

AN ABSTRACT OF THE THESIS OF

Laurel J. Standley for the degree of Doctor of Philosophy in Oceanography presented on June 12, 1987.

Title: Determination of Molecular Signatures of Natural and Thermogenic Products in Tropospheric Aerosols - Input and Transport

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Abstract approved:

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A chemotaxonomic study of natural compounds and their thermally altered products in rural and smoke aerosols within Oregon is presented. Correlation with source vegetation provided information on the formation of aerosols and their transport. Distributions and concentrations of straight-chain homologous series such as n-alkanes, n-alkanoic acids, n-alkan-2-ones, n-alkanols and n-alkanals were analyzed in rural aerosols, aerosols produced by prescribed burning and residential wood combustion, and extracts of source vegetation. Cyclic di- and triterpenoids were also examined. The latter components provided more definitive correlations between source vegetation and aerosols. Results included: (1) an increase in C_{max} in regions of warmer climate; (2) possible correlation of aerosols with source vegetation 100 km to the east; (3) the tracing of input from combustion of various fuels such as pine, oak and alder in aerosols produced by residential wood combustion; and (4) preliminary results that demonstrate a potentially large input of thermally altered diterpenoids via direct deposition rather than diagenesis of unaltered sedimentary diterpenoids.

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DETERMINATION OF MOLECULAR SIGNATURES OF NATURAL
AND THERMOGENIC PRODUCTS IN TROPOSPHERIC
AEROSOLS - INPUT AND TRANSPORT

by

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little bits of inspiration during that last year.

And finally, I appreciate the various characters along the way whose work or discussion brought additional inspiration, for science moves slowly in a vacuum.

I can't conceive
the nucleus of all
begins inside a tiny seed.

And what we see
as insignificant
provides the purest air we breathe...

And yet we take from it without consent
our shelter, food...

But far too many give them in return
a stoke, a drown, a burn,
as if they're nothing.

But if you ask yourself where would you be,
Without them you will find you would not.

But who am I to doubt
or question the inevitable being.
For these are but a few discoveries
we find inside the secret life of plants.

- Stevie Wonder, "The Secret Life of Plants", 1979

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DETERMINATION OF MOLECULAR SIGNATURES OF NATURAL
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AEROSOLS - INPUT AND TRANSPORT

I: Introduction

The tropospheric boundary layer acts as a global dispersal mechanism for atmospheric particulate material, i.e. aerosols (Jaenicke, 1980), produced by numerous biogenic and anthropogenic mechanisms. The compositions of tropospheric aerosols are complex and their effects on global processes and human health are just beginning to be understood. At present, the bulk of the organic matter in aerosols has yet to be characterized. Although biogenic emissions are thought to equal or exceed the anthropogenic contribution, in comparison to the extensive studies that have been carried out on urban particulates, no systematic study has been made of the biogenic emissions of organic carbon to the troposphere (Duce et al., 1983).

The goal of this thesis was to further characterize the extractable organic matter in tropospheric aerosols produced by biomass and the combustion of biomass such as prescribed burning and residential wood combustion. The molecular signatures derived from these aerosols would be used in source correlation and the determination of transport and fate. Utilizing capillary gas chromatography and capillary gas chromatography/mass spectrometry, the predominant lipid fractions were analyzed for homologous series such as n -alkanes, n -alkanoic acids and n -alkanals, and cyclic

components such as diterpenoids originating in resins and triterpenoids.

The region studied, the State of Oregon, provided an excellent location for obtaining rural aerosols without a major background signal from anthropogenic processes. The state is predominantly rural and is situated on the western edge of the United States at the Pacific Ocean. Although some anthropogenic input from outside the state is possible from industrial and urban regions in California, the predominant air mass trajectories for the aerosols in this work were off the Pacific Ocean.

Three general types of samples were collected. The largest sample suite consisted of an extensive coverage of aerosols in rural regions of Oregon along a transect which traced the predominant wind trajectories of the season, and in addition, extracts of waxes from the major vegetation in the respective areas. This study resulted in the determination of reproducibility between replicate samples and between aerosols and source vegetation. Long-range transport was also evaluated by the correlation of molecular markers with sources.

Aerosol samples produced by prescribed burns of logging sites were also collected. They yielded information on burning characteristics and processes of thermal alteration of biomarkers, which in turn could be used as tracers.

Finally, samples of aerosols generated by residential wood combustion were collected. Correlations of components in ambient

smoky aerosols collected in three residential communities of Oregon were made with the distributions of tracers in source smoke aerosols collected directly adjacent to stoves burning a specific type of wood fuel.

Since direct vegetative emissions and biomass combustion, such as residential wood burning and natural and prescribed fires, are major contributors to the tropospheric load of organic matter, an increased understanding of their specific sources, concentrations and compositions is essential. Thus, a beginning has been attempted here.

II: Characterization of Extractable Plant Wax, Resin, and
Thermally Matured Components in Smoke Particles from
Prescribed Burns

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ABSTRACT

Atmospheric particles from two slash burns in the Oregon Coast Range were solvent-extracted, and this higher weight organic matter was analyzed by capillary gas chromatography/mass spectrometry. The extractable organic matter that was characterized for the smoke particles was comprised predominantly of unresolved polar organic material, with plant wax and resin components dominating the resolved fraction. Pyrogenic components (polycyclic aromatic hydrocarbons) were present in minor amounts. Homologous series of *n*-alkanes, alkanolic acids, and alcohols were present in patterns characteristic of plant wax signatures. The diterpenoid resin components were in thermally altered and unaltered forms. These components are useful as molecular markers in source correlation. Triterpenoid components present may be indicative of instantaneous thermal maturation.

INTRODUCTION

Natural fires, prescribed burns and residential wood combustion contribute significant amounts of particulate matter to the troposphere (Fahnestock, 1979; Greenberg et al., 1984; Wong, 1979). Localized impact on air quality can be extreme with turbidity levels resulting from natural and prescribed fires at times exceeding those found for heavily polluted urban regions (Eaton and Wendler, 1983). Residential wood combustion also has been demonstrated to impact air quality in various communities, contributing 20-73% to wintertime particulate levels (Core et al., 1984; Dasch, 1982; Murphy et al., 1984; Ramdahl et al., 1984; Sexton et al., 1984). Additionally, since the majority of particulate matter produced is fine, it can be transported over long distances. Plumes from forest fires in Canada were detected up to 5000 km away by satellite imagery (Chung and Le, 1984).

Characterization of these particles is critical in order to understand their impact. The predominant organic components characterized thus far are only the polycyclic aromatic hydrocarbons (PAH) and their derivatives (Dasch, 1982; Murphy et al., 1984; Ramdahl et al., 1984; Mast et al., 1984; Morales et al., 1979; Ramdahl and Becher, 1982; Schmeltz and Hoffman, 1976). Shum and Loveland (1974) characterized particulate matter emitted during prescribed grass burns with respect to trace elements.

The solvent-extractable organic matter (lipids) has not been characterized in detail besides the PAH components, and since this

fraction accounts for up to 50% of the particulate matter produced by biomass burning (Dasch, 1982; Cooper, 1980), it will affect the overall chemical behavior of the particles. These lipids are comprised of higher molecular weight organic compounds from biogenic, pyrogenic, geogenic and anthropogenic sources (Simoneit, 1984; 1985; Simoneit and Mazurek, 1982; Simoneit et al., 1980). Measurable amounts of these components survive combustion, and they or their slightly altered counterparts serve as markers for source correlations. For example, the presence of resin components such as abietic acid (Appendix IV) allows the distinction between smoke from forest (coniferous) and smoke from grass or brush fires to be made. Ramdahl (1983) has demonstrated the use of retene (Appendix IV), a thermally altered product of abietane series resin components, as a molecular marker of residential wood combustion.

In this paper we present results from the molecular analysis of the lipid fractions of atmospheric particles produced by "slash" burning (prescribed burning of indigenous shrubs, ferns and mosses, small fir and hardwood trees, and litter from logging operations, which consists primarily of fir, spruce, and cedar litter). Prescribed burning not only contributes significantly to regional particulate loads (Stith et al., 1981) but also provides logistically convenient sampling opportunities that wildfires do not. Results from the analyses of smoke from prescribed burning can be used as first approximations for smoke from a natural fire in a region of similar vegetation.

EXPERIMENTAL SECTION

Sampling. Particulate matter was sampled from the smoke of two prescribed slash burns located in the Beaver Creek area of the Oregon Coastal Range (Figure II.1). The first burn sampled was conducted by Boise Cascade Corp. on July 26, 1983. Two time periods were sampled, the first for 7 h (600 m^3) during the burn (BCB I) and the second for 14 h (1200 m^3) after burning was complete and smoldering had begun (BCB II). During the burn the sampler was located approximately 600 m across a valley and directly in the plume of the slash burn. After burning was complete, the sampler was placed in the valley between the burn and the original sampling site. This second sample consisted of the settling smoke produced by smoldering.

The second burn, conducted by Georgia-Pacific Corp. on September 21, 1983, was sampled as above (GPB I for 4 h, 400 m^3 , and GPB II for 13 h, 1100 m^3). However in this case, both samples were taken at the same site, which was approximately 200 m away from the burn.

Particles $>0.5 \mu\text{m}$ were collected on annealed (500°C for 4-8 h) quartz fiber filters in a high-volume air sampler with a flow rate of approximately $1.5 \text{ m}^3/\text{min}$ (Simoneit, 1984; Simoneit and Mazurek, 1982). Sample filters were placed in annealed glass jars immediately after collection, spiked with a few milliliters of methylene chloride to inhibit microbial activity, and then stored at 4°C until analysis.

FIGURE II.1

Location of sampling sites (Lincoln County, Central Oregon Coast): (*) Boise Cascade burn (July 1983); (+) Georgia Pacific burn (September 1983)

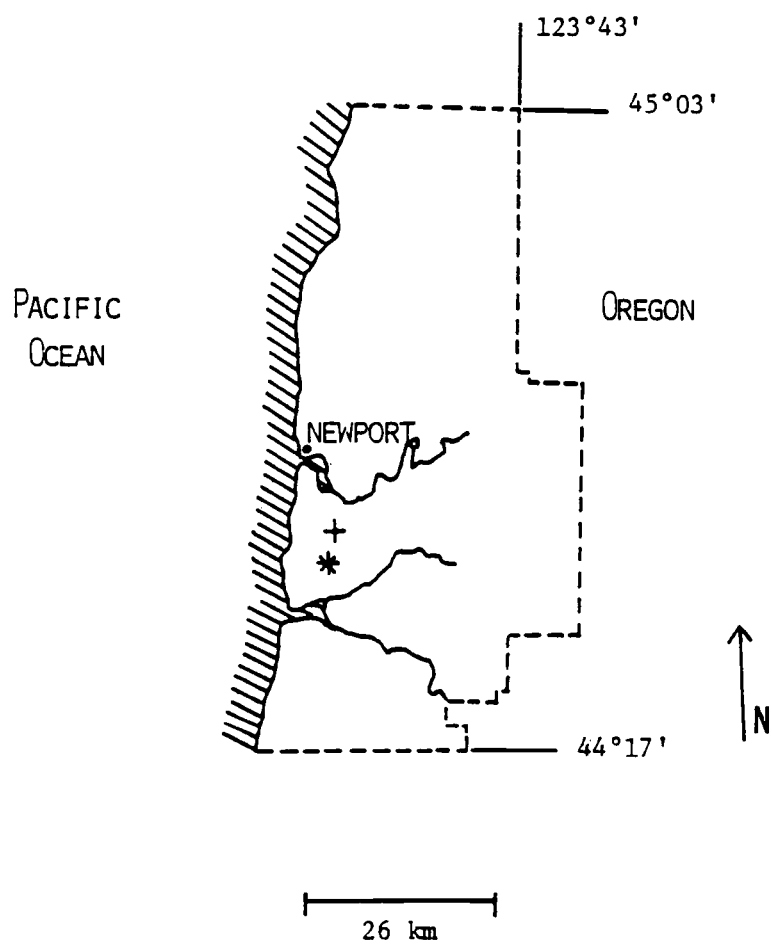


FIGURE II.1

Lipid Analysis. Sample filters were extracted by sonication with three sequential 300-mL aliquots of a 2:1 hexane/diethyl ether mixture. The extracts were then reduced in volume to 5 mL in a rotary evaporator with a water bath at approximately 30°C. One hundred microliter aliquots of the total extracts were evaporated to dryness in the presence of air at room temperature and weighed on a microbalance to determine the extract yields.

Additional aliquots (approximately half) of the total extracts were derivatized using diazomethane in ether and separated by thin-layer chromatography (silica gel phase with 20 parts hexane to 1 part ether as the mobile phase) into fractions of varying polarity (i.e., fractions containing hydrocarbons, fatty acids as methyl esters, ketones and alcohols/polar compounds) (Simoneit, 1984; 1985; Simoneit and Mazurek, 1982). These fractions were analyzed by capillary gas chromatography (GC, Varian 4600 with a 30 m X 0.25 mm i.d. capillary column coated with DB-1701, J&W Scientific, 65°C for 6 min, then to 310°C at a rate of 4°C/min) and capillary gas chromatography/mass spectrometry (GC/MS Finnigan 4000 mass spectrometer coupled to a 9610 GC with a 30 m X 0.25 mm i.d. capillary column coated with DB-5, J&W Scientific) (Simoneit, 1984; Simoneit and Mazurek, 1982). A blank carried through the procedure contained 6 µg of total extractable organic matter, which is approximately 0.02-0.08% of the total extract weights.

RESULTS AND DISCUSSION

Analytical Results. The analytical results are summarized in Table II.1, with comparative data from some ambient rural aerosols (Simoneit and Mazurek, 1982). Total extract yields of the smoke aerosols ranged from 6 to 43 $\mu\text{g}/\text{m}^3$, quite high when compared to an ambient loading of 2 $\mu\text{g}/\text{m}^3$ sampled in a meadow near Corvallis. Filters of smoke samples were a light ash grey. The Boise Cascade Corp. burn (BCB) aerosols yielded 32 $\mu\text{g}/\text{m}^3$ directly in the plume of the active burn and 6 $\mu\text{g}/\text{m}^3$ overnight during the smoldering phase. Smoke aerosols from the Georgia-Pacific Corp. burn (GPB) yielded 43 $\mu\text{g}/\text{m}^3$ during active burning and 27 $\mu\text{g}/\text{m}^3$ during smoldering. The extract yields of GPB I and II are higher than those of BCB I and II due to the proximity of the sampler to the GPB site.

Total hydrocarbon and fatty acid (as methyl ester) fractions ranged from 220 to 1000 ng/m^3 and from 50 to 600 ng/m^3 , respectively. Ambient levels were 230 and 240 ng/m^3 for the hydrocarbon and fatty acid fractions, respectively. Only one of the four samples, GPB II, had a significantly greater concentration of hydrocarbons and fatty acids than found in ambient aerosols. The other three samples deviated only slightly from the comparative ambient levels in spite of their significantly enhanced yields of extractable organic matter.

The Carbon Preference Index (CPI, defined in Appendix I), a measure of the carbon number predominance of homologous compound series, is useful to determine the degree of plant wax vs. fossil

TABLE II.1 ANALYTICAL DATA ON PRESCRIBED BURN AEROSOLS

Sample identification	Total solvent extract yield (ng/m ³)	Total hydrocarbons (ng/m ³)	n-Alkanes		Total acid fraction (ng/m ³)	n-Alkanoic acids CPI (C ₁₄ -C ₃₁)	n-Alkanones		n-Alkanols	
			CPI (C ₂₅ -C ₃₄)	U:R			total ng/m ³	CPI (C ₁₆ -C ₃₃)	total ng/m ³	CPI (C ₁₁ -C ₂₈)
BCB I (active burning)	31,800	420	4.6	0.8	630	9.0	0.8	5.0	0.6	∞
BCB II (smoldering phase)	6,000	220	1.2	0.3	50	16.0	0.1	6.9	0.8	13
GPB I (active burning)	42,900	380	3.6	0.3	50	6.4	24.0	3.9	1.1	∞
GPB II (smoldering phase)	26,800	1,100	2.2	3.3	600	7.4	12.9	3.1	2.1	∞
Corvallis Meadow (for comparison, ref. Simoneit and Mazurek, 1982)	2,400	230	8.1	0.2	240	8.9	-	-	96.0	5

fuel input (Simoneit, 1984; 1985; Simoneit and Mazurek, 1982; Mazurek and Simoneit, 1982). Reflecting biochemical specificity, the straight-chain components of plant waxes exhibit pronounced CPIs (significantly greater than one); for example, n -alkanes and n -alkanones have strong odd carbon number predominances, and n -alkanols and n -alkanoic acids have strong even carbon number predominances. Petroleum hydrocarbons, on the other hand, have a relatively smooth distribution of n -alkanes (i.e., CPI = 1). In the Corvallis forest aerosols the dominating contribution from plant waxes is demonstrated by the high CPI values of 8 for n -alkanes and 8 and 5 for n -alkanoic acids and n -alkanols, respectively (Simoneit and Mazurek, 1982).

The CPIs of the n -alkanes in smoke (calculated using n -alkanes in the plant wax range of C_{24} to C_{34}) varied from 1.2 to 4.6. A trend toward slightly lower CPIs was observed as the burns shifted from active burning of plants (brush, ferns and small trees) and surface litter (branches and/or logging debris) to the smoldering of surface litter and soil. Thus, the CPIs dropped from 4.6 to 1.2 (BCB) and from 3.6 to 2.2 (GPB). A potential source for the alkanes of lower CPI is fossil fuel input or a random mechanism (i.e. - non-biological) such as thermal cracking from macromolecular material that is found in the humus present in the soil surface and that burns during smoldering. For example, thermal release of bound primary alcohols, which are dominated by even chain length homologs might contribute even alkanes to the signature.

The n -alkanoic acids and alkanols retained a predominantly

plant wax character, i.e., strong even carbon number predominance, in all four smoke aerosol samples, with CPIs ranging from 6 to 16 for the acids and CPIs ranging from 13 to ∞ for the alkanols. n-alkanones were predominated by odd chain lengths and had CPIs ranging from 3.1 to 6.9.

Plant Wax Components/Straight-Chain Homologs. Homologous distributions of normal alkanes, alkanolic acids, alkanones, alkanals, and alkanols present in the samples are displayed in Figure II.2. The n-alkanes of all samples except BCB II display a pronounced plant wax signature, with a carbon number maximum (C_{max} , homolog of greatest concentration) at C_{27} or C_{29} and odd carbon number predominance above C_{25} . Superimposed on these plant wax distributions in samples BCB I and GPB I and II is a pattern characteristic possibly of diesel exhaust. The distribution analogous to diesel is comprised on n-alkanes with a carbon number range of C_{18} to C_{26} , no carbon number predominance, and a maximum at C_{22} to C_{23} (Simoneit, 1984; 1985). The estimated contribution of n-alkanes from non-biogenic sources is represented by the envelope under the dashed lines (cf. Figure II.2).

The distribution of n-alkanes in the particles of BCB II (Figure II.2b), however, cannot be traced to plant wax or petroleum source materials. As there is a maximum at C_{26} to C_{27} with essentially no carbon number predominance (CPI = 1.2), diesel exhaust which has a C_{max} around C_{23} and plant waxes with pronounced

CPIs cannot be the predominant contributors to the signature. It is possible that these alkanes are formed by combustive cracking as mentioned earlier, though this requires further study.

