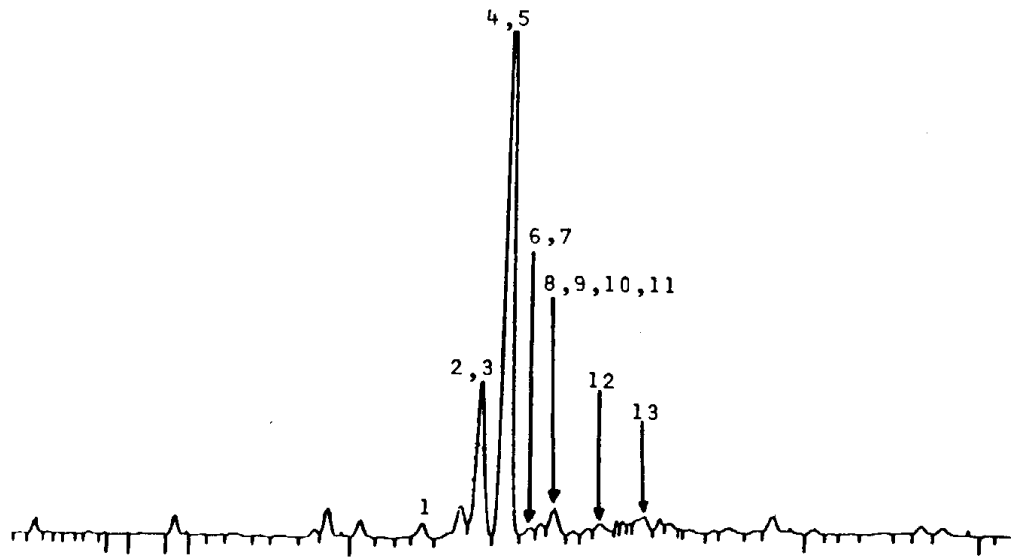

Figure V-12. GC-FID analysis of 1.3 ℓ Tenax/Carbosieve sample of carrot (Imperator) emissions (NH-36C). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-13.

Table V-15. Emissions Identified from Cherry (Bing) by GC/MS Analysis of Survey Sample NH-54B (TIC Shown in Figure V-13)

Peak No.	Compound Identification[a]
1	unknown (m.w. 100)
2	n-hexanal
3	cis-3-hexen-1-ol
4	p-xylene (internal standard)
5	1-decene
6	3-hexenylacetate
7	trans-ocimene[b]
8	1-dodecene
9	1-tetradecene
10	β-caryophyllene
11	unknown sesquiterpene (m.w. 204)

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.
[b]See footnote c on Table V-3.

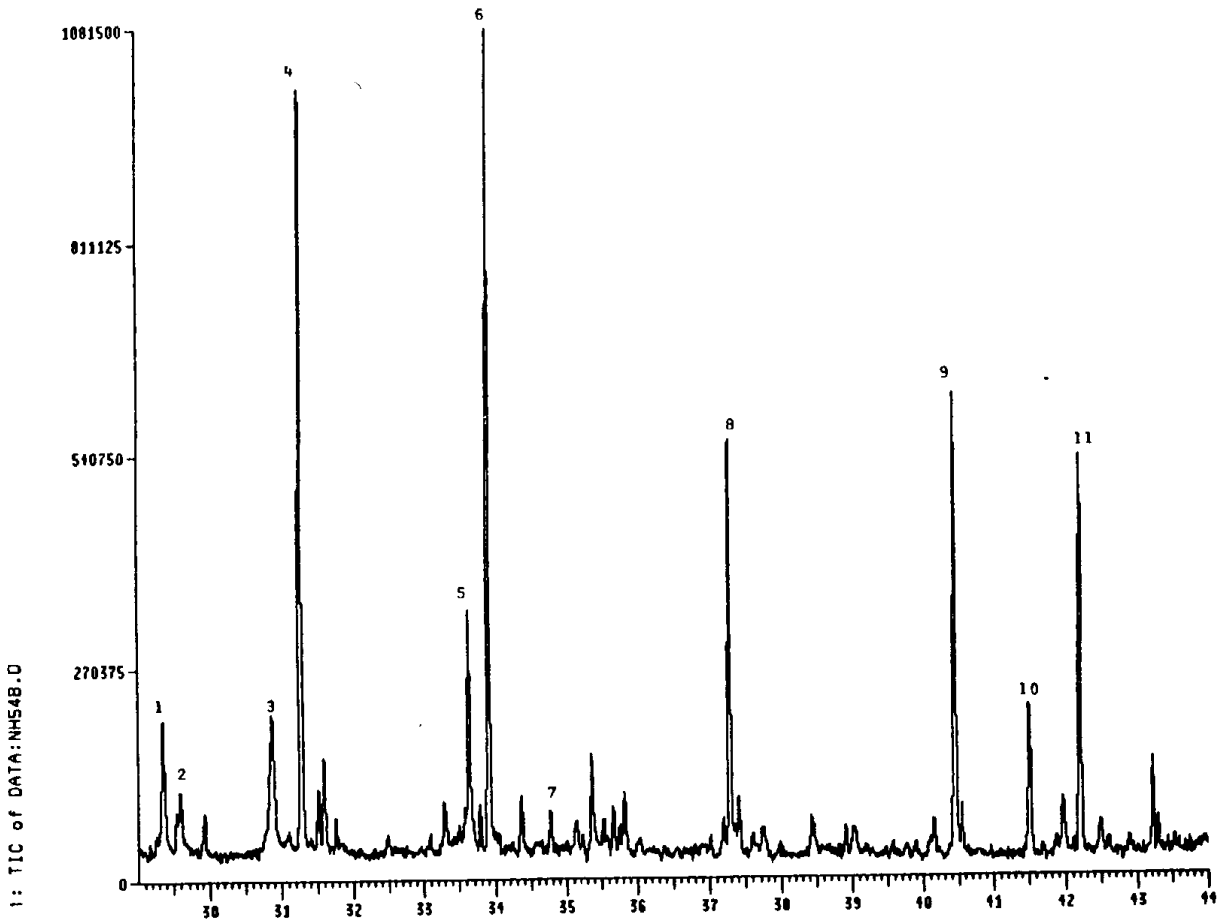

Figure V-13. TIC from GC/MS analysis of 6.6 ℓ Tenax sample of cherry (Bing) emissions (NH-54B). Identities of numbered peaks given in Table V-15.

Table V-16. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Cherry (Bing) - 1989 June 6

Assigned Peaks[a]	NH-54A 0900	NH-54B 1030	NH-54C 1200	NH-54D 1330	NH-54E 1445	Identification
2[b]	2	5	3	4	5	n-hexanal
4	d	d	d	d	d	p-xylene
5	3	12	11	8	7	1-decene
6	17	24	20	11	14	3-hexenylacetate
7	n.d.[f]	4	3	7	2	trans-ocimene
8	7	10	15	13	13	1-dodecene
9	3	6	11	12	17	1-tetradecene
10	1	2	3	4	5	β-caryophyllene
11[b]	<1	4	n.d.	8	n.a.[e]	unknown sesquiterpene (m.w. 204)
toluene[g]	<1	1	n.d.	n.d.	<1	
Σ(Assigned Peaks)[h]	34	67	66	55	53	
ΣMonoterpenes	n.d.	4	3	7	2	
ΣSesquiterpenes	<2	6	3	12	5	
$\Sigma C_7 \rightarrow C_{15}$[i]	118	106	131	109	146	
C_5[j]	<1	<1	<1	<1	<1	
$\Sigma C_3 \rightarrow C_5$[k]	33	29	34	36	40	
$\Sigma C_3 \rightarrow C_6$[t]	17	48	55	50	30	
Total Plant Emissions[l]	34	67	66	55	53	
Total Carbon[m]	151	135	165	145	186	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-14. The numbers correspond to the GC/MS identifications as given on Figure V-13 and in Table V-15.
[b-t]Footnotes given on Table V-73.

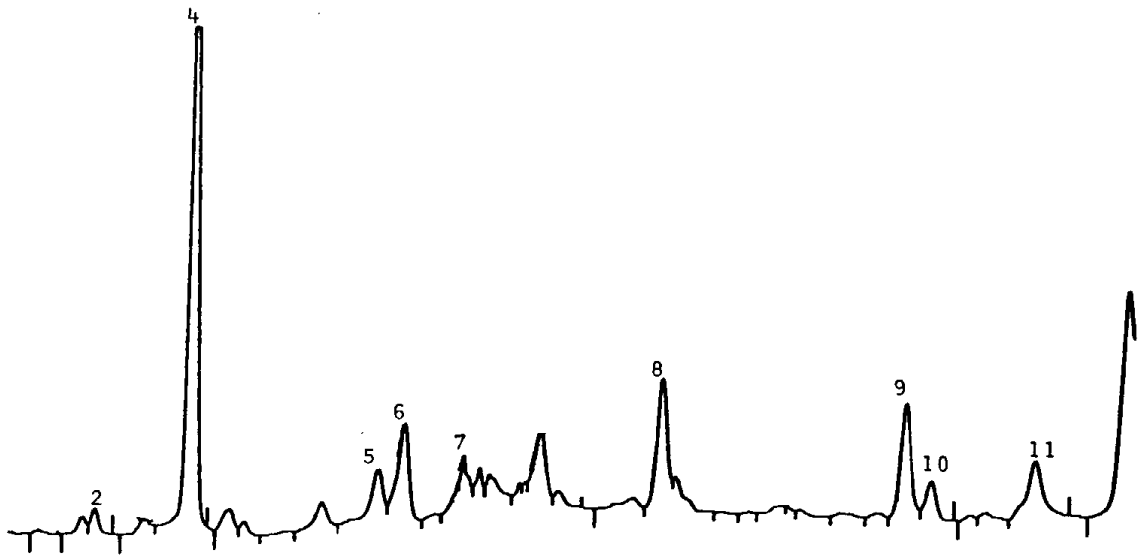

Figure V-14. GC-FID analysis of 1.3 ℓ Tenax/Carbosieve sample of cherry (Bing) emissions (NH-54D). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-15.

Table V-17. Emissions Identified from Grain Corn (Pioneer 3183) by GC/MS Analysis of Survey Sample NH-86 (TIC Shown in Figure V-15)

Peak No.	Compound Identification[a]
1	unknown (m.w. 100)
2	n-hexanal
3	p-xylene (internal standard)
4	1-decene
5	1-dodecene
6	1-tetradecene
7	unknown sesquiterpene (m.w. 204)

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.

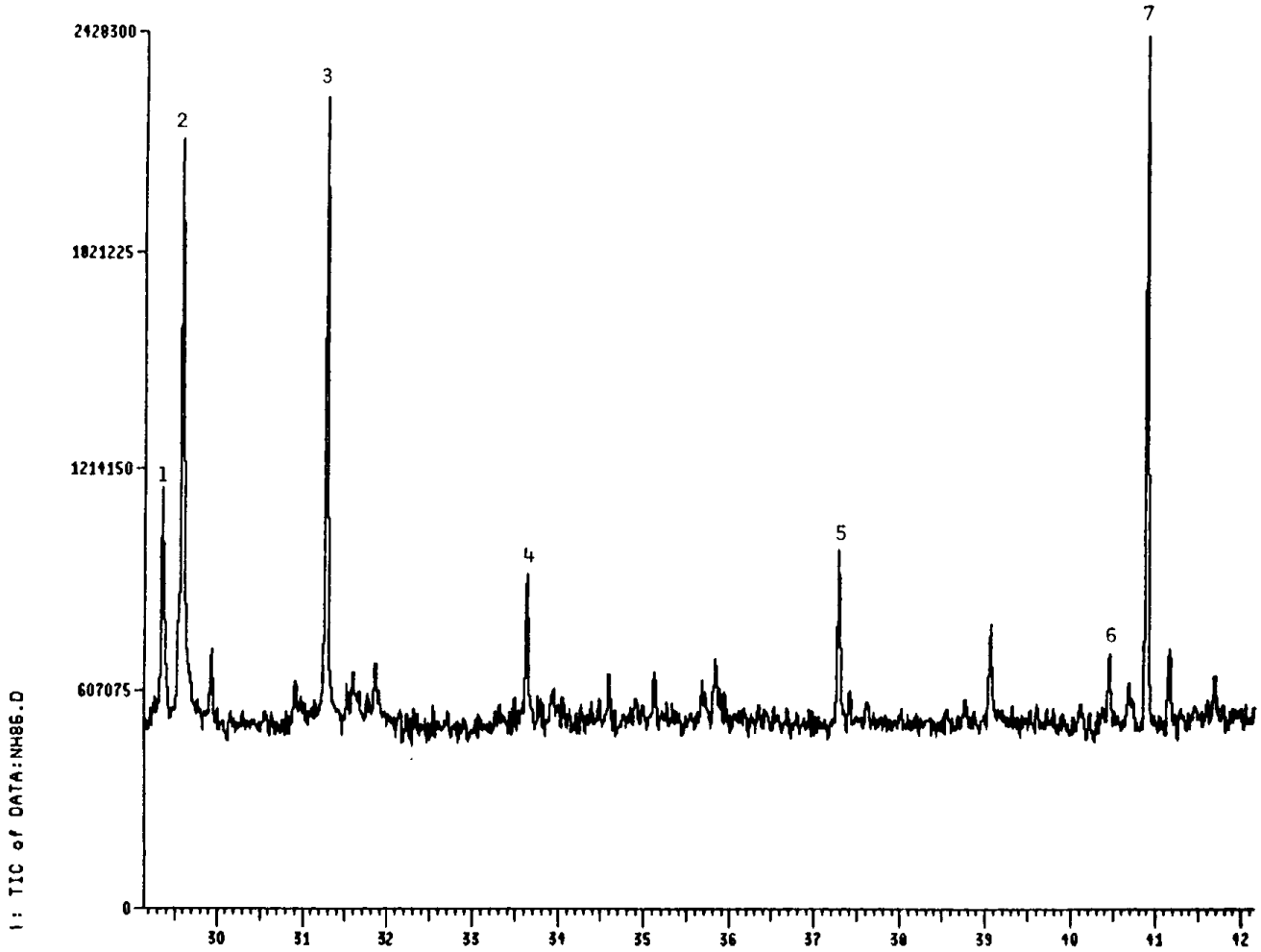

Figure V-15. TIC from GC/MS analysis of 6.4 ℓ Tenax sample of grain corn (Pioneer 3183) emissions (NH-86). Identities of numbered peaks given in Table V-17.

Table V-18. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Grain Corn (Pioneer 3183) - 1989 July 13

Assigned Peaks[a]	NH-86 1345	Identification
1,2	10	unknown (m.w. 100) and n-hexanal
3	d	p-xylene
4	10	1-decene
5	17	1-dodecene
6	18	1-tetradecene
7	13	unknown sesquiterpene (m.w. 204)
toluene[g]	<1	
ΣC_6[s]	13	
Σ(Assigned Peaks)[h]	68	
ΣMonoterpenes	n.d.[f]	
ΣSesquiterpenes	13	
$\Sigma C_7 \rightarrow C_{15}$[i]	199	
C_5[j]	<1	
$\Sigma C_3 \rightarrow C_5$[k]	27	
Total Plant Emissions[l]	68	
Total Carbon[m]	226	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-16. The numbers correspond to the GC/MS identifications as given on Figure V-15 and in Table V-17.
[b-t]Footnotes given on Table V-73.

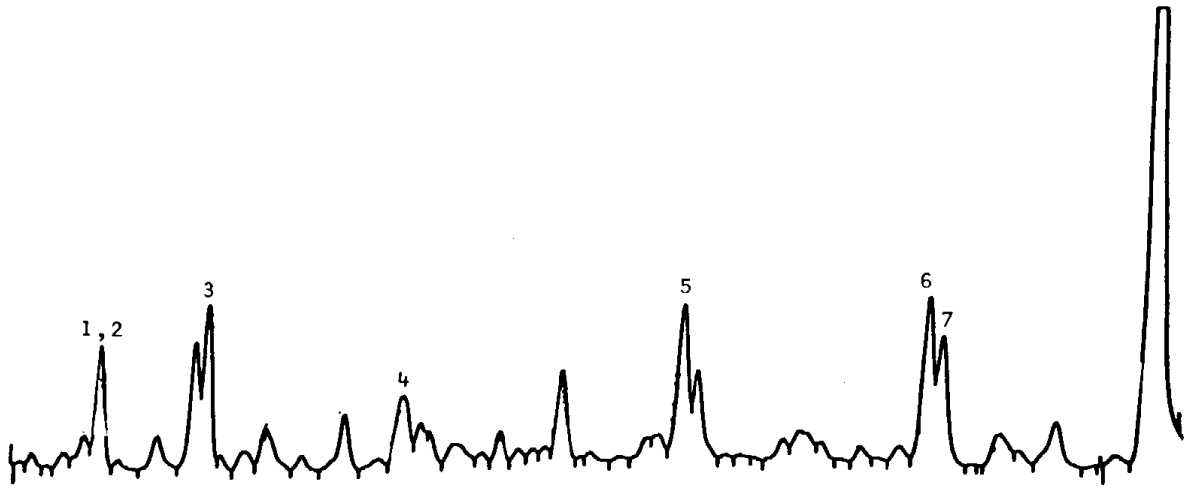

Figure V-16. GC-FID analysis of 2.6 ℓ Tenax sample of grain corn (Pioneer 3183) emissions (NH-86). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-17.

Table V-19. Emissions Identified from Lint Cotton (SJ2) by GC/MS Analysis of Survey Sample NH-84B (TIC Shown in Figure V-17)

Peak No.	Compound Identification[a]
1	unknown (m.w. 100)
2	n-hexanal
3	cis-3-hexen-1-ol
4	p-xylene (internal standard)
5	α-pinene
6	benzaldehyde (possibly a Tenax artifact)
7	myrcene + β-pinene
8	3-hexenylacetate
9	2-carene
10	unknown (m.w. 134)
11	unknown
12	p-cymene
13	cis-ocimene[b]
14	d-limonene
15	β-phellandrene
16	trans-ocimene[b]
17	acetophenone (possibly Tenax artifact)
18	n-undecane
19	unknown (m.w. 150)
20	2-methyl-6-methylene-1,7-octadien-3-one (tentative)
21	unknown
22	unknown (m.w. 150)
23	1-dodecene
24	n-dodecane
25	1-tetradecene
26	n-tetradecane
27	β-caryophyllene

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.
[b]See footnote c on Table V-3.

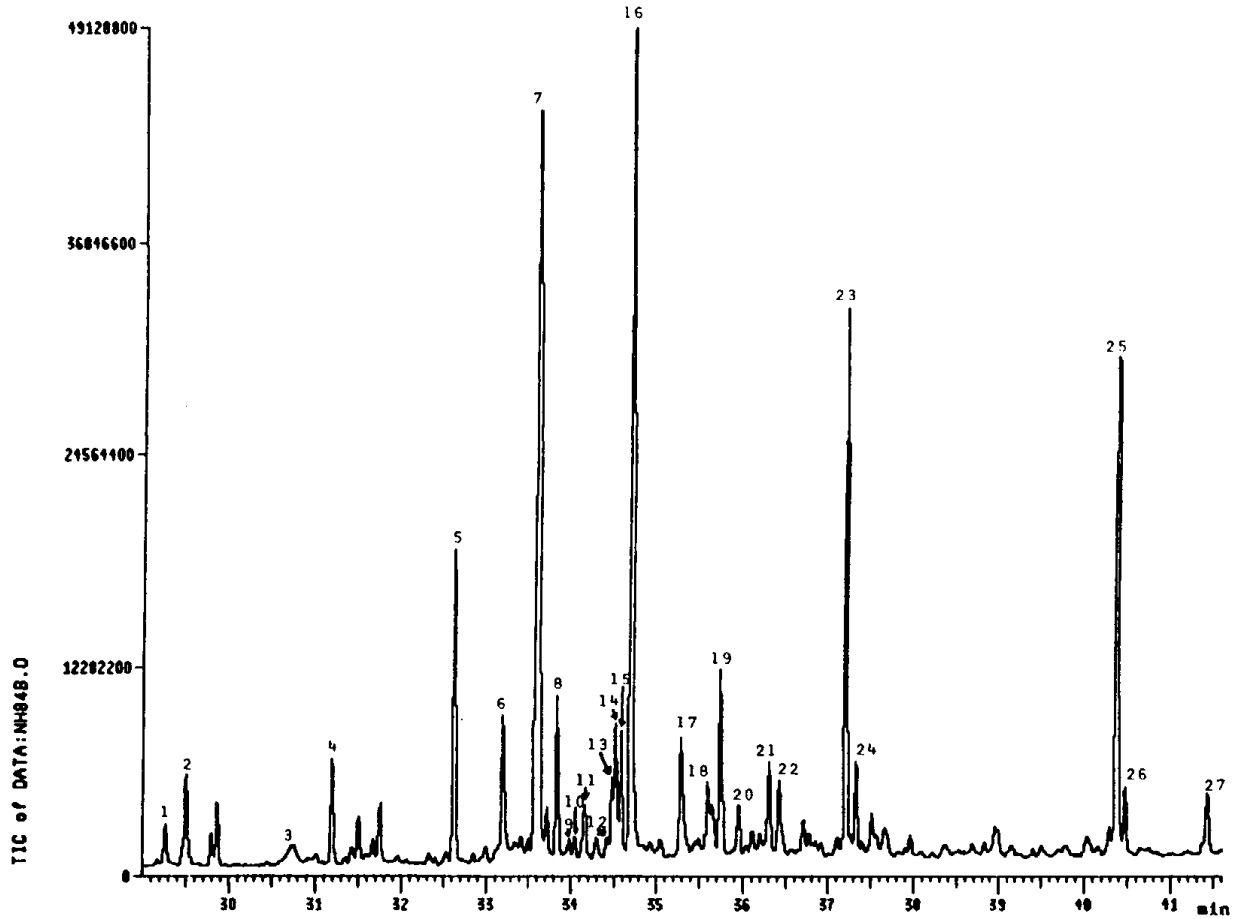

Figure V-17. TIC from GC/MS analysis of 6.4 ℓ Tenax sample of lint cotton (SJ2) emissions (NH-84B). Identities of numbered peaks given in Table V-19.

Table V-20. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Lint Cotton (SJ2) - 1989 July 18

Assigned Peaks[a]	NH-89A 0900	NH-89B 1030	NH-89C 1200	NH-89D 1330	NH-89E 1450	Identification
2[b]	3	4	6	10	12	n-hexanal
3	3	3	3	10	3	cis-3-hexen-1-ol
4	d	d	d	d	d	p-xylene
5	8	15	11	44	13	α-pinene
7[n]	3	n.a.[e]	4	n.a.	6	β-pinene
7[n]	14	36	20	105	33	myrcene
8→10, 11[b]	8	38	12	22	7	3-hexenylacetate, 2-carene, unknown (m.w. 134) and unknown
12,14,15	8	17	8	17	9	p-cymene, d-limonene and β-phellandrene
13	n.d.[f]	n.d.	n.d.	n.d.	1	cis-ocimene
16	3	18	14	69	27	trans-ocimene
20[b]	3	7	9	14	8	2-methyl-6-methylene-1,7-octadien-3-one (tentative)
21,22[b]	6	4	9	4	9	unknowns
23[b]	4	9	15	16	14	1-dodecene
24[b]	2	2	8	6	7	n-dodecane
25,26[b]	2	5	12	11	12	1-tetradecene and n-tetradecane
27	1	4	2	14	2	β-caryophyllene
toluene[g]	5	2	3	10	3	
ΣC_6[s]	7	c	c	c	7	
Σ(Assigned Peaks)[h]	68	162	133	342	163	
ΣMonoterpenes	36	86	57	235	89	
ΣSesquiterpenes	1	4	2	14	2	
$\Sigma C_7 \rightarrow C_{15}$[i]	95	228	207	420	216	
C_5[j]	<1	2	2	2	2	
$\Sigma C_3 \rightarrow C_5$[k]	63	64	28	69	30	
Total Plant Emissions[l]	68	162	133	342	163	
Total Carbon[m]	158	290	235	489	246	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-18. The numbers correspond to the GC/MS identifications as given on Figure V-17 and in Table V-19.
[b-t]Footnotes given on Table V-73.

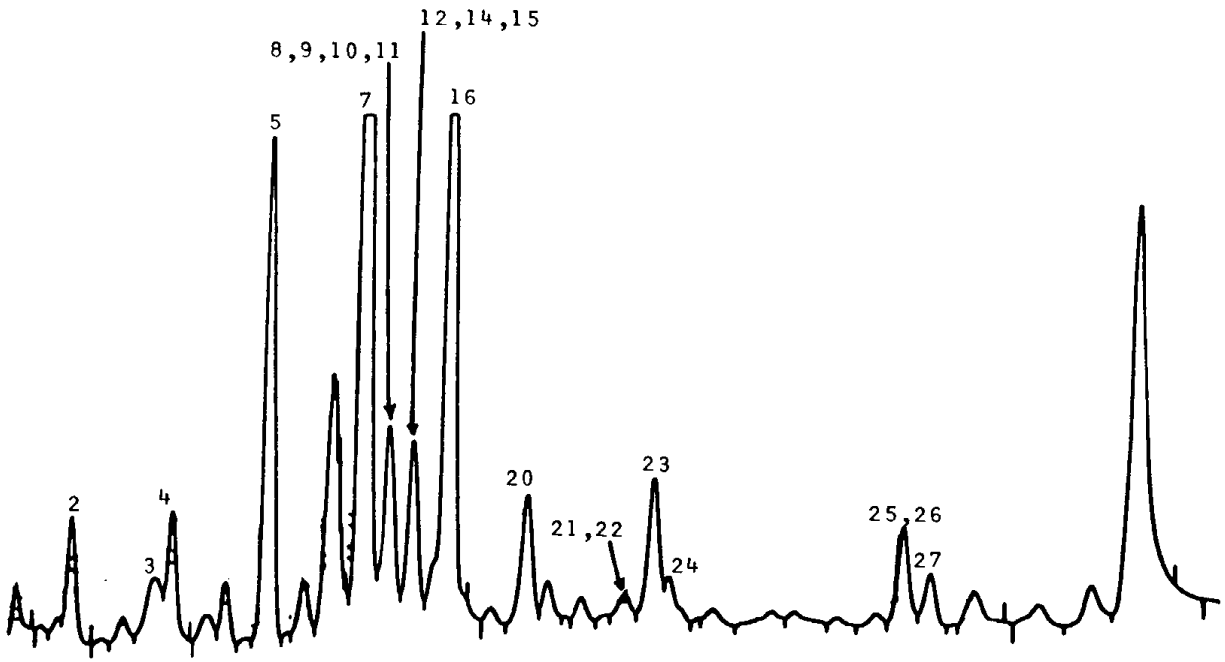

Figure V-18. GC-FID analysis of 2.5 ℓ Tenax sample of lint cotton (SJ2) emissions (NH-89D). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-19.

Table V-21. Emissions Identified from Table Grape (Thompson Seedless) by GC/MS Analysis of Survey Sample NH-44 (TIC Shown in Figure V-19)

Peak No.	Compound Identification[a]
1	unknown (m.w. 100)
2	p-xylene (internal standard)
3	3-hexenylacetate
4	unknown
5	unknown (m.w. 156)
6	unknown
7	1-dodecene
8	n-dodecane
9	1-tetradecene
10	n-tetradecane
11	n-pentadecane

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.

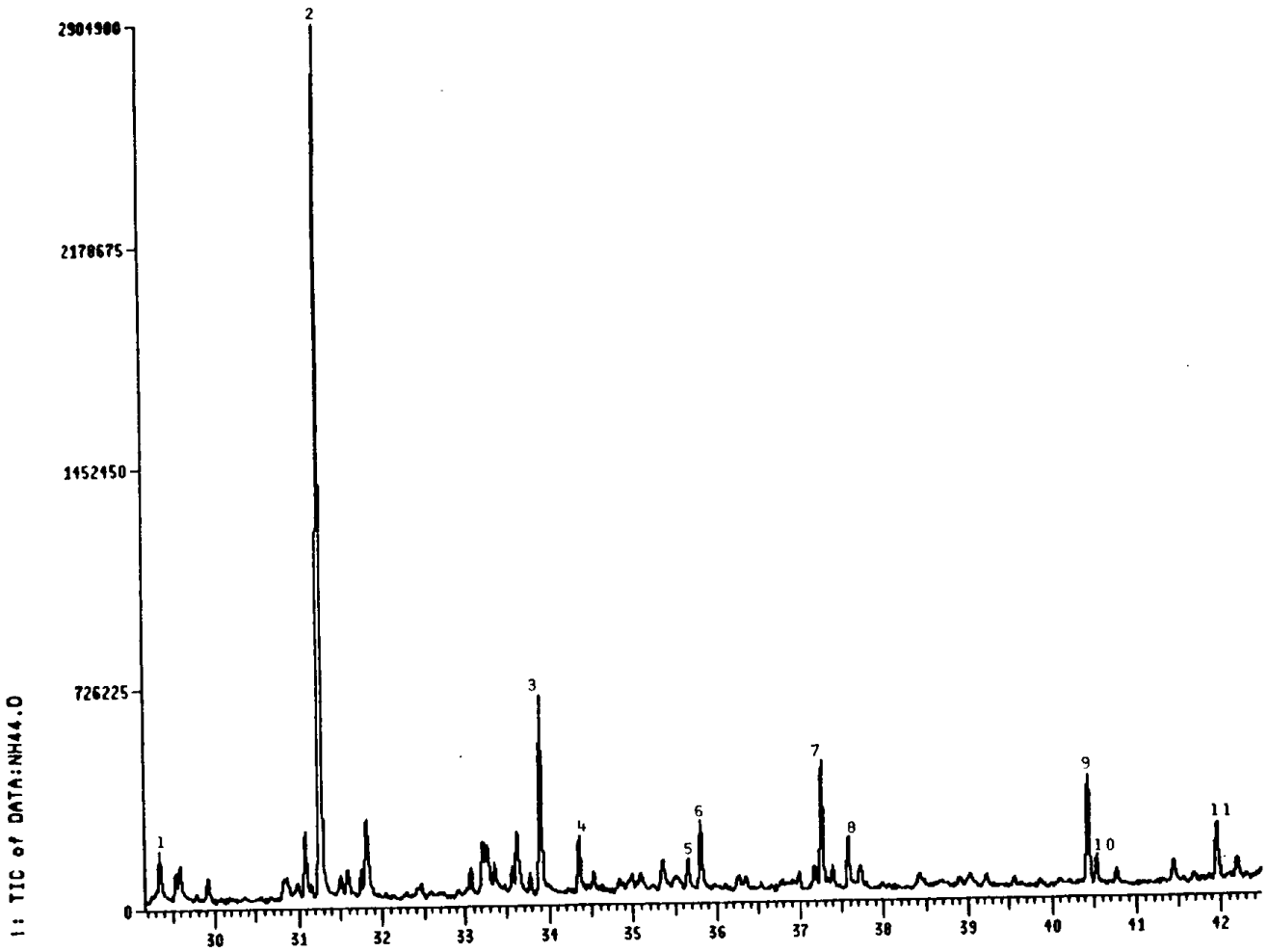

Figure V-19. TIC from GC/MS analysis of 3.8 ℓ Tenax sample of grape (Thompson Seedless) emissions (NH-44). Identities of numbered peaks given in Table V-21.