The alkanolic acid distributions of the smoke particles (Figure II.2e-h) show distinct biogenic, probably plant wax, signatures (Simoneit and Mazurek, 1982). In BCB I, BCB II, and GPB II, there are strong even carbon number predominances with maxima at C₂₂ and C₂₄. However, the distribution of the \underline{n} -fatty acids of GPB I differs somewhat from the other smoke samples. The even carbon number predominance is retained, but the maximum is shifted from C₂₂ or C₂₄ to C₃₀. Since the detritus being combusted comes from similar starting material for both GPB I and II, this difference is intriguing. The source for these higher weight alkanolic acids is as yet uncertain but may reflect a difference in litter vs. soil composition at that site. \underline{N} -alkan-2-ones exhibited CPIs ranging from 3.1 to 6.9 (Figure II.2i-1) and an odd carbon number predominance. These compounds have been determined previously in sediments (Volkman et al., 1981) in which they sometimes closely resembled the \underline{n} -alkanes. The distribution of \underline{n} -alkan-2-ones in the smoke aerosols follows closely the \underline{n} -alkanes attributable to plant waxes (above the dashed envelope enclosing non-biologically formed components) with C_{max} of C₂₇ and odd carbon number predominance. These may result from oxidation of the \underline{n} -alkanes.

\underline{N} -alkanals were detected in GPB II at concentrations up to 1 ng/m³ (Figure II.2k). There is a C_{max} of C₂₂ and even carbon number predominance which is indicative of plant wax components

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FIGURE II.2

Distribution diagrams (concentration vs. carbon number) for straight-chain homologous compounds: (a-d) n -alkanes (dashed line drawn to emphasize contribution from plant wax components); (e-h) n -alkanoic acids; (i-l) n -alkanones (dashed lines n -alkanals); and (m-p) n -alkanols. Boise Cascade burn, active burning (a,e,i,m); Boise Cascade burn, smoldering (b,f,j,n); Georgia Pacific burn, active burning (c,g,k,o); Georgia Pacific burn, smoldering (d,h,l,p).

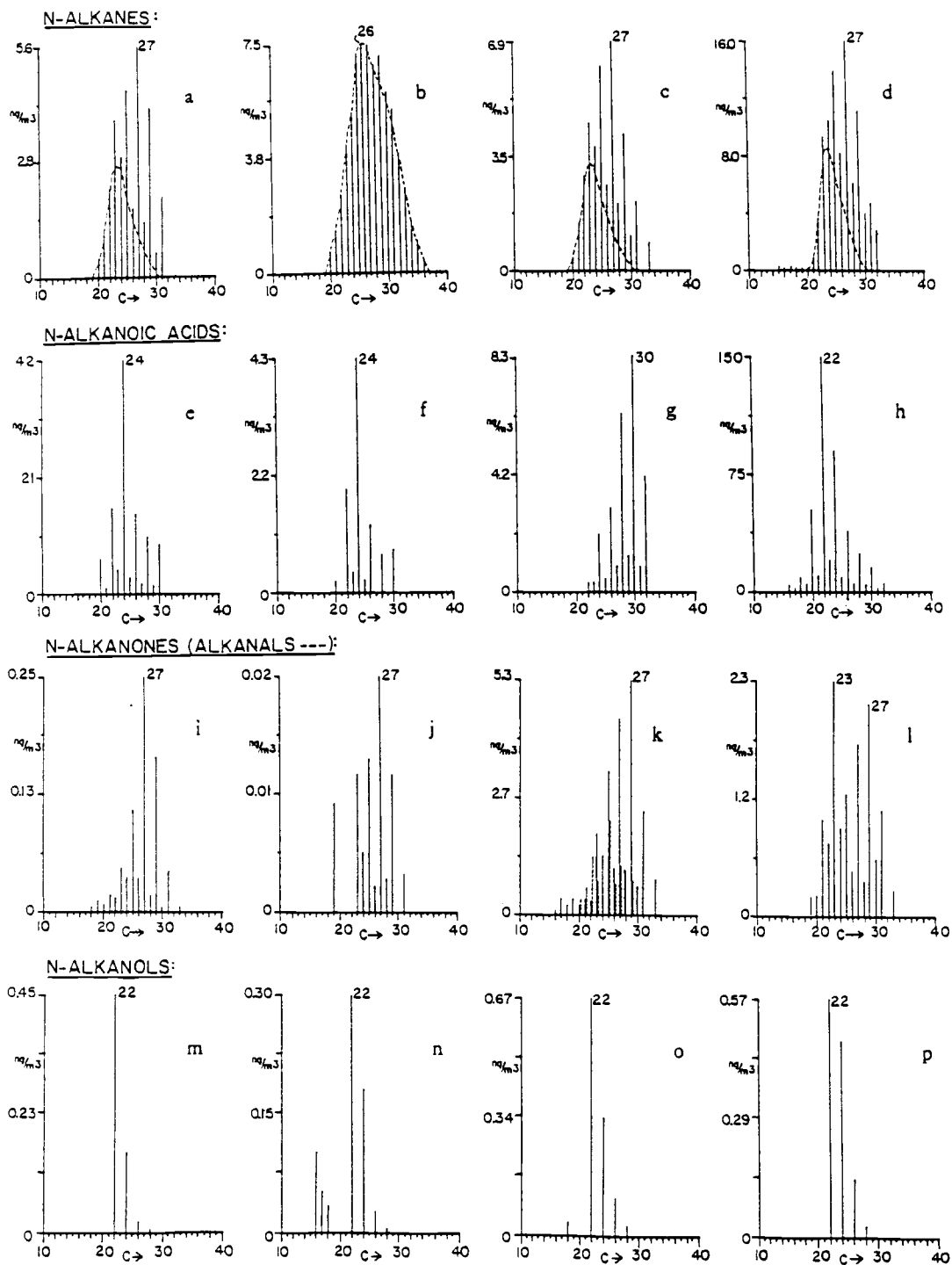


FIGURE II.2

CPIs cannot be the predominant contributors to the signature. It is possible that these alkanes are formed by combustive cracking as mentioned earlier, though this requires further study.

The alkanolic acid distributions of the smoke particles (Figure II.2e-h) show distinct biogenic, probably plant wax, signatures (Simoneit and Mazurek, 1982). In BCB I, BCB II, and GPB II, there are strong even carbon number predominances with maxima at C_{22} and C_{24} . However, the distribution of the n -fatty acids of GPB I differs somewhat from the other smoke samples. The even carbon number predominance is retained, but the maximum is shifted from C_{22} or C_{24} to C_{30} . Since the detritus being combusted comes from similar starting material for both GPB I and II, this difference is intriguing. The source for these higher weight alkanolic acids is as yet uncertain but may reflect a difference in litter vs. soil composition at that site. N -alkan-2-ones exhibited CPIs ranging from 3.1 to 6.9 (Figure II.2i-1) and an odd carbon number predominance. These compounds have been determined previously in sediments (Volkman et al., 1981) in which they sometimes closely resembled the n -alkanes. The distribution of n -alkan-2-ones in the smoke aerosols follows closely the n -alkanes attributable to plant waxes (above the dashed envelope enclosing non-biologically formed components) with C_{max} of C_{27} and odd carbon number predominance. These may result from oxidation of the n -alkanes.

N -alkanals were detected in GPB II at concentrations up to 1 ng/m^3 (Figure II.2k). There is a C_{max} of C_{22} and even carbon number predominance which is indicative of plant wax components

(Kolattakudy, 1971).

The n -alkanol (Figure II.2m-p) distributions also show a distinct plant wax source character, with even carbon number predominances maximizing at C_{22} and ranging from 13 to ∞ . A measure of the relative degree of thermal degradation of plant waxes is the ratio of normal alkanols ($>C_{20}$) to alkanes (C_{24}), since alkanols are more easily degraded. The ratio of n -alkanols to alkanes in a Corvallis meadow aerosol is 1.6 (Simoneit and Mazurek, 1982). However, n -alkanol to alkane ratios of the smoke aerosols ranged from 0.014 to 0.044, reflecting a 2 order of magnitude drop in alkanol concentration relative to alkanes possibly due to thermal degradation. Phytosterols, major molecular markers from plant waxes in aerosols (Simoneit et al., 1983), were not detectable in the smoke samples.

Intact wax esters were also detected in the smoke samples. A mass spectrum of the C_{40} wax peak from GPB I is shown in Figure II.3a and the fragmentation pattern represents a mixture of four isomers that have eluted at the same time. They are as follows (with alcohol moieties in parentheses): $C_{15}H_{31}CO_2(C_{24}H_{49})$; $C_{17}H_{35}CO_2(C_{22}H_{45})$; $C_{19}H_{39}CO_2(C_{20}H_{41})$; $C_{21}H_{43}CO_2(C_{18}H_{37})$. The fragment peaks 257, 285, 313, and 341 in the mass spectrum represent the ions $C_{16}H_{33}O_2^+$, $C_{18}H_{37}O_2^+$, $C_{20}H_{41}O_2^+$, AND $C_{22}H_{45}O_2^+$, respectively. These same C_{40} wax esters were characterized in various rural aerosols (Simoneit and Mazurek, 1982).

Diterpenoids. The predominant diterpenoids found in the smoke

FIGURE II.3

Mass spectra of example components: (a) mixture of four isomers of C_{40} wax esters; (b and c) isomers of dehydroabietin and (d) friedel-14-en -3-one with major fragment ions (a) $C_{15}H_{24}^+$ (m/z 204) and (b) $C_{21}H_{32}O_2^+$ (m/z 300) indicated.

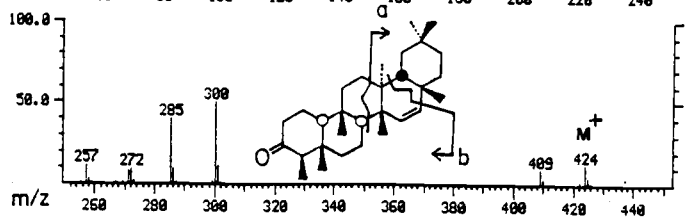
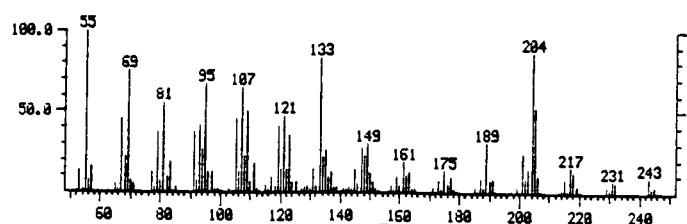
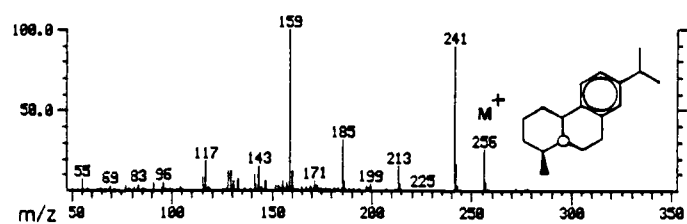
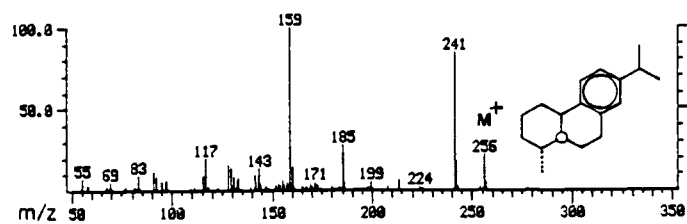
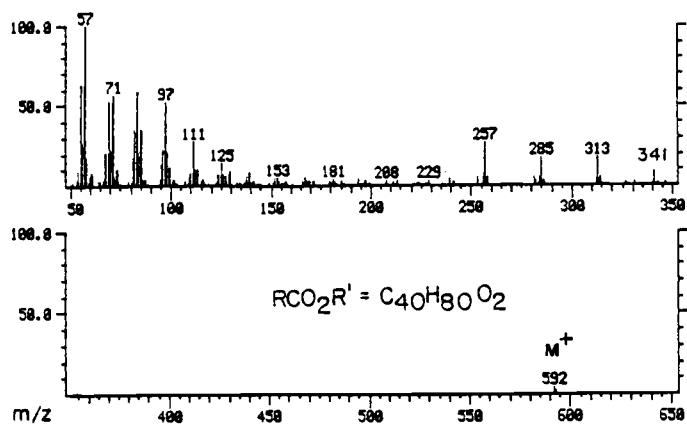


FIGURE II.3

samples are derived from the abietane skeletal precursors in resins (see Appendix IV) (Simoneit and Mazurek, 1982; Simoneit, 1986). Three isomers of dehydroabietic acid, with concentrations ranging from 0.7 to 60 ng/m³, constitute the major components present, and abietic acid ranges from 1 to 30 pg/m³. The dehydroabietin isomers, shown in Appendix IV, hydrocarbon derivatives also from abietane skeletal precursors in resins (Simoneit and Mazurek, 1982; Simoneit, 1986), are found in the ranges of 90-100 pg/m³ and 160-250 pg/m³, respectively. Dehydroabietane is not detectable.

Retene (Appendix IV) as mentioned earlier, is an incomplete combustion product of compounds with the abietane skeleton. Ramdahl (1983) has demonstrated its use as an indicator of residential coniferous wood combustion. Our data support this application as a tracer for such combustion, and in addition, retene can be used during dry seasons as a tracer for forest fires or prescribed burning. Its concentration in the smoke particles is about 8 ng/m³.

Various intermediates along the pathway of thermal degradation of abietic acid to retene were also detected in the smoke particles. These intermediates can also be useful as tracers for coniferous wood combustion. Additional detail on this suite of components will be published in a later paper.

Triterpenoids. Triterpenoids are useful as molecular markers in source correlation due to their molecular specificity (Simoneit, 1986). There are two classes of triterpenoids that will be discussed in this paper. These are the pentacyclic hopanoids (with a five-membered E ring) and triterpenoids with a six-membered E

ring. Triterpenoids of the latter class are produced by many higher plants (Simoneit, 1986). Shown in Figure II.3d is the interpreted mass spectrum of the mono-unsaturated triterpenoid friedel-14-en-3-one, which was characterized in the extracts of GPB I and II. At present, it is uncertain whether this double bond was derived thermally or diagenetically or if this compound was produced directly by the source vegetation.

The hopanoid series is also useful in this discussion since 17β (H), 21β (H)-hopanes are produced by microbiota and some higher plants, and their presence indicates an input from biological sources as immature organic matter in this case from plants, litter, and soil (Simoneit, 1986). The 17α (H), 21β (H)-hopanes are the geologically mature isomers of the 17β (H), 21β (H)-hopanes and are evidence of petroleum input or thermal maturation (Simoneit, 1984). The 17β (H), 21α (H)-hopanes (also called moretanes) are thought to be intermediates in the thermal maturation of 17β (H), 21β (H)-hopanes or other biogenic hopanoid precursors (Simoneit, 1986; Ourisson et al., 1984).

In Figure II.4, the relative concentrations of hopanes present in the smoke aerosols are plotted vs. carbon number (Figure II.4a-d). Included for comparison purposes are the distributions of hopanes in aerosols from vehicular exhaust of gasoline and diesel engines (Figure II.4e and f). The hopane signatures from the exhaust samples can be attributed to the presence of lubricating oil, which is characteristic of thermally mature (fossil) organic

FIGURE II.4

Distribution diagrams for hopane series: (a) Boise Cascade burn, active burning; (b) Boise Cascade burn, smoldering; (c) Georgia Pacific burn, active burning; (d) Georgia Pacific burn, smoldering; (e) auto exhaust; (f) diesel truck exhaust.

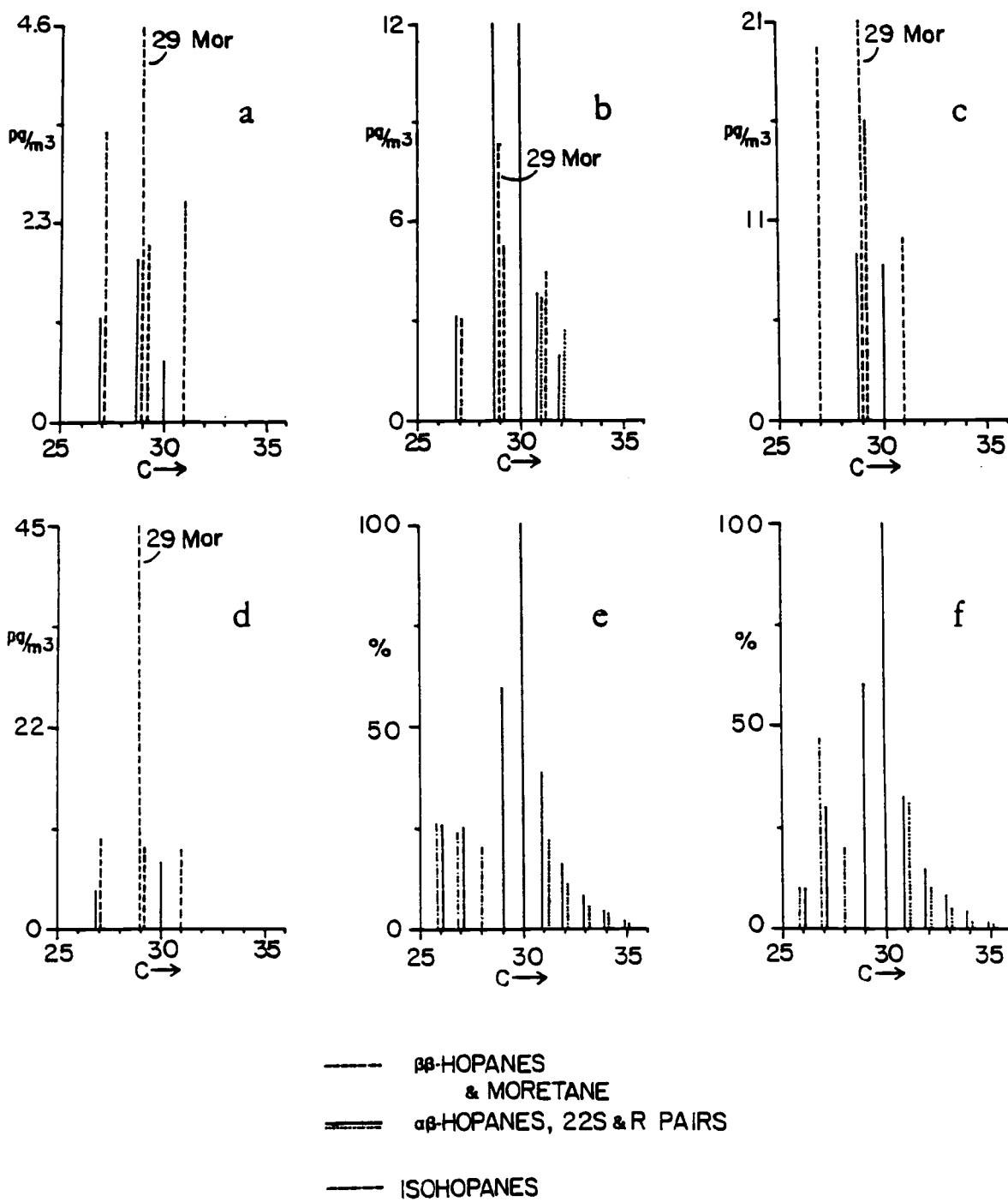


FIGURE II.4

matter. No $17\beta\text{H}, 21\beta\text{H}$ -hopanes or moretanes are present. The C_{31} to C_{35} hopanes consist of approximately equivalent amounts of the 22S and 22R isomers. BCB I and GPB I and II contain predominantly $17\beta\text{H}, 21\beta\text{H}$ -hopanes and the C_{29} moretane. Minor amounts of $17\alpha\text{H}, 21\beta\text{H}$ -are present but do not resemble the hopane distribution present in the exhaust aerosols, possibly due to the fact that they are near the detection limit. BCB II, however, contains predominantly $17\alpha\text{H}, 21\beta\text{H}$ -hopanes and 22S and 22R pairs, with lesser amounts of $17\beta\text{H}, 21\beta\text{H}$ -hopanes and C_{29} moretane. There are a few possible explanations for the distributions of the hopanes present in these samples.

Both these sites are in rural regions 10-15 km from a major highway. A potential source for a fossil fuel contribution to GPB I and II is the exhaust from the diesel generator used to power the sampler. Although the generator was placed 120 m downwind from the sample, it is possible that contamination occurred during the initial phase of burning. Slash burns are planned to burn hot enough to create a vertical column of smoke that dissipates when it reaches the inversion layer rather than at ground level. Therefore, during the initial stages of the burn, surrounding air would have been drawn toward the column of smoke, and exhaust from the generator could have passed the sampler. The presence of mature hopanes in BCB I and II, however, cannot be so easily explained. A major contribution of vehicular exhaust from a highway 10 km away is possible. Another explanation, though not yet determined as quantitatively important, is the volatilization of diesel exhaust

residues deposited on the site by the logging trucks used in removing the timber from the area.

One source of the mature hopanes could be the instantaneous thermal maturation of the $17\beta\text{H}, 21\beta\text{H}$ -hopanoids produced by higher plants such as ferns and moss (e.g. Ourisson et al., 1984; Ageta et al., 1964; 1968). These plant species are abundant in the Oregon Coast Range. Maturation of organic matter in sedimentary basins has been shown to occur with time inversely related to temperature (Simoneit, 1983); i.e., maturation occurs more quickly in hotter regimes.

Table II.2 presents the ratios of thermally mature to immature (biogenic) hopanes and n -alkanes. Both ratios are very consistent for the samples BCB I, GPB I and II. Both ratios rise significantly for BCB II. A common source for the mature components is therefore likely.

Polycyclic Aromatic Hydrocarbons (PAH). Production of PAH by combustion of organic matter has been well documented (Schmeltz and Hoffman, 1976). Although PAH are considered to be ubiquitous in the environment (Hites et al., 1980), localized elevations in concentration due to urban processes and biomass burning can occur (Ramdahl, 1983; Handa et al., 1980).

Levels of total PAH (alkylated and non-alkylated) range from 0.1 to 16 ng/m^3 , with retene contributing up to half the total PAH content. Individual PAH are present at levels 1-3 orders of magnitude higher than those measured levels in rural and urban

TABLE II.2. COMPARISON OF THERMALLY MATURE WITH BIOGENIC COMPONENTS

	BCB I	BCB II	GPB I	GPB II
$\alpha\beta$ -hopanes/($\beta\beta$ -hopanes + $\beta\alpha$ -hopanes)	0.26	1.82	0.25	0.26
nonbiogenic/biogenic n -alkanes	0.9	34.5	0.7	0.7

regions of the western United States (Simoneit, 1984; 1985; Grosjean et al., 1983). However, the PAH levels in these smoke samples are 10-100 times less than those determined for the urban atmospheres of Elverum, Norway (Ramdahl et al., 1984), which is influenced by residential wood combustion, and Iidabashi, Japan (Handa et al., 1980), which is heavily influenced by vehicular exhaust. No appreciable amounts of oxygenated or nitrated PAH, other than fluorenone, are detectable. However, this method does not comprise the most sensitive search for these particular compounds.

The two slash burns sampled produced different suites of PAH. Retene was not present in appreciable amounts in the smokes from the Boise Cascade Corp. burn, whereas it was the predominant PAH in the smokes from the Georgia-Pacific Corp. burn. Combustion conditions, i.e., temperature and oxygen levels, determine the predominance of products from thermal alteration vs. those from pyrosynthesis (Ramdahl, 1983). Under low temperatures and depleted oxygen regimes, products of thermal alteration such as retene will predominate from resinous plant detritus. A difference in the intensity of the two burns or the degree of oxygen depletion within the smoke column would account for this variation.

A loss of reactive PAH upon extended exposure to transformation reactants has been demonstrated to be an accurate assessment of aging (time in transport since emission from the source) (Nielsen, 1984; Nielsen et al., 1984; Roberts et al., 1984). Ratios of the more reactive benzo(a)pyrene (BaP) to benzo(e)pyrene (BeP) approximately equal to 1 indicate a low level of transformation

(Nielsen, 1984; Nielsen et al., 1984). As BaP was below the detection limit in all smokes analyzed here, rapid transformation is thought to be occurring due to enhanced levels of oxidizing and/or nitrating reactants in the smoke column and/or plume.

Total Extract Summary. Plant waxes, resin-derived compounds, and PAH comprised 0.3-2.4% of the total extractable organic matter of the smoke aerosols. Unresolved and polar (not amenable to gas chromatographic separation) components make up the bulk of the extracts, accounting for 99.5% (BCB I) and 99.7% (GPB I) of the total extracts of aerosols produced during active burning. Their contribution dropped to 98.6% (BCB II) and 97.6% (GPB II) in extracts of aerosols produced during the smoldering phase.

In an effort to ascertain the nature of the bulk of the extractable matter, a rough analysis was performed of the methylated extract of GPB I. Only 25% was soluble in hexane (a fraction roughly comparable to material amenable to nonpolar capillary gas chromatographic analysis) and that >90% was volatilized at temperatures up to 300°C. Therefore, the bulk of the extracted material was polar organic or inorganic matter (salts which were dissolved in the polar solvent) and not fine particulate matter that may have passed our filtration steps during sample workup.

Relative contributions of plant waxes, resins, PAH, and pyrogenic products are shown in Figure II.5. Plant wax constituents predominate in the aerosols from active burning. Resin-derived components have a fairly constant, though lesser, contribution to

FIGURE II.5

Pie diagrams of relative contributions of plant waxes, resin components, PAH, and thermally matured components (UCM plus nonbiogenic hydrocarbons). (BCB I) Boise Cascade burn, active burning; (BCB II) Boise Cascade burn, smoldering; (GPB I) Georgia Pacific burn, active burning; (GPB II) Georgia Pacific Burn, smoldering.

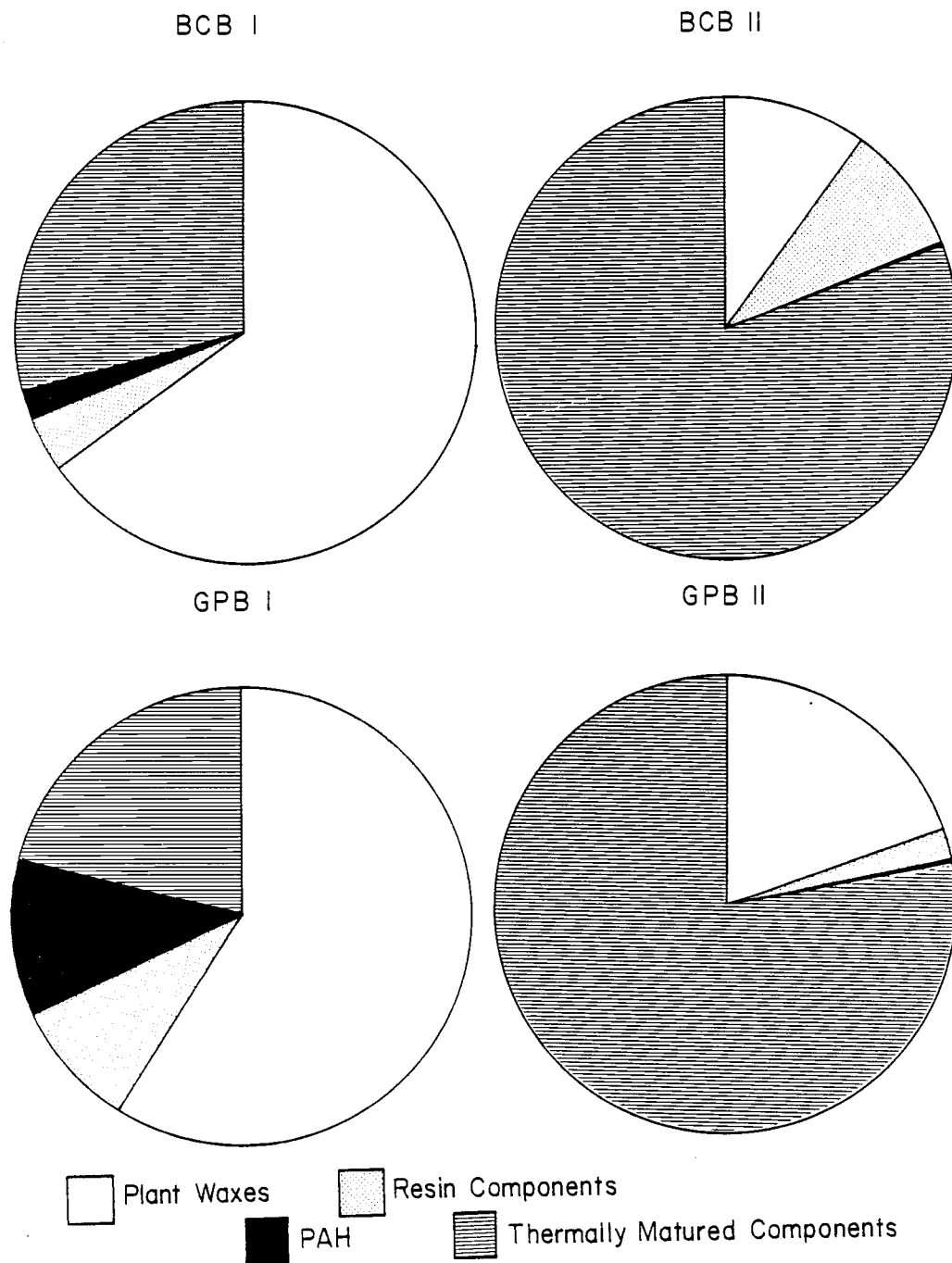


FIGURE II.5

the extractable fraction. Pyrogenic compounds i.e., PAH, exhibit a distinct difference between aerosols produced during active burning and smoldering, where greater amounts are generated under the hotter conditions of active burning. Thermally generated components dominate the characterized extracts of the smoldering aerosols.

CONCLUSIONS

The lipids characterized for smoke particles indicate a predominantly biogenic signature with lesser amounts of PAH. Plant wax constituents such as normal alkanes, alkanolic acids, alkanals, alkanols and minor resin compounds dominate the resolvable fraction. Thermally altered resin components are also present in appreciable amounts, and they can be utilized as tracers for coniferous wood combustion. An indication that the thermally sensitive constituents of plant waxes have been degraded is apparent in the low ratio of n -alkanols to n -alkanes, with the labile alkanols being depleted by up to 2 orders of magnitude.

The distributions of thermally altered and pyrosynthetic components depend on the nature of the burn. The temperature and degree of oxygen depletion varied between the two burns as reflected in the predominance of retene to PAH levels in smoke particles from one burn and not the other. Levels of reactive species, i.e., oxidizers, are postulated to be high in the smoke column and/or plume, since reactive PAH such as BaP are not detectable. Elevated levels of PAH produced during forest fires and prescribed burning in remote and rural regions have a measurable impact on air quality.

III: Thermally Altered Resin Diterpenoids in Aerosols Produced
by Prescribed Burns

ABSTRACT

Atmospheric particles produced by two slash burns in the Oregon Coast Range were solvent-extracted, and the diterpenoid components analyzed by capillary gas chromatography and capillary gas chromatography/mass spectrometry. The suite of diterpenoids, originating in the resinous higher plants which were combusted, was comprised of reaction intermediates in the sequence of thermal transformation of components such as abietic acid and dehydroabietin to retene. This sequence parallels the diagenetic decomposition noted in sedimentary records. As global transport of combustion aerosols has been well documented, it is possible that the thermally altered diterpenoids documented in this study are directly deposited to the sediments. Preliminary calculations demonstrated that the contribution from directly deposited, altered diterpenoids may be as much as 3 to 1,000 times the contribution from diagenesis of unaltered diterpenoids originating in transported plant wax aerosols. Their relative contribution to the sedimentary record needs to be explored further.

INTRODUCTION

Biomass combustion contributes 0.5 to 2×10^{15} g of carbon annually to the atmosphere (Seiler and Crutzen, 1980). Since the particle matter produced is fine (i.e. - Stith et al., 1981) it can be transported on a global scale as demonstrated by Chung and Le (1984) who used satellite imagery to trace forest fire plumes up to 5000 km.

Chemical characterization of these particles is essential for their use in source reconciliation, as on a local scale in the determination of the impact of residential wood combustion, on a regional scale in the tracing of plumes from natural and prescribed fires, and on a global scale in the deposition to the oceans.

In this paper we present a discussion of the cyclic diterpenoids detected in smoke particles produced by two slash burns (prescribed burns of coniferous slash and debris and brush left after clear-cut logging) conducted in the coastal range of western Oregon. Analysis of the remaining higher molecular weight organic components present in the smoke aerosols was published previously (Chapter II). The diterpenoid class of compounds was chosen to be highlighted for two reasons. Diterpenoids have a relatively large degree of molecular specificity as compared to other plant wax components such as straight chain alkanes and are thus more definitive in source correlation. Further, they were present in these samples in quantities which made analysis reasonably straightforward by GC-MS and were represented by numerous

intermediates along a pathway of thermal degradation to an aromatized product, retene. As will be discussed later, their presence proved very informative.

Cyclic diterpenoids originating in essential oils and resins of higher plants have been reported in various segments of the geosphere (Simoneit, 1986). The predominant components determined in this study are derived from the abietane and pimarane skeletons (Appendix IV), which are the major diterpenoids produced by plants in the northern hemisphere (Thomas, 1970). Diterpenoids with varying degrees of aromatization and decarboxylation have been reported in ambient rural aerosols (Simoneit and Mazurek, 1982), aerosols resulting from residential coniferous wood combustion (Ramdahl, 1983), in ash produced during the volcanic eruption of Mount St. Helens (Pereira et al., 1982), in contemporary and fossil resinous plant detritus (Simoneit et al., 1986), and in lake and oceanic sediments (e.g. - LaFlamme and Hites, 1978; Simoneit, 1977a; Wakeham et al., 1980).

The prevalent mechanism evoked in explaining the presence of degraded diterpenoids in soils and sediments is diagenesis (LaFlamme and Hites, 1978, Simoneit, 1975; 1977a; Wakeham et al., 1980). However, the presence of resin components and their thermally altered products in coniferous smoke aerosols as discussed in this paper and by Ramdahl (1983) provokes thought about the relative contribution from combustion versus diagenetically derived diterpenoids in the sedimentary record.

EXPERIMENTAL SECTION

Sampling.

Smoke particles ($>0.5 \mu\text{m}$) produced by two prescribed slash burns were collected on annealed (500°C for four to eight hours) quartz fiber filters using a high volume air sampler with a flow rate of approximately $1.5 \text{ m}^3/\text{min}$. Filters were stored immediately after sampling in annealed glass jars, spiked with a few ml of dichloromethane to inhibit microbial growth, and stored at 4°C until analysis (Simoneit and Mazurek, 1982).

The two burns were located in the Beaver Creek area of the Oregon Coastal range (see Figure II.1). The first burn sampled was conducted by Boise Cascade Corp. on July 26, 1983. During the active stage of the burning, the sampler was placed directly in the plume of the burn approximately one km across an interceding valley. This comprised the first sample (BCB I, 600 m^3). The sampler was moved down to the base of the valley, approximately 500 m from the burn, to collect a second sample comprised of the smoke produced from the overnight smoldering of the fire (BCB II, 1200 m^3).

The second burn sampled was conducted by Georgia-Pacific Corp. on September 21, 1983. Two samples were collected in the same manner as above, with one comprised of the smoke produced by active burning (GPB I, 400 m^3) and the second a sampling of aerosols produced by smoldering (GPB II, 1100 m^3). Both samples in this case were collected within 200 m of the burn site.

Extraction and analysis.

Sample filters were extracted by sonication for 15 minutes with three aliquots of a hexane:diethyl ether mixture (2:1). The extracts were then evaporated under vacuum to approximately 5 ml using a rotary evaporator and a nitrogen blowdown apparatus for the final phase.

Aliquots (approximately half) of the extracts were derivatized with diazomethane prepared in diethyl ether from N-methyl-N'-nitro-N-nitrosoguanidine (Pierce) and separated into four fractions of varying polarity using silica gel thin-layer chromatography (mobile phase 19:1 hexane:diethyl ether)(Simoneit and Mazurek, 1982). The non-polar diterpenoids co-eluted with the normal alkanes and the polar diterpenoids, such as dehydroabietic acid, formed a band in the middle of the plate. Analysis and quantitation of the diterpenoid components were carried out by co-injection with known standards on capillary gas chromatography/mass spectrometry (Finnigan 4000 mass spectrometer coupled to a 9610 gas chromatograph with a 30 m X 0.25 mm i.d. capillary column coated with DB-5, J&W Scientific) (Simoneit and Mazurek, 1982). Component structures were identified by comparison with standard retention times and mass spectra (components A, C, Ga, Ha, Ia, La and b, R, S, and Ta and Tb, in Table III.1 and Figures III.1 and III.2), literature mass spectra (D^1 , Hb^1 , Ib^1 , N^2 ; 1. Simoneit and Mazurek, 1982; 2. Enzell and Wahlberg, 1969), and by interpretation (B, E, F, Gb, c, and d, J, K, M, O, P and Q). Mass spectra are presented in Appendix V.

RESULTS AND DISCUSSION

In the smoke aerosol samples collected from slash burns diterpenoid components are present which document the step-wise thermal alteration of resin components such as abietic acid and dehydroabietin to retene. A parallel reaction sequence has been proposed by the various researchers mentioned previously for the diagenetic production of altered diterpenoids in the sedimentary record. The four samples are quite distinct with respect to the presence and concentrations of the intermediates in the reaction sequence. GPB I and II contained the most extensive sequence of intermediates as well as the highest concentrations. Components which were relatively unaltered and at levels comparable to those found in ambient aerosols collected in the same region under clean conditions (no burning) dominated BCB I and II.

Table III.1 is a compilation of the concentrations of the diterpenoids present in the smoke aerosols sampled. Included for comparison purposes are results from aerosols collected under clean conditions in the same region where the burns were carried out and the extract from the bleed resin of a Brewer Spruce also collected in the coastal forest near the burn sites (Chapter V). The letters signifying the components in Table III.1 correspond to those presented in Figures III.1 and III.2.