Table V-22. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Table Grape (Thompson Seedless) - 1989 July 25

Assigned Peaks[a]	NH-92A 0900	NH-92B 1030	NH-92C 1200	NH-92D 1330	NH-92E 1445	Identification
2	d	d	d	d	d	p-xylene
3	27	76	11	15	12	3-hexenylacetate
7	11	23	14	19	27	1-dodecene
8	3	6	8	9	13	n-dodecane
9	5	10	8	17	26	1-tetradecene
10	n.d.[f]	n.d.	n.d.	4	n.d.	n-tetradecane
11	1	n.a.[e]	<1	1	1	n-pentadecane
toluene[g]	13	8	5	2	2	
ΣC_6[s]	12	14	10	11	13	
Σ(Assigned Peaks)[h]	47	115	42	65	79	
ΣMonoterpenes	n.d.	n.d.	n.d.	n.d.	n.d.	
ΣSesquiterpenes	n.d.	n.d.	n.d.	n.d.	n.d.	
$\Sigma C_7 \rightarrow C_{15}$[i]	135	254	187	194	221	
C_5[j]	6	6	3	<2	4	
$\Sigma C_3 \rightarrow C_5$[k]	112	111	49	74	80	
Total Plant Emissions[l]	47	115	42	65	79	
Total Carbon[m]	247	365	236	268	301	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-20. The numbers correspond to the GC/MS identifications as given on Figure V-19 and in Table V-21.
[b-t]Footnotes given on Table V-73.

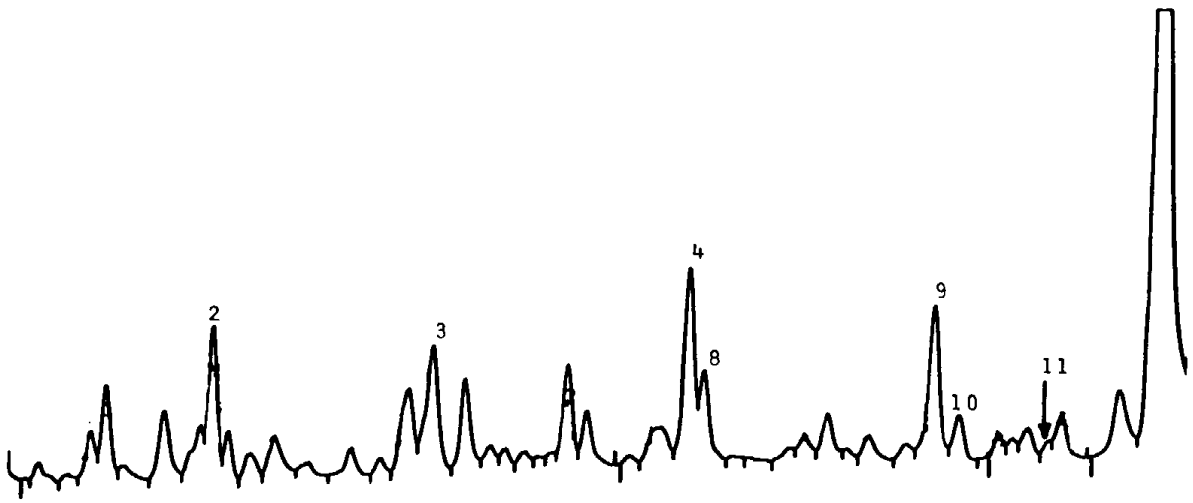

Figure V-20. GC-FID analysis of 1.3 ℓ Tenax sample of table grape (Thompson Seedless) emissions (NH-92D). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-21.

Table V-23. Emissions Identified from Wine Grape (French Columbard) by GC/MS Analysis of Survey Sample NH-74 (TIC Shown in Figure V-21)

Peak No.	Compound Identification[a]
1	trans-2-hexenal
2	cis-3-hexen-1-ol
3	p-xylene (internal standard)
4	1-decene
5	n-decane
6	3-hexenylacetate
7	d-limonene
8	n-undecane
9	unknown
10	1-dodecene
11	n-dodecane
12	1-tetradecene
13	n-tetradecane
14-16	unknown sesquiterpenes (m.w. 204)
17	n-pentadecane
18-19	unknown sesquiterpenes (m.w. 204)
20	1-hexadecene (tentative)
21	n-hexadecane
22	n-heptadecane

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.

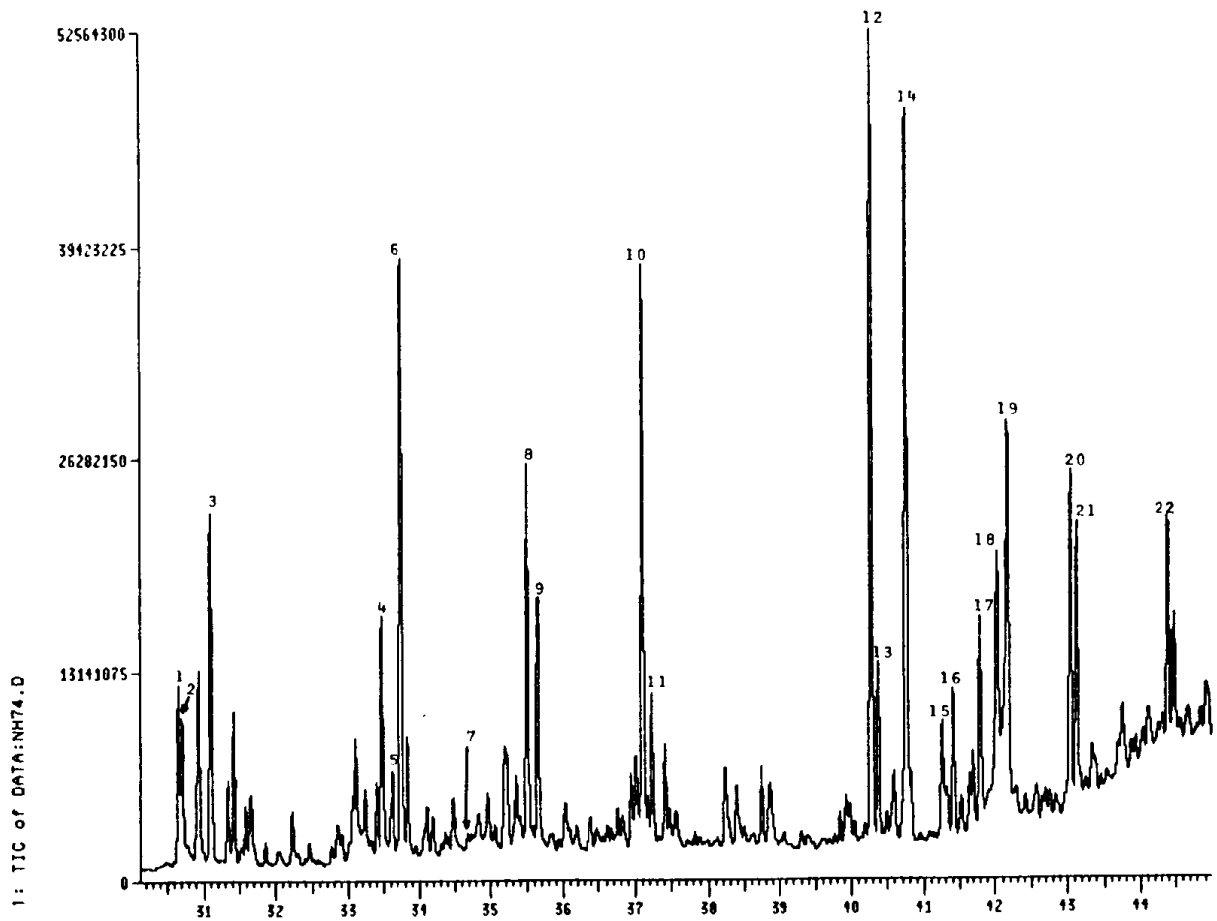

Figure V-21. TIC from GC/MS analysis of 5.3 ℓ Tenax sample of wine grape (French Columbard) emissions (NH-74). Identities of numbered peaks given in Table V-23.

Table V-24. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Wine Grape (French Columbard) - 1989 July 27

Assigned Peaks[a]	NH-93A 0900	NH-93B 1030	NH-93C 1200	NH-93D 1330	NH-93E 1445	Identification
1[b]	18	8	14	17	20	trans-2-hexenal
2	15	5	9	13	9	cis-3-hexen-1-ol
3	d	d	d	d	d	p-xylene
4,5	11	12	15	12	16	1-decene, n-decane
6	44	13	19	41	20	3-hexenylacetate
10	6	8	12	19	21	1-dodecene
11	5	6	11	12	16	n-dodecane
12,13,14	3	6	9	13	20	1-tetradecene, n-tetradecane and unknown sesquiterpene (m.w. 204)
15,16	n.d.	4	n.d.	n.d.	n.d.	unknown sesquiterpenes (m.w. 204)
17[b]	1	3	4	3	4	n-pentadecane
18[b],19[b]	3	3	5	9	7	unknown sesquiterpenes (m.w. 204)
20	c	c	c	c	c	1-hexadecene (tentative)
21	c	c	c	c	c	n-hexadecane
toluene[g]	6	7	4	2	2	
ΣC_6[s]	9	10	16	10	7	
Σ(Assigned Peaks)[h]	106	68	98	139	133	
ΣMonoterpenes	n.d.	n.d.	n.d.	n.d.	n.d.	
ΣSesquiterpenes	3	7	5	9	7	
$\Sigma C_7 \rightarrow C_{15}$[i]	157	126	192	244	239	
C_5[j]	2	2	2	1	2	
$\Sigma C_3 \rightarrow C_5$[k]	46	76	38	38	30	
Total Plant Emissions[l]	106	68	98	139	133	
Total Carbon[m]	203	202	230	293	269	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-22. The numbers correspond to the GC/MS identifications as given on Figure V-21 and in Table V-23.
[b-t]Footnotes given on Table V-73.

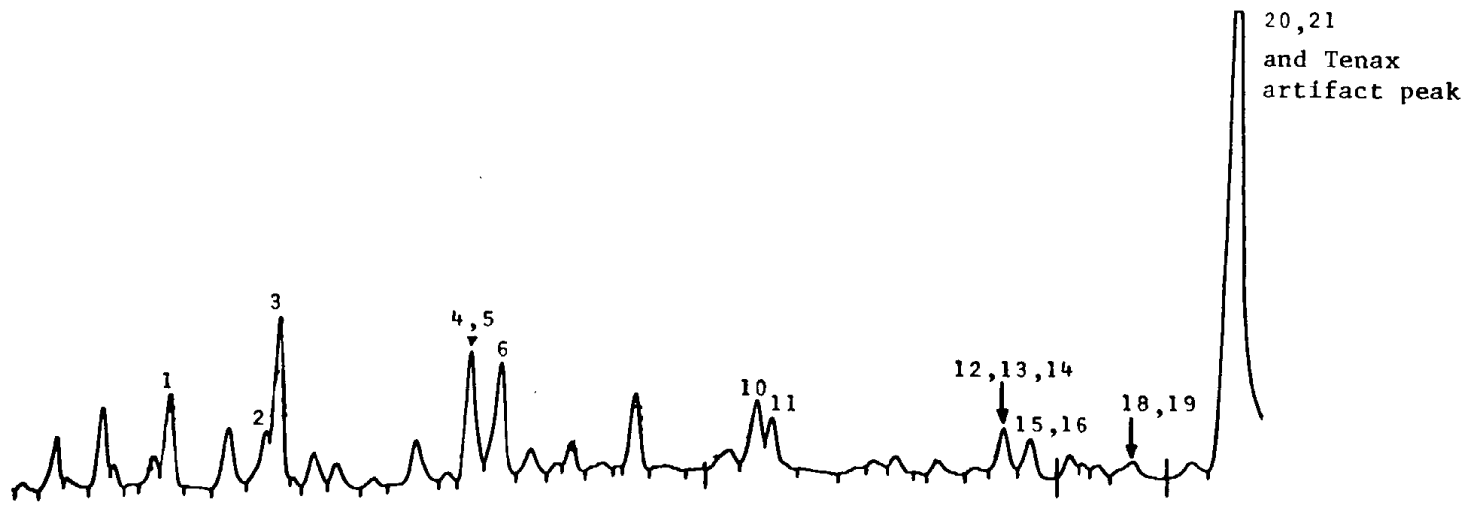

Figure V-22. GC-FID analysis of 1.3 ℓ Tenax sample of wine grape (French Columbard) emissions (NH-93B). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-23.

Table V-25. Emissions Identified from Lemon (Lisbon) by GC/MS Analysis of Survey Sample NH-5 (TIC Shown in Figure V-23)

Peak No.	Compound Identification
1	α-pinene
2	sabinene
3	β-pinene
4	myrcene
5	1,2,4-trimethylbenzene (internal standard)
6	3-hexenylacetate
7	α-terpinene
8	p-cymene
9	d-limonene
10	1,8-cineole
11	trans-ocimene[a]
12	γ-terpinene
13	unknown

[a]See footnote c on Table V-3.

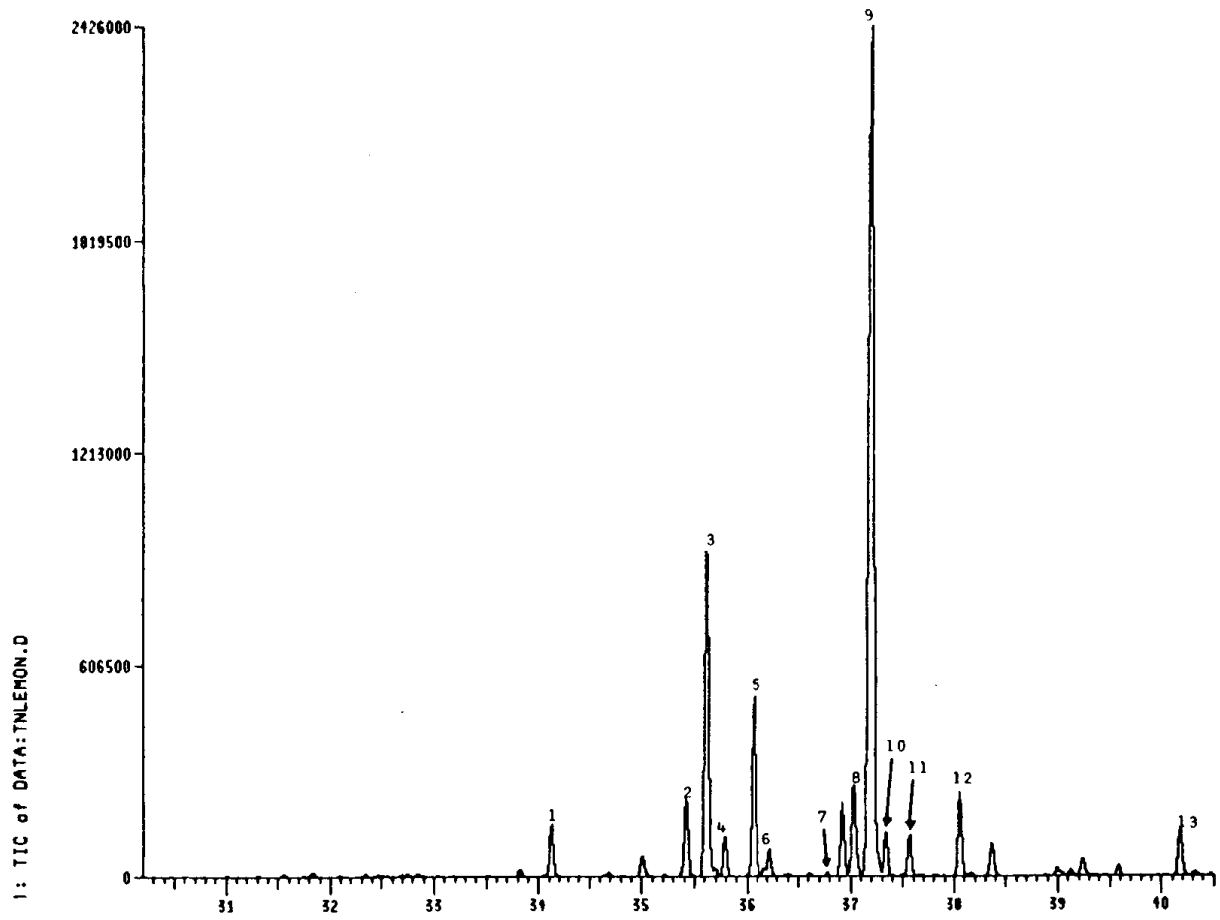

Figure V-23. TIC from GC/MS analysis of 1 ℓ Tenax sample of lemon (Lisbon) emissions (NH-5). Identities of numbered peaks given in Table V-25.

Table V-26. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Lemon (Lisbon) - 1988 September 8

Assigned Peaks[a]	NH-26A 0900	NH-26B 1030	NH-26C 1200	NH-26D 1330	NH-26E 1445	Identification
1	<1	<1	<1	<1	<1	α-pinene
2,3	15	6	4	6	8	sabinene and β-pinene
4	6	3	5	9	4	myrcene (peaks 4 and 5 coeluted, area of marker subtracted to estimate myrcene)
5	d	d	d	d	d	1,2,4-trimethylbenzene
6	2	2	n.d.	1	1	3-hexenylacetate
7,8,9,10	68	39	13	17	19	α-terpinene, p-cymene, d-l[illegible]onene and 1,8-cineole
11	1	<1	n.d.	n.d.	n.d.	trans-ocimene
12	2	1	<1	n.d.	n.d.	γ-terpinene
13[b]	9	6	<1	1	1	unknown
toluene[g]	4	4	3	2	1	
Σ(Assigned Peaks)[h]	104	58	24	35	34	
ΣMonoterpenes	93	50	23	33	32	
ΣSesquiterpenes	c	c	c	c	c	
$\Sigma C_7 \rightarrow C_{15}$[i]	126	100	60	67	76	
C_5[j]	c	c	c	c	c	
$\Sigma C_3 \rightarrow C_6$[q]	20	26	15	16	19	
Total Plant Emissions[l]	104	58	24	35	34	
Total Carbon[m]	146	126	75	83	95	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-24. The numbers correspond to the GC/MS identifications as given on Figure V-23 and in Table V-25.
[b-t]Footnotes given on Table V-73.

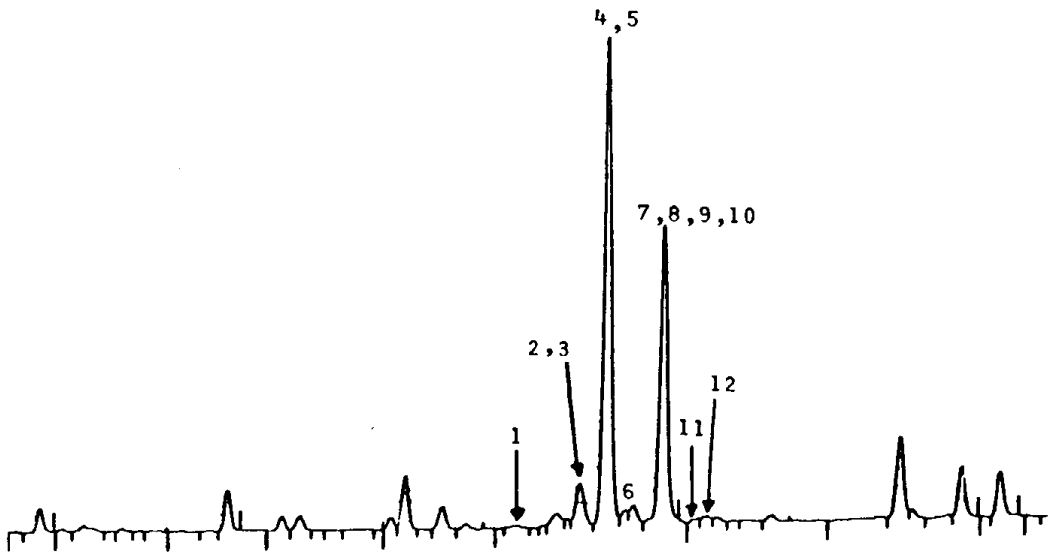

Figure V-24. GC-FID analysis of 1.3 ℓ Tenax/Carbosieve sample of lemon (Lisbon) emissions (NH-26B). The assigned peaks correspond to the GC/MS identifications given in Table V-25.

Table V-27. Emissions Identified from Lettuce (Empire) by GC/MS Analysis of Survey Sample NH-34 (TIC Shown in Figure V-25)

Peak No.	Compound Identification
1	*cis*-3-hexen-1-ol
2	1,2,4-trimethylbenzene (internal standard)
3	3-hexenylacetate

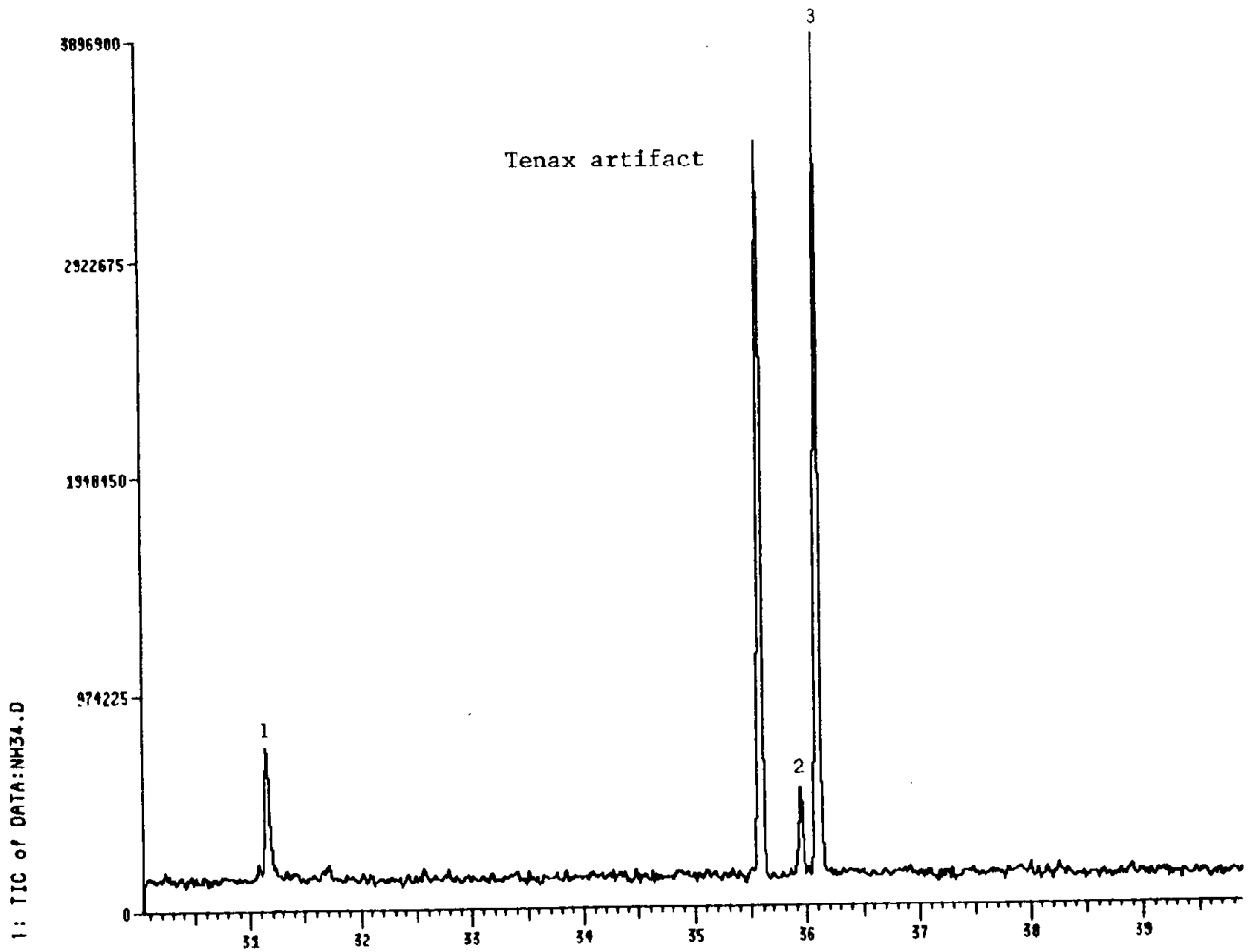

Figure V-25. TIC from GC/MS analysis of 2.7 ℓ Tenax sample of lettuce (Empire) emissions (NH-34). Identities of numbered peaks given in Table V-27.

Table V-28. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Lettuce - 1988 September 12 and October 6

Assigned Peaks[a]	NH-27[u] 0930	NH-31 1100	Identification
1	671	n.d.[f]	cis-3-hexen-1-ol
2	d	d	1,2,4-trimethylbenzene
3	1114	5	3-hexenylacetate
toluene[g]	3	3	
Σ(Assigned Peaks)[h]	1785	5	
ΣMonoterpenes	n.d.	n.d.	
ΣSesquiterpenes	n.d.	n.d.	
$\Sigma C_7 \rightarrow C_{15}$[i]	1866	53	
C_5[j]	c	c	
$\Sigma C_3 \rightarrow C_6$[q]	175	59	
Total Plant Emissions[l]	1785	5	
Total Carbon[m]	2041	112	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-26. The numbers correspond to the GC/MS identifications as given on Figure V-25 and in Table V-27.

[b-t]Footnotes given on Table V-73.

[u]cis-3-Hexen-1-ol and 3-hexenylacetate emissions unrealistically high due to disturbance of plants. See Section VII for full discussion.

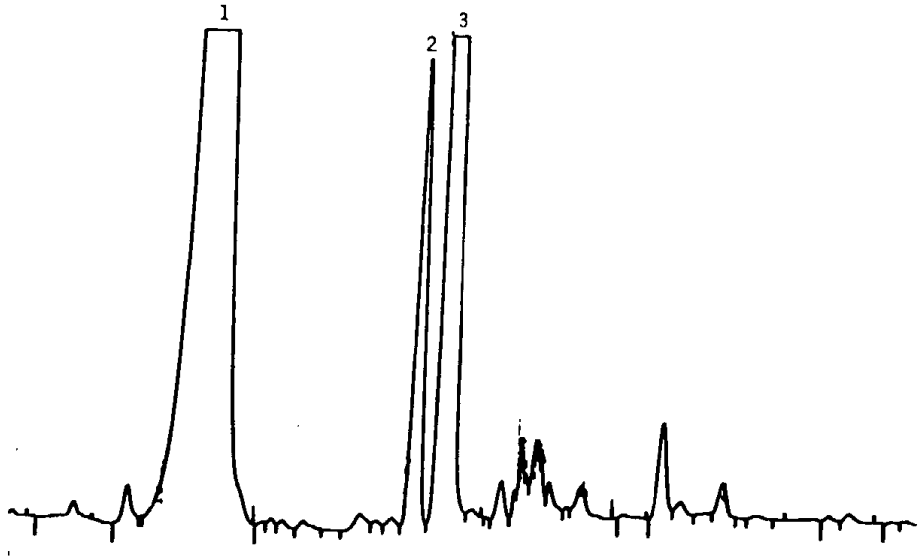

Figure V-26. GC-FID analysis of 1.5 ℓ Tenax/Carbosieve sample of lettuce (Empire) emissions (NH-27). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-27.

Table V-29. Emissions Identified from Nectarine (Silver Lode) by GC/MS Analysis of Survey Sample NH-11 (TIC Shown in Figure V-27)

Peak No.	Compound Identification[a]
1	cis-3-hexen-1-ol
2	1,2,4-trimethylbenzene (internal standard)
3	3-hexenylacetate
4	cis-ocimene[b]
5	trans-ocimene[b]
6	unknown
7	2-methyl-6-methylene-1,7-octadien-3-one (tentative)
8	unknown (m.w. 182)

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.
[b] See footnote c on Table V-3.