Diterpenoids with the Abietane Skeleton

The proposed scheme for the thermal degradation of resin

TABLE III.1: CONCENTRATIONS OF CYCLIC DITERPENOIDs PRESENT IN SMOKE AEROSOLS PRODUCED BY SLASH BURNING (in pg/m³)

<u>Compound¹</u>		<u>Compositional</u>		<u>BCB I</u>	<u>BCB II</u>	<u>GPB I</u>	<u>GPB II</u>	<u>Ambient³</u>	<u>Brewer Spruce³</u>
<u>Code</u>	<u>Name</u>	<u>Formula</u>	<u>M.W.²</u>					<u>Aerosol</u>	<u>Bleed Resin</u>
PAH	various	various		4100	140	15,840	5,800		
A	retene	C ₁₈ H ₁₈	234	-	-	8,100	1,600	-	-
B	dihydroretene	C ₁₈ H ₂₀	236	-	-	-	80	-	-
C	tetrahydroretene	C ₁₈ H ₂₂	238	-	-	-	100	-	-
D	16,17-bisnordehydroabietane	C ₁₈ H ₂₆	242	-	110	-	-	-	-
E	a	methylretenes	C ₁₉ H ₂₀	248	-	-	2,400	23	-
	b						-	64	-
	c					1,900	18	-	-
	d					-	49	-	-
	e					-	24	-	-
F	a	dehydrosimonellite and others	C ₁₉ H ₂₂	250	-	-	100	-	-
	b						34	-	-
	c						50	-	-
	d						56	-	-
G	a	simonellite and others	C ₁₉ H ₂₄	252	-	-	92	7	-
	b						72	-	-
	c						19	7	-
	d						61	-	-
H	a	19-norabieta-4(18),8,11,13-tetraene	C ₁₉ H ₂₆	254	-	62	440	20	-
	b	19-norabieta-3 or 4,8,11,13-tetraene					120	15	+
I	a	19-norabieta-8,11,13-triene	C ₁₉ H ₂₈	256	-	90	100	110	0.4
	b	18-norabieta-8,11,13-triene (dehydroabietin)				160	380	120	3.3
J	a	dimethylretenes	C ₂₀ H ₂₄	262	-	-	-	14	-
	b						-	5	-
K	a	e.g. 3-oxonorabieta-6,8,11,13-tetraene	C ₁₉ H ₂₄ O	268	10	6	-	-	-
	b	e.g. 7-oxonorabieta-5,8,11,13-tetraene			14	11	-	50	-
L	a	7-oxo-19-norabieta-8,11,13-triene	C ₁₉ H ₂₆ O	270	110	78	430	110	-
	b	7-oxo-18-norabieta-8,11,13-triene (7-oxodehydroabietin)			230	91	560	150	-

Compound ¹		Compositional		BCB I	BCB II	GPB I	GPB II	Ambient ³	Brewer Spruce ³
Code	Name	Formula	M.W. ²					Aerosol	Bleed Resin
M	e.g. 1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylic acid	C ₁₇ H ₂₂ O ₂	272	90	87	230	104	-	-
N	a dehydroabietal	C ₂₀ H ₂₈ O	284	44	37	-	-	9.0	+
	b e.g. 16,17-bisnordehydroabietic acid	C ₁₈ H ₂₄ O ₂	286	-	18	-	-	-	-
O	e.g. 1-methyl-7-isopropyl-1,2,3,4-tetrahydrophenanthrene-1-carboxylic acid	C ₁₉ H ₂₂ O ₂	296	330	460	420	1,100	-	-
P	a e.g. 1,4a-dimethyl-7-ethyl-1,2,3,4,4a,9 or 10a-hexahydrophenanthrene-1-carboxylic acid	C ₁₉ H ₂₄ O ₂	298	-	13	-	73	-	-
	b e.g. 1,4a-dimethyl-7-ethyl-1,2,3,4,4a,9 or 10a-hexahydrophenanthrene-1-carboxylic acid			-	100	-	72	-	-
	c e.g. 1-methyl-7-isopropyl-1,2,3,4,9,10-hexahydrophenanthrene-1-carboxylic acid			-	-	-	180	-	-
Q	a e.g. 1,4-dimethyl-7-isopropyl-1,2,3,4-tetrahydrophenanthrene-1-carboxylic acid	C ₂₀ H ₂₄ O ₂	310	9	11	-	48	-	-
	b			-	-	-	55	-	-
R	13-isopropyl-5 α -podocarpa-6,8,11,13-tetraen-16-oic acid	C ₂₀ H ₂₆ O ₂	312	4	14	-	47	-	+
S	dehydroabietic acid	C ₂₀ H ₂₈ O ₂	314	12	37	-	-	42	+
T	a,b pimaric acids	C ₂₀ H ₃₀ O ₂	316	present	-	-	16	-	4 isomers
	c abietic acid			-	-	-	53	-	4 isomers

¹ Note - isomers of each compound are listed in the order that they elute on a DB5 (J&W Scientific) 0.25 mm X 30 m capillary column.

² Molecular weights of acidic components as methyl esters.

³ Ambient levels of components present in aerosols and the presence of these components in Brewer Spruce bleed resin collected in the coastal range of the State of Oregon (Chapter V).

FIGURE III.1

Scheme of thermal degradation of abietane skeleton
diterpenoids

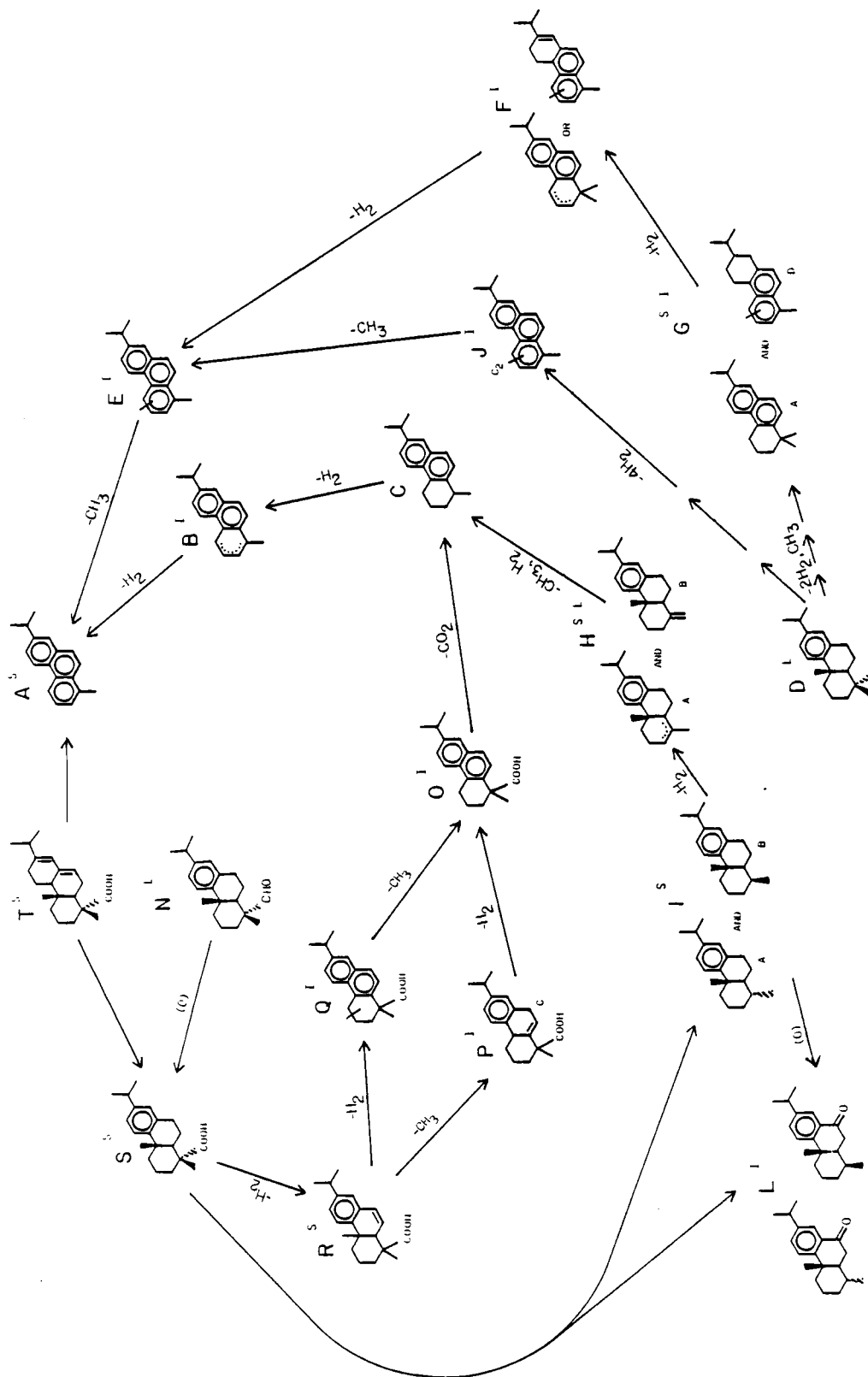


FIGURE III.1

components with the abietane skeleton is presented in Figure III.1. Sequential dehydrogenation, dealkylation and decarboxylation result in the aromatic product retene. All of the intermediates shown (except dehydroabietane which is shown for comparison purposes) were identified in one or several of the four slash burn aerosol samples. GPB II contained the most extensive group of intermediates documenting almost all stages of thermal alteration of the abietane skeleton. Also presented in Figure III.1 are the structures of diterpenoid ketones and an aldehyde identified as components of the smoke aerosols. These components may have various sources, including production by the original plant and thermal or microbial oxidation of the original resin components. These factors will be addressed later in the discussion.

As noted in the introduction, degraded diterpenoids have been found previously in the following environmental samples. Sediments from Lake Washington (Wakeham et al., 1980), the Northeastern Pacific, North Atlantic Ocean, Black Sea and Cariaco Trench (Simoneit, 1975; 1977a; 1986); in soils from coniferous forests (LaFlamme and Hites, 1978; Simoneit et al., 1986); and atmospheric particulate matter (Ramdahl, 1983; Simoneit and Mazurek, 1982). The most common components which were determined to be present were retene, dehydroabietin, simonellite, dehydroabietane, and dehydroabietic acid. Also mentioned as present in several of the studies were tetrahydroretene, norsimonellite and 19-norabieta-6,8,11,13-tetraene. The aerosols collected in the rural western United States (Simoneit and Mazurek, 1982) contained additional

intermediates such as abieta-6,8,11,13-tetraenoic acid, 16,17-bisnorabietic acid and 16,17-bisnordehydroabietane. The diterpenoids identified in these studies provided the basis for schematic interpretations of the successive decarboxylation, dehydrogenation and dealkylation of resin diterpenoids (e.g. abietic acid) to form retene. However, gaps remained in the sequence due either to the absence of the intermediates in the samples, or the fact that researchers did not search for them. The detailed sequence of intermediates present in the smoke samples from this study confirmed the proposed reaction pathways.

Processes producing the various suites of resin components seen in the four smoke samples can include (1) primary production by the vegetation being combusted, (2) oxidative diagenesis of this fresh resin matter upon exposure to the elements (occurring after expulsion from the plant as a bleed resin or exposure of litter after logging), (3) microbial oxidation and (4) thermal alteration. To distinguish thermal products from those of the other processes, a comparison of component suites in ambient aerosols and an understanding of typical products formed via other processes is important.

Resin components which will be considered primary for the purpose of this discussion are those which are produced by the vegetation or formed quickly from unstable intermediate compounds. Included in this group are the compounds present in ambient aerosols and the conifer bleed resins (e.g. Brewer Spruce resin) such as

abietic and dehydroabietic acids (T and S), dehydroabietin and isomer (Ia and b) and the resin aldehyde dehydroabieta1 (N). Since certain resin components such as neoabietic and levopimaric acids are thermally unstable (Schuller and Conrad, 1966), the original conformation of resins in the vegetation suite that was combusted is unclear.

Diagenesis of certain components upon extended environmental exposure cannot be discounted as a process responsible for some of the intermediates present in the aerosols; however, comparisons with the diterpenoids of the ambient aerosols and bleed resin which have undergone a moderate amount of exposure, account for the easily altered intermediates. A second process which must be distinguished from thermal alteration is microbial oxidation. The favored sites for microbial oxidation to the ketone functionality are carbon numbers 3 and 7 on the abietane skeleton (see Appendix IV for numbering system) (Biellman and Wennig, 1971). Components La and b in Figure III.1 might very well be produced by microbial oxidation of resin precursors. Of course, any of the oxidation processes might result in products with ketone functionalities at these positions if these are thermodynamically favored. The relative importance of various potential oxidation processes will be discussed later.

The distributions of the various intermediates are controlled by the conditions present in the burns such as temperature, starting materials, oxidizing/reducing characteristics of the combustion zone, and distance the aerosols were sampled from the burn which

would have an effect on the relative exposure to light and reactive components in the plume. It was noted by Ramdahl (1983) that the ratio of retene to PAH was higher with lower combustion temperatures and air supply. Included in Table III.1 are the amounts of polynuclear aromatic hydrocarbons (PAH, alkylated plus non-alkylated). Note the absence of retene in samples BCB I and II. This absence coupled with the significant quantities of PAH, especially in the case of BCB I, may be indicative of burning conditions which include high temperatures and an abundant air supply. This may explain the scarcity of altered diterpenoids in these samples. As the collection site was directly in the plume of the burn and visibility was greatly reduced due to the level of smoke present, the absence of these diterpenoids is not due to a low particle count. GPB I and II, on the other hand, have relatively high concentrations of retene as compared to total PAH. Coincidentally, the concentrations of other diterpenoids are also elevated. This may be indicative of a cooler burn or one in which zones of oxygen depletion have occurred.

Among the primary components in the abietane suite of diterpenoids such as abietic acid, dehydroabietic acid and abietal, concentrations when present were in the range of ambient levels. These compounds were absent in GPB I and II, except for a level of abietic acid in GPB II which was comparable to ambient levels. The absence of dehydroabietic acid is significant since this component is usually the predominant diterpenoid present in environmental

samples (Simoneit, 1986).

Dehydroabietin and its isomer (Ib and a, respectively), also in the bleed resin and ambient aerosols, were present in the smoke aerosols at concentrations ranging from 90 to 110 and 120 to 380 pg/m^3 , respectively. These levels are two orders of magnitude higher than concentrations of these compounds in ambient aerosols. This elevation of concentration may be due to a thermal generation of these components or a volatilization at the flame front. However, concentrations ranged up to 120 pg/m^3 in aerosols collected inland (Chapter V). Thus, a contribution directly from surrounding vegetation not involved in the burn cannot be discounted.

As was noted in research on plant waxes and rural ambient aerosols collected across the State of Oregon (Chapter V), dehydroabietin always predominates over the 19-norabieta-8,11,13-triene. The presence of a corresponding set of isomers with a ketone functionality at position C-7 (according to the abietane skeleton numbering system, compounds La and b) with a predominance of 7-oxodehydroabietin over 7-oxonorabietatriene supports the possibility of a relationship between the sets of compounds. Components La and b may be oxidative products of the hydrocarbons Ia and b or they could be derived from a similar source. By examining the structures of Ia and b to determine a reason for the predominance of dehydroabietin (Ib), it was determined that of the two, Ib has greater inherent steric hindrance between the C-19 and C-20 methyl groups than C-18 and C-20 for Ia. No other difference can be seen. This would not explain the predominance of isomer Ib.

Thus, analysis of possible precursors becomes essential. A likely starting material is dehydroabietic acid (S), which is a predominant diterpenoid in environmental samples (Simoneit, 1986) and is found in the resin fractions of local vegetation (Standley and Simoneit, 1987). Decarboxylation of dehydroabietic acid would result in the direct formation of dehydroabietin, the predominant isomer. Callitrisic acid (see Appendix IV for the structure), which was not identified in the samples thus far but which is produced by Juniperus sabina berries (dePascual et al., 1983) and by cypress in the southern hemisphere (Carman and Deeth, 1967) would upon loss of the carboxylic acid group form the 19-norabieta-8,11,13-triene isomer. The other two epimers of dehydroabietic acid which have the 5 α configuration at C-5 (abietane skeleton numbering system) are structurally relatively strained (chair/strained boat configuration as compared to the chair/chair configuration of dehydroabietic acid) and would thus be expected to be the least stable.

There was an unidentified isomer of dehydroabietic acid present in BCB I and the Brewer Spruce bleed resin at 5 and 2% the concentration of dehydroabietic acid, respectively. This may be the callitrisic acid. In any case, the most likely precursor to component Ia is callitrisic acid.

The corresponding ketone isomers, La and b, were present at 78 to 430 pg/m³ for isomer La and 91 to 560 pg/m³ for Lb. Though these were not found in the ambient aerosols collected in the region, they were determined in aerosols collected at rural sites inland at

concentrations up to 12 and 64 pg/m^3 for isomers La and b, respectively (Chapter V). Their absence in the coastal aerosols is postulated to be due to insufficient time for photochemical or microbial oxidation. The levels present in the smoke aerosols are clearly elevated and as such are indicative of thermal oxidation. They may result from oxidation of the dehydroabietin isomers or by direct oxidation and decarboxylation of the same precursors. Present in the study of the extract of berries of Juniperus sabina mentioned previously was the component 7-oxocallitrisate. This resulted from oxidation upon storage of the extract and demonstrates a possible reaction intermediate between callitrisic acid and 7-oxo-19-norabietatriene, which would result from a decarboxylation of the 7-oxocallitrisic acid.

Two isomers with the formula $\text{C}_{19}\text{H}_{24}\text{O}$ (K) were present only in relatively low levels ranging from 6 to 50 pg/m^3 . These might be formed by dehydrogenation of components La and b, since the ratio of the two isomers is similar to those seen between the components Ia and b and La and b. It is impossible to tell without further information whether these keto-diterpenoids result from microbial, photochemical or thermal oxidation.

Concentrations of the partially aromatized resin acids, compounds R and Q (Figure III.1), are relatively low in BCB I and II (4 to 14 pg/m^3), absent in GPB I and slightly elevated in GPB II at 47 to 55 pg/m^3 . They are predominated in all samples by the dealkylated intermediate, compound O (e.g. 1-methyl-7-isopropyl-1,2,3,4-tetrahydrophenanthrene-1-carboxylic acid), which ranges in

concentration from 330 to 1100 $\mu\text{g}/\text{m}^3$. From its presence in all samples at relatively high concentrations, component O appears to be quite a stable intermediate in the scheme of thermal alteration.

The degraded diterpenoids further along in the scheme (i.e. - compounds B, C, E, F, G, H, and J) were only present in GPB I and II, except for one isomer of H in BCB II. They completed the documentation of the aromatization of abietane skeleton components to retene. There were several pathways possible with respect to the sequence of dealkylation and dehydrogenation; however, though it can be said that certain characteristics associated with the burns affect the alteration path followed, the numerous variabilities inherent and the limited number of samples makes the correlation of suites of intermediates with conditions present during the burns impractical.

Diterpenoids with the Pimarane and Podocarpane Skeletons

Trends noted in the abietane series were mirrored in the pimarane skeleton diterpenoids (Figure III.2). However, there were fewer representative intermediates, probably due to their generally lower concentrations in resins. In BCB I, reflecting the low levels and scant representation of intermediates in the abietane series, there were no measurable levels of pimarane skeleton diterpenoids. BCB II contained moderately low levels of the slightly altered components D and Pa and b, with no contribution from the unaltered pimaric acid. This distribution was essentially the same as that in

FIGURE III.2

Intermediates in the scheme of thermal degradation of
pimarane and podocarpene skeleton diterpenoids

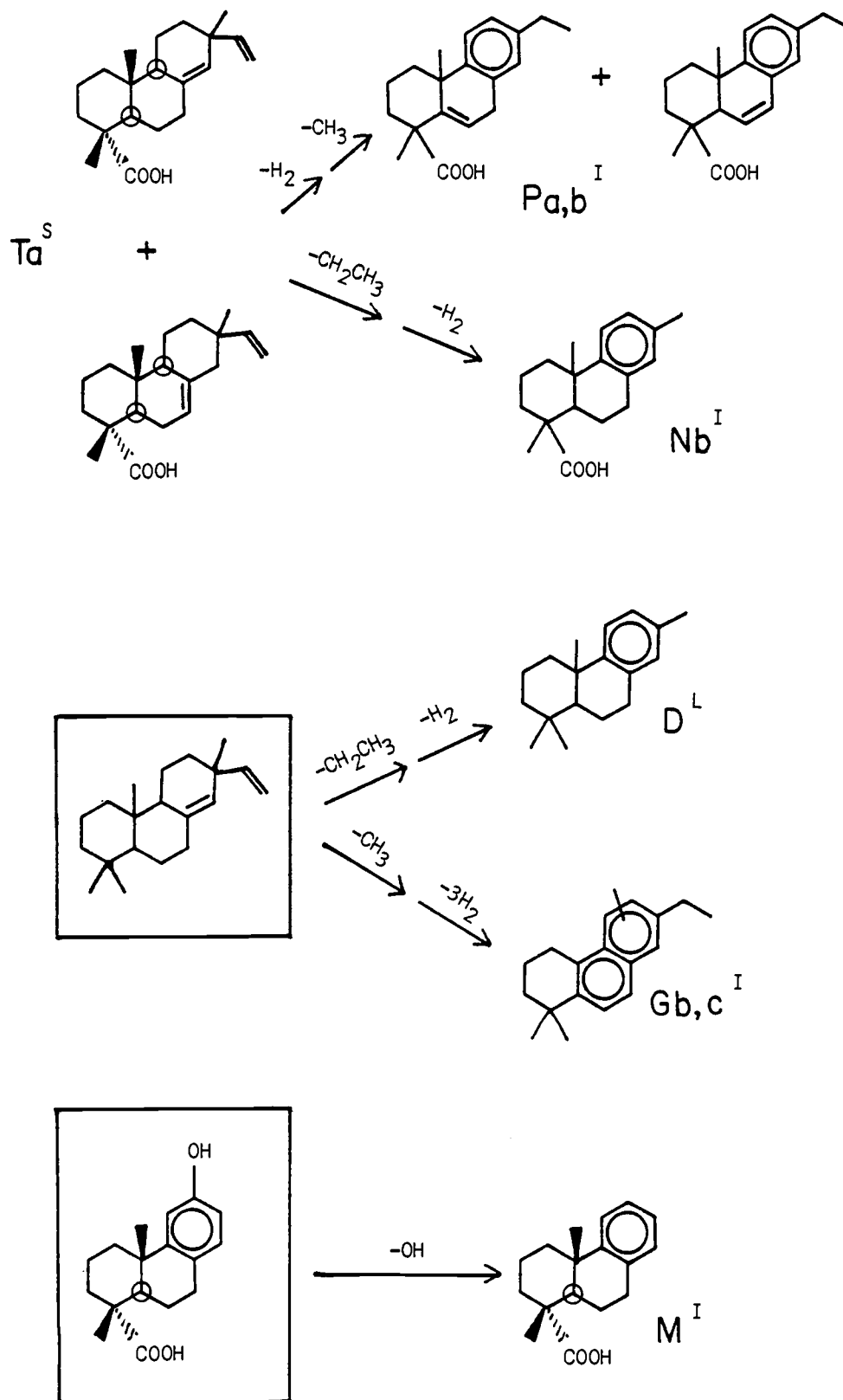


FIGURE III.2

the abietane series, with no measurable contribution from abietic acid but moderate levels of the slightly altered intermediates. Both suites of diterpenoids in GPB I were skewed toward the thermally altered components as demonstrated by the presence only of component G in the pimarane series. GPB II, which contained the broadest range of intermediates in the abietane suite of diterpenoids also contained pimarane-type diterpenoids from the unaltered T compound to the moderately altered P and G compounds.

One diterpenoid present, which was probably derived from podocarpic acid, was 1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylic acid (M, Figure III.2). This compound was present in all four samples at level ranging from 90 to over 200 pg/m^3 .

Altered Diterpenoids: Direct Input versus Diagenesis

To estimate the relative contribution of resin components emitted to the troposphere from biomass burning and natural input, which in part may eventually be deposited to the ocean, the following calculations were made. These results should give a first approximation to the relative concentrations in oceanic sediments of directly deposited versus diagenetically produced decarboxylated and aromatized resin components.

Seiler and Crutzen (1980) estimated that 0.5 to 2×10^{15} g of carbon are produced annually by biomass combustion. I estimate that 10-50% of that is contributed by the combustion of coniferous fuel by taking into account the following: (1) forest fires produce more

particulate matter per km^2 than grass and shrub fires; (2) 50% of the world's land mass is thought to be vegetated by coniferous trees and shrubs (Box, 1981); and (3) biomass burning in the southern hemisphere is dominated by the clearing of tropical forest (non-coniferous), which would limit the amount of emissions attributable to the combustion of coniferous biomass. An analysis by Gray et al. (1984) determined that aerosols in Los Angeles contained 14.9% carbon to 26.7% extractable organic matter (combustion aerosols may differ but this figure is useful as a first approximation). Finally, diterpenoids (predominantly thermally altered) analyzed in this study (Chapters III and IV) comprised 0.06 to 1.0% of the extractable organic matter fraction in combustion aerosols. The tropospheric load of diterpenoids produced from biomass combustion would therefore be 0.5 to 200×10^8 g/yr. The average concentration of diterpenoids in aerosols collected in rural regions of Oregon (Chapter V) was 0.8 ng/m^3 . As mentioned previously, it was estimated (Box, 1981) that 50% of the world's land mass, or $80 \times 10^6 \text{ km}^2$, was covered by coniferous trees and shrubs. Deposition can be estimated by multiplying the atmospheric concentration and area of contributing vegetation by a flux factor, 1.0 cm/sec (i.e. McVeety, 1986; McClure, 1976). The resulting flux would be on the order of $2 \times 10^7 \text{ kg/yr}$.

Therefore, the estimated relative contribution of altered diterpenoids via direct deposition versus diagenesis of unaltered resins would be 3 to 1,000 times as much. Since transport of plant

wax particles would not be as long-range due to their relatively larger size (Van Vaeck and Van Cauwenberghe, 1978; 1985), this estimate may even be lower than the actual value.

As these calculations present a first approximation, it would be highly recommended that additional work, such as the analysis of the physical characteristics of the carbon particles co-occurring with diterpenoids (i.e. - Goldberg, 1984), be done to refine the above figures. However, these figures demonstrate that previous theories proposing diagenesis of unaltered transported resin material as the primary process resulting in aromatized, decarboxylated diterpenoids may need to be revised.

CONCLUSIONS

In an investigation of the resin components present in the smoke aerosols produced during slash burning, we have accounted for the reaction intermediates which document the complete sequence of thermal transformation of resinous components such as abietic acid and dehydroabietin to retene, the fully aromatized component. We believe this demonstrates the process of instantaneous thermal maturation which parallels the diagenetic pathways described in soils and in sedimentary records (LaFlamme and Hites, 1978; Simoneit, 1977a; Simoneit et al., 1986; Wakeham et al., 1980). In addition, since transport of tropospheric aerosols produced by combustion is well documented on a global scale (Chung and Le, 1984), this study may also demonstrate a source of partially or completely aromatized diterpenoids deposited directly to sediments.

As it can be assumed that natural forest fires emitting smoke containing thermally altered diterpenoids have occurred since conifers originated in the late Carboniferous period (Scott, 1974; Thomas, 1970), the possibility exists that a significant portion (3 to 1,000 times the amount) of the degraded diterpenoids present in the sedimentary record which previously have been attributed to diagenesis may have been directly deposited via atmospheric transport of smoke particles. The relative contribution of these thermally-altered diterpenoids to aerosols and ultimately to sedimentary sinks, needs to be explored further.

IV: Correlation of Organic Molecular Tracers in
Residential Wood Combustion Products with the
Source of Fuel

ABSTRACT

Polar cyclic di- and triterpenoids were analyzed in the extracts of residential wood combustion aerosols collected in suburban sections of Eugene, Oakridge and Corvallis, Oregon. Additional samples collected included smoke from two wood stoves burning only alder or pine as fuel, soot from the alder burning stove and a fireplace where oak was the predominant fuel, and alder wood. Due to the relatively cooler temperatures present under residential wood combustion smoldering conditions, as compared to the active burning of slash burns, incomplete combustion resulted in preservation of high levels of the natural products discussed.

There were three distinct signatures which could be used to trace relative input from coniferous, alder and oak combustion products, i.e. - diterpenoids, lupane derived triterpenoids and friedelin, respectively. Conifer combustion products dominated the smoke aerosols.

INTRODUCTION

Residential wood combustion (RWC), most specifically combustion using wood stoves, has increased dramatically in the last decade as a major source of home space heating. Nationwide, ten percent of home heating input is from firewood combustion (Lipfert and Dungan, 1983). In the State of Oregon, greater than half of the households use RWC for some space heating (Oregon Department Environmental Quality (ODEQ), 1981). Emissions are relatively high compared to other sources of space heating such as oil and gas, ranging from one to two orders of magnitude higher in production of inhalable particulate matter ($< 0.25 \mu\text{m}$) (Cooper, 1980; ODEQ, 1981). Since many stoves are operated at a slow smoldering rate to conserve fuel, elevated levels of partially combusted particulate material are released (ODEQ, 1981). The levels of respirable particulate matter produced by RWC in Oregon are greater than any other identified state-wide source except slash burns (ODEQ, 1981).

Researchers have demonstrated the presence of carcinogens in RWC smoke and the production of mutagens upon exposure to light and oxidizers such as NO_2 and O_3 (Alfheim et al., 1984; Kamens et al., 1984; Ramdahl et al., 1984). Additionally, emissions are generated at ground level with little thermal buoyancy, primarily at night when temperature inversions are most likely to occur, and are concentrated in residential sections where impact to human health, especially that of people with respiratory ailments, can be severe (Cooper, 1980).

Using various tracer methods developed thus far, researchers have demonstrated significant impacts in certain communities, with RWC contributing 20 to 73% to ambient levels of particulate matter (e.g. - Dasch, 1982; Carlson, 1982; Cooper et al., 1981; Kowalczyk et al., 1982; Murphy et al., 1982; Ramdahl et al., 1984; Sexton et al., 1984). The methods chosen to quantify the contribution from RWC included radiotracers (Cooper, 1980), chemical element balances (Friedlander, 1973), gaseous tracers (Khalil et al., 1983) and atmospheric dispersion models (Dobbins, 1979).

In this preliminary study of smoke aerosols produced by residential wood combustion, we present the characterization of higher weight organic components useful in tracing specific fuels and general combustion conditions. Residential neighborhoods in three Oregon cities were chosen as sampling sites due to the high contribution from RWC and minimal contamination from automotive and industrial sources.

SAMPLING AND ANALYSIS

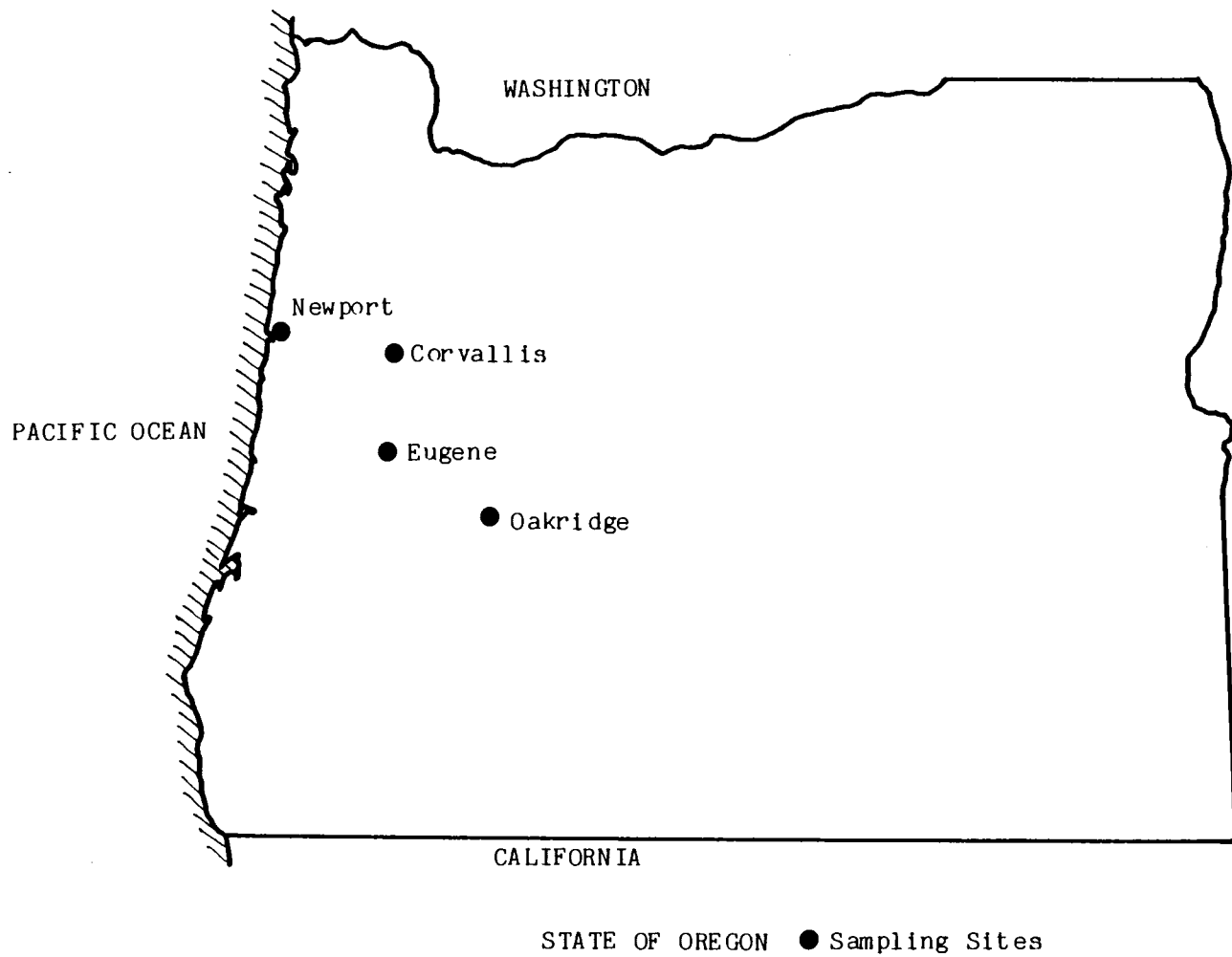
Sampling.

Smoke particles ($>0.5 \mu\text{m}$) produced predominantly by residential wood combustion were collected on precombusted (500°C for four to eight hours) quartz fiber filters (Pallflex QAS) using high volume air samplers operated at a flow rate of approximately $1.5 \text{ m}^3/\text{min}$. Filters were stored directly in the jars in which they would be extracted and spiked with a few ml of methylene chloride to inhibit microbial growth (Simoneit and Mazurek, 1982). Samples were kept at 4°C until analysis.

Locations of the sampling sites are shown in Figure IV.1. Residential neighborhoods in three Oregon cities were chosen for the sampling of ambient RWC aerosols: Eugene, Oakridge and Corvallis. Sample volumes ranged from 2,300 to $11,000 \text{ m}^3$. The first sample, collected on top of the Lane County Regional Air Pollution Authority (L.C.R.A.P.A) trailer in Amazon Park in south Eugene, is comprised of aerosols collected over a 28 hour period between January 26 and 27, 1985. The sample collected at Oakridge was also collected at a L.C.R.A.P.A. site, which was located on the roof of the Willamette Activity Center one block south of Highway 58. Sampling proceeded for approximately 25 hours between February 12 and 13, 1985. The final ambient RWC sample was collected on the roof of the B.R.T. Simoneit residence in a residential section of north Corvallis. The sampler was operated between December 14 and 20 for a total of 146

FIGURE IV.1
Sampling sites in the State of Oregon

FIGURE IV.1



hours. All filters were a dark brown after sampling.

For purposes of source characterization, two samples of relatively pure smoke from wood stoves at residences in rural regions of the Oregon Coast were collected. Samplers were placed within a couple of meters of the stove pipes on the roofs of the homes where one stove burned predominantly alder and one burned only pine. Additional samples collected were the soot from an oak burning fireplace, soot from the wood stove burning alder and a piece of alder wood taken from the source wood pile.

Extraction and Analysis.

Samples were extracted by ultrasonic agitation for fifteen minutes using five aliquots of three solvent mixtures: one aliquot of benzene; three aliquots of a three to one toluene:chloroform mixture; and one aliquot of a one to three mixture of toluene:chloroform. All sample extracts were then processed according to the filtering and transfer procedure developed by Mazurek (1985).

The extracts were evaporated under vacuum to approximately 5 to 10 ml. Final evaporation to 1 to 2 ml was performed using a nitrogen blowdown apparatus. Extract weights were determined by the evaporation of a 100 microliter aliquot of the extract under a gentle stream of nitrogen. Aliquots containing approximately 2 to 10 mg of higher molecular weight organic matter (in a toluene:methanol solvent mixture to facilitate methylation, Schlenk and Gellerman, 1960) were derivatized using an excess of

diazomethane in benzene prepared from the precursor N-methyl-N'-nitro-N-nitrosoguanidine (Pierce Chemical Co.).

The methylated extracts were then separated into four fractions of varying polarity by silica gel thin layer chromatography with a 19:1 hexane:ethyl acetate mixture as the mobile phase. The fraction which eluted midway on the plate (R_f 0.3 -0.7) contained the polar di- and triterpenoids. This is the fraction which will be discussed in this paper. Data from the other fractions will be analyzed at a later date.

Extract fractions were analyzed using capillary gas chromatography (GC, Varian 4600 with a 30 m X 0.25 mm i.d. capillary column coated with DB-1701, J&W Scientific, temperature programmed for 65°C for 5 minutes, then to 130°C at a rate of 15°C/min, then to 275°C at a rate of 6°C/min) and capillary gas chromatography/mass spectrometry (GC/MS, Finnigan 4000 quadrupole mass spectrometer coupled to a 9610 GC with a 30 m X 0.25 mm i.d. capillary column coated with DB-5, J&W Scientific, temperature programmed for 65°C for 6 min, then to 310°C at a rate of 4°C/min). Components were quantified on GC/MS by coinjection of a known standard (hexamethyl benzene). Structures which were identified are presented in Appendix IV. The structures of Fc, Gc and d, Hb and I were determined by comparison with the GC retention times and mass spectra of the authentic standards. Structures C and E were identified by comparison with published mass spectra (Enzell and Wahlberg, 1969; Simoneit and Mazurek, 1982). The remaining structures were elucidated by interpretation of the mass spectra.