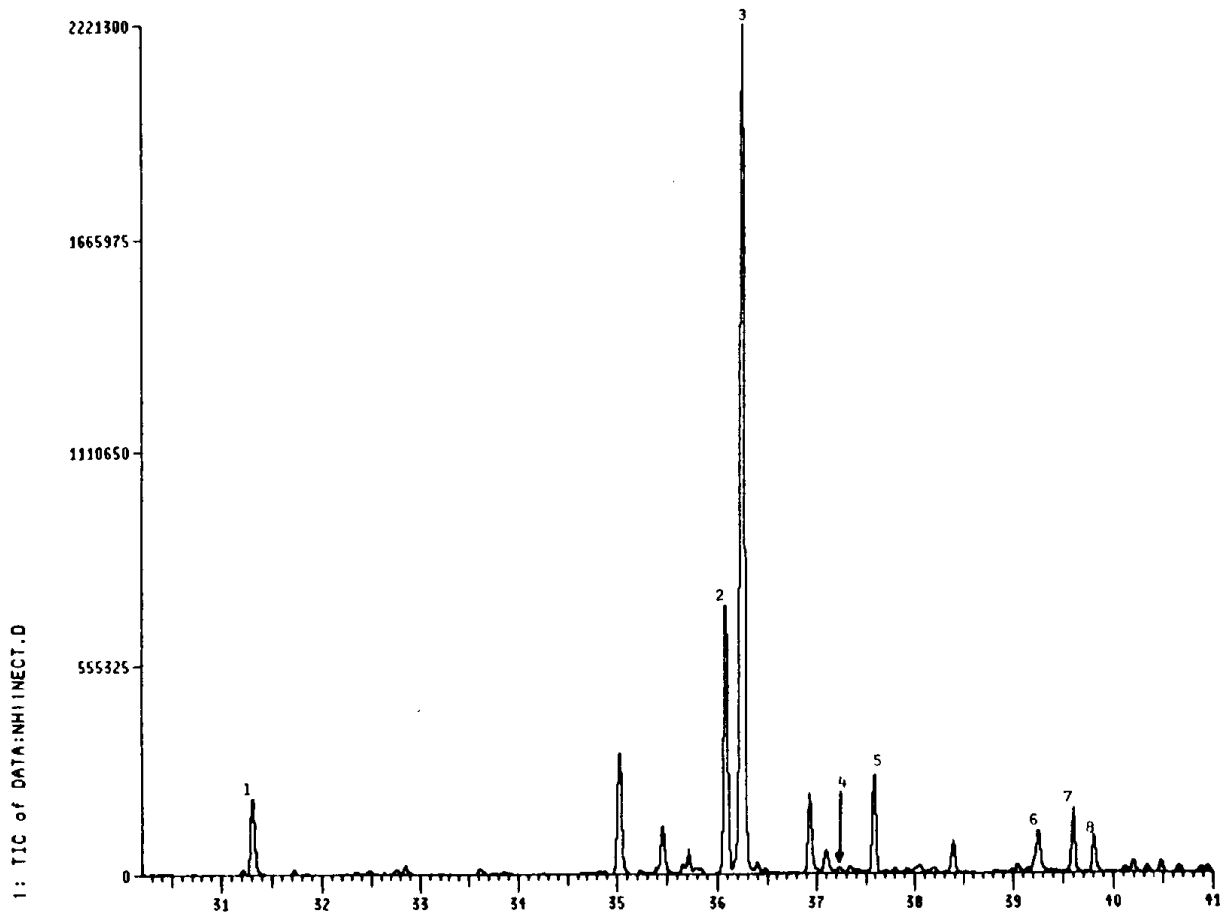

Figure V-27. TIC from GC/MS analysis of 1 ℓ Tenax sample of nectarine (Silver Lode) emissions (NH-11). Identities of numbered peaks given in Table V-29.

Table V-30. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Nectarine (Armking) - 1988 October 4

Assigned Peaks[a]	NH-30A 0900	NH-30B 1030	NH-30C 1200	NH-30D 1330	NH-30E 1445	Identification
1[b]	3	2	1	<1	1	cis-3-hexen-1-ol
2	d	d	d	d	d	1,2,4-trimethylbenzene
3	17	12	10	15	8	3-hexenylacetate
5	3	1	<1	n.d.[f]	<1	trans-ocimene
7[b]	1	2	5	5	3	2-methyl-6-methylene-1,7-octadien-3-one (tent.)
toluene[g]	10	7	4	2	2	
Σ(Assigned Peaks)[h]	24	17	17	20	13	
ΣMonoterpenes	3	1	<1	0	<1	
ΣSesquiterpenes	c	c	c	c	c	
$\Sigma C_7 + C_{15}$[i]	98	73	72	83	62	
C_5[j]	c	c	c	c	c	
$\Sigma C_3 + C_6$[q]	91	69	46	18	32	
Total Plant Emissions[l]	24	17	17	20	13	
Total Carbon[m]	189	142	118	101	94	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-28. The numbers correspond to the GC/MS identifications as given on Figure V-27 and in Table V-29.
[b-t]Footnotes given on Table V-73.

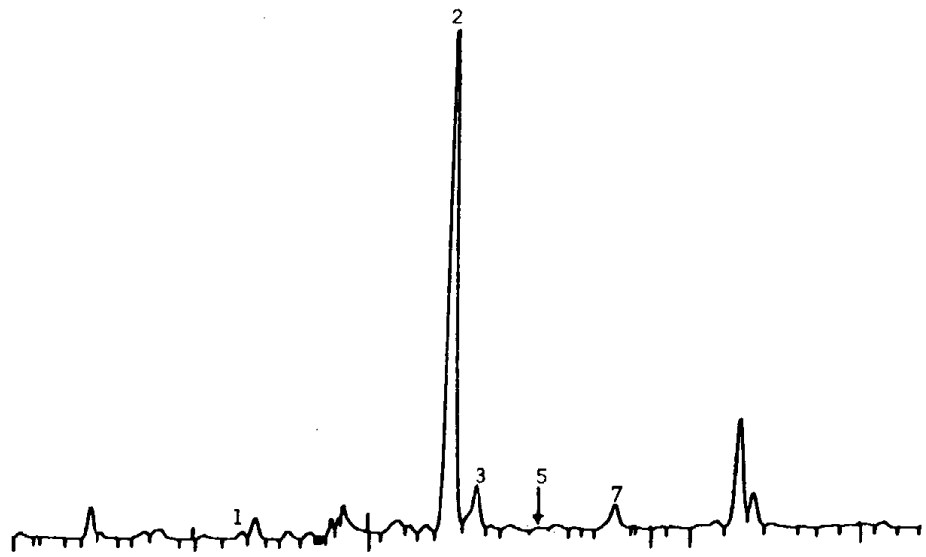

Figure V-28. GC-FID analysis of 1.2 ℓ Tenax/Carbosieve sample of nectarine (Armking) emissions (NH-30C). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-29.

Table V-31. Emissions Identified from Olive (Manzanillo) by GC/MS Analysis of Survey Sample NH-79D (TIC Shown in Figure V-29)

Peak No.	Compound Identification[a]
1	cis-3-hexen-1-ol
2	p-xylene (internal standard)
3	1-decene
4	3-hexenylacetate
5	trans-ocimene[b]
6	unknown
7	1-dodecene
8	unknown
9	1-tetradecene
10	unknown sesquiterpene (m.w. 204)
11	β-caryophyllene

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.
[b]See footnote c on Table V-3.

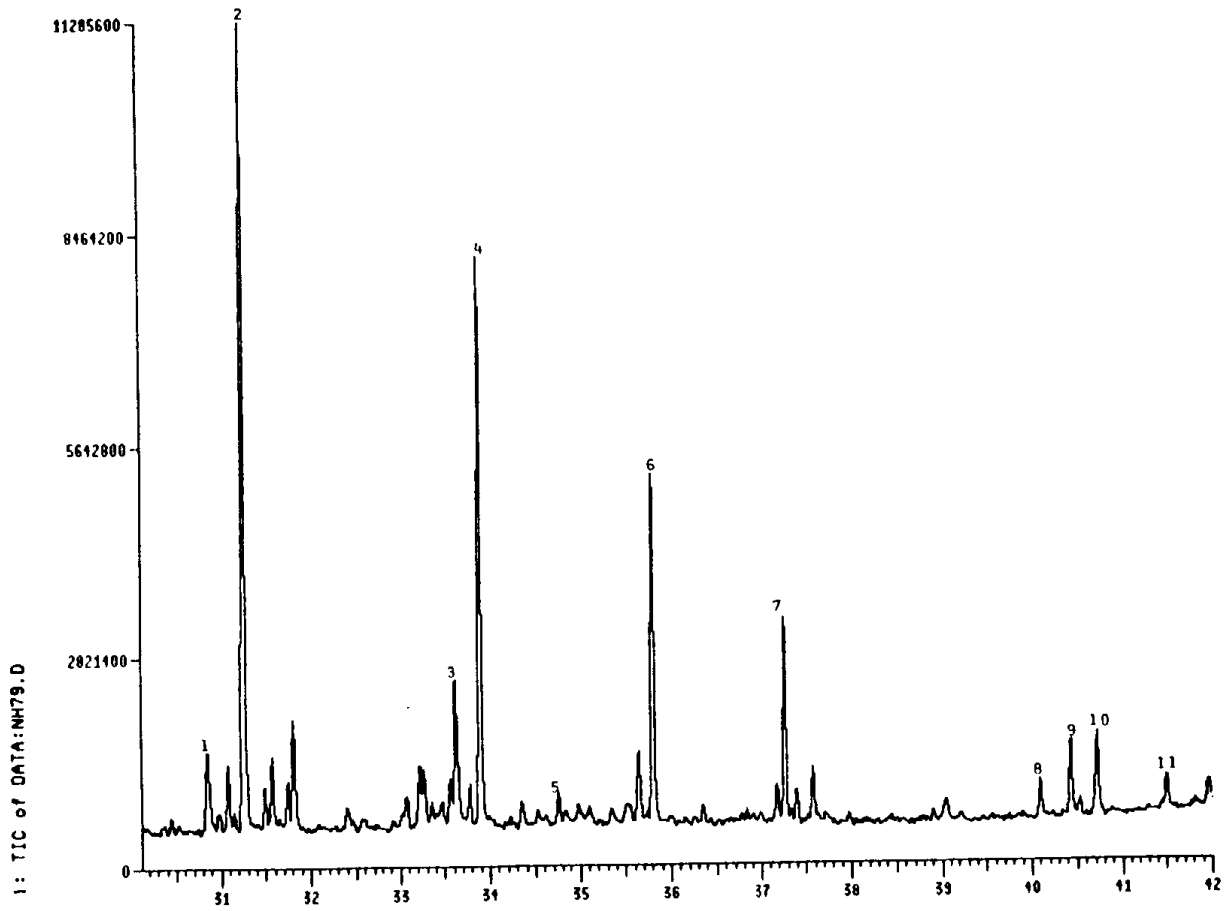

Figure V-29. TIC from GC/MS analysis of 5 ℓ Tenax sample of olive (Manzanillo) emissions (NH-79D). Identities of numbered peaks given in Table V-31.

Table V-32. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Olive (Manzanillo) - 1989 June 29

Assigned Peaks[a]	NH-79A 0900	NH-79B 1030	NH-79C 1200	NH-79D 1330	NH-79E 1445	Identification
1	12	3	3	4	<1	cis-3-hexen-1-ol
2	d	d	d	d	d	p-xylene
3	8	6	8	6	5	1-decene
4	12	7	7	11	7	3-hexenylacetate
5	1	2	5	1	2	trans-ocimene
6	8	6	8	7	6	unknown
7	5	7	9	7	8	1-dodecene 1-tetradecene
9,10	3	4	6	4	8	unknown sesquiterpene (m.w. 204)
11	3	3	3	<1	4	β-caryophyllene
toluene[g]	10	4	3	2	1	
ΣC_6[s]	10	5	6	3	3	
Σ(Assigned Peaks)[h]	52	38	49	41	41	
ΣMonoterpenes	1	2	5	1	2	
ΣSesquiterpenes	3	3	3	<1	4	
$\Sigma C_7 \rightarrow C_{15}$[i]	121	91	116	89	78	
C_5[j]	3	2	3	2	3	
$\Sigma C_3 \rightarrow C_5$[k]	59	29	29	20	49	
Total Plant Emissions[l]	52	38	49	41	41	
Total Carbon[m]	180	120	145	109	127	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-30. The numbers correspond to the GC/MS identifications as given on Figure V-29 and in Table V-31.
[b-t]Footnotes given on Table V-73.

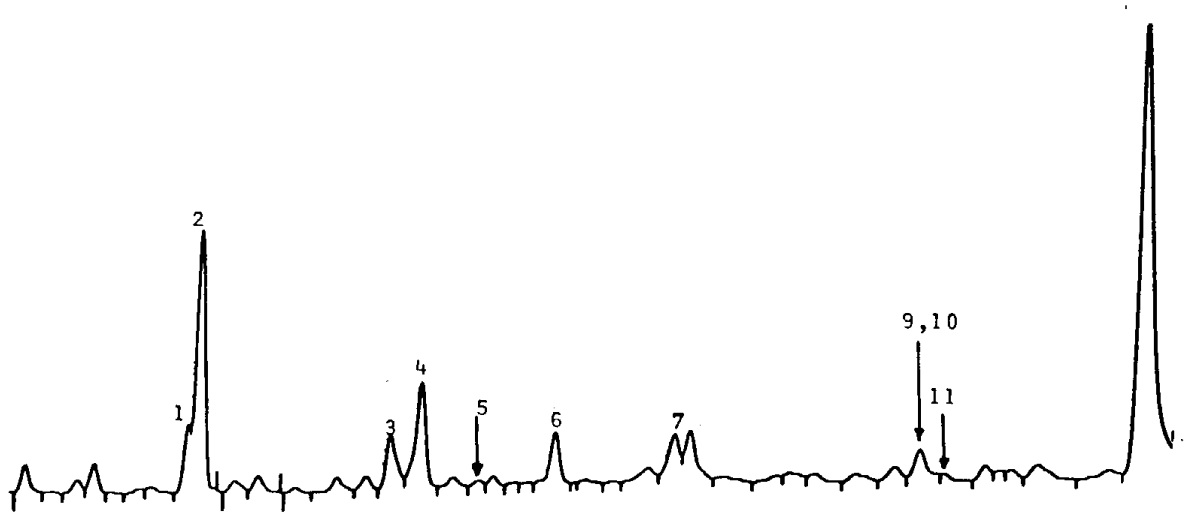

Figure V-30. GC-FID analysis of 2.5 ℓ Tenax sample of olive (Manzanillo) emissions (NH-79D). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-31.

Table V-33. Emissions Identified from Onion (South Port White Globe) by GC/MS Analysis of Survey Sample NH-32 (TIC Shown in Figure V-31)

Peak No.	Compound Identification[a]
1	*cis*-3-hexen-1-ol
2	1,2,4-trimethylbenzene (internal standard)
3	unknown (m.w. 150)

[a]Molecular weights given for unknown indicate the presence of an apparent molecular ion.

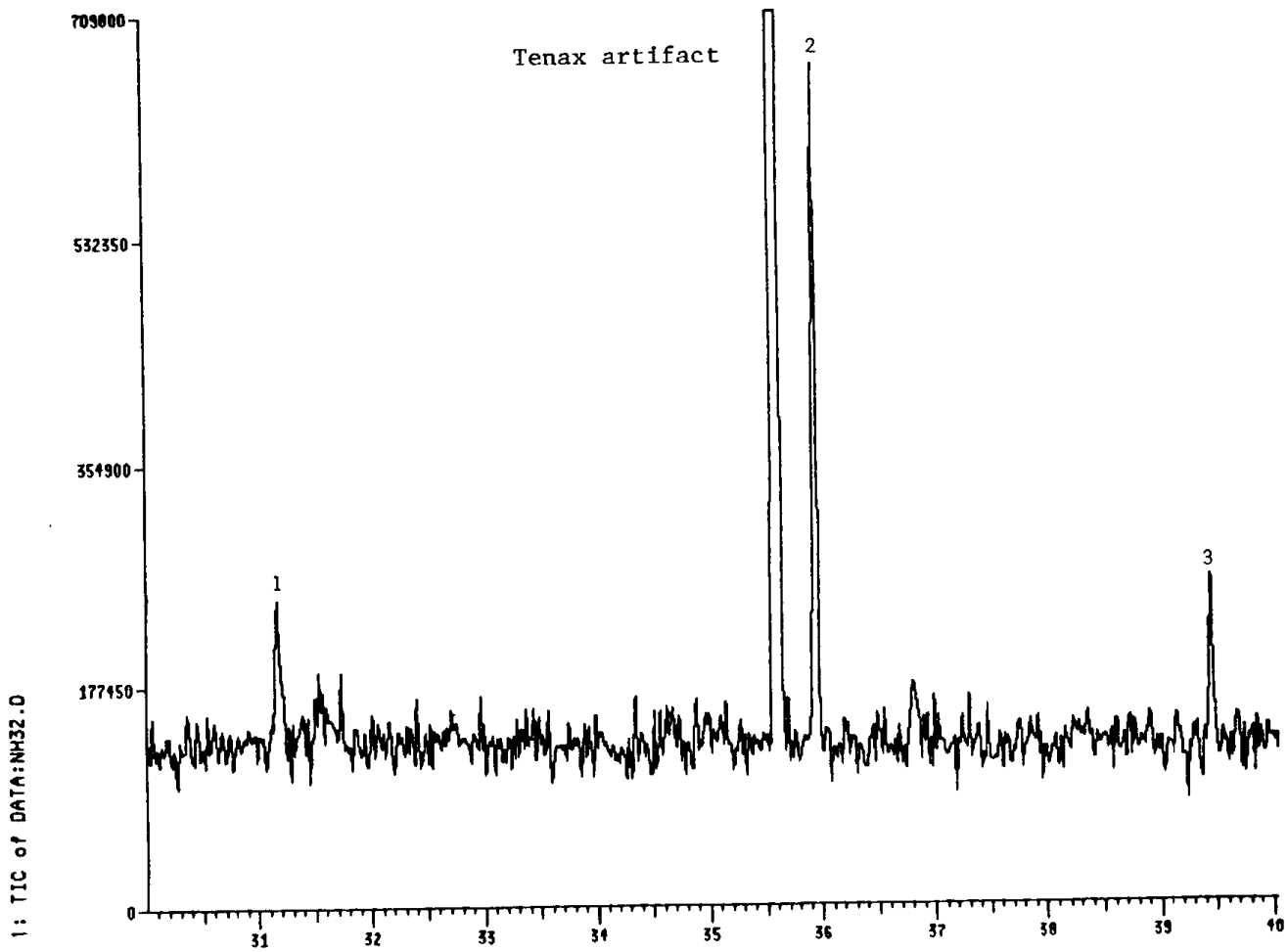

Figure V-31. TIC from GC/MS analysis of 1 ℓ Tenax sample of onion (South Port White Globe) emissions (NH-32). Identities of numbered peaks given in Table V-33.

Table V-34. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Onion - 1988 October 6

Assigned Peaks[a]	NH-32 1400	Identification
1	43	cis-3-hexen-1-ol
2	d	1,2,4-trimethylbenzene
3[b]	14	unknown (m.w. 150)
toluene[g]	1	
Σ(Assigned Peaks)[h]	57	
ΣMonoterpenes	n.d.[f]	
ΣSesquiterpenes	n.d.	
$\Sigma C_7 \rightarrow C_{15}$[i]	84	
C_5[j]	c	
$\Sigma C_3 \rightarrow C_6$[q]	58	
Total Plant Emissions[l]	57	
Total Carbon[m]	142	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-32. The numbers correspond to the GC/MS identifications as given on Figure V-31 and in Table V-33.
[b-t]Footnotes given on Table V-73.

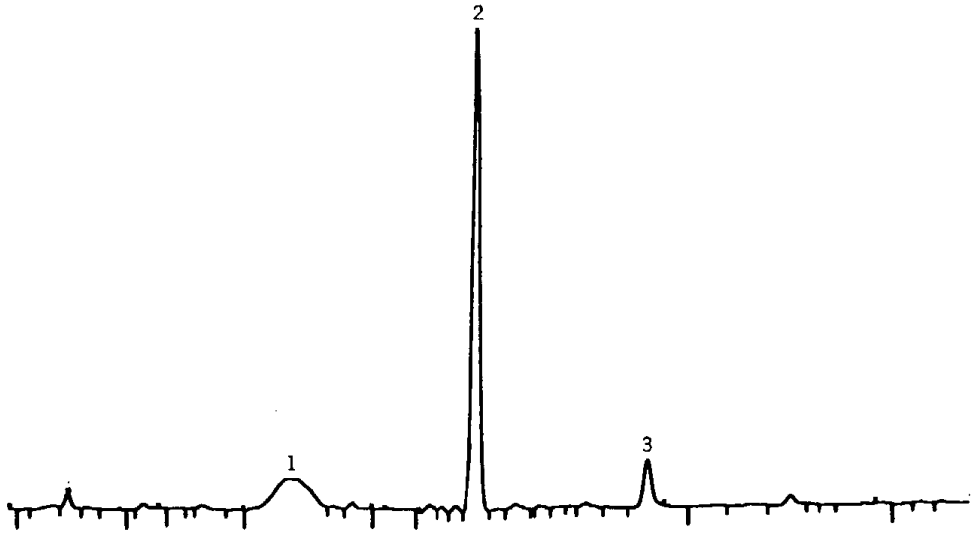

Figure V-32. GC-FID analysis of 1.3 ℓ Tenax/Carbosieve sample of onion (South Port White Globe) emissions (NH-32). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-33.

Table V-35. Emissions Identified from Navel Orange (Washington) by GC/MS Analysis of Survey Sample NH-37D (TIC Shown in Figure V-33)

Peak No.	Compound Identification[a]
1	sabinene
2	1,2,4-trimethylbenzene (internal standard)
3	3-hexenylacetate
4	unknown (m.w. 154)
5	d-limonene

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.

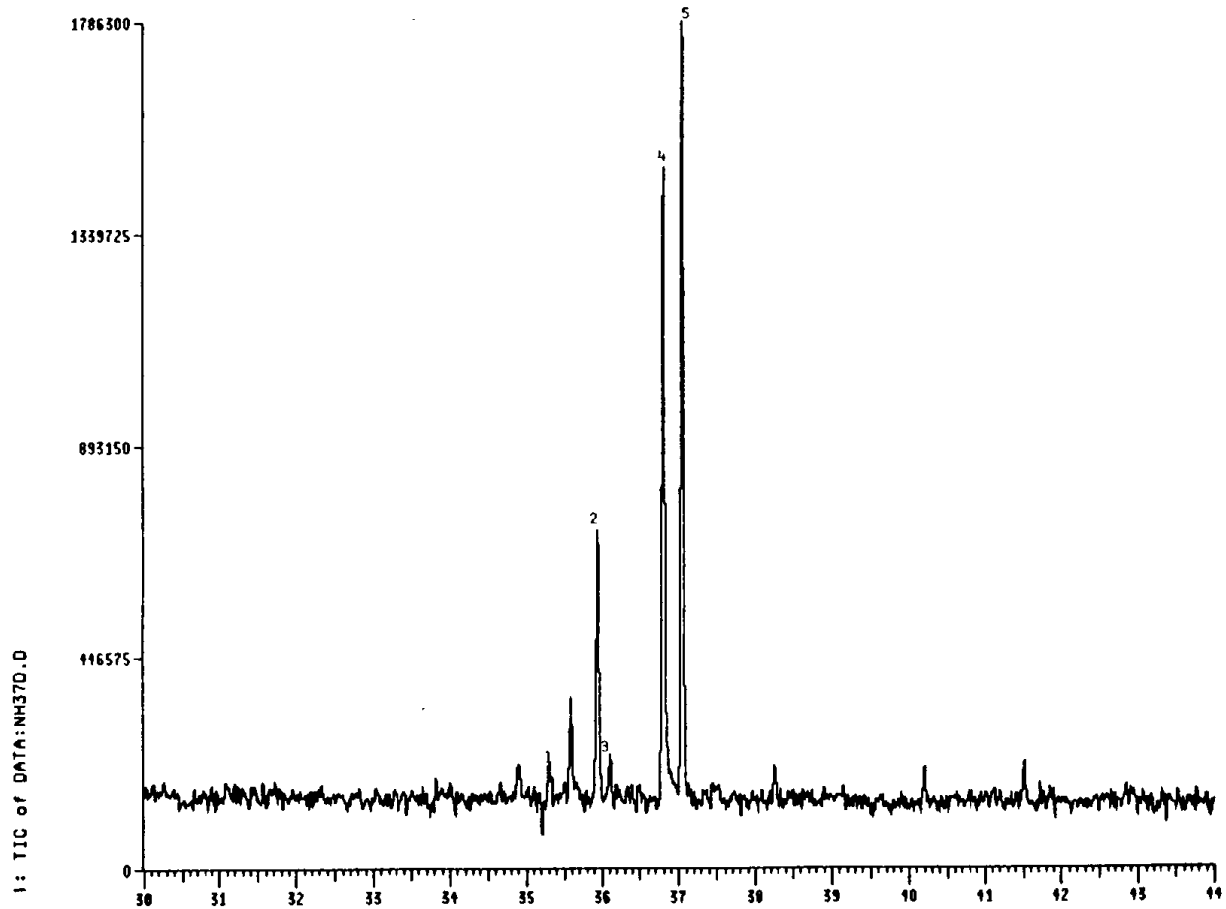

Figure V-33. TIC from GC/MS analysis of 4 ℓ Tenax sample of navel orange (Washington) emissions (NH-37D). Identities of numbered peaks given in Table V-35.

Table V-36. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Navel Orange (Washington) - 1988 October 13

Assigned Peaks[a]	NH-37A 0900	NH-37B 1030	NH-37C 1200	NH-37D 1330	NH-37E 1445	Identification
1	n.d.[f]	2	n.d.	7	n.d.	sabinene
2	d	d	d	d	d	1,2,4-trimethylbenzene
3	<1	1	n.d.	12	2	3-hexenylacetate
4,5	10	44	11	203	3	unknown (m.w. 154) and d-limonene
toluene[g]	1	2	2	2	2	
Σ(Assigned peaks)[h]	11	47	11	222	5	
ΣMonoterpenes	10	46	11	210	3	
ΣSesquiterpenes	c	c	c	c	c	
$\Sigma C_7 \rightarrow C_{15}$[i]	21	58	24	242	18	
C_5[j]	c	c	c	c	c	
$\Sigma C_3 \rightarrow C_6$[q]	6	14	12	14	11	
Total Plant Emissions[l]	11	47	11	222	5	
Total Carbon[m]	27	72	36	256	29	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-34. The numbers correspond to the GC/MS identifications as given on Figure V-33 and in Table V-35.
[b-t]Footnotes given on Table V-73.

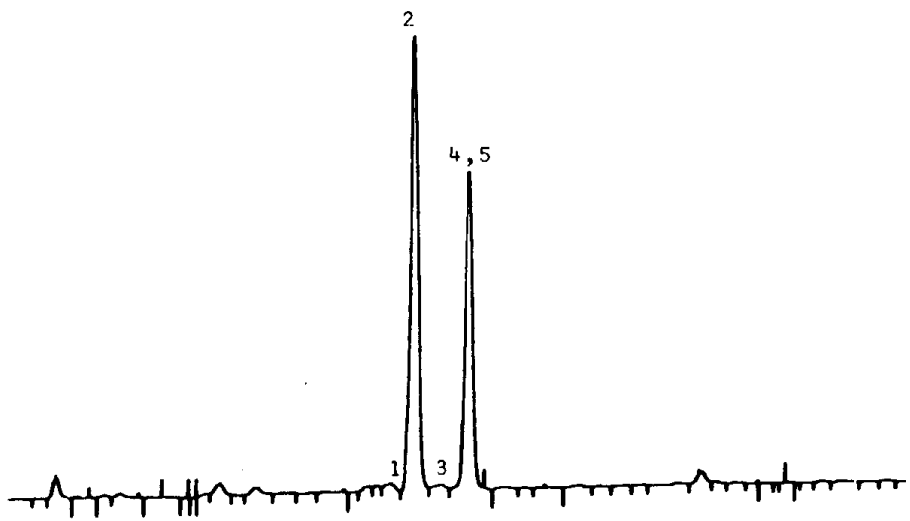

Figure V-34. GC-FID analysis of 2.5 ℓ Tenax/Carbosieve sample of navel orange (Washington) emissions (NH-37B). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-35.

Table V-37. Emissions Identified from Valencia Orange by GC/MS Analysis of Survey Sample NH-4 (TIC Shown in Figure V-35)

Peak No.	Compound Identification[a]
1	*cis*-3-hexen-1-ol
2	α-pinene
3	sabinene
4	myrcene
5	1,2,4-trimethylbenzene (internal standard)
6	3-hexenylacetate
7	unknown (m.w. 134)
8	Δ^3-carene
9	α-terpinene
10	p-cymene
11	d-limonene
12	*trans*-ocimene[b]
13	γ-terpinene
14	unknown
15	unknown
16	unknown

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.
[b]See footnote c on Table V-3.