RESULTS AND DISCUSSION

Extract weights of the smoke produced by two wood stoves and ambient aerosols collected in the residential sections of three Oregon towns are listed in Table IV.1. Included for comparison purposes is the range of extract weights determined for smoke particles produced by the prescribed burning (slash burns) of logging litter and brush on clear cut sites in the Oregon Coast Range (Standley and Simoneit, 1987).

Concentrations of solvent extractable organic matter ranged from 40 to 120 $\mu\text{g}/\text{m}^3$ in the ambient aerosols and from 87 to 600 $\mu\text{g}/\text{m}^3$ in the smoke particles collected from the flues of the wood stoves. Since the Oregon State Standard for attainable air particulate loading is 60 $\mu\text{g}/\text{m}^3$ (ODEQ, 1981), and the extractable fraction of fresh and degraded particles produced by RWC has been measured to be between 50 and 89% of the total particulate weight (Kamens et al., 1984), it can be inferred that all three localities clearly exceeded the allowable particle load as legislated by the state of Oregon. In comparison, slash burn aerosols, with extract weights ranging from 6 to 43 $\mu\text{g}/\text{m}^3$, were at times so concentrated that visibility was reduced to less than several hundred meters.

Extracts of the polar di- and triterpenoid fractions of the various samples were analyzed to determine the presence of molecular markers (e.g. natural products) which could be traced back to the source material, i.e.- alder, oak or conifer fuel. For example, smoke from wood stoves burning only pine or alder was collected to

TABLE IV.1. ANALYTICAL DATA ON SMOKE AND AEROSOL PARTICLES

<u>Sample</u>	<u>Volume (m³)</u>	<u>Extract Weight (µg/m³)</u>
Wood stove smoke from alder	400	600
Wood stove smoke from pine	1,500	87
Eugene aerosols	2,600	65
Oakridge aerosols	2,300	120
Corvallis aerosols	11,000	40
Slash burn smoke (for comparison, ref. Chapter II)		6-43

determine the compound signature from these specific fuels. Extracts of alder wood, soot from the flue of the alder burning stove, and particles collected a meter from the stove pipe formed a trio of samples intended to trace the molecular markers through combustion and particle formation. An extract of oak soot was also collected and analyzed. Since no smoke sample of purely oak combustion was obtained and hard woods are a common fuel used in wood stoves, the results from this sample were extrapolated as a first approximation of the oak smoke signature. The validity of this extrapolation was demonstrated by the sample suite for alder, as will be explained later.

The molecular markers determined in the source samples and their corresponding concentrations in ambient aerosols collected in Eugene, Oakridge and Corvallis, are presented in Table IV.2. Concentrations of markers in aerosols are presented in ng/m^3 for the purpose of comparisons with results from other studies and also normalized to extract weight ($\mu\text{g/g}$ extract) to assist in tracing the fate of components during production of particles by combustion. Plotted in Figures IV.2 and IV.3 are the select ion monitoring (SIM) plots of the major components identified, detailing elution order and relative abundance in the smoke aerosols collected in Corvallis. It is clear that this sample is dominated by dehydroabiatic acid, which is also the predominant diterpenoid found in most western United States aerosols and other environmental samples (Simoneit, 1986; Simoneit and Mazurek, 1982).

Comparisons with levels of the predominant diterpenoids present

TABLE IV.2: CONCENTRATIONS OF CYCLIC DI- AND TRITERPENOIDS IN RESIDENTIAL WOOD COMBUSTION SAMPLES
($\mu\text{g/g}$ extract included for comparison purposes)

COMPOUND Code	COMPOSITIONAL Name	FORMULA	M.W. ²	ALDER		ALDER		PINE SMOKE		EUGENE		OAKRIDGE		CORVALLIS			
				OAK SOOT ($\mu\text{g/g}$)	WOOD ($\mu\text{g/g}$)	SOOT ($\mu\text{g/g}$)	ALDER SMOKE (ng/m^3)	($\mu\text{g/g}$)	(ng/m^3)	($\mu\text{g/g}$)	(ng/m^3)	($\mu\text{g/g}$)	(ng/m^3)	($\mu\text{g/g}$)	(ng/m^3)		
A	unknown	-	262	-	-	-	-	-	47	560	24	360	74	630	13	330	
B	e.g. 1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydro-phenanthrene-1-carboxylic acid	$\text{C}_{17}\text{H}_{22}\text{O}_2$	272	-	-	-	-	-	13	160	3.6	54	18	150	2.0	50	
C	dehydroabietal	$\text{C}_{20}\text{H}_{28}\text{O}$	284	-	-	-	-	-	5.5	66	2.7	41	6.2	53	-	-	
D	e.g. 1-methyl-7-isopropyl-1,2,3,4-tetrahydro-phenanthrene-1-carboxylic acid	$\text{C}_{19}\text{H}_{22}\text{O}_2$	296	-	-	-	-	-	15	180	0.98	15	4.0	34	0.12	3	
E	13-isopropyl-5 α -podocarpa-6,8,11,13-tetraen-16-oic acid	$\text{C}_{20}\text{H}_{26}\text{O}_2$	312	-	-	-	-	-	-	-	5.7	86	27	230	0.40	10	
F	a dehydroabietic acid + b isomers c	$\text{C}_{20}\text{H}_{28}\text{O}_2$	314	-	-	-	-	-	2.6 5.9	31 71	-	-	-	-	-	-	
G	a abietic and pimaric acids b c d isopimaric acid	$\text{C}_{20}\text{H}_{30}\text{O}_2$	316	-	-	-	-	-	17 27 240	200 320 2900	2.2 - 64	33 - 960	440 6.0 5.1 180	3700 51 43 1500	270 - - 7.8	- - 1.0 200	
H	a unknown b Lup-22(29)-en-3-one c unknown	$\text{C}_{30}\text{H}_{48}\text{O}$ $\text{C}_{30}\text{H}_{48}\text{O}$ $\text{C}_{30}\text{H}_{48}\text{O}$	424	-	0.02 0.11 0.06	4.7 61 16	26 150 58	44 260 99	-	-	-	-	-	-	-	0.77 0.72 0.63	19 18 16
I	friedelin	$\text{C}_{30}\text{H}_{50}\text{O}$	426	0.62	-	-	-	-	-	-	0.37	6	-	-	2.2	55	
J	unknown	$\text{C}_{33}\text{H}_{56}\text{O}$	468	-	-	1.5	12	20	-	-	-	-	-	-	-	-	
K	unknown	$\text{C}_{34}\text{H}_{58}\text{O}$	482	-	4	2.5	9.4	16	-	-	-	-	-	-	0.32	8	

¹ Note - isomers of each compound are listed in the order that they elute on a DB5 (J&W Scientific) 0.25 mm x 30 m capillary column.

² Molecular weights of acidic components as methyl esters.

FIGURE IV.2

Plots of characteristic ions of the major diterpenoid
components present in Corvallis ambient aerosols

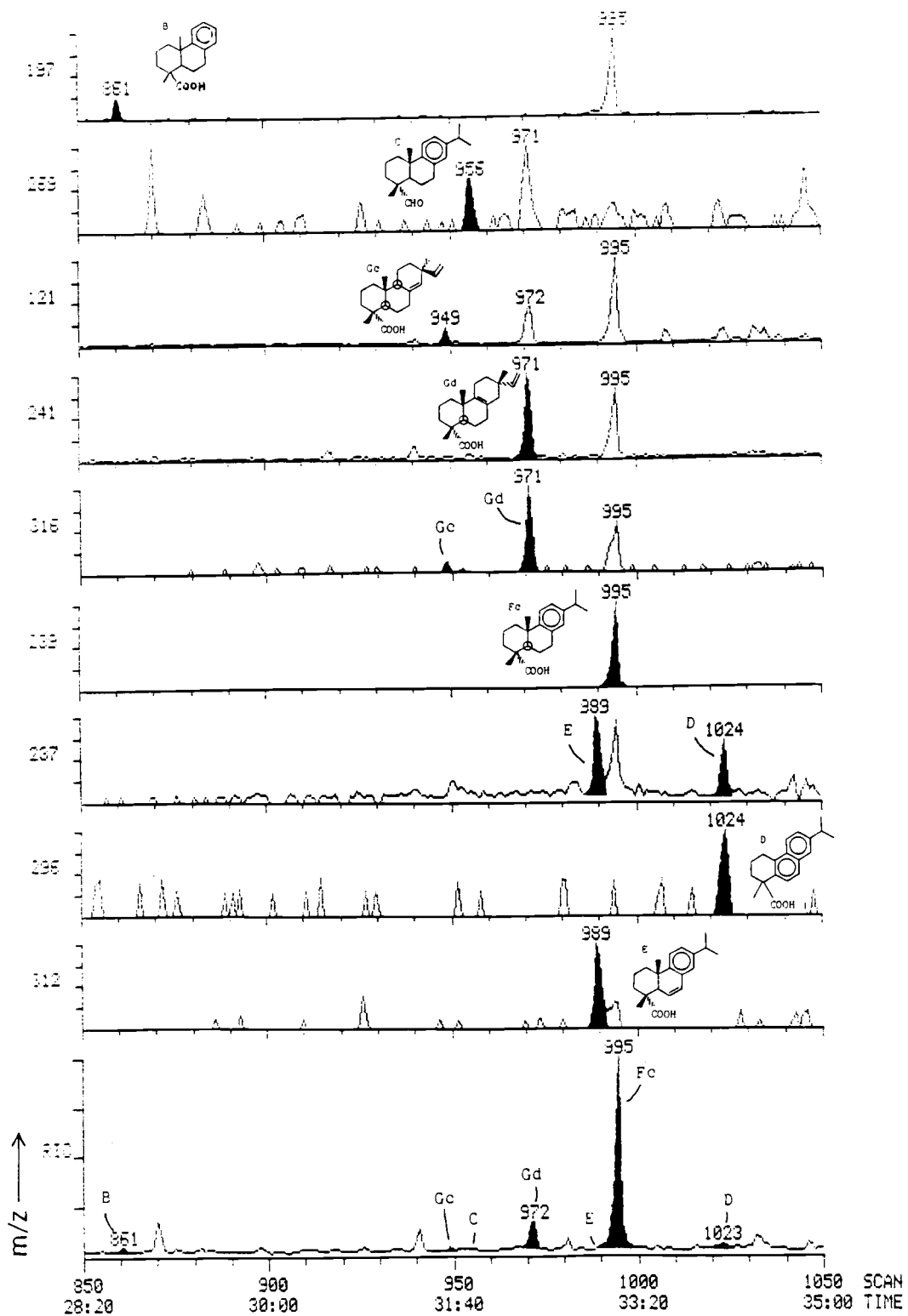


FIGURE IV.2

FIGURE IV.3

Plots of characteristic key ions of the major triterpenoids (lupenone and friedelin) present in Corvallis ambient aerosols

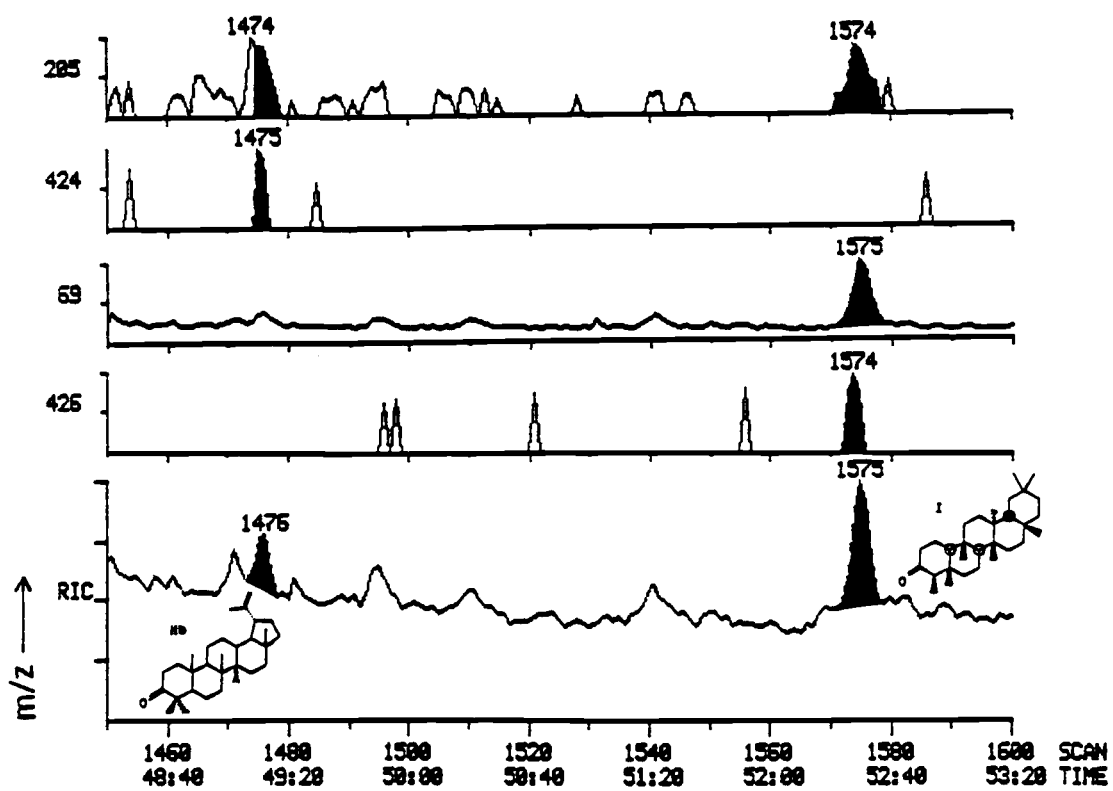


FIGURE IV.3

in rural ambient aerosols across the state of Oregon and smoke from slash burns conducted in the Oregon Coast Range (Chapters III and V) show that there is an elevation of concentration in the range of one to three orders of magnitude. This demonstrates that these aerosols were produced under relatively low temperature and oxygen combustion regimes, as in smoldering which produces greater levels incompletely combusted material such as the aromatized diterpenoids (Chapter III; Ramdahl, 1983; ODEQ, 1981). This preservation of molecular structures enhances the correlation with specific woods used as fuel in residential wood combustion.

Three general groups of components can be elucidated among those present in the samples. First, the most predominant suite in terms of concentration and variety is the cyclic diterpenoids, compounds A through Gd (Table IV.2). Except for the minor presence of dehydroabietic acid in the oak soot, these components are only found in the pine stove smoke and the three ambient aerosol samples. Second, the oxygenated cyclic triterpenoids (compounds Ha,b and c, J and K), are found only in the trio of samples derived from alder and Corvallis ambient aerosols. Third, friedelin (component I) is found only in the oak soot and the Eugene and Corvallis aerosol samples. Though signature assignment is preliminary with just these few markers, especially for the oak combustion signature, trends can be discerned.

Plotted in Figure IV.4 are histograms of the predominant markers for each of the three fuel types, normalized to the most

concentrated compound in each sample. Dehydroabietic and isopimaric acids (Fc and Gd) represent coniferous input. Lupenone, which predominates the alder distributions, and friedelin, representing tentatively the oak signature, are also plotted. The only incongruity was the presence in the oak soot of dehydroabietic acid, a predominant diterpenoid in coniferous vegetation. This may have originated from coniferous fuel such as pine or cedar kindling chips combusted in the fireplace. No other diterpenoids were present. A reversal of the ratio of isopimaric to dehydroabietic acid in pine smoke as compared with the ambient aerosols may be due to their relative stability in the atmosphere, with isopimaric decomposing upon extended exposure. Another possible explanation would be that the fuel being utilized was coniferous but not the same species as the fuel burned in the stove sampled. In general, it appears that the predominant fuel utilized in Oakridge is coniferous, an inexpensive and readily available wood. Eugene and Corvallis aerosols, which are also predominated by resin components, show some influence from oak combustion. A measurable amount of lupenone in the Corvallis aerosols may indicate a contribution from alder combustion.

The validity of extrapolating the oak and alder combustion signatures from the soot can be seen in Figure IV.5. Three isomers with a molecular weight of 424, including lup-22(29)-en-3-one, are present in the alder sample trio. The relative ratios of the three compounds are quite similar; however, concentrations normalized to the extract weight vary. Lupenone is present at 0.11, 61 and 260

FIGURE IV.4

Normalized concentrations of predominant source signature components

FIGURE IV.4

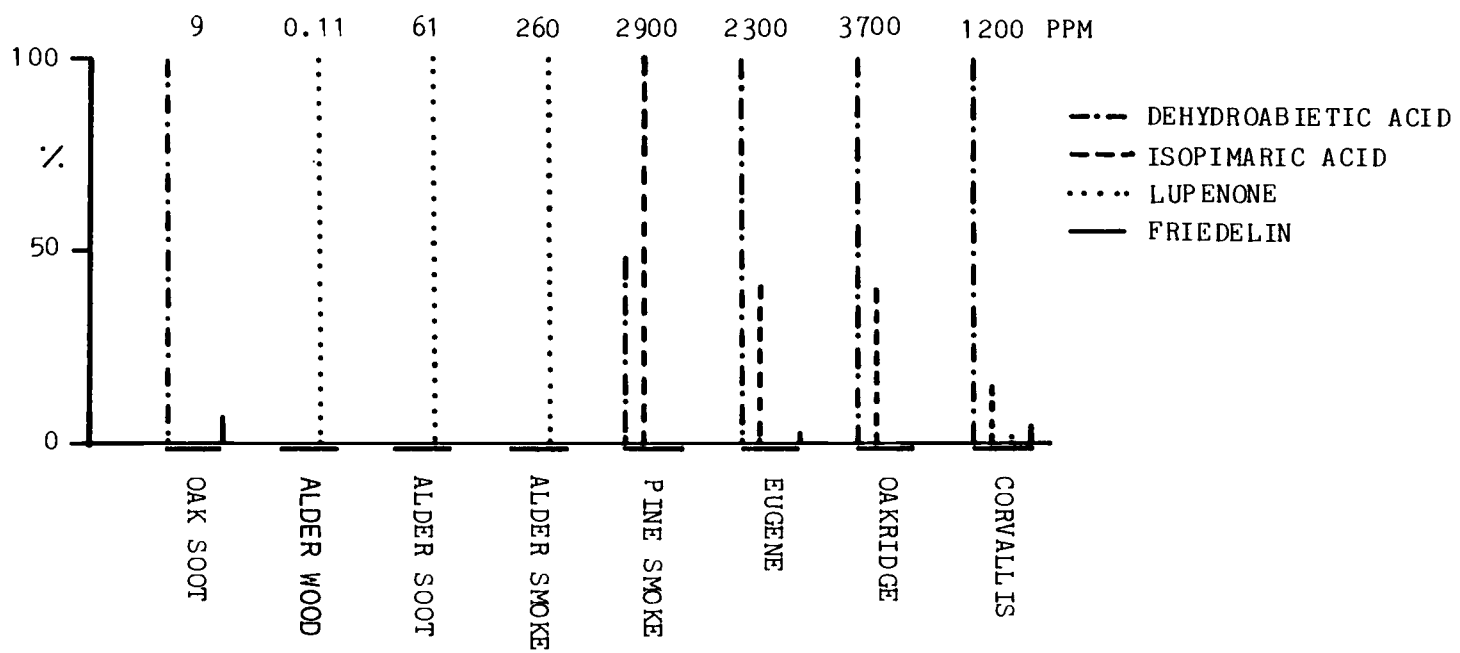


FIGURE IV.5

Normalized concentrations of lup-22(29)-en-3-one and isomers present in residential wood combustion samples

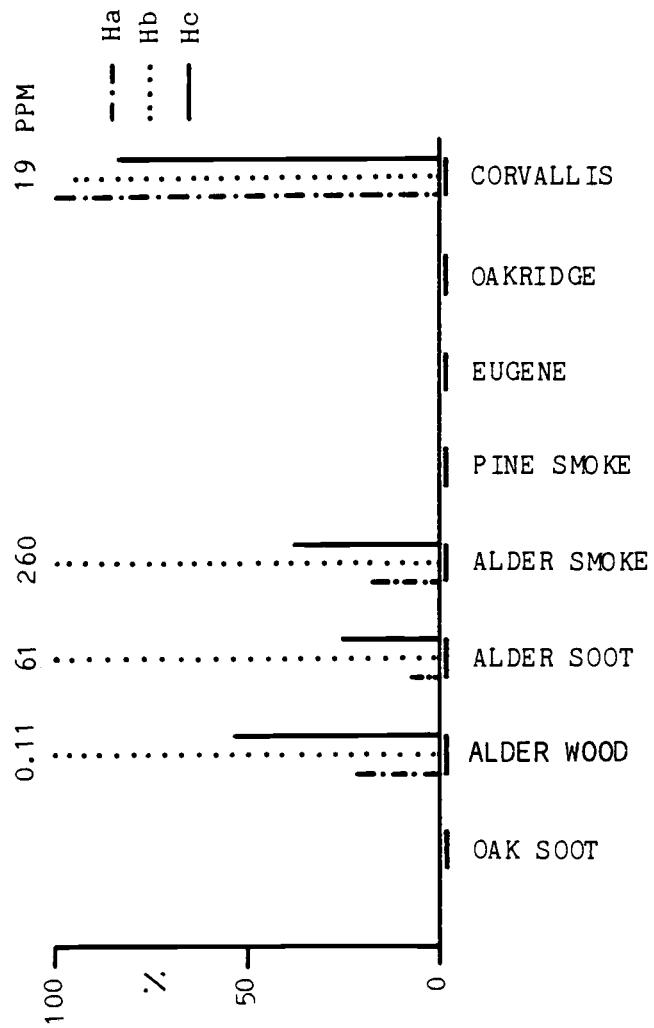


FIGURE IV.5

$\mu\text{g/g}$ (ppm) extract in the alder wood, soot and smoke aerosols, respectively. An enrichment of these components in the extract of the smoke as compared to the alder which may document the relative loss of other extractable material, with these isomers being relatively resistant to heat. The distributions of the three lupenone-type isomers in the Corvallis aerosols does not match that of the alder source trio. This may be a result of different source compositions or different stabilities of the compounds upon extended exposure to light and oxidizing conditions.

CONCLUSIONS

In an examination of the molecular markers present in a set of smoke samples from residential wood combustion, cyclic di- and triterpenoids were found to be useful in correlating signatures of combustion products of specific fuels to signatures present in ambient aerosols collected in three Oregon communities. In earlier research (Cooper et al., 1981), it was thought that no unique or reproducible signature could be obtained from higher molecular weight organic matter. Though reproducibility still needs to be ascertained, I have demonstrated that natural products such as the cyclic terpenoids are definitive tracers of specific types of fuel used in residential wood combustion.

The smoldering nature of RWC, as compared to processes of relatively high temperature combustion such as slash burning, is reflected in the compositional signatures of the organic fractions of smoke aerosols by the elevated concentrations of incomplete combustion products.

There was a clear predominance of coniferous combustion products as recognizable diterpenoids in the ambient aerosols collected, which is likely to be due to the availability and inexpense of pine and fir wood in the state.

V: Natural Product Signatures in Tropospheric Aerosols:
Reproducibility, Sources and Transport

ABSTRACT

Sources, fates and variability of plant wax components were measured in aerosols collected across a transect in the state of Oregon. Compositions and concentration were determined by the analysis of the solvent extracts utilizing capillary gas chromatography and capillary gas chromatography/mass spectrometry.

The degree of variability, both with respect to concentration and signature, ranged between 2 and 190%, depending partially on the physical aspects of the sampling site and the degree of heterogeneity of the predominant vegetation in the region.

Correlations between the homologous series of n -alkanes and n -alkanoic acids of the predominant regional vegetation and aerosols permitted, in some cases, direct signature fingerprinting between plant waxes and the corresponding aerosols. Where aerosols resulted from heterogeneous regional vegetation or the sites were situated too closely to vegetation, these correlations became complex, with high uncertainties. Correlation between source vegetation and aerosols of molecular markers such as di- and triterpenoids proved more definitive and suggested long-range transport.

INTRODUCTION

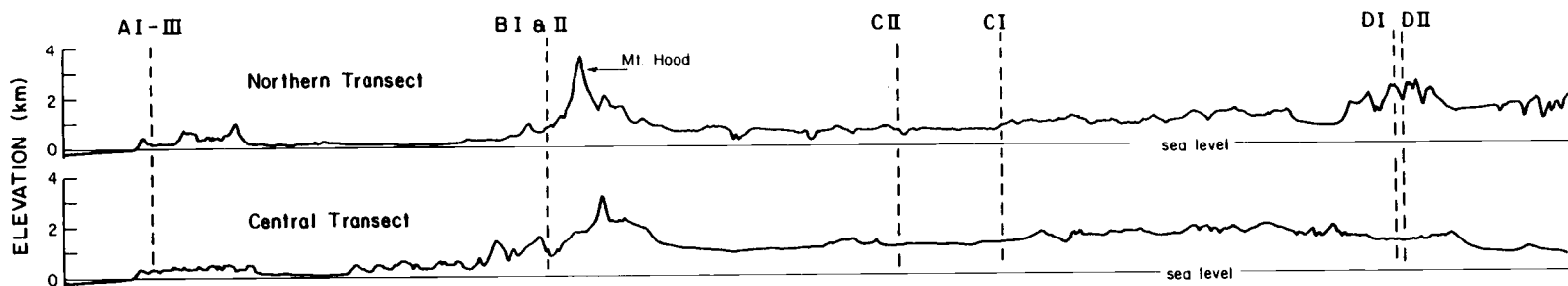
The presence of aerosols containing higher plant waxes in the troposphere has been well documented (for example: Arpino et al., 1972; Broddin et al., 1980; Duce et al., 1983; Gagosian et al., 1981; Mazurek and Simoneit, 1984; Matsumoto and Hanya, 1980; Simoneit, 1977b; 1984; Simoneit and Mazurek, 1982; Simoneit et al., 1980). However, in comparison to the relatively extensive studies that have been carried out on urban aerosols, few systematic investigations have been made of the rural contributions of organic carbon to the troposphere (Duce et al., 1983; Hahn, 1980; Jaenicke, 1980). Processes involved in biosphere/atmosphere interactions are not well documented with respect to higher molecular weight organic compounds.

The goal of this study was to systematically study the sources and transport of higher plant waxes in aerosols and the reproducibility of their signatures. The study was carried out along a transect across the state of Oregon, which had the advantage of being predominantly rural with a source of relatively clean air entering the state from the Pacific Ocean. This transect, originating on the central Oregon coast and terminating in the northeastern corner of the state (see Figures V.1a-d), traced the predominant wind trajectories. Thus, the air masses sampled in northeastern Oregon traversed the other three regions in the state which were characterized with respect to aerosol and plant wax signatures (Figure V.1b).

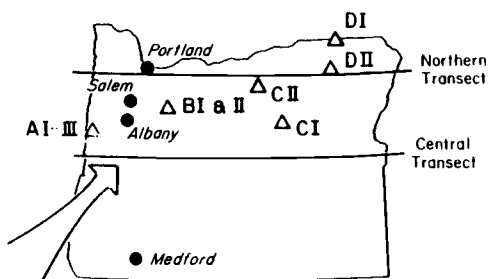
FIGURE V.1

Sampling sites in the state of Oregon: AI-III - Coast Range; BI&II - Willamette National Forest; CI - Rowe Creek; CII - Wilson Ranch; DI&II - Umatilla National Forest. (a) Transects of topography, (b) Sampling sites, (c) Predominant vegetation, and (d) Average annual temperature

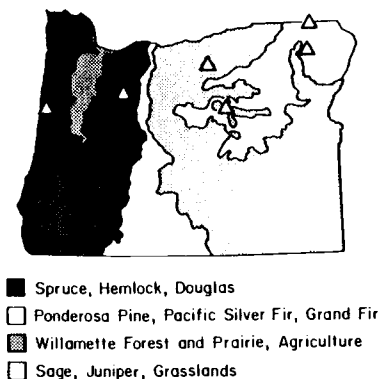
a. SAMPLING REGION: TRANSECTS OF TOPOGRAPHY



b. SAMPLING SITES



c. VEGETATION



d. AVERAGE ANNUAL TEMPERATURE RANGE

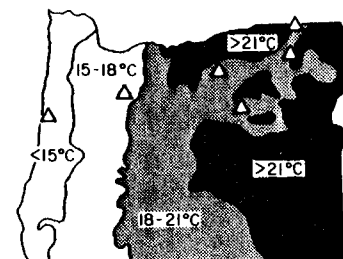


FIGURE V.1

In recent work by Gagosian et al. (1987), a combination of organic tracers and trajectory analysis of aerosols collected in a remote oceanic region provided a preliminary method of assigning the regional sources of air parcels. However, in a discussion on tracers of atmospheric transport, Levy (1987) noted that horizontal trajectories were not appropriate for complex terrain or where vertical movement was involved. Flow around hills has been demonstrated to be highly dependent on the degree of stratification of the flow field, with neutral and unstable conditions resulting in a three dimensional recirculation zone in the lee of the hill (Ryan et al., 1984). As can be seen from the topographical cross sections shown in Figure V.1a, the complexity of the terrain in the study region is substantial. The inherent turbulence as well as vertical and horizontal deviations from the trajectory would greatly influence the source assignment of aerosols collected at ground level.

This paper presents the results from the molecular characterization of organic matter in tropospheric aerosols and predominant vegetation extracts utilizing capillary gas chromatography (GC) and capillary gas chromatography/mass spectrometry (GC/MS), with quantitation using selected ion monitoring (SIM) GC/MS. Correlation with sources and the uncertainties inherent in interpretation due to variation are discussed.

EXPERIMENTAL

Sampling Locations and Descriptions

Ten aerosol samples, particles $> 0.5 \mu\text{m}$, were collected in each of four rural regions along a transect tracing the prevalent southwesterly wind pattern across the state of Oregon (Figure V.1a-d). Two 20 hour samples were collected simultaneously on each of five consecutive days. This sampling scheme was designed to give data on the variability in aerosol concentration and composition both on a day to day basis and between samples collected side-by-side. A summation of the meteorological data is presented in Table V.1. As expected for the season in which the samples were collected, the predominant winds were from the southwest, except for the final four days of sampling when the wind direction shifted to the west and finally a wind from the northwest on the last day of sampling.

Extracts of the wax, bark and sap of the predominant vegetation were also collected in each of the regions. Descriptions of the sampling sites and the predominant vegetation follow.

The Oregon Coastal Range.

The three sites sampled in the first region were within the canopy of a mixed coniferous stand, within the canopy of an homogeneous alder grove, and on an open range adjacent to and southwest of the alder grove. All three sites were approximately 5-10 km from the Pacific Ocean. A two lane highway, U.S. Route 101,

TABLE V.1: WEATHER CONDITIONS

<u>SITE</u>	<u>WIND</u> ¹	<u>DAYTIME</u> <u>T°C</u>	<u>SKY</u> <u>CONDITION</u>
Coast I (mixed coniferous canopy)	SWm	10-23	sunny/cloudy
II (Alder grove)	SWm	10-23	"
III (open range)	SWm	10-23	"
Willamette I (on range just above treeline)	SWmWb	~20	sunny
II (mixed coniferous canopy)	WmNWm	~20	"
Columbia Basin I (Rowe Creek valley)	SWmod	25	sunny
II (Wilson Ranch)	SWbrisk	6-28	cloudy
Umatilla I (open range)	SWm	5-13	sunny/cloudy
II (border-mixed coniferous forest)	SWm	13-28	sunny

¹ Wind direction from . m = mild, mod. = moderate (~ 10-20 km/h), brisk (~ >20 km/h)

runs along the coast between the ocean and the sampling sites and the small town of Waldport (population less than 1000) lies approximately 10 km southwest; otherwise there is little anthropogenic influence on the aerosol compositions which originate from oceanic sources and the 5-10 km of coniferous and alder trees and fields of brush. The predominant vegetation sampled in the region includes: moss, Salmonberry leaves, Red Alder bark and leaves, Wood Fern, Sword Fern, Norway Spruce needles and sap, Brewer Spruce needles and sap, and Douglas-fir needles.

The Willamette National Forest.

The two sites where sampling occurred were adjacent to each other, the first just above the tree line near the top of a ridge on the western edge of the Cascade mountain range in the Willamette National Forest. The second site was 10 m below the first site and within the canopy of a mixed coniferous forest. This mountain ridge lies just west of the Willamette Valley, a populated region which is primarily agricultural but includes several industrial regions (see Figure V.1b). These include wood and paper processing, rare earth metals extraction and processing, agricultural products, and miscellaneous industries such as electronics. Collection of the major regional vegetation included: moss/lichen, Rhododendron leaves, Mountain Hemlock leaves, big-cone Douglas-fir needles, and Brewer Spruce needles.

The Columbia Basin and Edge of the Umatilla National Forest.

The first sampling site in this region was on Rowe Creek which is at the southwestern edge of the Umatilla National Forest. The predominant vegetation in this area was grass, brush, juniper and sage. The second site was on the Wilson Ranch, a cattle ranch and wheat farm on a high plain in the Columbia Basin which lies between the Willamette and the Umatilla National Forests. Samples were collected on a harvested wheat field still containing wheat stubble. Other vegetation was sparse and limited to sage and grasses. This site was 100 km from the Cascade Mountain Range and coniferous forests.

The Umatilla National Forest.

The first of two sites where samples were collected lies on a ridge above the tree line at an approximate altitude of 2 km at the northeastern corner of Oregon. The predominant vegetation included brush, small trees such as alder and maple, and some coniferous trees. The surrounding mountains contained many sites which were logged by clear cutting and still relatively clear or grown over with small trees and brush. The second site in this region was in the southwestern region of the Umatilla National Forest and at the edge of a mixed coniferous forest. This site was within a few km of a four-lane highway. The predominant vegetation in the region of which extracts were obtained are as follows: Douglas-fir needles, elm leaves, alder leaves, fern, laurel leaves, maple leaves, Ponderosa Pine needles, White Fir needles, and Pacific Silver Fir

needles.

Pacific Ocean.

Two aerosol samples were collected on board the R.V. Wecoma during the October 1985 cruise. The transect was at approximately 45°N, 8 to 20 km offshore Oregon. Due to contamination from the ship's stacks, interpretation of the hydrocarbon fraction was not possible. Results from the n-alkanoic acid fractions are presented.

Collection of Aerosols

Aerosols >0.5 μm were collected on precombusted quartz fiber filters (Pallflex QAS) using high volume air samplers (Simoneit and Mazurek, 1982). The average flow rate was 1.5 m^3/min and sample volumes ranged from 1300 to 2100 m^3 . The samplers were powered by Honda EG 1400X generators, which had been converted for use with propane as fuel. After collection the sample filters were stored in annealed glass jars and spiked with 5-10 ml of dichloromethane to inhibit microbial growth. Samples were then stored at 4°C until analysis (for some samples refrigeration was delayed until return from the field). Extraction of the sample aerosols was carried out within the jars used for storage to minimize contamination or loss in transferring (Mazurek, 1985).

During aerosol collection, samplers were placed on a platform approximately 2 m in height to minimize contamination from soil and debris. Sampler exhaust was vented approximately 30 m downwind

using tubes attached to the exhaust ports. Generators were also placed 30 to 50 m downwind from the samplers to minimize contamination from their exhaust.

Sample Work-up and Analysis

Sample filters were extracted by ultrasonic agitation using the following sequence of solvent mixtures: one aliquot of pure benzene, three aliquots of a 2:1 mixture of toluene:chloroform mixture and then one aliquot of a 1:2 mixture of toluene:chloroform. The duration of each sonication was fifteen minutes. Extracts were combined, filtered and transferred to round bottom flasks using an apparatus developed by Mazurek (1985).

Extracts of the vegetation samples were obtained by briefly dipping leaves or bark in dichloromethane to dissolve the external waxes. Care was taken to not leave the specimens in the solvent too long so as to minimize the extraction of significant amounts of the internal cellular lipids. Bleed resin was merely dissolved in dichloromethane. All vegetation extracts were then filtered through annealed glass wool before sample work-up (Mazurek, 1985).

The filtered extracts were evaporated under vacuum to approximately 2 ml. Aliquots were then taken for the determination of extract weights and derivatization. Alkanoic acid and phenolic moieties in the extracts were methylated using diazomethane in benzene prepared from the precursor N-methyl-N'-nitro-N-nitrosoguanidine (Pierce Chemical Co.).

Aliquots of the methylated extract were separated into four fractions on silica gel by thin layer chromatography. The mobile phase was a mixture of 19:1 hexane:chloroform. The four fractions collected contained the following classes of compounds: (1) n -alkanes and saturated and unsaturated cyclic di- and triterpenoid hydrocarbons, (2) mid-chain alkanones and polynuclear aromatic hydrocarbons, (3) n -alkanoic acid-methyl esters and saturated and unsaturated di- and triterpenoid ketones and methyl esters, and (4) n -alcohols and polar organics.

The first three of the four fractions collected will be discussed in this paper. Analysis of the components present in the fourth fraction (alcohols and polar organics) will be presented in a later paper. Extract fractions were analyzed using capillary gas chromatography (GC, Varian 4600 with a 30 m X 0.25 mm i.d. capillary column coated with DB-1701, J&W Scientific, programmed: 65°C for 5 min, then to 130°C at a rate of 15°C/min, then to 275°C at a rate of 6°C/min) and capillary gas chromatography/mass spectrometry (GC/MS, Finnigan 4000 quadrupole mass spectrometer coupled to a 9610 GC with a 30 m X 0.25 mm i.d. capillary column coated with DB-5, J&W Scientific, temperature programmed: 65°C for 6 min, then to 310°C at a rate of 4°C/min, MS conditions were as follows: filament 0.45eV, multiplier 70eV, ionizer 330°C, manifold 120°C).