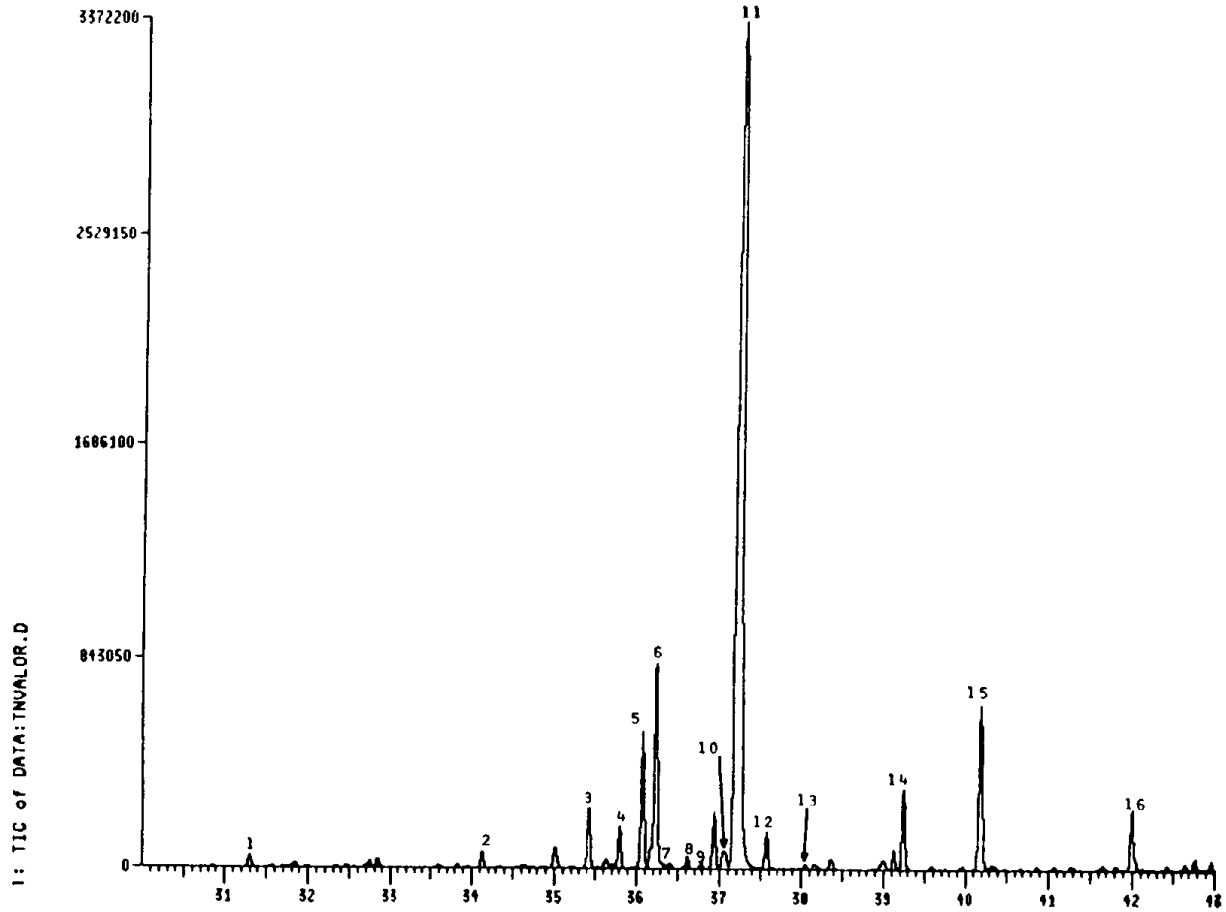

Figure V-35. TIC from GC/MS analysis of 1 ℓ Tenax sample of Valencia orange emissions (NH-4). Identities of numbered peaks given in Table V-37.

Table V-38. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Valencia Orange - 1988 September 1

Assigned Peaks[a]	NH-24A 0900	NH-24B 1030	NH-24C 1200	NH-24D 1330	NH-24E 1445	Identification
1[b]	2	<1	2	<1	1	cis-3-hexen-1-ol
2	<1	n.d.[f]	n.d.	<1	n.d.	α-pinene
3	n.d.	n.d.	5	8	6	sabinene
4	4	2	20	18	14	myrcene (peaks 4 and 5 coeluted, area of marker subtracted to estimate myrcene)
5	d	d	d	d	d	1,2,4-trimethylbenzene
6,7,8	2	3	n.a.[e]	n.d.	n.d.	3-hexenylacetate, unknown (m.w. 134), Δ^3-carene
9,10,11	34	15	15	31	15	α-terpinene, p-cymene, d-limonene
12	2	<1	2	2	1	trans-ocimene
14[b]	n.d.	<1	7	6	7	unknown
15[b]	n.d.	<1	43	43	38	unknown
toluene[g]	10	1	4	2	4	
Σ(Assigned Peaks)[h]	45	22	94	109	82	
ΣMonoterpenes	39	18	42	59	36	
ΣSesquiterpenes	c	c	c	c	c	
$\Sigma C_7 \rightarrow C_{15}$[i]	81	33	175	176	141	
C_5[j]	c	c	c	c	c	
$\Sigma C_3 \rightarrow C_6$[q]	50	9	44	46	50	
Total Plant Emissions[l]	45	22	94	109	82	
Total Carbon[m]	131	42	219	222	191	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-36. The numbers correspond to the GC/MS identifications as given on Figure V-35 and in Table V-37.
[b-t]Footnotes given on Table V-73.

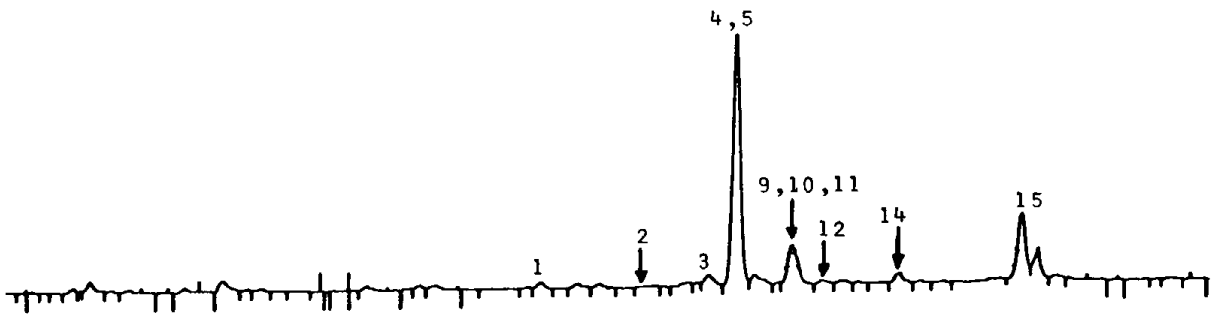

Figure V-36. GC-FID analysis of 1.3 ℓ Tenax/Carbosieve sample of Valencia orange emissions (NH-24D). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-37.

Table V-39. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Irrigated Pasture - 1989 May 26

Assigned Peaks[a]	NH-48A 0900	NH-48B 1030	NH-48C 1200	NH-48D 1330	NH-48E 1445	Tentative Identification[a]
1	34	14	31	79	13	*cis*-3-hexen-1-ol
2	d	d	d	d	d	p-xylene
3,4	n.a.[e]	23	39	37	32	1-decene and n-decane
5	41	20	57	277	22	3-hexenylacetate
6	3	6	10	11	8	1-dodecene
7	2	10	19	13	17	n-dodecane
8	n.d.[f]	n.a.	5	5	n.a.	1-tetradecene
toluene[g]	4	3	15	8	10	
Σ(Assigned Peaks)[h]	80	73	161	422	92	
$\Sigma C_7 \rightarrow C_{15}$[i]	305	371	523	840	492	
C_5[j]	5	6	8	6	5	
$\Sigma C_3 \rightarrow C_5$[r]	268	506	733	509	737	
$\Sigma C_3 \rightarrow C_6$[t]	160	253	493	504	779	
Total Plant Emissions[l]	80	73	161	422	92	
Total Carbon[m]	572	877	1256	1349	1229	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-37. Tentative identifications made by GC-FID analysis using retention time comparisons.
[b-t]Footnotes given on Table V-73.

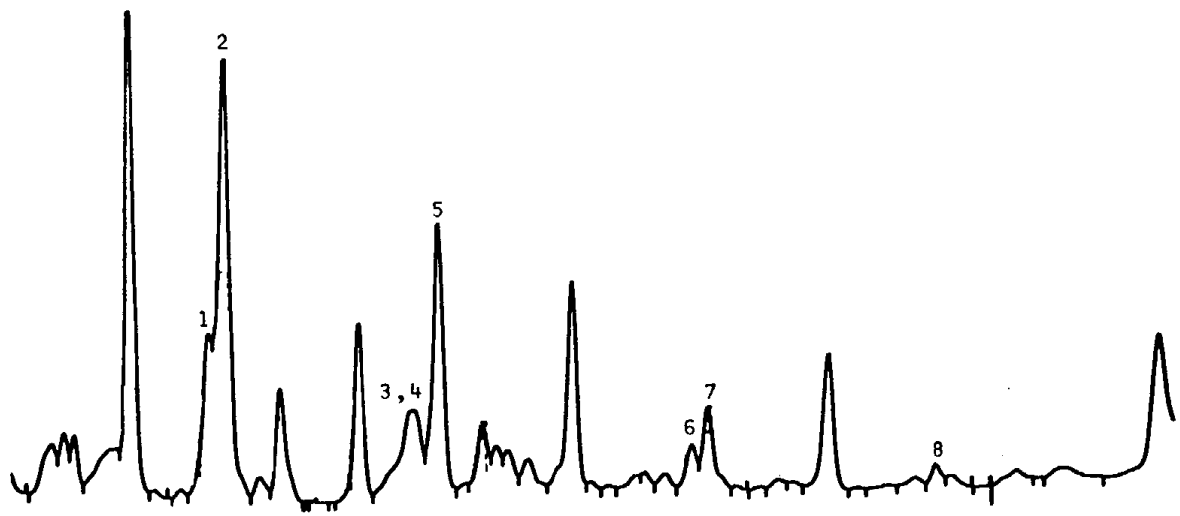

Figure V-37. GC-FID analysis of 1.3 ℓ Tenax/Carbosieve sample of irrigated pasture emissions (NH-48C). Peak identities as indicated in Table V-39 have been assigned on the basis of GC-FID retention times.

Table V-40. Emissions Identified from Peach (Halford) by GC/MS Analysis of Survey Sample NH-70 (TIC Shown in Figure V-38)

Peak No.	Compound Identification[a]
1	cis-3-hexen-1-ol
2	p-xylene (internal standard)
3	α-pinene
4	1-decene
5	3-hexenylacetate
6	Δ^3-carene
7	cis-ocimene[b]
8	trans-ocimene[b]
9	terpinolene
10	2-methyl-6-methylene-1,7-octadien-3-one (tentative)
11	1-dodecene
12	methyl salicylate (tentative)
13	1-tetradecene
14	β-caryophyllene
15-17	unknown sesquiterpenes (m.w. 204)

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.
[b]See footnote c on Table V-3.

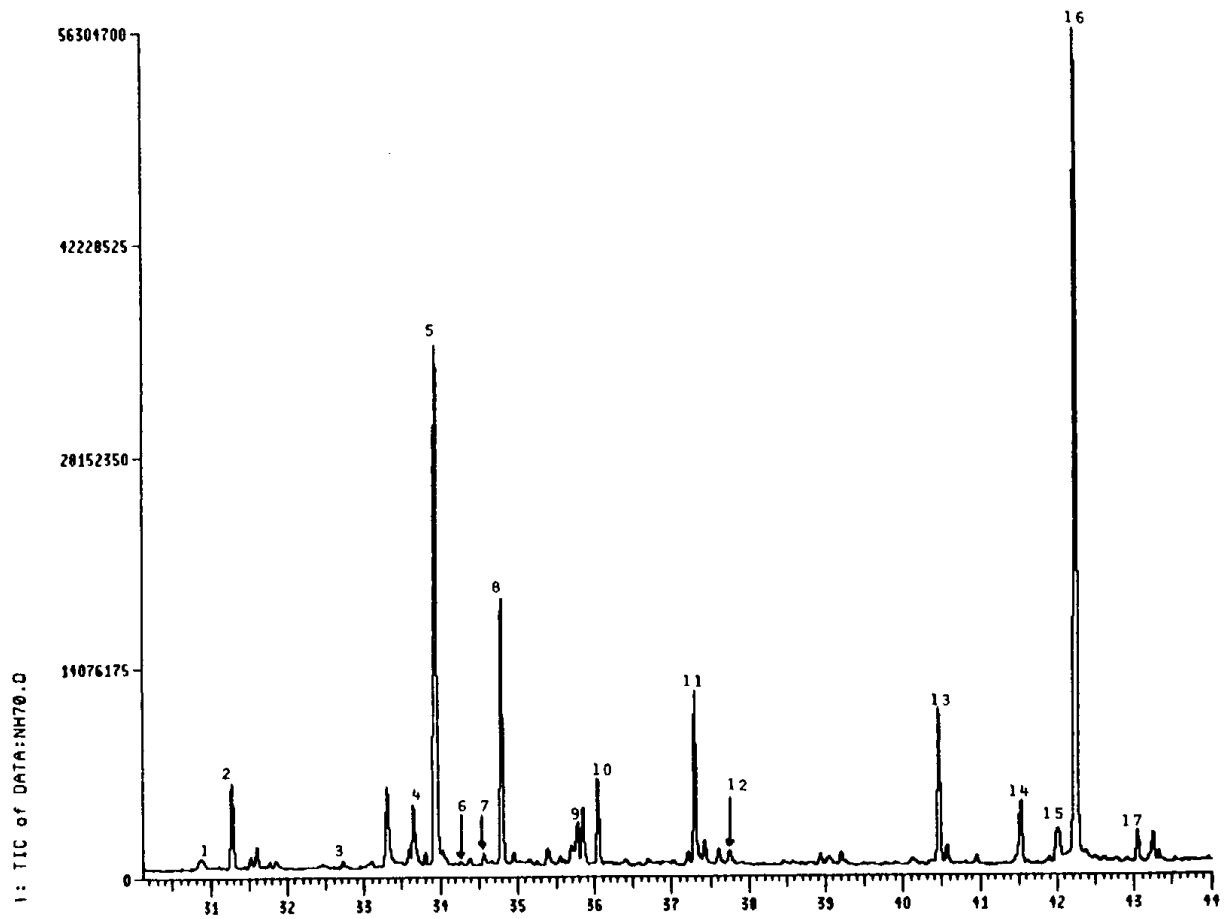

Figure V-38. TIC from GC/MS analysis of 6.3 ℓ Tenax sample of peach (Halford) emissions (NH-70). Identities of numbered peaks given in Table V-40.

Table V-41. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Peach (Halford) - 1989 June 30

Assigned Peaks[a]	NH-80A 0900	NH-80B 1030	NH-80C 1200	NH-80D 1330	NH-80E 1445	Identification
1	137	39	46	58	20	cis-3-hexen-1-ol
2	d	d	d	d	d	p-xylene
4	8	6	8	n.a.[e]	8	1-decene
5,6	485	375	206	237	114	3-hexenylacetate and Δ^3-carene
7	n.d.[f]	n.d.	1	n.d.	n.d.	cis-ocimene
8	18	19	20	17	32	trans-ocimene
9	1	n.d.	n.d.	n.d.	1	terpinolene
10	11	11	17	16	23	2-methyl-6-methylene-1,7-octadien-3-one (tentative)
11	19	12	14	18	13	1-dodecene
13	4	7	11	15	13	1-tetradecene
14	2	3	3	2	4	β-caryophyllene
15,16	30	45	46	102	81	unknown sesquiterpenes (m.w. 204)
toluene[g]	5	3	2	2	1	
ΣC_6[s]	9	8	10	15	14	
Σ(Assigned Peaks)[h]	715	517	372	465	309	
ΣMonoterpenes	19	19	21	17	33	
ΣSesquiterpenes	32	48	49	104	85	
$\Sigma C_7 \rightarrow C_{15}$[i]	823	597	502	611	413	
C_5[j]	2	<1	<1	<1	<1	
$\Sigma C_3 \rightarrow C_5$[k]	30	21	23	20	23	
Total Plant Emissions[l]	715	517	372	465	309	
Total Carbon[m]	853	618	525	631	436	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-39. The numbers correspond to the GC/MS identifications as given on Figure V-38 and in Table V-40.
[b-t]Footnotes given on Table V-73.

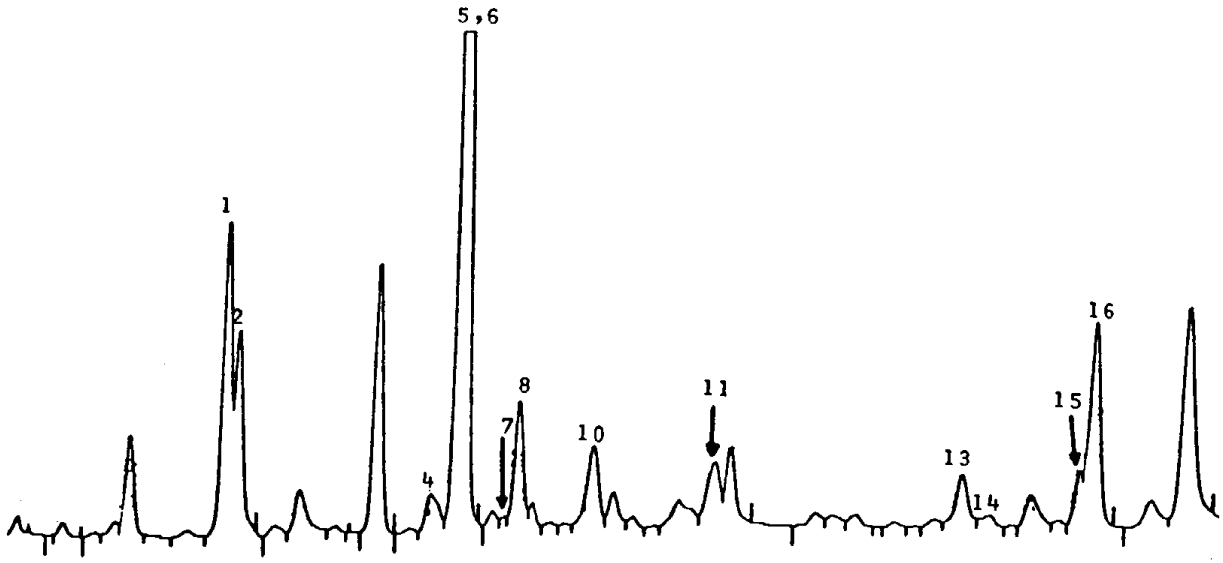

Figure V-39. GC-FID analysis of 1.3 ℓ Tenax sample of peach (Halford) emissions (NH-80C). The assigned peaks correspond to the GC/MS identifications given in Table V-40.

Table V-42. Emissions Identified from Pistachio (Kerman) by GC/MS Analysis of Survey Sample NH-69 (TIC Shown in Figure V-40)

Peak No.	Compound Identification[a]
1	cis-3-hexen-1-ol
2	p-xylene (internal standard)
3	tricyclene or α-thujene (tentative)
4	α-pinene
5	camphene
6	myrcene and β-pinene
7	2-carene
8	α-phellandrene
9	unknown (m.w. 150)
10	Δ^3-carene
11	α-terpinene
12	p-cymene
13	d-limonene
14	β-phellandrene
15	unknown terpene (m.w. 136)
16	γ-terpinene + unknown (m.w. 154)
17	terpinolene
18	unknown (m.w. 150)
19	1,3,8-p-menthatriene (tentative)
20	unknown (m.w. 168)
21	1-dodecene
22	unknown (m.w. 152)
23	p-cymen-8-ol (tentative)
24	bornyl acetate

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.

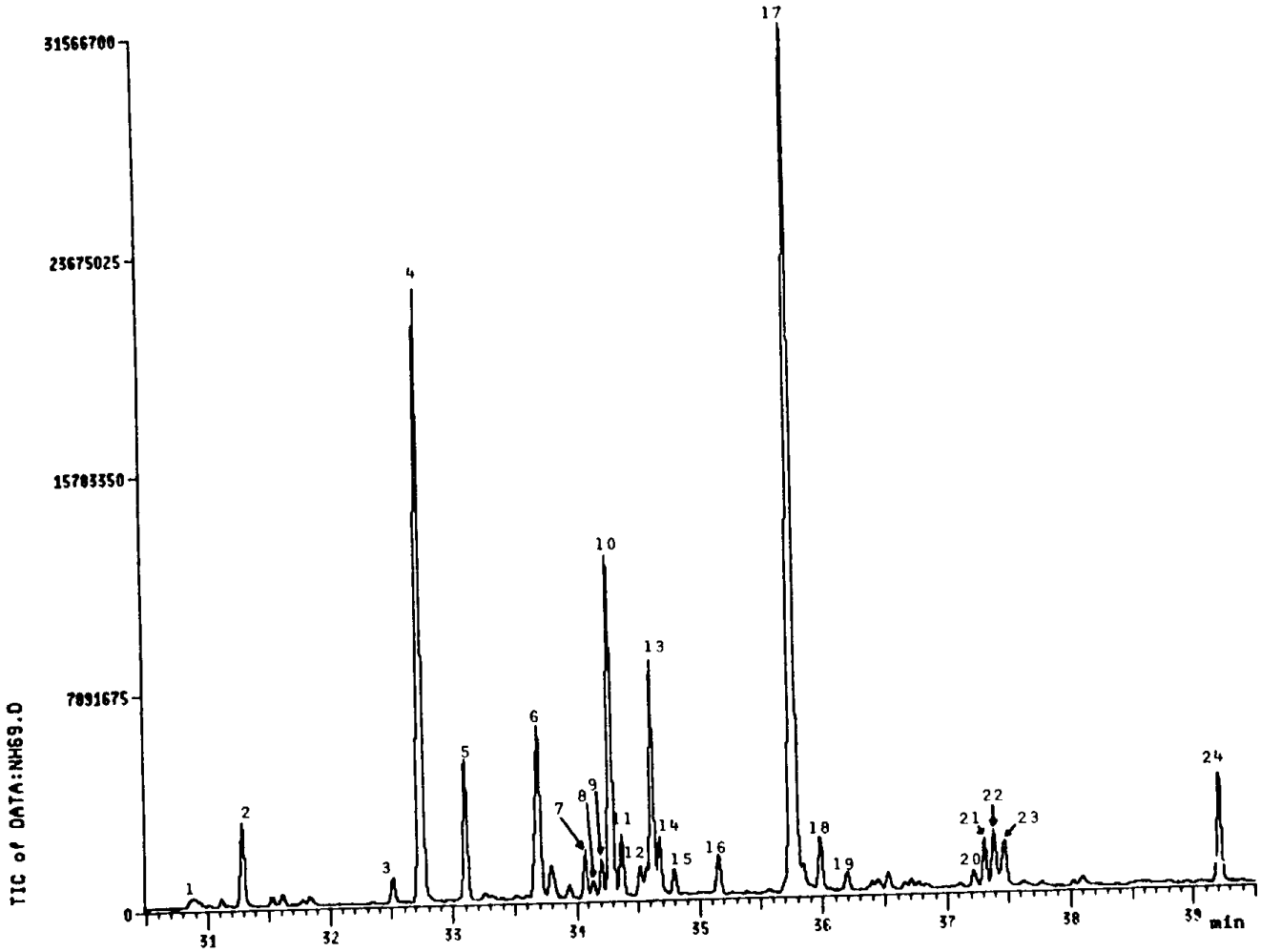

Figure V-40. TIC from GC/MS analysis of 6.3 ℓ Tenax sample of pistachio (Kerman) emissions (NH-69). Identities of numbered peaks given in Table V-42.

Table V-43. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Pistachio (Kerman) - 1989 June 22

Assigned Peaks[a]	NH-76A[v] 0900	NH-76B 1030	NH-76C 1200	NH-76D 1330	NH-76E 1445	Identification
1	20	65	199	46	26	cis-3-hexen-1-ol
2	d	d	d	d	d	p-xylene
3[b]	92	33	13	6	8	tricyclene or α-thujene
4	1,660	427	257	127	185	α-pinene
5	150	86	54	24	36	camphene
6[n]	160	77	38	25	30	β-pinene
6[n]	129	50	39	17	33	myrcene
7→11	401	125	88	19	78	2-carene, α-phellandrene, Δ^3-carene, α-terpinene and unknown (m.w. 150)
12,13	269	92	60	14	43	p-cymene and d-limonene
14	11	5	6	6	12	β-phellandrene
15	14	6	20	80	156	unknown terpene (m.w. 136)
16	33	13	10	n.d.[f]	n.d.	γ-terpinene and unknown (m.w. 154)
17	1,781	610	305	53	306	terpinolene
18	33	49	54	29	52	unknown (m.w. 150)
20→23[b]	78	95	100	46	76	1-dodecene, p-cymen-8-ol (tentative) and unknown (m.w. 152)
24	102	49	52	31	51	bornyl acetate
toluene[g]	5	6	3	2	2	
ΣC_6[s]	11	10	17	17	11	
Σ(Assigned Peaks)[h]	4,933	1,782	1,295	523	1,092	
ΣMonoterpenes	4,700	1,524	890	371	887	
ΣSesquiterpenes	n.d.	n.d.	n.d.	n.d.	n.d.	
$\Sigma C_7 \rightarrow C_{15}$[i]	5,096	1,896	1,541	651	1,290	
C_5[j]	<1	<1	<1	<1	<1	
$\Sigma C_3 \rightarrow C_5$[k]	19	21	11	16	11	
Total Plant Emissions[l]	4,933	1,782	1,295	523	1,092	
Total Carbon[m]	5,115	1,917	1,552	667	1,301	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-41. The numbers correspond to the GC/MS identifications as given on Figure V-40 and in Table V-42.
[b-t]Footnotes given on Table V-73.
[v]Rough handling of this sample may have caused elevated emissions.

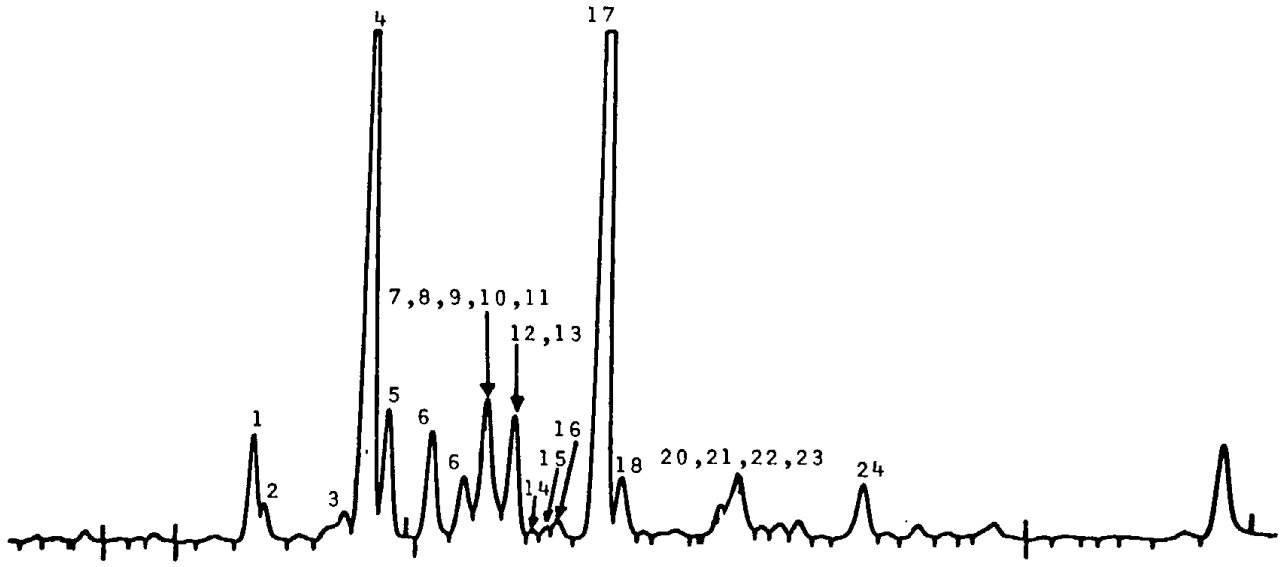

Figure V-41. GC-FID analysis of 1.3 ℓ Tenax sample of pistachio (Kerman) emissions (NH-76B). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-42.

Table V-44. Emissions Identified from Plum (Santa Rosa) by GC/MS Analysis of Survey Sample NH-73 (TIC Shown in Figure V-42)

Peak No.	Compound Identification[a]
1	unknown (m.w. 100)
2	unknown
3	1-butylacetate (tentative)
4	trans-2-hexenal
5	cis-3-hexen-1-ol
6	p-xylene (internal standard)
7	1-decene
8	n-decane
9	3-hexenylacetate
10	trans-ocimene[b]
11	n-undecane
12	unknown (m.w. 154)
13	1-dodecene
14	n-dodecane
15	unknown (m.w. 208)
16	1-tetradecene

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.
[b]See footnote c on Table V-3.

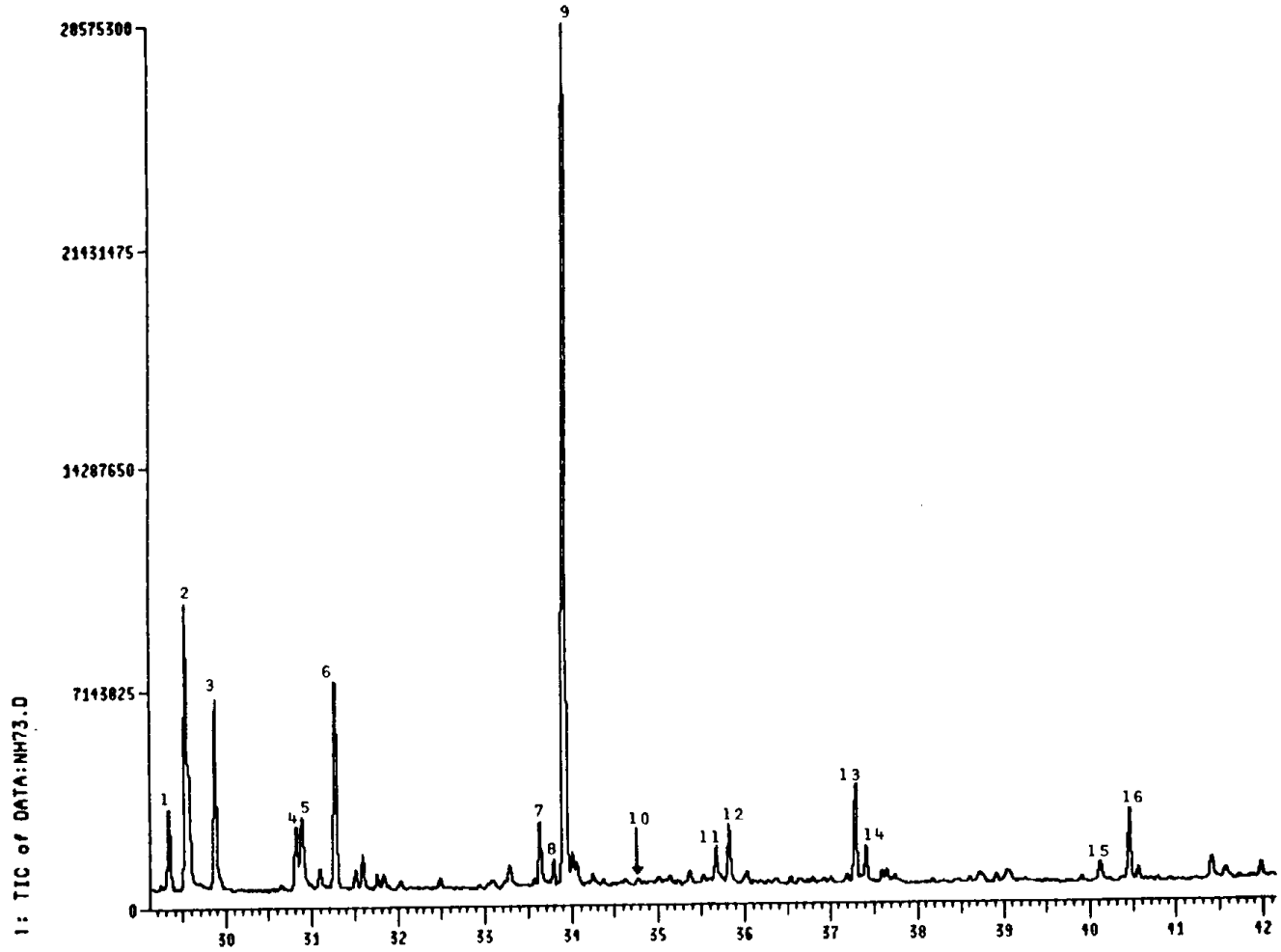

Figure V-42. TIC from GC/MS analysis of 5.1 ℓ Tenax sample of plum (Santa Rosa) emissions (NH-73). Identities of numbered peaks given in Table V-44.

Table V-45. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Plum (Santa Rosa) - 1989 July 28

Assigned Peaks[a]	NH-94A 0900	NH-94B 1030	NH-94C 1200	NH-94D 1330	NH-94E 1445	Identification
2[b]	23	8	16	15	13	unknown
3[b]	7	2	5	2	3	1-butyl acetate (tentative)
4	n.d.[f]	n.d.	10	5	28	trans-2-hexenal
5	39	9	10	5	10	cis-3-hexen-1-ol
6	d	d	d	d	d	p-xylene
7,8	8	7	11	8	10	1-decene and n-decane
9	230	57	42	29	24	3-hexenylacetate
10	<1	<1	<1	n.d.	3	trans-ocimene
11[b]	8	6	10	7	10	n-undecane
12[b]	n.d.	n.d.	9	2	14	unknown (m.w. 154)
13	12	9	19	18	22	1-dodecene
14	7	4	9	9	9	n-dodecane
16	7	8	23	25	27	1-tetradecene
toluene[g]	6	6	7	3	1	
ΣC_6[s]	9	9	15	5	10	
Σ(Assigned Peaks)[h]	342	111	155	125	173	
ΣMonoterpenes	<1	<1	<1	n.d.	3	
ΣSesquiterpenes	n.d.	n.d.	n.d.	n.d.	n.d.	
$\Sigma C_7 \rightarrow C_{15}$[i]	399	155	232	168	232	
C_5[j]	2	5	6	2	1	
$\Sigma C_3 \rightarrow C_5$[k]	29	76	46	26	23	
Total Plant Emissions[l]	342	111	155	125	173	
Total Carbon[m]	428	231	278	194	265	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-43. The numbers correspond to the GC/MS identifications as given on Figure V-42 and in Table V-44.
[b-t]Footnotes given on Table V-73.

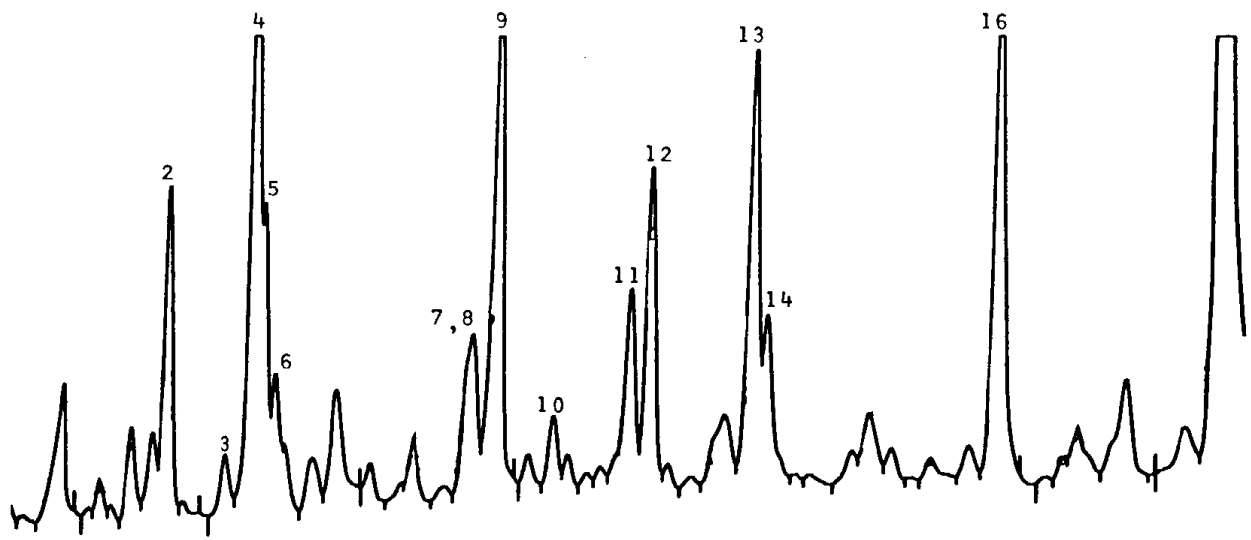

Figure V-43. GC-FID analysis of 2.6 ℓ Tenax sample of plum (Santa Rosa) emissions (NH-94E). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-44.

Table V-46. Emissions Identified from French Prune (Mariana) by GC/MS Analysis of Survey Sample NH-87 (TIC Shown in Figure V-44)

Peak No.	Compound Identification[a]
1	unknown (m.w. 100)
2	unknown (m.w. 114)
3	cis-3-hexen-1-ol
4	p-xylene (internal standard)
5	1-decene
6	n-decane
7	3-hexenylacetate
8	trans-ocimene[b]
9	1-dodecene
10	n-dodecane
11	1-tetradecene
12	n-tetradecane

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.
[b]See footnote c on Table V-3.

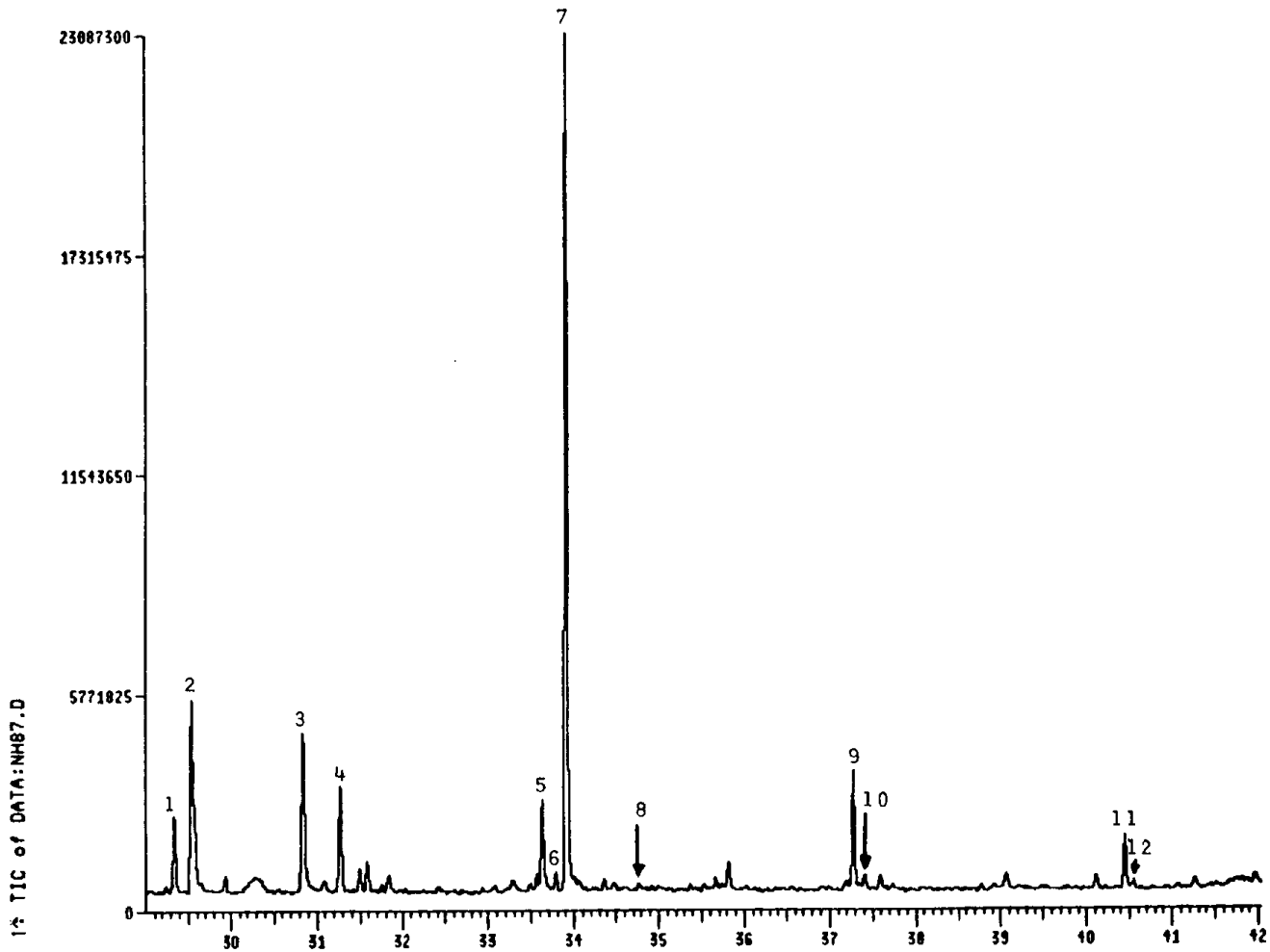

Figure V-44. TIC from GC/MS analysis of 6.5 ℓ Tenax sample of French prune (Mariana) emissions (NH-87). Identities of numbered peaks given in Table V-46.

Table V-47. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for French Prune - 1989 July 14

Assigned Peaks[a]	NH-87 1130	Identification
1,2	23	unknowns (m.w. 100 and 114)
3	32	cis-3-hexen-1-ol
4	d	p-xylene
5,6	7	1-decene and n-decane
7	83	3-hexenylacetate
8	1	trans-ocimene
9	11	1-dodecene
10	8	n-dodecane
11	11	1-tetradecene
toluene[g]	<1	
Σ(Assigned Peaks)[h]	176	
ΣMonoterpenes	1	
ΣSesquiterpenes	n.d.[f]	
$\Sigma C_7 \rightarrow C_{15}$[i]	233	
ΣC_6[s]	5	
C_5[j]	<1	
$\Sigma C_3 \rightarrow C_5$[k]	18	
Total Plant Emissions[l]	179	
Total Carbon[m]	251	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-45. The numbers correspond to the GC/MS identifications as given on Figure V-44 and in Table V-46.
[b-t]Footnotes given on Table V-73.

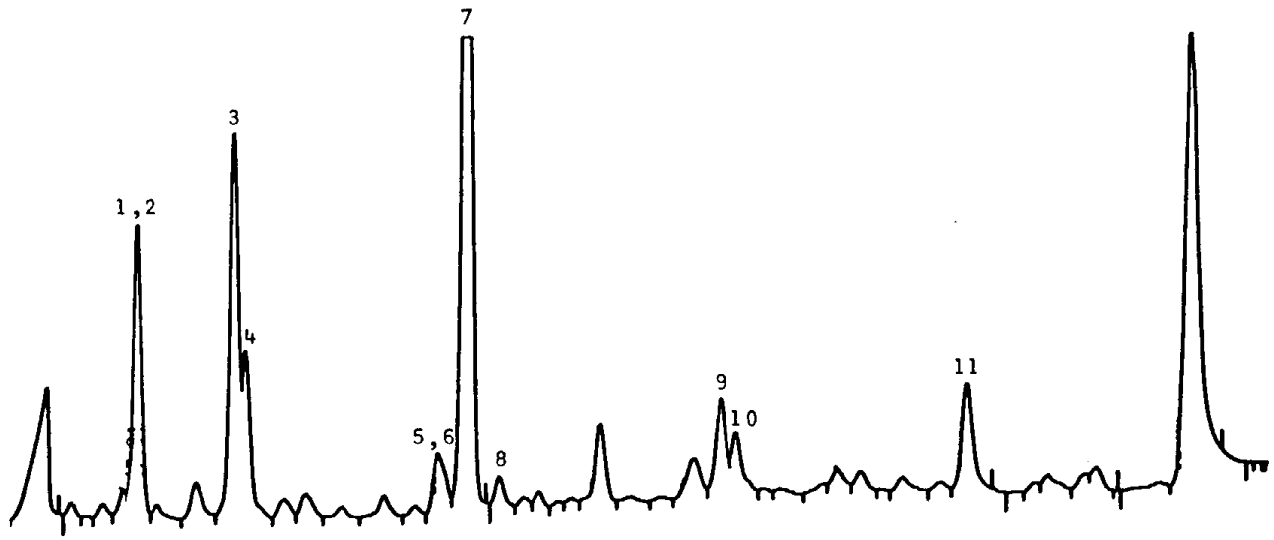

Figure V-45. GC-FID analysis of 2.5 ℓ Tenax sample of French prune (Mariana) emissions (NH-87). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-46.

Table V-48. Emissions Identified from Rice (M202) by GC/MS Analysis of Survey Sample NH-90E (TIC Shown in Figure V-46)

Peak No.	Compound Identification[a]
1	unknown (m.w. 100)
2	unknown
3	n-hexanal
4	p-xylene (internal standard)
5	2-heptanone
6	1-decene
7	unknown
8	1-dodecene
9	n-dodecane
10	unknown
11	unknown
12	1-tetradecene
13	unknown (m.w. 220)

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.

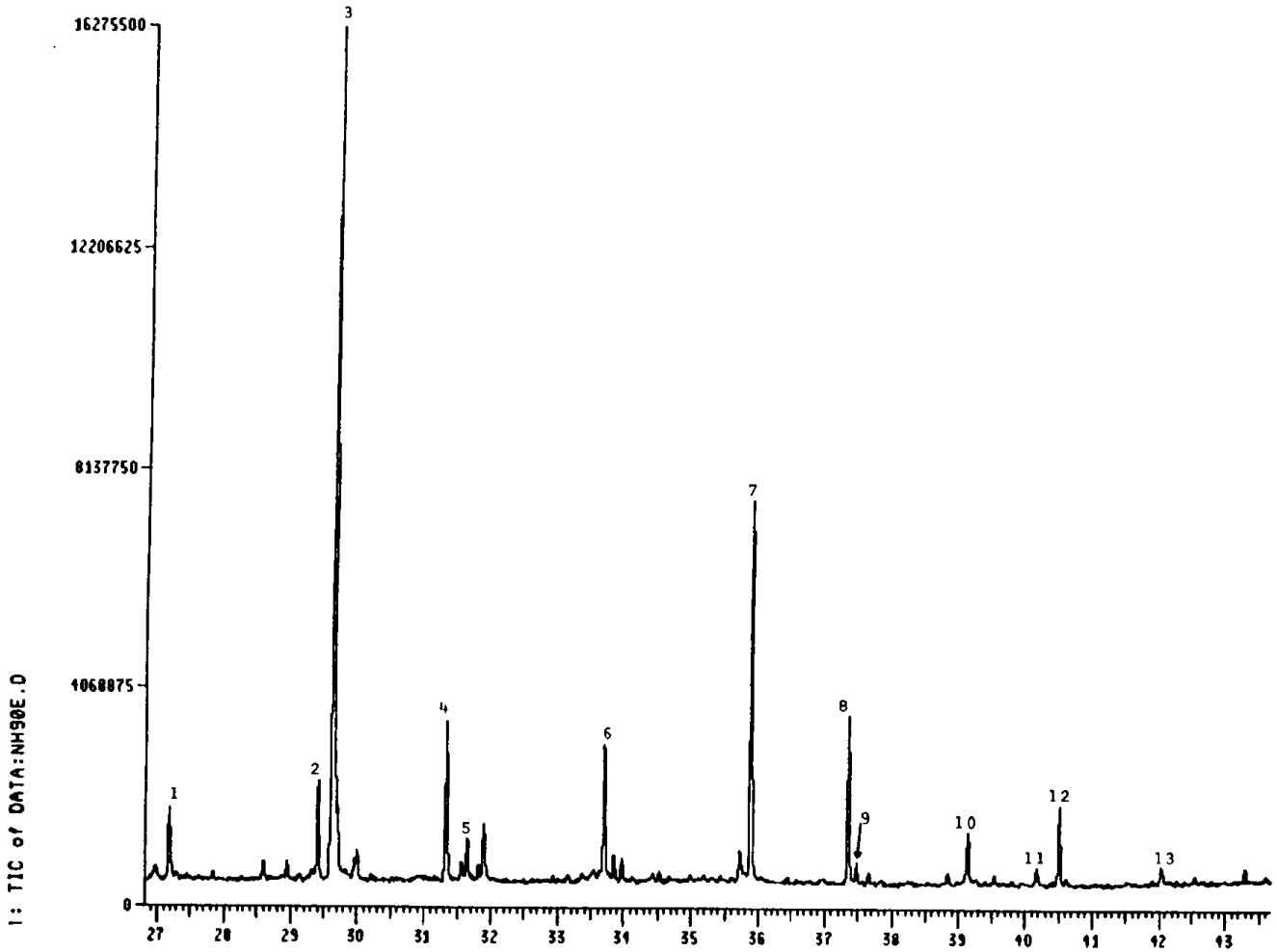

Figure V-46. TIC from GC/MS analysis of 6.3 ℓ Tenax sample of rice (M202) emissions (NH-90E). Identities of numbered peaks given in Table V-48.

Table V-49. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Rice (M202) - 1989 July 20

Assigned Peaks[a]	NH-90A 0900	NH-90B 1030	NH-90C 1200	NH-90D 1330	NH-90E 1445	Identification
3[b]	9	7	7	7	8	n-hexanal
4	d	d	d	d	d	p-xylene
5	3	3	3	3	2	2-heptanone
6	12	14	17	18	13	1-decene
8	18	27	38	37	24	1-dodecene
9	7	11	11	15	11	n-dodecane
10[b]	4	7	7	11	5	unknown
12	11	29	43	44	25	1-tetradecene
toluene[g]	7	4	<1	2	2	
ΣC_6[s]	11	8	c	11	6	
Σ(Assigned Peaks)[h]	72	106	136	147	98	
ΣMonoterpenes	n.d.[f]	n.d.	n.d.	n.d.	n.d.	
ΣSesquiterpenes	n.d.	n.d.	n.d.	n.d.	n.d.	
$\Sigma C_7 \rightarrow C_{15}$[i]	146	170	216	247	183	
C_5[j]	<1	<1	1	<1	c	
$\Sigma C_3 \rightarrow C_5$[k]	17	22	22	20	13	
Total Plant Emissions[l]	72	106	136	147	98	
Total Carbon[m]	163	192	238	267	196	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-47. The numbers correspond to the GC/MS identifications as given on Figure V-46 and in Table V-48.
[b-t]Footnotes given on Table V-73.

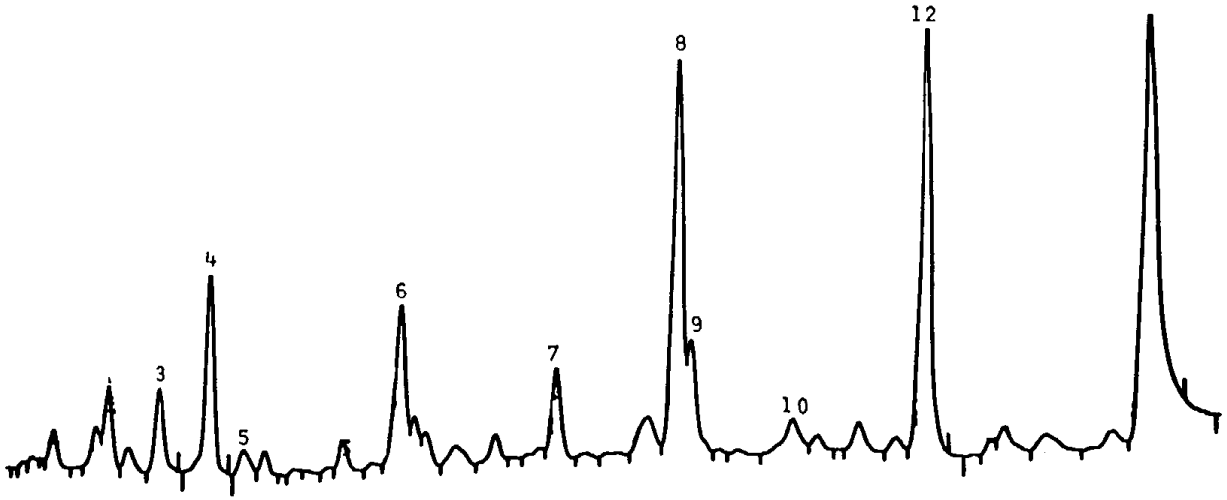

Figure V-47. GC-FID analysis of 1.3 ℓ Tenax sample of rice (M202) emissions (NH-90C). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-48.

Table V-50. Emissions Identified from Safflower (UC 26) by GC/MS Analysis of Survey Sample NH-75A (TIC Shown in Figure V-48)

Peak No.	Compound Identification[a]
1	cis-3-hexen-1-ol
2	p-xylene (internal standard)
3	α-pinene
4	sabinene
5	β-pinene + myrcene
6	d-limonene
7	trans-ocimene[b]
8	unknown (m.w. 180)
9	2-methyl-6-methylene-1,7-octadien-3-one (tentative)
10	1-dodecene
11	verbenone (tentative)
12	1-tetradecene
13	unknown sesquiterpene (m.w. 204)
14	cyperene
15	β-caryophyllene
16	unknown sesquiterpene (m.w. 204)
17	1-pentadecene (tentative)
18	α-humulene
19-21	unknown sesquiterpenes (m.w. 204)

[a]Molecular weights given for unknowns indicate the presence on an apparent molecular ion.
[b]See footnote c on Table V-3.

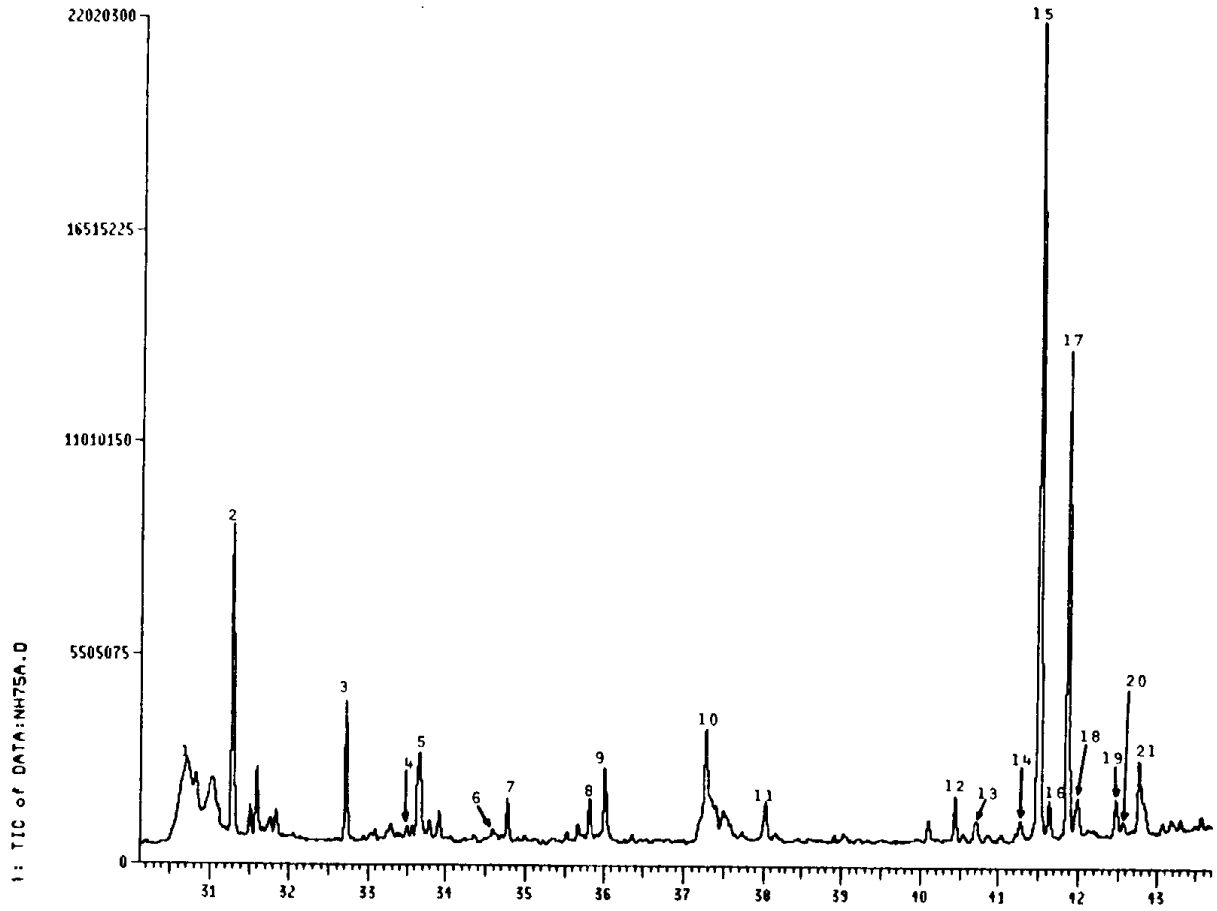

Figure V-48. TIC from GC/MS analysis of 5 ℓ Tenax sample of safflower (UC 26) emissions (NH-75A). Identities of numbered peaks given in Table V-50.

Table V-51. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Safflower (UC 26) - 1989 June 20

Assigned Peaks[a]	NH-75A 0900	NH-75B 1030	NH-75C 1200	NH-75D 1330	NH-75E 1445	Identification
1	c	c	c	c	c	cis-3-hexen-1-ol
3	5	2	8	n.d.[f]	n.d.	α-pinene
4,5[n]	2	1	5	n.d.	1	sabinene and β-pinene
5[n]	c	8	c	n.a.[e]	2	myrcene
6	1	n.d.	2	n.a.	n.d.	d-limonene
7	2	8	4	n.a.	2	trans-ocimene
9	6	6	8	15	11	2-methyl-6-methylene-1,7-octadien-3-one (tentative)
10	c	22	18	25	18	1-dodecene
12	13	29	26	36	22	1-tetradecene
15	47	144	46	81	64	β-caryophyllene
17	133	327	151	211	239	1-pentadecene (tentative)
18	c	52	14	49	24	α-humulene
19,20,21	3	11	20	13	6	unknown sesquiterpenes (m.w. 204)
toluene[g]	<1	2	2	2	3	
Σ(Assigned Peaks)[h]	212	610	302	430	389	
ΣMonoterpenes	10	19	19	n.a.	5	
ΣSesquiterpenes	50	207	80	143	94	
$\Sigma C_7 \rightarrow C_{15}$[i]	401	955	516	992	612	
C_5[j]	2	2	<1	<1	<1	
$\Sigma C_3 \rightarrow C_5$[k]	173	41	22	33	60	
$\Sigma C_3 \rightarrow C_6$[t]	77	97	95	86	81	
Total Plant Emissions[l]	212	610	302	430	389	
Total Carbon[m]	574	996	538	1,025	672	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-49. The numbers correspond to the GC/MS identifications as given on Figure V-48 and in Table V-50.
[b-t]Footnotes given on Table V-73.

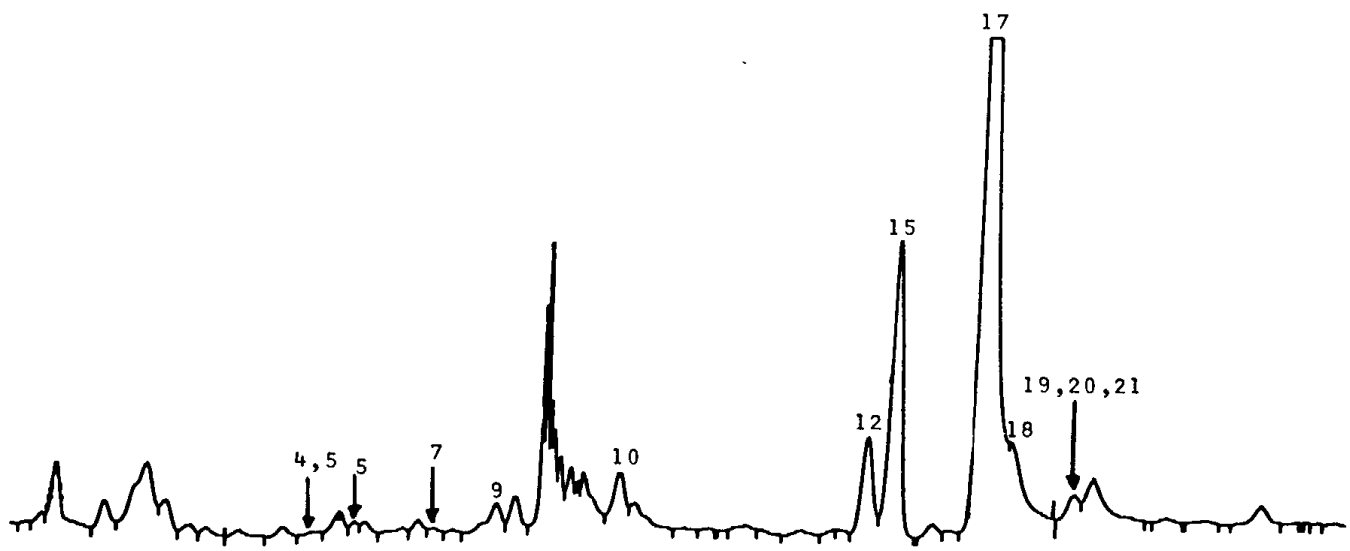

Figure V-49. GC-FID analysis of 1.2 ℓ Tenax/Carbosieve sample of safflower (UC 26) emissions (NH-75E). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-50.

Table V-52. Emissions Identified from Grain Sorghum (Dekalb 424) by GC/MS Analysis of Survey Sample NH-81D (TIC Shown in Figure V-50)

Peak No.	Compound Identification
1	p-xylene (internal standard)
2	α-pinene
3	1-decene
4	3-hexenylacetate
5	unknown
6	1-dodecene
7	n-dodecane
8	1-tetradecene
9	n-tetradecane

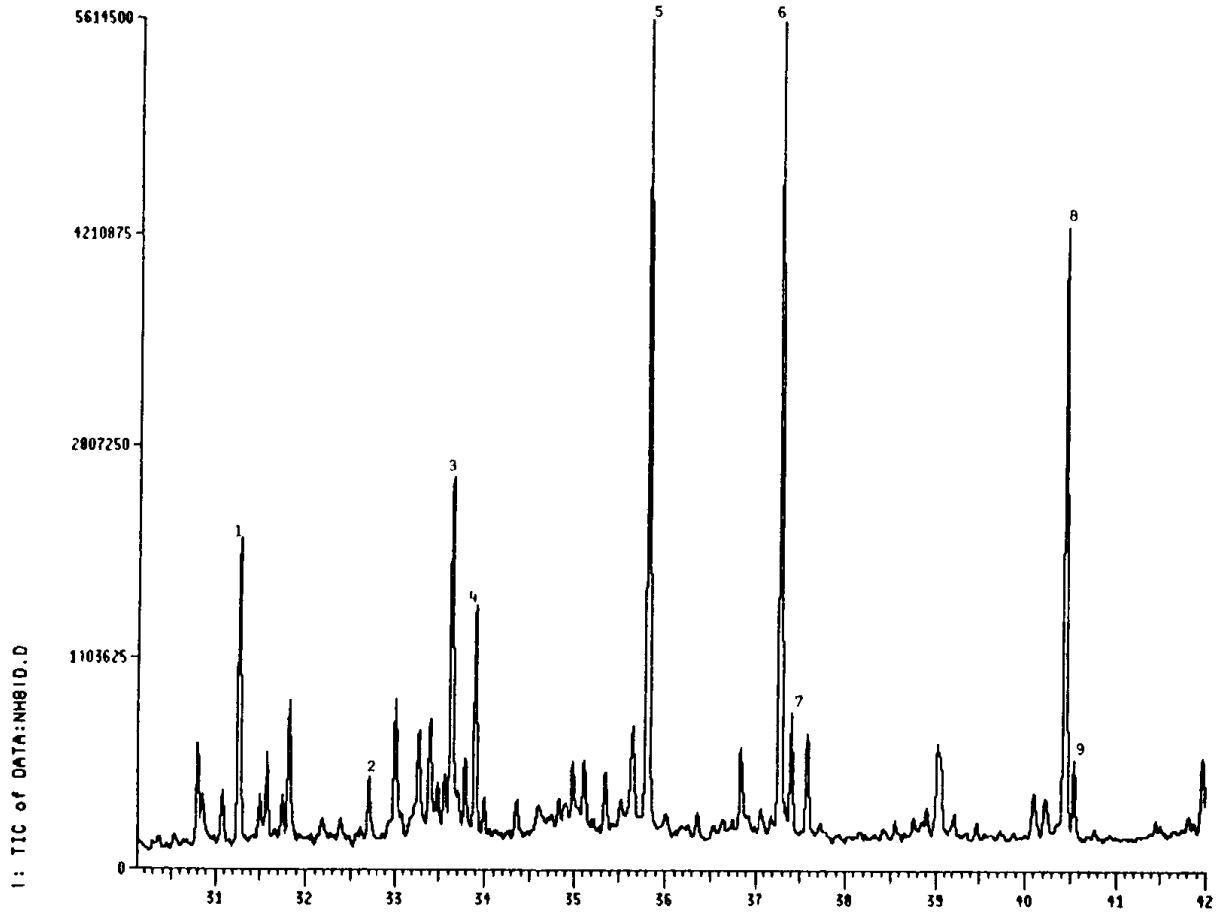

Figure V-50. TIC from GC/MS analysis of 4.8 ℓ Tenax sample of grain sorghum (Dekalb 424) emissions (NH-81D). Identities of numbered peaks given in Table V-52.

Table V-53. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Grain Sorghum (Dekalb 421) - 1989 July 5

Assigned Peaks[a]	NH-81A 0900	NH-81B 1030	NH-81C 1200	NH-81D 1330	NH-81E 1445	Identification
1	d	d	d	d	d	p-xylene
2	6	4	3	4	5	α-pinene
3	15	17	18	27	15	1-decene
4	21	27	16	20	10	3-hexenylacetate
5[b]	19	23	21	35	26	unknown
6	13	22	23	27	12	1-dodecene
7	14	11	17	21	20	n-dodecane
8[b],9[b]	12	24	29	30	15	1-tetradecene, n-tetradecane
toluene[g]	6	9	2	3	2	
ΣC_6[e]	18	12	8	22	20	
Σ(Assigned Peaks)[h]	100	128	127	164	103	
ΣMonoterpenes	6	4	3	4	5	
ΣSesquiterpenes	n.d.[f]	n.d.	n.d.	n.d.	n.d.	
$\Sigma C_7 \rightarrow C_{15}$[i]	218	249	226	369	229	
C_5[j]	2	c	<1	2	1	
$\Sigma C_3 \rightarrow C_5$[k]	28	21	39	36	32	
Total Plant Emissions[l]	100	128	127	164	103	
Total Carbon[m]	246	270	265	405	261	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-51. The numbers correspond to the GC/MS identifications as given on Figure V-50 and in Table V-52.
[b-t]Footnotes given on Table V-73.

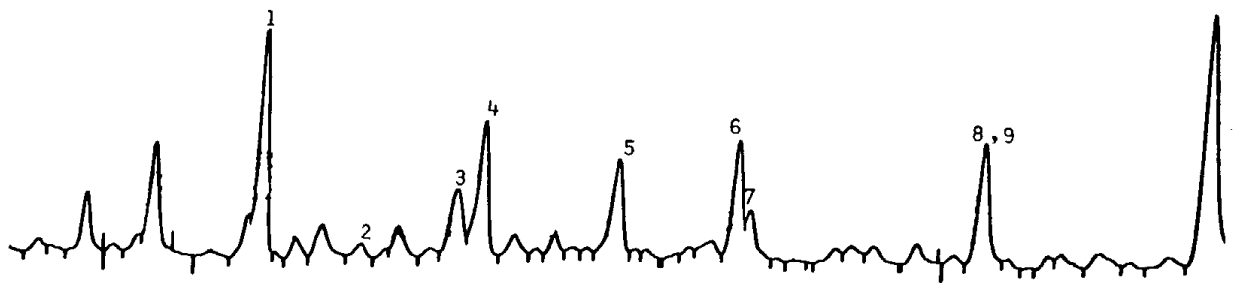

Figure V-51. GC-FID analysis of 1.4 ℓ Tenax sample of grain sorghum (Dekalb 424) emissions (NH-81B). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-52.

Table V-54. Emissions Identified from Fresh Market Tomato (Sunny) by GC/MS Analysis of Survey Sample NH-57 (TIC shown in Figure V-52)

Peak No.	Compound Identification[a]
1	p-xylene (internal standard)
2	α-pinene
3	unknown (m.w. 134)
4	unknown terpene (m.w. 136)
5	2-carene
6	α-phellandrene
7	α-terpinene
8	p-cymene
9	unknown terpene (m.w. 136)
10	d-limonene
11	β-phellandrene
12	unknown (m.w. 158)
13	β-caryophyllene

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.

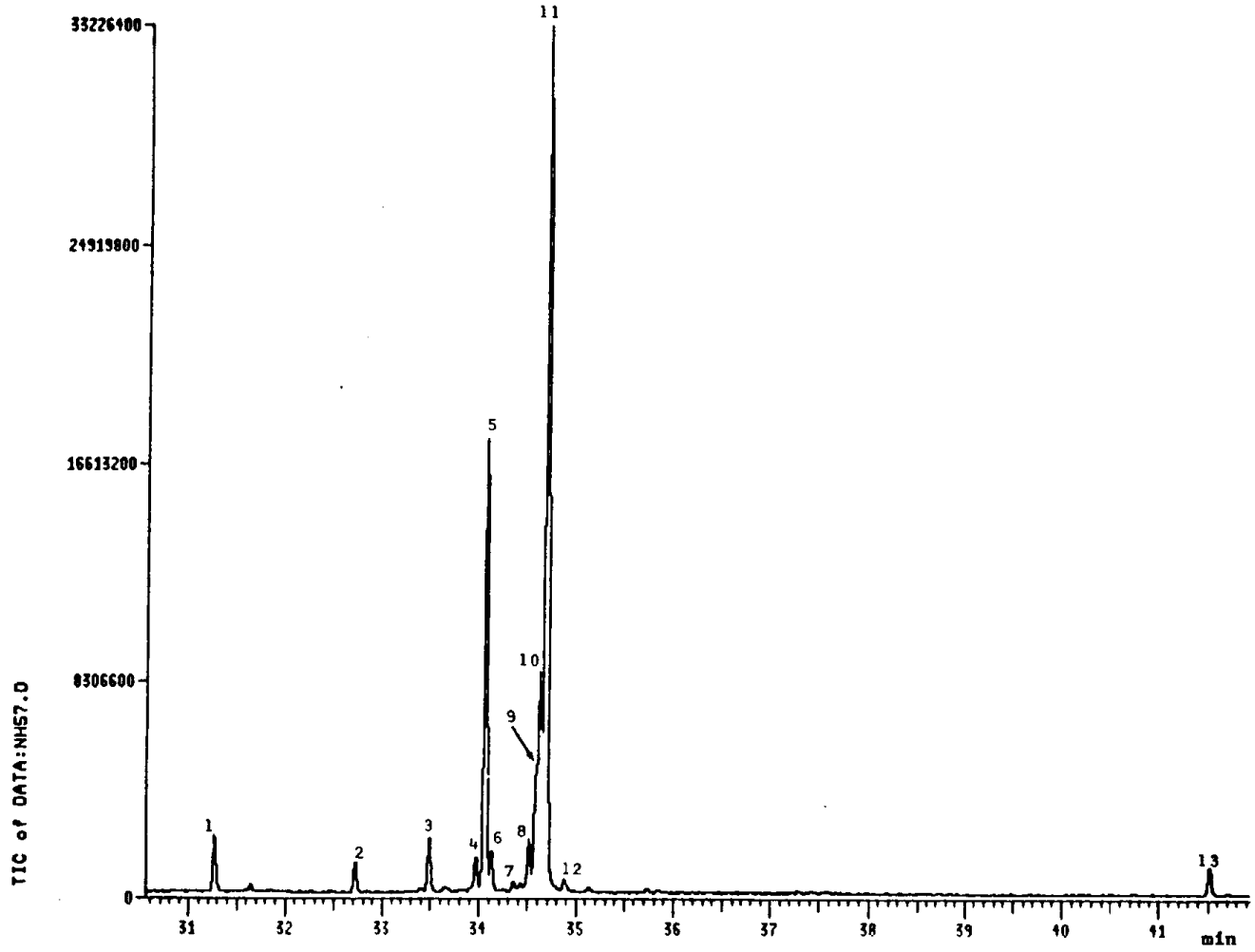

Figure V-52. TIC from GC/MS analysis of 7.4 ℓ Tenax sample of fresh market tomato (Sunny) emissions (NH-57). Identities of numbered peaks given in Table V-52.

Table V-55. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Fresh Market Tomato (Sunny) - 1989 June 27

Assigned Peaks[a]	NH-78A 0900	NH-78B 1030	NH-78C 1200	NH-78D 1330	NH-78E 1445	Identification
1	d	d	d	d	d	p-xylene
2	108	144	160	351	64	α-pinene
3	124	251	141	344	46	unknown (m.w. 134)
4,5,6	1,194	2,565	1,463	4,010	471	unknown terpene (m.w. 136), 2-carene, and α-phellandrene
7→11	3,058[p]	4,744[p]	3,752	8,773[p]	1,211	α-terpinene, p-cymene, unknown terpene (m.w. 136) d-limonene and β-phellandrene
13	12	33	18	49	5	β-caryophyllene
toluene[g]	20	19	<2	3	2	
ΣC_6[a]	14	12	c	c	c	
Σ(Assigned Peaks)[h]	4,496	7,737	5,534	13,527	1,797	
ΣMonoterpenes	4,360	7,453	5,375	13,134	1,746	
ΣSesquiterpenes	12	33	18	49	5	
$\Sigma C_7 \rightarrow C_{15}$[i]	4,757	8,146	5,886	14,199	2,182	
$-C_5$[j]	3	3	5	4	2	
$\Sigma C_3 \rightarrow C_5$[k]	24	27	29	41	39	
Total Plant Emissions[l]	4,496	7,737	5,534	13,527	1,797	
Total Carbon[m]	4,781	8,172	5,915	14,240	2,221	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-53. The numbers correspond to the GC/MS identifications as given on Figure V-52 and in Table V-54.
[b-t]Footnotes given on Table V-73.

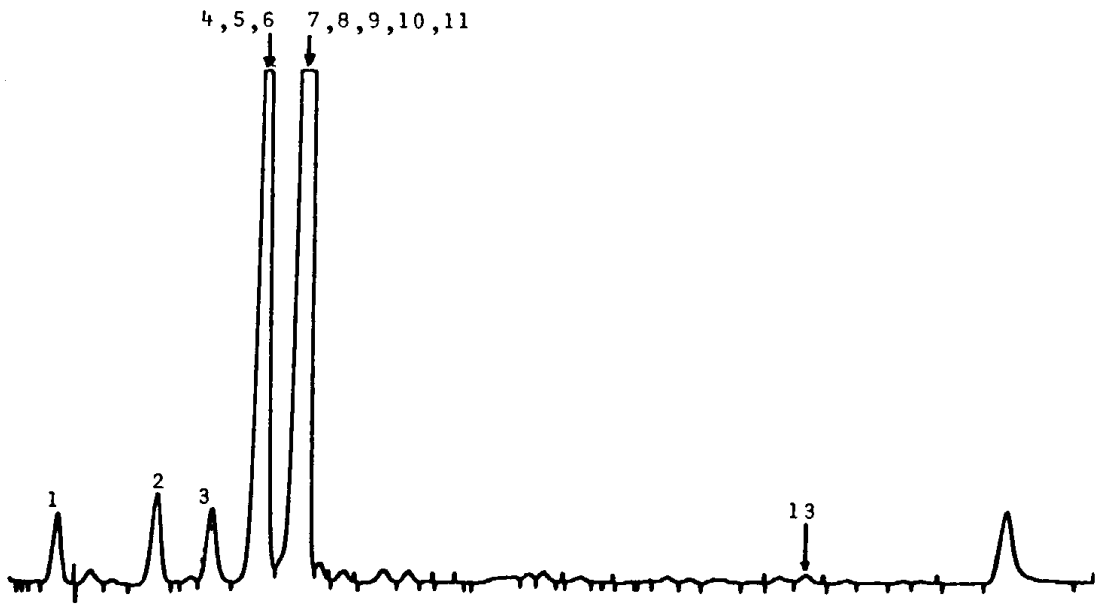

Figure V-53. GC-FID analysis of 530 mℓ Tenax sample of fresh market tomato (Sunny) emissions (NH-78C). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-54.

Table V-56. Emissions Identified from Processing Tomato (6203 Canning Tomato) by GC/MS Analysis of Survey Sample NH-64 (TIC Shown in Figure V-54)

Peak No.	Compound Identification[a]
1	unknown (m.w. 100)
2	n-hexanal
3	cis-3-hexen-1-ol
4	p-xylene (internal standard)
5	α-pinene
6	unknown (m.w. 134)
7	2-carene
8	α-phellandrene
9	α-terpinene
10	p-cymene
11	d-limonene
12	β-phellandrene
13	unknown (m.w. 134)
14	γ-terpinene
15	terpinolene
16	β-caryophyllene
17	α-humulene

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.

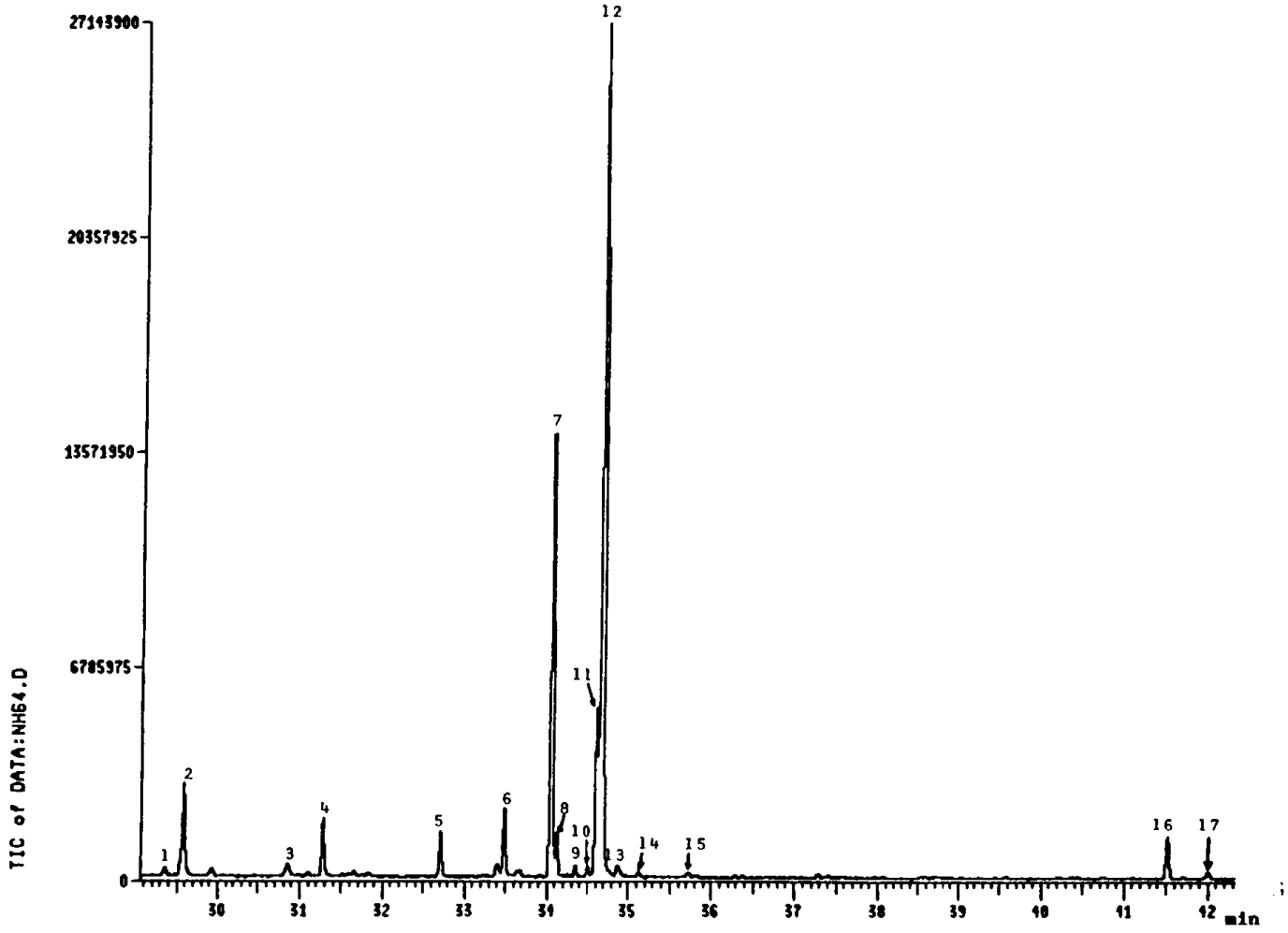

Figure V-54. TIC from GC/MS analysis of 5.1 ℓ Tenax sample of processing tomato (6203) emissions (NH-64). Identities of numbered peaks given in Table V-56.

Table V-57. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Processing Tomato (#6203 Canning) - 1989 July 6

Assigned Peaks[a]	NH-82A 0900	NH-82B 1030	NH-82C 1200	NH-82D 1330	NH-82E 1445	Identification
2[b]	75	36	16	15	15	n-hexanal
4	d	d	d	d	d	p-xylene
5	177	59	23	28	29	α-pinene
6	252	78	26	32	27	unknown (m.w. 134)
7,8	2,124	735	256	277	269	2-carene, α-phellandrene,
9,10,11,12	5,638	2,099	696	809	740	α-terpinene, p-cymene, d-limonene, and β-phellandrene
13[b]	17	23	10	9	13	unknown (m.w. 134)
14	15	13	6	5	7	γ-terpinene
15	44	17	10	5	11	terpinolene
16	13	10	n.d.[f]	n.d.	n.d.	β-caryophyllene
17[b]	8	12	10	6	10	α-humulene
toluene[g]	28	8	8	6	4	
ΣC_6[e]	27	19	12	15	17	
Σ(Assigned Peaks)[h]	8,363	3,082	1,052	1,186	1,121	
ΣMonoterpenes	7,998	2,923	991	1,124	1,056	
ΣSesquiterpenes	21	22	10	6	10	
$\Sigma C_7 \rightarrow C_{15}$[i]	8,660	3,302	1,264	1,453	1,470	
C_5[j]	10	2	1	2	c	
$\Sigma C_3 \rightarrow C_5$[k]	63	28	16	15	c	
Total Plant Emissions[l]	8,363	3,082	1,052	1,186	1,121	
Total Carbon[m]	8,723	3,330	1,280	1,468	1,470[o]	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-55. The numbers correspond to the GC/MS identifications as given on Figure V-54 and in Table V-56.
[b-t]Footnotes given on Table V-73.

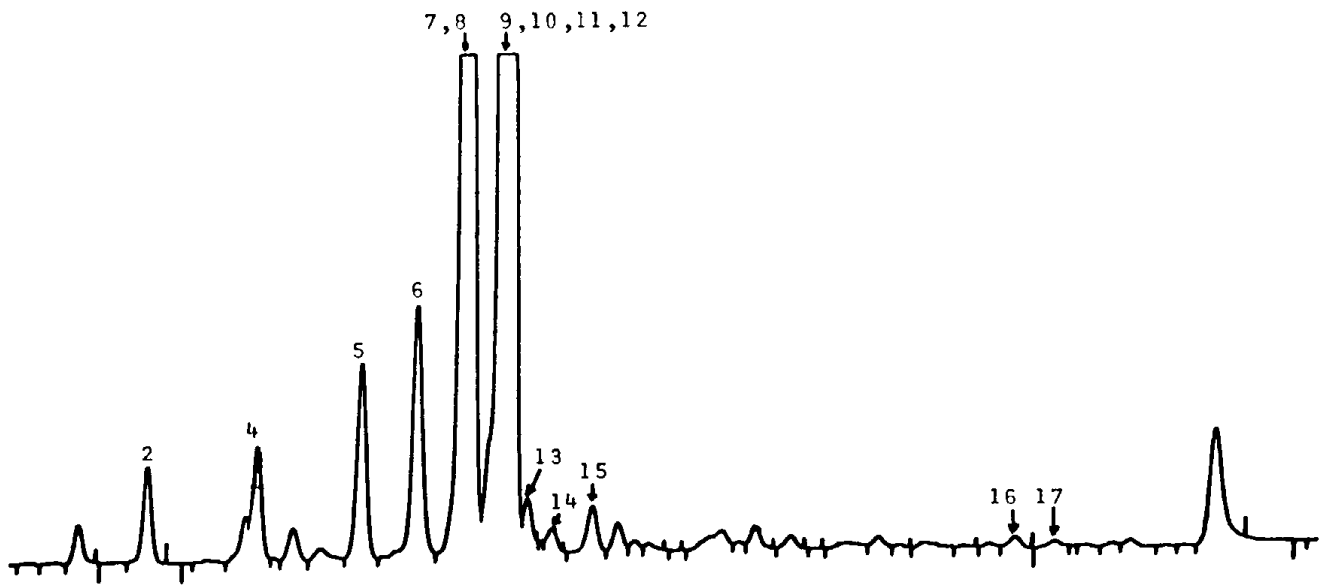

Figure V-55. GC-FID analysis of 520 mℓ Tenax sample of processing tomato (6203) emissions (NH-82A). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-56.

Table V-58. Emissions Identified from English Walnut (Hartley) by GC/MS Analysis of Survey Sample NH-88 (TIC Shown in Figure V-56)

Peak No.	Compound Identification[a]
1	unknown (m.w. 100)
2	n-hexanal
3	cis-3-hexen-1-ol
4	p-xylene (internal standard)
5	α-pinene
6	camphene
7	unknown (m.w. 134)
8	sabinene
9	β-pinene + myrcene
10	3-hexenylacetate
11	p-cymene
12	d-limonene
13	1,8-cineole
14	trans-ocimene[b]
15	unknown
16	unknown
17	pinocarvone (tentative)
18	1-dodecene
19	bornyl acetate
20	1-tetradecene
21	unknown sesquiterpene (m.w. 204)
22	β-caryophyllene
23	unknown sesquiterpene (m.w. 204)
24	1-hexadecene (tentative)
25	unknown

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.
[b]See footnote c on Table V-3.

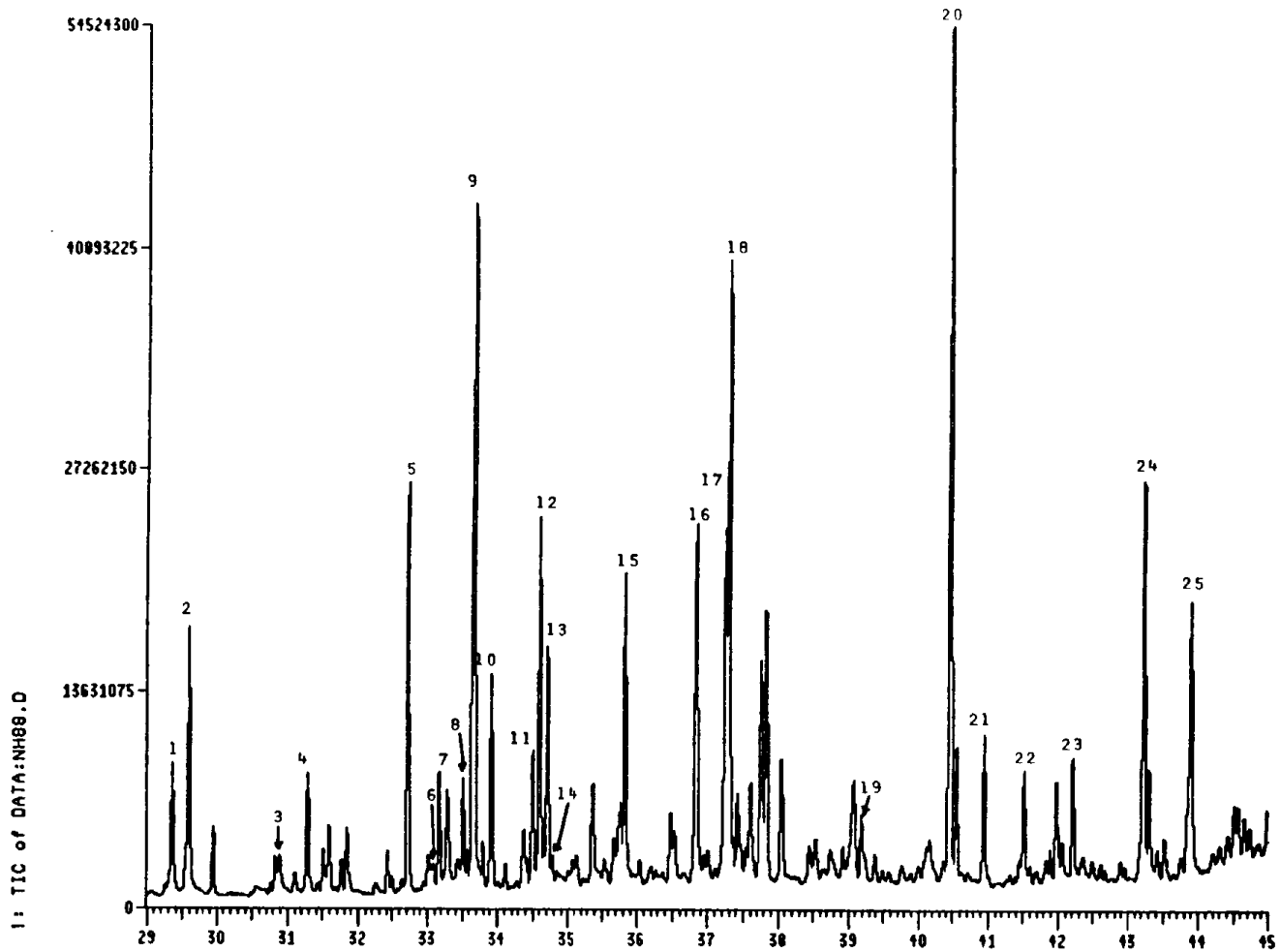

Figure V-56. TIC from GC/MS analysis of 6.4 ℓ Tenax sample of English walnut (Hartley) emissions (NH-88). Identities of numbered peaks given in Table V-58.

Table V-59. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for English Walnut (Hartley) - 1989 July 21

Assigned Peaks[a]	NH-91A 0900	NH-91B 1030	NH-91C 1200	NH-91D 1330	NH-91E 1445	Identification
3	23	4	7	n.d.[f]	14	cis-3-hexen-1-ol
4	d	d	d	d	d	p-xylene
5	40	39	47	21	52	α-pinene
6	2	2	2	1	3	camphene
7	5	3	4	3	5	unknown (m.w. 134)
8,9	65	63	83	33	91	sabinene and β-pinene
9	9	10	10	9	9	myrcene
10	29	8	14	3	20	3-hexenylacetate
11,12,13	17	13	22	11	25	p-cymene, d-limonene, 1,8-cineole
14	2	n.d.	<1	<1	<1	trans-ocimene
15[b]	10	9	15	11	16	unknown
16[b]	10	11	16	11	21	unknown
17[b]	6	6	11	5	16	pinocarvone (tentative)
18	17	23	32	22	29	1-dodecene
20,21	9	15	30	19	22	1-tetradecene and unknown sesquiterpene (m.w. 204)
22	3	2	4	2	5	β-caryophyllene
24	c	c	4	c	9	unknown sesquiterpene (m.w. 204)
toluene[g]	5	3	2	1	1	
ΣC_6[s]	8	7	9	10	23	
Σ(Assigned Peaks)[h]	264	208	298	152	329	
ΣMonoterpenes	135	127	165	76	181	
ΣSesquiterpenes	3	2	8	2	14	
ΣC_7-C_{15}[i]	326	274	379	233	424	
C_5[j]	<1	1	<1	2	2	
ΣC_3-C_5[k]	23	22	20	29	32	
Total Plant Emissions[l]	264	208	298	152	329	
Total Carbon[m]	349	296	399	262	456	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-57. The numbers correspond to the GC/MS identifications as given on Figure V-56 and in Table V-58.
[b-t]Footnotes given on Table V-73.

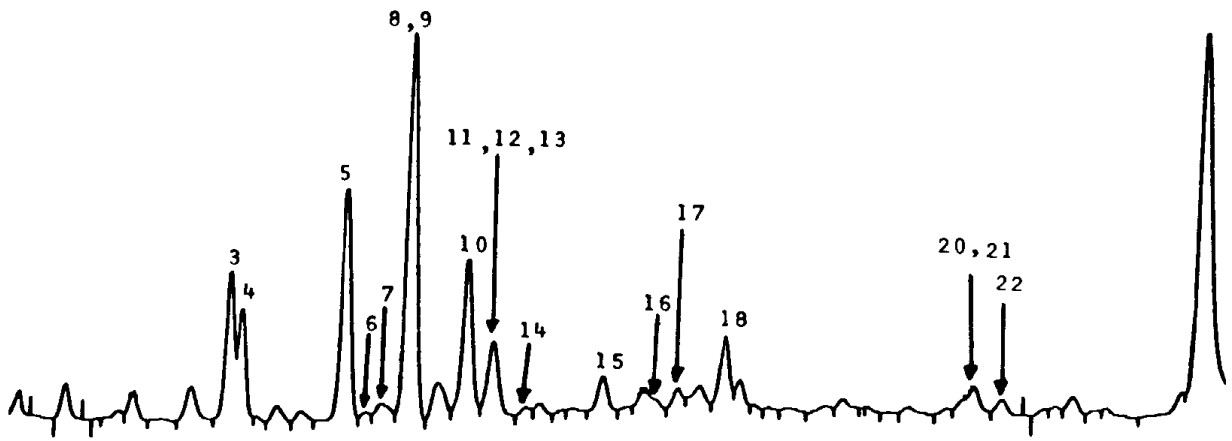

Figure V-57. GC-FID analysis of 1.3 ℓ Tenax sample of English walnut (Hartley) emissions (NH-91A). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-58.

Table V-60. Emissions Identified from Wheat (Yecorro Rojo) by GC/MS Analysis of Survey Sample NH-72 (TIC Shown in Figure V-58)

Peak No.	Compound Identification[a]
1	unknown (m.w. 84)
2	hexane
3	unknown (m.w. 98)
4	n-hexanal
5	p-xylene (internal standard)
6	unknown (m.w. 170)
7	1-dodecene
8	n-tridecane
9	1-tetradecene

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.

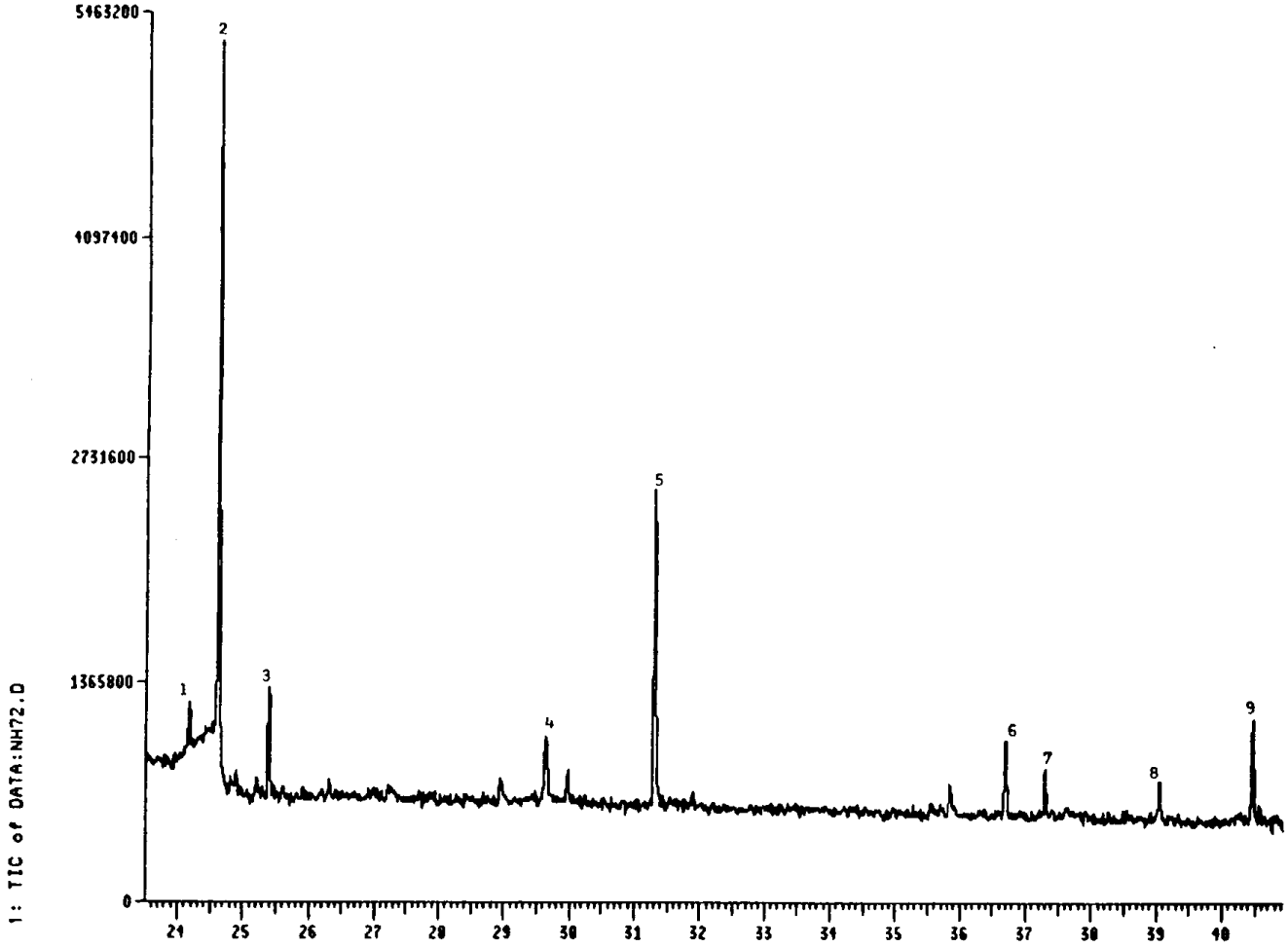

Figure V-58. TIC from GC/MS analysis of 700 mℓ Tenax/Carbosieve sample of wheat (Yecorro Rojo) emissions (NH-72). Identities of numbered peaks given in Table V-60.

Table V-61. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Wheat (Yecorro Rojo) - 1989 May 25

Assigned Peaks[a]	NH-47A 0900	NH-47B 1030	NH-47C 1200	NH-47D 1330	NH-47E 1445	Identification
4[b]	10	17	17	32	18	n-hexanal
5	d	d	d	d	d	p-xylene
6[b]	5	22	13	29	22	unknown (m.w. 170)
7	5	12	11	30	12	1-dodecene
8	3	5	7	20	5	n-tridecane
9	4	13	13	39	13	1-tetradecene
toluene[g]	<1	2	<1	2	2	
Σ(Assigned Peaks)[h]	27	69	61	150	70	
ΣMonoterpenes	n.d.[f]	n.d.	n.d.	n.d.	n.d.	
ΣSesquiterpenes	n.d.	n.d.	n.d.	n.d.	n.d.	
$\Sigma C_7 \rightarrow C_{15}$[i]	82	215	187	325	194	
C_5[j]	3	4	3	4	1	
$\Sigma C_3 \rightarrow C_5$[r]	219	398	439	668	489	
$\Sigma C_3 \rightarrow C_6$[t]	120	154	234	374	c	
Total Plant Emissions[l]	27	69	61	150	70	
Total Carbon[m]	301	613	626	993	683	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-59. The numbers correspond to the GC/MS identifications as given on Figure V-58 and in Table V-60.
[b-t]Footnotes given on Table V-73.

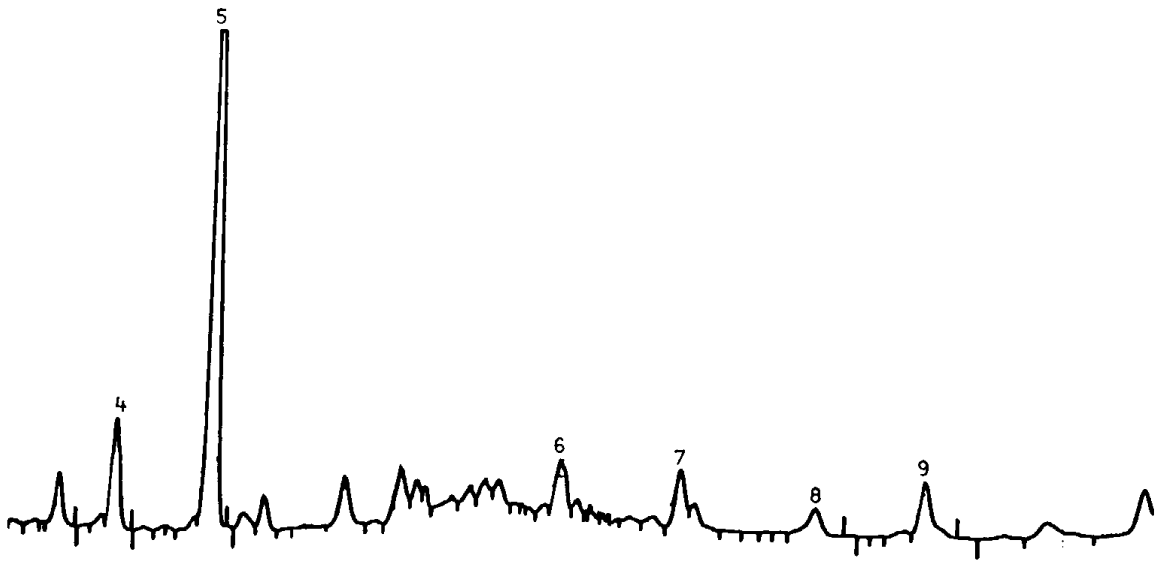

Figure V-59. GC-FID analysis of 1.3 ℓ Tenax sample of wheat (Yecorro Rojo) emissions (NH-47C). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-60.

Table V-62. Emissions Identified from Chamise by GC/MS Analysis of Survey Sample NH-41 (TIC Shown in Figure V-60)

Peak No.	Compound Identification[a]
1	unknown (m.w. 100)
2	n-hexanal
3	trans-2-hexenal
4	p-xylene (internal standard)
5	α-pinene
6	camphene
7	1-decene
8	myrcene
9	3-hexenylacetate
10	α-phellandrene
11	p-methylanisole (tentative)
12	p-cymene
13	d-limonene
14	β-phellandrene
15	unknown
16	unknown (m.w. 150)
17	2-methyl-6-methylene-1,7-octadien-3-one (tentative)
18	1,4-dimethoxybenzene (tentative)
19	1-dodecene
20	unknown
21	estragole (tentative)
22	1-tetradecene

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.

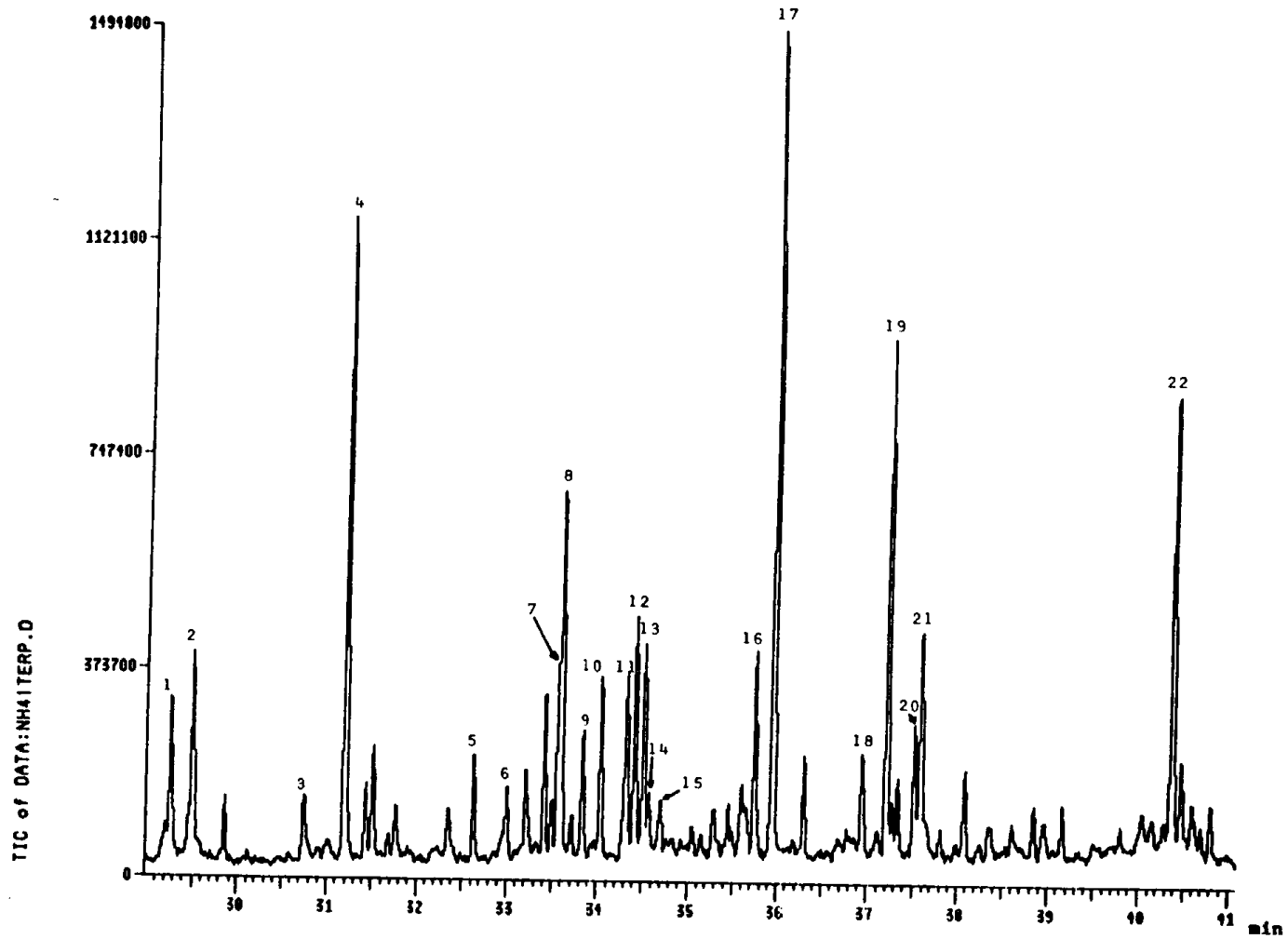

Figure V-60. TIC from GC/MS analysis of 8.5 ℓ Tenax sample of chamise emissions (sample NH-41). Identities of numbered peaks given in Table V-62.

Table V-63. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Chamise - 1989 May 30

Assigned Peaks[a]	NH-49A 0900	NH-49B 1030	NH-49C 1200	NH-49D 1330	NH-49E 1445	Identification
2[b]	31	13	8	12	11	n-hexanal
3[b]	c	c	2	6	9	trans-2-hexenal
4	d	d	d	d	d	p-xylene
5	6	10	7	7	7	α-pinene
6	1	n.d.[f]	n.d.	7	1	camphene
7,8	14	12	9	10	10	1-decene and myrcene
9,10	71	18	18	25	18	3-hexenylacetate and α-phellandrene
12,13,14	n.d.	9	3	5	2	p-cymene, d-limonene and β-phellandrene
16[b]	4	4	2	5	2	unknown (m.w. 150)
17[b]	6	6	6	6	5	2-methyl-6-methylene-1,7-octadien-3-one (tentative)
19	6	9	12	9	13	1-dodecene
22[b]	2	4	5	7	9	1-tetradecene
toluene[g]	2	2	2	7	1	
Σ(Assigned Peaks)[h]	141	85	72	99	87	
ΣMonoterpenes	21	31	19	29	20	
ΣSesquiterpenes	n.d.	n.d.	n.d.	n.d.	n.d.	
$\Sigma C_7 \rightarrow C_{15}$[i]	175	142	94	157	128	
C_5[j]	1	2	5	2	4	
$\Sigma C_3 \rightarrow C_5$[k]	48	43	83	44	57	
$\Sigma C_3 \rightarrow C_6$[t]	65	39	52	85	56	
Total Plant Emissions[l]	141	85	72	99	87	
Total Carbon[m]	223	185	177	201	185	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-61. The numbers correspond to the GC/MS identifications as given on Figure V-60 and in Table V-62.
[b-t]Footnotes given on Table V-73.

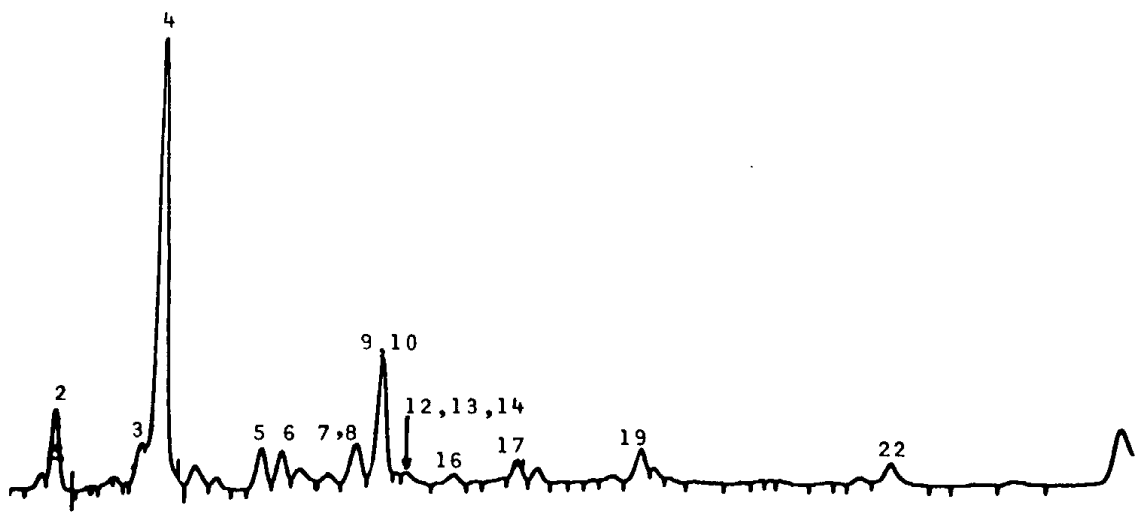

Figure V-61. GC-FID analysis of 1.3 ℓ Tenax/Carbosieve sample of chamise emissions (NH-49D). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-62.

Table V-64. Emissions Identified from Annual Grassland by GC/MS Analysis of Survey Sample NH-42 (TIC Shown in Figure V-62)

Peak No.	Compound Identification[a]
1	unknown (m.w. 100)
2	n-hexanal
3	p-xylene (internal standard)
4	α-pinene
5	β-pinene
6	d-limonene
7	terpinolene
8	unknown
9	1-dodecene
10	n-dodecane
11	unknown
12	1-tetradecene

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.

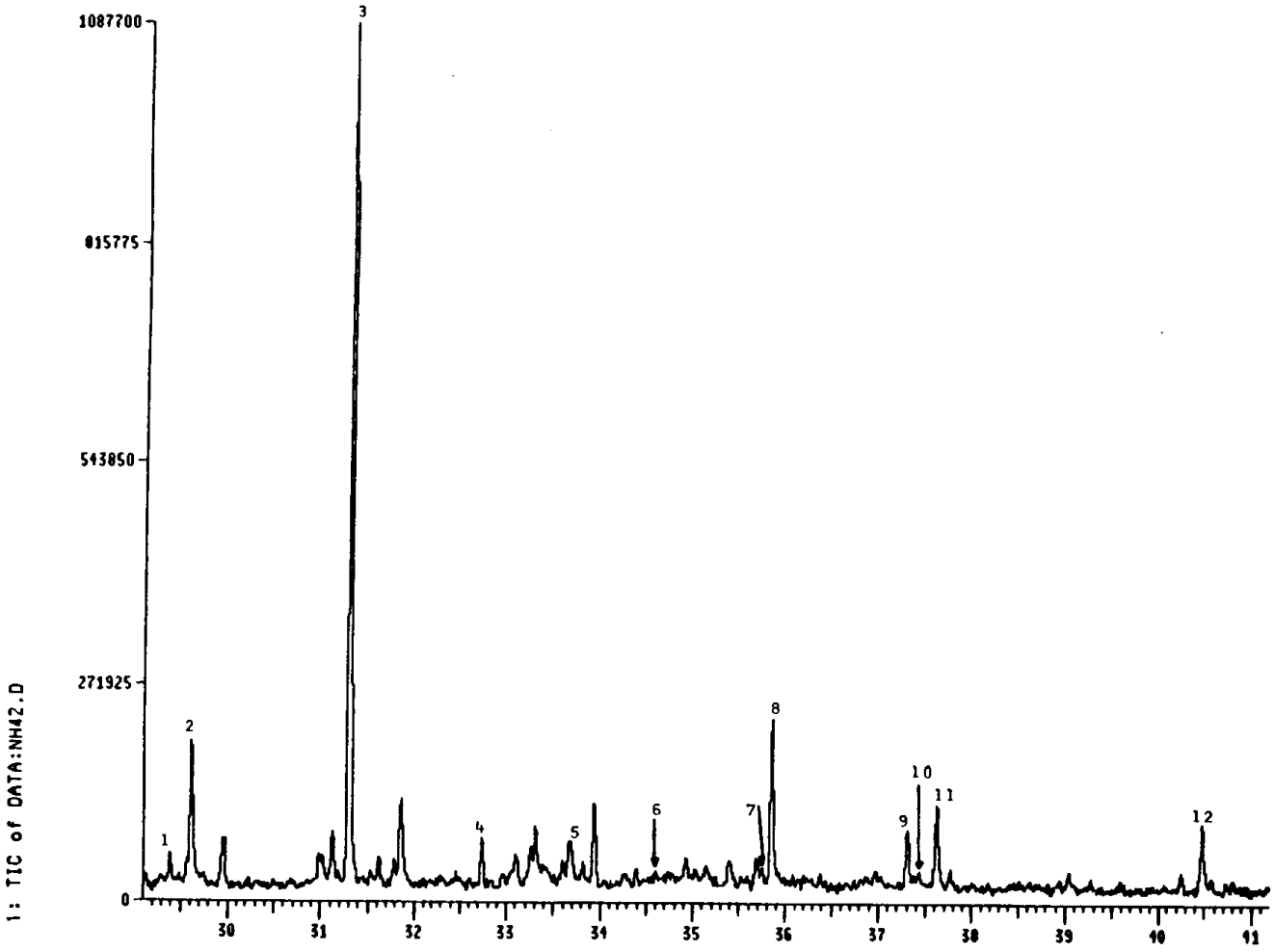

Figure V-62. TIC from GC/MS analysis of 2.5 ℓ Tenax sample of annual grasslands emissions (NH-42). Identities of numbered peaks given in Table V-64.

Table V-65. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Annual Grasslands - 1989 June 2

Assigned Peaks[a]	NH-51A 0900	NH-51B 1030	NH-51C 1200	NH-51D 1330	NH-51E 1445	Identification
1,2	3	n.d.[f]	7	8	7	unknown (m.w. 100) and n-hexanal
3	d	d	d	d	d	p-xylene
5	n.d.	n.d.	1	1	1	β-pinene
6	n.d.	n.d.	3	1	1	d-limonene
8[b]	2	1	4	5	5	unknown
9	n.d.	n.d.	3	4	3	1-dodecene
10,11	1	<1	3	4	4	n-dodecane and unknown
12	n.d.	n.d.	2	3	3	1-tetradecene
toluene[g]	1	n.d.	<1	<1	1	
Σ(Assigned Peaks)[h]	6	2	23	26	24	
ΣMonoterpenes	n.d.	n.d.	4	2	2	
ΣSesquiterpenes	n.d.	n.d.	n.d.	n.d.	n.d.	
$\Sigma C_7 \rightarrow C_{15}$[i]	37	6	75	82	61	
C_5[j]	3	2	3	2	2	
$\Sigma C_3 \rightarrow C_5$[k]	60	51	120	121	97	
$\Sigma C_3 \rightarrow C_6$[t]	47	17	110	98	63	
Total Plant Emissions[l]	6	2	23	26	24	
Total Carbon[m]	97	57	175	203	158	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-63. The numbers correspond to the GC/MS identifications as given on Figure V-62 and in Table V-64.
[b-t]Footnotes given on Table V-73.

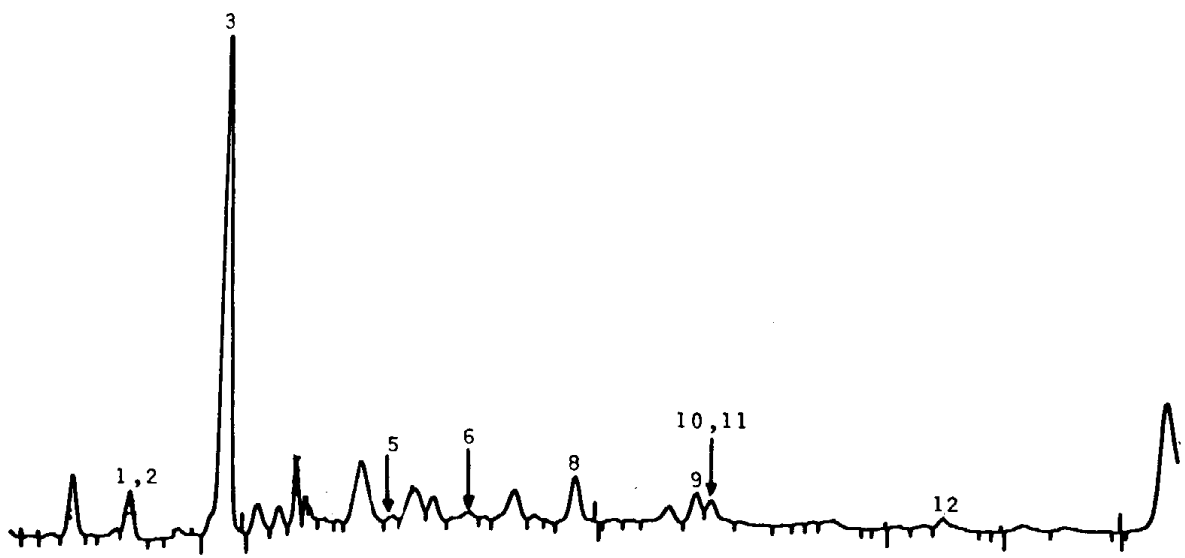

Figure V-63. GC-FID analysis of 1.4 ℓ Tenax/Carbosieve sample of annual grasslands emissions (NH-51C). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-64.

Table V-66. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Bigberry Manzanita - 1989 May 19

Assigned Peaks[a]	NH-45A 0900	NH-45B 1030	NH-45C 1200	NH-45D 1330	NH-45E 1445	Tentative Identification[a]
1	d	d	d	d	d	p-xylene
2	7	20	13	47	6	3-hexenylacetate
3	3	4	8	18	17	1-dodecene
4	3	2	2	3	1	n-dodecane
toluene[g]	c	n.d.[f]	<1	n.d.	<1	
Σ(Assigned Peaks)[h]	13	26	23	68	24	
$\Sigma C_7 \rightarrow C_{15}$[i]	57	102	85	176	83	
C_5[j]	<1	n.d.	n.d.	n.d.	n.d.	
$\Sigma C_3 \rightarrow C_5$[k]	72	79	58	99	50	
$\Sigma C_3 \rightarrow C_6$[t]	40	56	35	53	37	
Total Plant Emissions[l]	13	26	23	68	24	
Total Carbon[m]	129	181	143	275	133	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-64. Tentative identifications made by GC-FID analysis using retention time comparisons.
[b-t]Footnotes given on Table V-73.

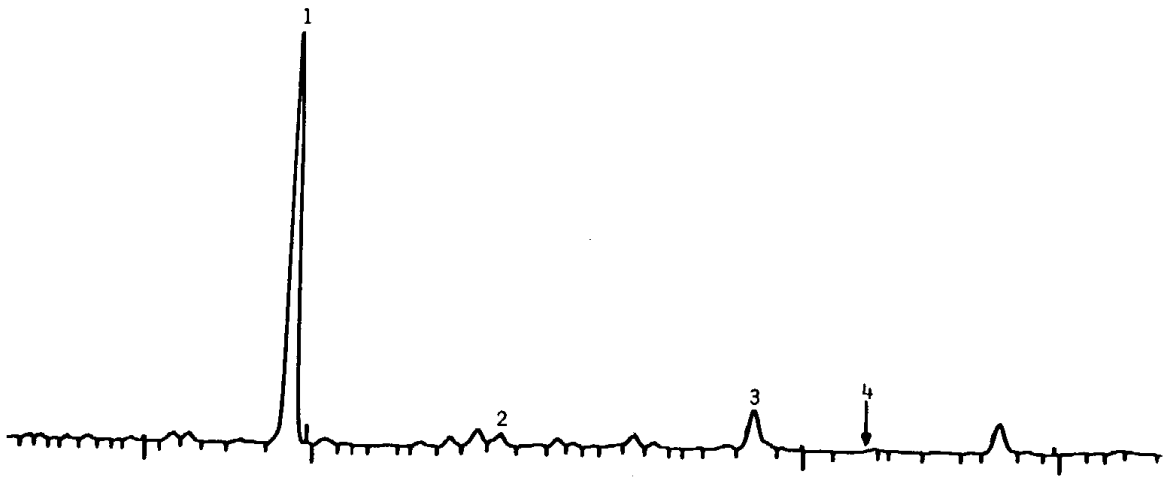

Figure V-64. GC-FID analysis of 1.4 ℓ Tenax/Carbosieve sample of Bigberry Manzanita emissions (NH-45E). Peak identities as indicated in Table V-66 have been assigned on the basis of GC-FID retention times.

Table V-67. Emissions Identified from Mountain Mahogany by GC/MS Analysis of Survey Sample NH-43 (TIC Shown in Figure V-65)

Peak No.	Compound Identification[a]
1	unknown (m.w. 100)
2	p-xylene (internal standard)
3	1-decene
4	n-decane
5	3-hexenylacetate
6	trans-ocimene[b]
7	terpinolene
8	1-dodecene
9	n-dodecane
10	1-tetradecene
11	n-tetradecane
12	n-pentadecane
13	n-hexadecane

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.
[b]See footnote c on Table V-3.

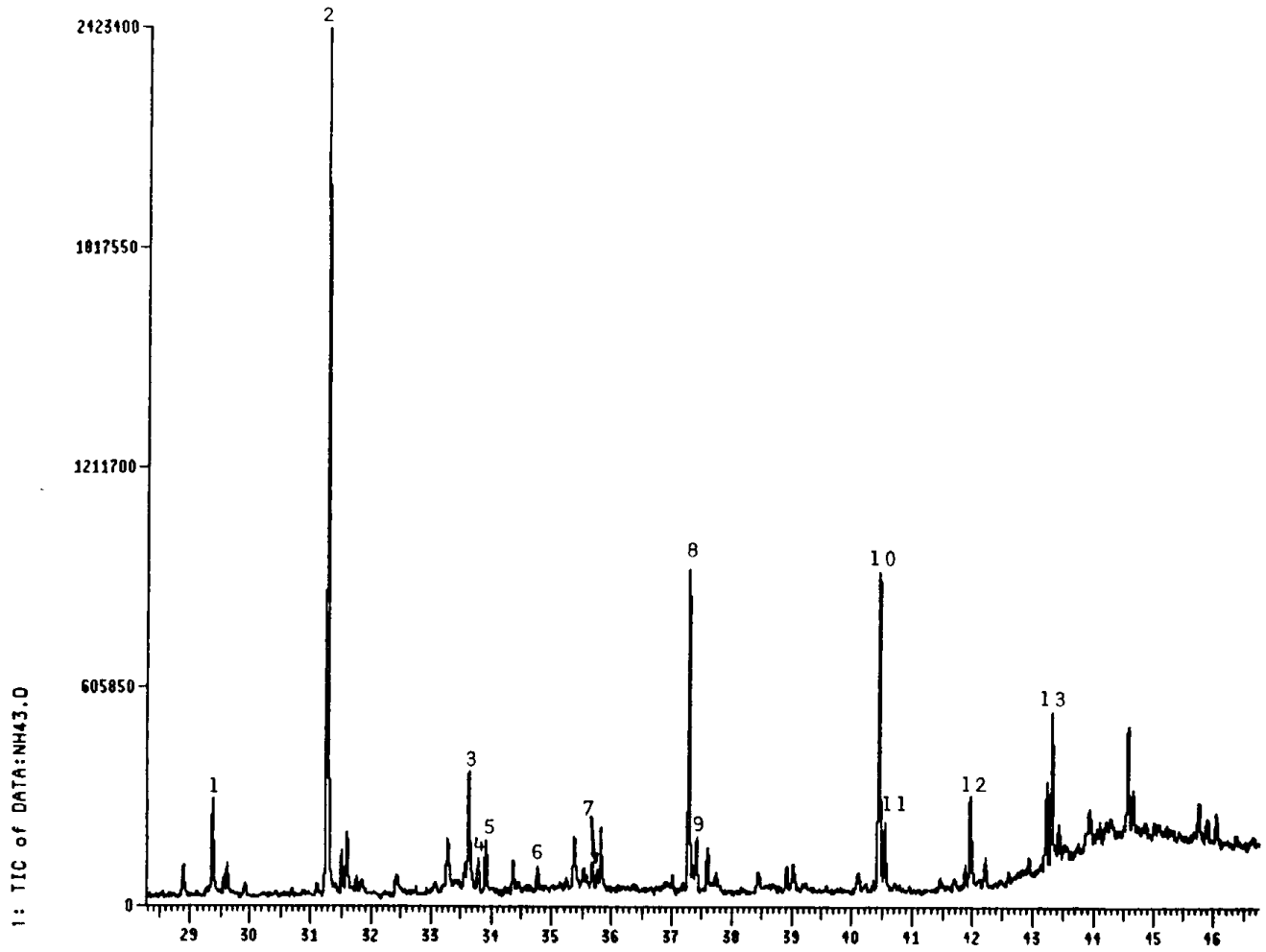

Figure V-65. TIC from GC/MS analysis of 3.9 ℓ Tenax sample of mountain mahogany emissions (NH-43). Identities of numbered peaks given in Table V-67.

Table V-68. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Mountain Mahogany - 1989 May 5

Assigned Peaks[a]	NH-43 1400	Identification
1[b]	9	unknown (m.w. 100)
2	d	p-xylene
3,4	8	1-decene, n-decane
5	2	3-hexenylacetate
6	3	trans-ocimene
8	12	1-dodecene
9	6	n-dodecane
10	7	1-tetradecene
toluene[g]	4	
Σ(Assigned Peaks)[h]	47	
ΣMonoterpenes	3	
ΣSesquiterpenes	n.d.[f]	
$\Sigma C_7 \rightarrow C_{15}$[i]	117	
C_5[j]	c	
$\Sigma C_3 \rightarrow C_6$[q]	93	
Total Plant Emissions[l]	47	
Total Carbon[m]	210	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-66. The numbers correspond to the GC/MS identifications as given on Figure V-65 and in Table V-67.
[b-t]Footnotes given on Table V-73.

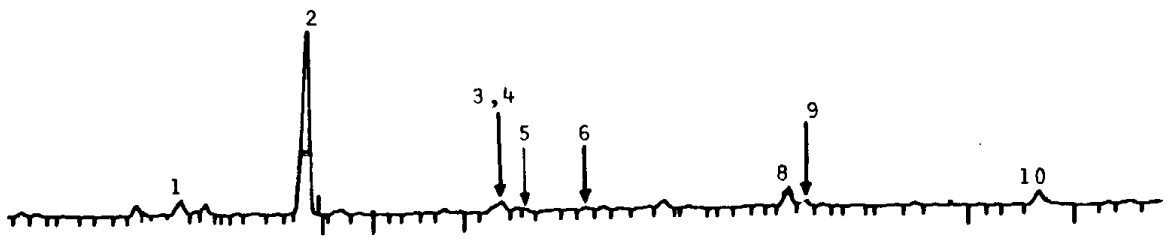

Figure V-66. GC-FID analysis of 1.3 ℓ Tenax/Carbosieve sample of mountain mahogany emissions (NH-43). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-67.

Table V-69. Emissions Identified from Valley Oak by GC/MS Analysis of Survey Samples NH-65 and NH-77E (TICs Shown in Figure V-67)

Peak No.	Compound Identification[a]
1	isoprene
2	cis-3-hexen-1-ol
3	p-xylene (internal standard)
4	α-pinene
5	3-hexenylacetate
6	trans-ocimene[b]
7	unknown
8	unknown
9	2-methyl-6-methylene-1,7-octadien-3-one (tentative)
10	1-dodecene
11	unknown (m.w. 154)

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.
[b]See footnote c on Table V-3.

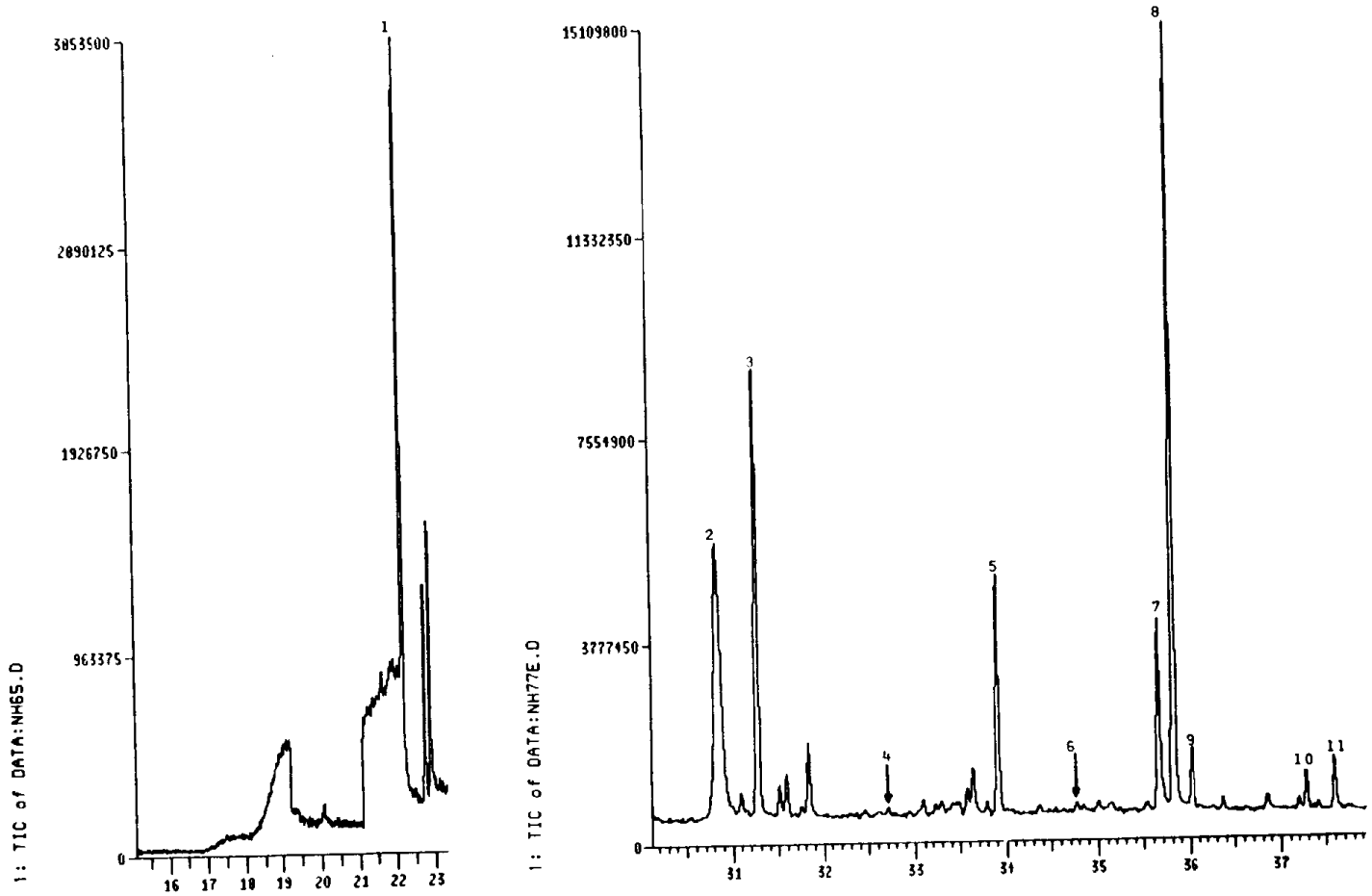

Figure V-67. TICs from GC/MS analyses of Valley oak emissions: 2.6 ℓ Tenax/Carbosieve sample shown at left (NH-65) and 5 ℓ Tenax sample shown at right (NH-77E). Identities of numbered peaks given in Table V-69.

Table V-70. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Valley Oak - 1989 June 23

Assigned Peaks[a]	NH-77A 0900	NH-77B 1030	NH-77C 1200	NH-77D 1330	NH-77E 1445	Identification
1	j	j	j	j	j	isoprene
2	68	61	16	n.a.	6	cis-3-hexen-1-ol
3	d	d	d	d	d	p-xylene
4	1	n.d.[f]	n.d.	<1	n.d.	α-pinene
5	34	n.a.	n.a.	13	n.d.	3-hexenylacetate
6	n.d.	<1	<1	2	<1	trans-ocimene
9	21	11	9	8	4	2-methyl-6-methylene-1,7-octadien-3-one (tentative)
10	6	8	8	4	5	1-dodecene
toluene[g]	2	2	1	1	c	
ΣC_6[s]	2	10	8	c	c	
Σ(Assigned Peaks)[h]	130	81	34	28	16	
ΣMonoterpenes	1	<1	<1	3	<1	
ΣSesquiterpenes	n.d.	n.d.	n.d.	n.d.	n.d.	
ΣC_7-C_{15}[i]	246	213	116	69	51	
C_5[j,w]	491	261	166	257	117	isoprene
ΣC_3-C_5[k]	535	281	188	273	133	
Total Plant Emissions[l]	621	342	200	285	133	
Total Carbon[m]	781	494	304	342	184	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-68 The numbers correspond to the GC/MS identifications as given on Figure V-67 and in Table V-69.

[b-t]Footnotes given on Table V-73.

[w]Isoprene was also quantified from 100 mℓ syringe samples analyzed with a 3 mℓ loop injection system on a 20 ft x 0.125 in. SS column of 5% DC 703/C20M on AW, DMCS, Chromosorb G(100/120 mesh), operated at 60°C. The FID was independently calibrated for isoprene. The following values were obtained for NH-77A thorugh NH-77E, respectively: 788, 315, 226, 394 and 124 ppbC isoprene.

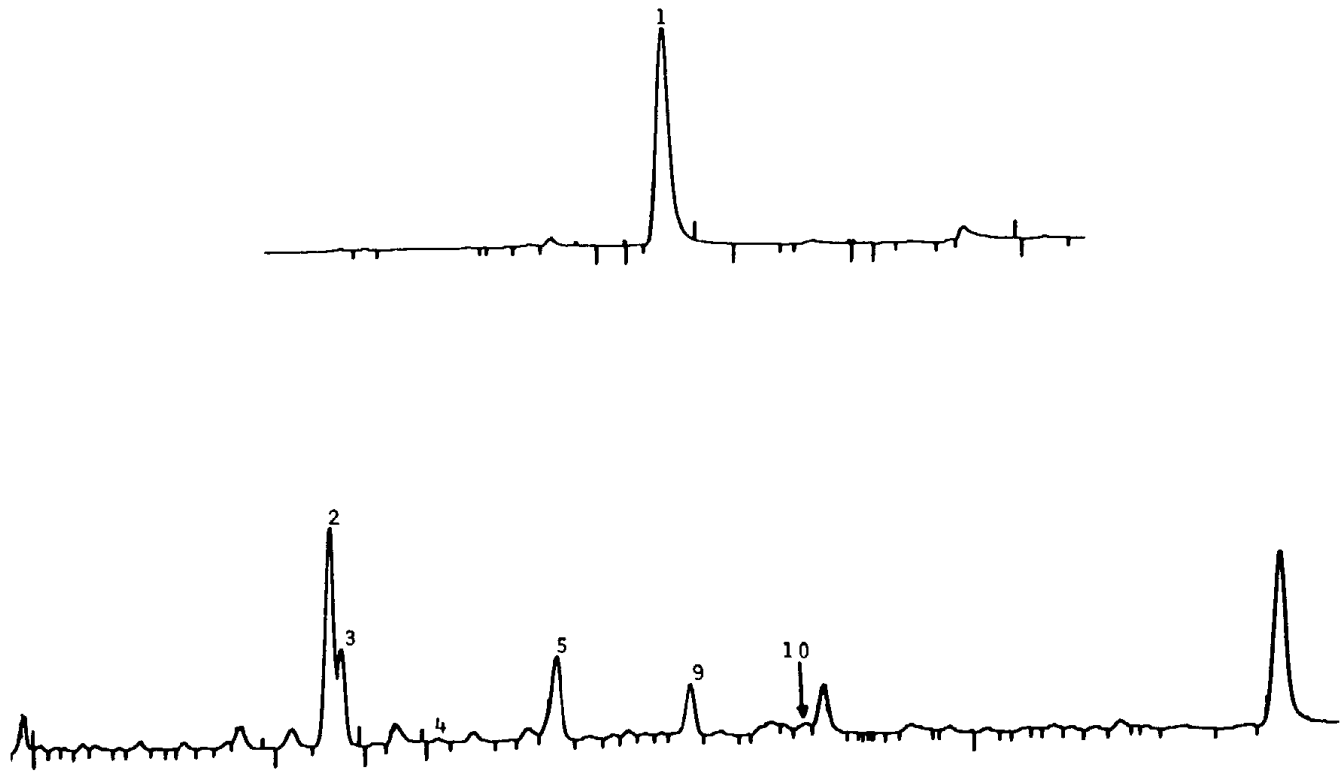

Figure V-68. GC-FID analyses of Valley oak emissions: 500 mℓ Tenax/Carbosieve sample analyzed on GS-Q column shown in upper chromatogram and 1.3 ℓ Tenax sample shown in lower chromatogram (NH-77A). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-69.

Table V-71. Emissions Identified from Whitethorn by GC/MS Analysis of Survey Sample NH-53 (TIC Shown in Figure V-69)

Peak No.	Compound Identification[a]
1	cis-3-hexen-1-ol
2	p-xylene (internal standard)
3	sabinene
4	myrcene
5	3-hexenylacetate
6	α-terpinene
7	d-limonene
8	trans-ocimene[b]
9	unknown (m.w. 150)
10	1-dodecene
11	β-caryophyllene
12,13	unknown sesquiterpenes (m.w. 204)

[a]Molecular weights given for unknowns indicate the presence of an apparent molecular ion.
[b]See footnote c on Table V-3.

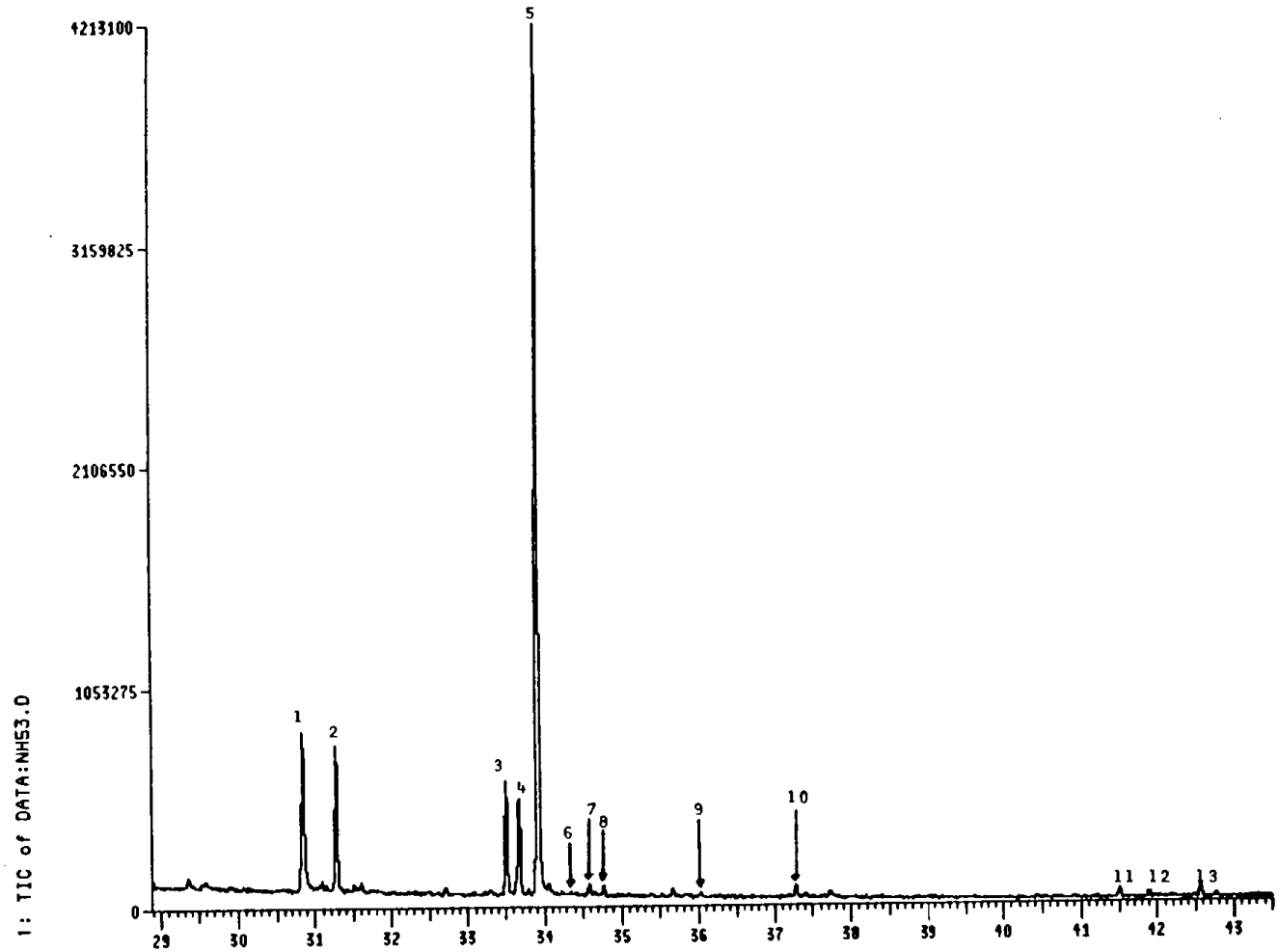

Figure V-69. TIC from GC/MS analysis of 5.3 ℓ Tenax sample of whitethorn emissions (NH-53). Identities of numbered peaks given in Table V-71.

Table V-72. Concentration Data for Assigned GC Peaks (ppbC) and Total Carbon (ppbC) for Whitethorn - 1989 June 1

Assigned Peaks[a]	NH-50A 0900	NH-50B 1030	NH-50C 1200	NH-50D 1330	NH-50E 1445	Identification
1	n.d.[f]	16	c	n.d.	4	cis-3-hexen-1-ol
2	d	d	d	d	d	p-xylene
3	6	30	58	126	46	sabinene
4	6	31	52	121	45	myrcene
5	41	124	76	118	35	3-hexenylacetate
6,7	2	6	10	24	9	α-terpinene + d-limonene
8	<1	3	3	9	9	trans-ocimene
9[b]	3	4	8	14	14	unknown (m.w. 150)
10	12	37	33	117	31	1-dodecene
11	n.d.	1	2	5	2	β-caryophyllene
12	n.d.	n.d.	<1	2	1	unknown sesquiterpene (m.w. 204)
13	n.d.	1	5	6	7	unknown sesquiterpene (m.w. 204)
toluene[g]	4	3	3	5	2	
Σ(Assigned Peaks)[h]	71	253	248	542	203	
ΣMonoterpenes	15	70	123	280	109	
ΣSesquiterpenes	n.d.	2	8	13	10	
$\Sigma C_7 \rightarrow C_{15}$[i]	100	287	304	605	265	
C_5[j]	<1	1	2	2	1	
$\Sigma C_3 \rightarrow C_5$[k]	56	61	51	70	61	
$\Sigma C_3 \rightarrow C_6$[t]	64	66	72	72	59	
Total Plant Emissions[l]	71	253	248	542	203	
Total Carbon[m]	156	348	355	675	326	

[a]Assigned peaks from GC-FID analyses as shown in Figure V-70. The numbers correspond to the GC/MS identifications as given on Figure V-69 and in Table V-71.
[b-t]Footnotes given on Table V-73.

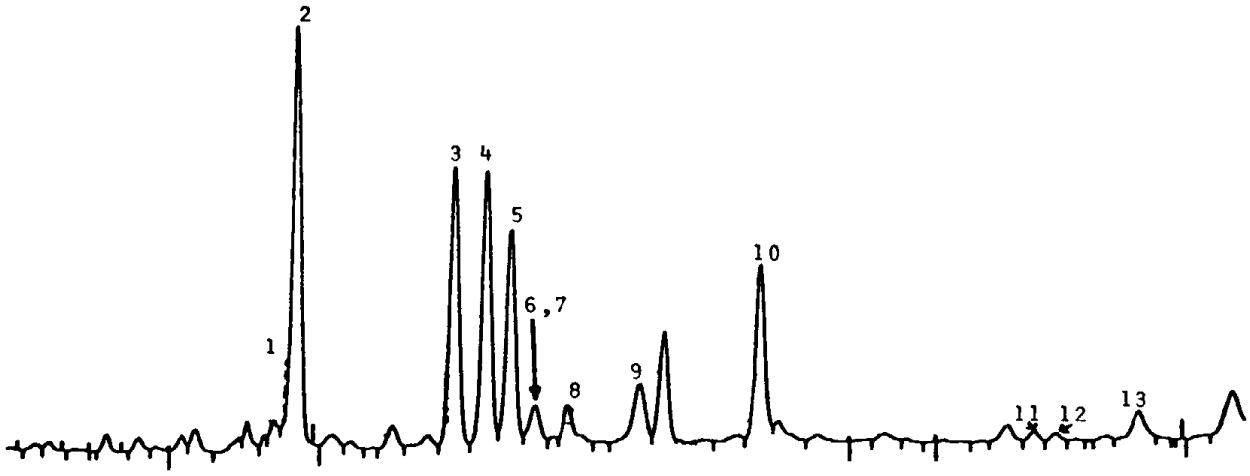

Figure V-70. GC-FID analysis of 1.4 ℓ Tenax/Carbosieve sample of whitethorn emissions (NH-50E). The assigned peaks have been numbered to correspond to the GC/MS identifications given in Table V-71.

Table V-73. Footnotes for Concentration Data Tables

[b]Tentative identification of GC-FID peak with GC/MS peak.
[c]No data.
[d]p-Xylene or 1,2,4-trimethylbenzene was added to each sample to serve as an internal retention time marker.
[e]n.a. = not assigned.
[f]n.d. = none detected.
[g]Toluene is considered to be an anthropogenic emission and is listed to show the magnitude of anthropogenics remaining in the sampling chamber.
[h]Total ppbC of the peaks assigned as plant emissions from the GC-FID analyses on the DB-5 column ($C_7 \rightarrow C_{15}$ and C_6-alcohol and C_6-aldehydes).
[i]Summation of all peaks after toluene and through the sesquiterpene region of the GC-FID chromatogram on the DB-5 column, i.e., roughly all C_7 through C_{15} hydrocarbons (excluding the trimethylbenzene or p-xylene marker) and including C_6-alcohol and C_6-aldehydes.
[j]C_5 = Isoprene or n-pentane from the GC-FID analyses on the GS-Q column. Some n-pentane was observed in the pure air blanks. If this peak was large, as for the Valley oak sample, GC/MS analysis was used to confirm the presence of isoprene.
[k]Total ppbC for the volatile $C_3 \rightarrow C_5$ species observed on the GS-Q column, with the exception of the acetone peak which was present in the pure air blanks.
[l]Total plant emissions is the sum of the ppbC given as assigned peaks and any confirmed isoprene.
[m]Summation of all peaks on the DB-5 column after toluene and through the sesquiterpene region of the chromatogram and the total ppbC for the volatile species observed on the GS-Q column (when the GS-Q column was not used, the volatile species as noted in footnote q below were added). Represents an upper limit to the plant emissions.
[n]β-Pinene and myrcene were not resolved in the GC/MS analyses, but were resolved in the GC-FID analyses.
[o]Volatile $C_3 \rightarrow C_5$ not included since no data available from GS-Q column for this sample.
[p]Integrator gave over-scale code.
[q]The GS-Q column was not used the first summer data was collected. Given is the total ppbC for the volatile species observed on the DB-5 column, using the factor for converting GC peak area to ppbC that has been used for all the data obtained from the DB-5 column. It is estimated that this area represents the $C_3 \rightarrow C_6$ species, excluding toluene and the 2,2-dimethylbutane added as a retention time marker. Unlike the data from the GS-Q column, certain components present in the pure air blanks, such as acetone, would be included in the total ppbC calculated.
[r]Total ppbC for the volatile $C_3 \rightarrow C_5$ species observed on the GS-Q column, including the acetone peak which was significantly larger than in the pure air blanks.
[s]An upper limit to the n-hexane plus benzene, i.e., the sum of the largest peak eluting within the expected retention time window for n-hexane plus the largest peak within the expected retention time window for benzene, or if several similar sized peaks were present, their sum.
[t]Total ppbC for the volatile $C_3 \rightarrow C_6$ species observed on the DB-5 column as noted in footnote q above.