Quantitation of the homologous series was carried out by comparison of the GC peak area with that of a co-injected known standard, hexamethyl benzene. Molecular markers were quantitated on GC/MS also by comparison with the peak area of the same standard

RESULTS AND DISCUSSION

Analyses of the distributions of homologous series of n -alkanes and n -alkanoic acids in aerosols and plant waxes yielded information on the variability of their distribution patterns and how closely the signatures of aerosols from a region reflected those of the predominant vegetation. It has been suggested that plant wax hydrocarbon distributions might have chemotaxonomic significance (Eglinton et al., 1962). However, due to the relatively simple structural nature of these components and the complexity of the assemblage of components present in waxes (Kolattukudy, 1976), the information present in the homologous series is not definitive enough to allow clear conclusions about source vegetation or transport of the resulting airborne waxes. Further, since free n -alkanoic acids are relatively minor wax components and intermediary in the production of other wax constituents, concentrations may be significantly influenced by processes occurring in the leaf and by degradation of wax esters, which decompose to give an alcohol and an alkanolic acid (Tulloch, 1976).

Homologous series in plant waxes and their corresponding aerosols exhibit pronounced carbon number preferences (CPI, the measure of the odd-to-even chain length predominance in n -alkanes and the even-to-odd predominance in n -alkanoic acids, Bray and Evans, 1961; Mazurek and Simoneit, 1984) and specific carbon number maxima (C_{max} , Mazurek and Simoneit, 1984), which can be used in the documentation of variation and trends and in preliminary

correlations with sources.

The cyclic di- and triterpenoids present had structures with a higher degree of complexity and thus specificity to species of plants. They are therefore more useful in chemotaxonomic correlations. These components are known as molecular markers (Simoneit, 1978, 1982, 1986) and have been useful in chemotaxonomic correlations by phytochemists (i.e. - Manners and Davis, 1984). Due to ground air mass turbulence these correlations tracing the atmospheric transport of regional plant waxes produced by the major vegetation must be made cautiously. As these aerosol samples were collected at ground level, it will be seen that this factor greatly complicated correlation with distant sources.

Homologous Distributions: Concentrations and Reproducibility

Presented in Tables V.2 and V.3 are summaries of the analytical data of the n -alkane and n -alkanoic acid homologs present in aerosol and vegetation extracts (note that samples which were collected side-by-side are connected by a line next to the sample letters). For comparison, regional averages are presented for all parameters. A complete file of the histograms of the aerosol and vegetation homolog distributions are presented in Appendices II and III. Certain distributions will be shown in this chapter's figures for purposes of discussion.

Total n -alkane and n -alkanoic acid concentrations in the transect aerosols ranged from 0.4 to 28 ng/m³ and 1.2 to 62 ng/m³, respectively. These values were two to three orders of magnitude

TABLE V.2 ANALYTICAL DATA OF TRANSECT AEROSOLS

SAMPLE	Total Volume		n-Alkanes			n-Alkanoic Acids		
	(m ³)	C _{max}	C _{max} (ng/m ³)	CPI _{C₂₀-C₃₆}	C _{max}	C _{max} (ng/m ³)	CPI _{C₁₅-C₃₇}	
A. Coast Range:								
I. Mixed coniferous forest	a.	2100	27	0.16	1.6	16(22)	1.7	16
	b.	2000	27(29)	0.18	1.7	16	1.1	31
	c.	1800	27	0.15	1.9	16(22,24)	0.78	15
	d.	1700	27	0.21	1.8	16(22,24)	1.0	10
II. Alder grove	a.	1800	27	0.16	4.1	16	5.3	21
	b.	1700	27	0.19	3.9	16	4.8	28
	c.	-	27	-	3.0	16	-	17
III. Open range	a.	2000	27(29,31)	0.05	2.3	16	2.6	21
	b.	2000	29	0.16	2.5	16	4.3	35
	c.	-	29	-	2.4	16	-	27
		Regional average	27.4	0.17	2.5	16	2.7	22
B. Willamette National Forest:								
I. Above tree line	a.	1600	25(27,29)	0.89	2.5	22(16)	0.70	3.3
	b.	1600	29(27)	0.64	2.9	22(16)	0.68	6.0
	c.	1500	31	10	6.6	16(22)	13	6.1
	d.	1600	31	0.94	4.0	22	0.28	4.7
	e.	1600	29(31)	1.0	3.2	26(16)	1.1	4.8
	f.	1600	31	4.0	5.0	16(26)	0.77	5.5
II. Mixed coniferous forest	a.	1600	29(27)	0.27	2.4	16(24)	1.8	5.9
	b.	1700	25(27)	0.43	2.4	16	2.7	5.5
	c.	1600	25	0.93	1.6	16(22)	1.5	3.4
	d.	1600	25	0.75	1.4	16	2.2	7.8
		Regional average	28.0	2.0	3.2	18.8	2.5	5.3

SAMPLE	Total Volume		n-Alkanes			n-Alkanoic Acids		
	(m ³)	C _{max}	C _{max} (ng/m ³)	CPI _{C₂₀-C₃₆}	C _{max}	C _{max} (ng/m ³)	CPI _{C₁₅-C₃₇}	
C. Columbia Basin:								
I. Rowe Creek	a.	-	29	-	2.9	16	-	6.3
	b.	1700	29	1.8	2.9	24(22,16)	0.84	4.2
	c.	1600	29(27)	0.63	1.9	16	0.79	6.3
	d.	1600	25(29,27)	0.58	1.9	14(16)	0.71	5.5
II. Wilson Ranch	a.	1600	29	1.8	3.2	16	1.5	7.4
	b.	1500	29	3.3	4.0	16	4.9	5.4
	c.	1700	29	1.9	2.9	22	4.9	6.2
	d.	1600	29	1.9	3.2	22(24)	9.2	7.3
	e.	1700	29(25)	1.3	1.9	16(22,24)	3.2	4.1
	f.	1600	29	3.4	2.5	22(16)	3.3	6.0
	Regional average		28.6	1.8	2.7	18.4	3.3	5.9
D. Umatilla National Forest:								
I. Open range	a.	-	31	-	2.5	16(22)	-	11
	b.	1600	29	0.22	2.7	16	0.75	12
	c.	1300	31(29)	0.33	2.1	16	1.6	21
	d.	1400	29(31)	0.34	2.3	16	0.72	8.3
II. Edgie mixed coniferous forest	a.	1700	31(29,27)	0.38	2.8	22(24)	1.4	6.7
	b.	1700	31(29)	0.54	3.0	16	0.65	7.1
	c.	1700	27(29,31)	0.75	5.2	16	1.0	9.1
	d.	1700	29(27)	0.72	4.3	16(22)	1.0	7.7
	e.	1500	31	1.0	4.0	16(22)	0.8	5.8
	f.	1500	29(31,27)	0.79	3.1	16	1.3	7.6
	Regional average		29.8	0.56	3.2	16.6	1.0	9.6
E. R.V. Wecoma Cruise								
	a.	1300	25	1.1	1.8	16	1.3	5.4
	b.	1300	27	0.56	1.3	16	0.76	7.2
	Regional average		26		1.6	16		6.3

TABLE V.3 ANALYTICAL DATA OF TRANSECT VEGETATION

Sample (Region)	n -Alkanes		n -Alkanoic Acids	
	C_{max}	$CPI_{C_{20}-C_{36}}$	C_{max}	$CPI_{C_{15}-C_{37}}$
I. Coast Range:				
a. Moss	27	14	24	18
b. Salmonberry	29	28	16(26)	37
c. Alder wax	29	23	22	72
d. Wood Fern	27	8.8	24	∞
e. Sword Fern	31	12	-	-
f. Norway Spruce wax	33	5.9	16	∞
g. Brewer Spruce wax	29	4.7	24(30)	17
h. Douglas-fir wax	29	7.4	24	15
II. Willamette National Forest:				
a. Moss/lichen	27	7.3	24	8.8
b. Rhododendron	33	15	-	-
c. Mountain Hemlock	31	17	28	2.3
d. Big-cone Douglas-fir wax	25	7.4	24(26)	7.8
e. Brewer Spruce wax	23	6.7	24	14
III. Columbia Basin:				
a. Sage	29	28	28	9.7
b. Juniper	25	5.3	-	-
c. Juniper/sage litter	33	11	28	7.0
d. Wilson Ranch soil	27(31)	10	16(22)	4.5
IV. Umatilla National Forest:				
a. Douglas-fir wax	25(27)	5.2	24(30)	9.7
b. "Green waxy bush"	29	36	22	21
c. Elm	29	56	22	8.1
d. Alder wax	31	49	24(28)	4.8
e. Fern	29	26	28(24)	19
f. Laurel	29	21	28	5.6
g. Maple	27	9.6	28	4.5
h. Ponderosa Pine wax	33	4.9	-	-
i. White Fir wax	33	6.0	-	-
j. Douglas-fir wax	25	6.8	24(26)	11
k. Pacific Silver Fir wax	25(27)	3.6	24	4.8
Range:	$C_{23}-C_{33}$	3.6-56	$C_{14}-C_{28}$	2.3- ∞

greater than loads measured in the remote Pacific by Gagosian and coworkers (1987), but were within the range of some measured oceanic levels, ranging from 5 to 30 ng/m³ for the n-alkanes (Marty and Saliot, 1982; Simoneit, 1977b; Van Vaeck et al., 1979) and from 3 to 300 ng/m³ for n-alkanoic acids (Barger and Garrett, 1976). These concentrations were at the low end of the range observed in rural aerosols analyzed by Simoneit and Mazurek (1982), which contained total hydrocarbon and fatty acid fraction concentrations ranging from 1 to 385 ng/m³ and 22 to 676 ng/m³, respectively.

Though n-alkane concentrations are relatively higher at the three eastern sites as compared to levels measured in the Coast Range aerosols (Table V.3), there does not appear to be a trend of gradually increased load as the air parcels move east. There is no eastward trend of increase in loading in the n-alkanoic acid fraction.

Quantitative variations between concentrations of homologous series from aerosol samples collected side-by-side and between samples collected on adjacent days (day-to-day) are presented in Table V.4 (an exact match would have a variance of 0 and one of 2 would reflect the highest degree of variation possible). In the n-alkane fraction, variations between samples collected side-by-side ranged from 0.02 to 1.6, with an average variance of 39%. On a day-to-day basis, variations ranged from 0.14 to 1.0 with an average of 0.52 or 52%. Variations in n-alkanoic acid concentrations were comparable to those of the n-alkanes with side-to-side and day-to-

TABLE V.4. VARIATION BETWEEN AEROSOL SAMPLES COLLECTED SIDE-BY-SIDE AND DAY-TO-DAY

<u>Sampling Sites</u>	<u>Σ N-alkanes</u>		<u>Σ N-alkanoic acids</u>		
	<u>side-by-side</u>	<u>day-to-day</u>	<u>side-by-side</u>	<u>day-to-day</u>	
A. Coast Range:	I (a-d)	0.09,0.20	0.14	0.35,0.24	0.05
	II (a-c)	0.29	-	0.17	-
	III (a-c)	-	0.67	-	0.19
B. Willamette:	I (a-f)	0.38,1.6,0.91	1.0,0.62	0.21,1.9,0.33	1.6,1.4
	II (a-d)	0.59,0.06	0.84	0.09,0.33	0.20
C. Columbia Basin:	I (a-d)	-,0.03	0.63	-,0.30	1.3
	II (a-f)	0.49,0.09,0.70	0.14,0.43	0.91,0.75,0.06	1.1,0.60
D. Umatilla:	I (a-d)	-,0.15	0.77	-,0.05	0.07
	II (a-f)	0.25,0.09,0.02	0.17,0.31	1.1,0.38,0.03	0.05,0.03
E. <u>R.V. Wecoma</u>	(a,b)	0.77	-	0.79	-
Overall Average		0.39 ± 0.42	0.52 ± 0.30	0.47 ± 0.49	0.60 ± 0.63

day ranges from 0.03 to 1.9 (ave. 0.47) and 0.03 to 1.6 (ave. 0.60), respectively. The average differences between samples collected from day-to-day were only slightly higher (13%) than between samples collected side-by-side. The relatively high variances measured for side-by-side samples are indicative of a large degree of heterogeneity in ambient aerosol loads, possibly caused by a large influence from local vegetation as opposed to transported aerosols, which should be well mixed by turbulent wind currents.

Anomalous concentrations in the homologous series of two sets of aerosol samples document one extreme with respect to variation. The two samples collected side-by-side on the second day of sampling at the first Willamette National Forest site (BIc and d) had respective n -alkane concentrations of 10 and 0.94 ng/m³. The set collected on the third day, BIE and f, contained 1 and 4 ng/m³, respectively. Since the sampling site for both sets was just above the tree line, it is likely that air parcels being sampled contained elevated levels of wax fragments formed by wind stress across the top of the canopy and that distribution of the particles was patchy.

Aerosol samples collected in the alder grove had differences between samples collected side-by-side of 29 and 17% for n -alkane and n -alkanoic acid concentrations, respectively. As proof of the homogeneity of the aerosols being sampled, the distributions of the homologs in the two samples were identical. These samples provided the best case of reproducibility in the study and gave a measure of the reproducibility of the high-volume air filtration method

employed. This will be discussed in further detail below.

There were no distinct correlations between degree of variation and site characteristics such as collection within a canopy versus on an open range. Nor were high variations in one homologous series necessarily reflected in the other. Variation between the three sample sets collected side-by-side at Wilson Ranch, for example, was 49%/9%/70% for the n -alkanes and 91%/75%/6% for the n -alkanoic acids. This lack of correlation with the nature of sites again demonstrated the complexity of the aerosols being sampled. In this case, however, the sampling site was on a high plain. Transported aerosols from the Willamette National Forest and mountain range 100 km east of the site should have had time to mix and homogenize.

Homolog Distributions: Correlation with Source Signatures

Recent work by Gagosian et al. (1987), discussed the tracing of the regional source of aerosols collected at a remote oceanic site by correlating the homologous distributions of straight chain plant wax components with trajectory analysis. Their approach differs from this work in that I correlated aerosol composition with a chemotaxonomic analysis of waxes in source vegetation. Similar conclusions could be drawn from both studies; however, on closer analysis, uncertainties become apparent. Gagosian et al. (1987), measured a shift upward in C_{max} in aerosols derived from tropical versus temperate regions. This shift was attributed to the adaptation of plants to more extreme temperatures, with longer chain

waxes necessary to withstand the heat in tropical regimes. We noted a shift in the C_{\max} of n -alkanes from $C_{27.4}$ to $C_{29.8}$ when moving from the cooler climate of the Oregon coast to the desert climate of eastern Oregon (see Figure V.1d for average temperature regions in the State of Oregon). Since the shift in C_{\max} measured across Oregon along roughly the same latitude is the same order of magnitude that Gagosian et al. (1987), attributed to the difference between tropical and temperate waxes, it becomes apparent that correlations of C_{\max} with latitude must be made cautiously. Climates can change drastically over relatively short geographical distances. Our research does support a preliminary correlation with climate. However, an additional complication with respect to the climatic correlations of homologous wax components can be demonstrated by the range of C_{\max} present in vegetation comprising one forest. For example, Douglas-fir and Ponderosa Pine within the Umatilla National Forest displayed C_{\max} of C_{25} and C_{33} , respectively. To reduce the uncertainty inherent in these correlations, one would have to determine the relative contributions of the various predominant vegetation species.

Furthermore, one aspect of the sampling suite that contributed to the uncertainty was that only one sample of each vegetation type was extracted at each site. Future work should include a systematic analysis of the reproducibility of plant wax signatures. Variations in both terpenoid and homolog distributions have been demonstrated as plants mature, though stability is usually reached during the flourishing stage in late summer and fall (Nishimoto, 1974; Zinkel

and Clarke, 1985). As this study was carried out during late summer/early fall and aerosols would reflect the distributions of the vegetation suite, this potential uncertainty should be minimized. However, as demonstrated by the variations in the signatures of alder leaf and Douglas-fir needle waxes collected at different sites (ranges of C_{29} to C_{31} and C_{25} to C_{29} , respectively), interpretation based on a C_{max} may be invalid and must be made cautiously.

An additional factor which complicates source correlation is the effect of terrain on air mass movement. In the study by Gagosian et al. (1987), the ocean provided no obstacles (neglecting vertical movements due to adiabatic lifting) and thus trajectory analysis was relatively simple. In this study, the complexity of the terrain of the study region as discussed previously would necessitate the use of a complex model to trace air flow, especially at ground level. In future transport studies, taking into account all three factors - aerosol composition, chemotaxonomic analysis of the source vegetation and air trajectory analysis - would reduce some of the uncertainties.

A variety of processes are involved in the production of rural aerosols and this is reflected in their relative complexity as compared to plant wax distributions. Part of that complexity derives from a suite of vegetation waxes being produced, dislodged and becoming airborne. Vegetation waxes in the sampling regions had a broad range of n -alkane C_{max} from C_{23} (Brewer Spruce) to C_{33}

(Ponderosa Pine, rhododendron, etc.). Plant waxes also have a narrower range of homologs than the aerosols. For example, elm wax n -alkanes are comprised predominantly of C_{29} , with insignificant contributions from homologs less than C_{27} and greater than C_{31} (see Appendix II). Some plant waxes have broader ranges, for example - White Fir with C_{21} - C_{35} and Douglas-fir with C_{21} - C_{31} , but most range no more than six consecutive chain lengths. Most aerosol samples had n -alkane distributions ranging from twelve to fifteen homologs.

Plant waxes and other biogenic sources have pronounced CPIs. In the vegetation sampled in this study, the CPIs ranged from 3.6 to 56 with an average of 16 (see Table V.2). CPIs of the aerosols, on the other hand, ranged from 1.3 to 6.6 with an average of 2.9. They reflect input from other sources. Additional processes that can contribute to rural aerosol signatures are combustion of organic matter, such as prescribed burning and residential wood combustion, and petroleum components from vehicular exhaust. Dilution by even chain length n -alkanes results in decreased CPIs. n -alkanes without carbon number predominance are produced in random processes such as combustion and thermal maturation in the sediments (Simoneit, 1983; Chapter II).

When contributions from n - C_{16} and lower n -alkanoic acid homologs are subtracted, there is no significant difference in the complexity between aerosols and vegetation waxes. This differs substantially from the increased complexity seen in the n -alkane fraction. CPIs for the aerosols ranged from 2.9 to 20 with an average of 8.4. For the vegetation waxes, CPIs ranged from 2.3 to

infinity, with an average of 14 not counting the sample with a CPI of infinity. As mentioned previously, information from n -alkanoic acid homologs must be viewed cautiously due to the various processes producing them.

Homolog distributions in aerosols collected in the alder grove on the Oregon Coast Range were highly reproducible in signature, both on a side-by-side and a day-to-day basis. As shown in Figure V.2, gas chromatograms of the n -alkanoic acid fraction of the three aerosol samples collected at this site are essentially superimposable. Even the location and shape of the hump of unresolved material is reproduced in all three samples. Histograms of both homologous series (Appendices II and III) detail an excellent reproducibility. The n -alkanoic acids in the aerosols mirror the signature of the alder n -alkanoic acids (see Figure V.3). The aerosols contained the following signature: a definitive C_{max} of C_{22} with C_{24} and C_{26} contributing approximately 69 (+/-9)% and 21 (+/-4)%, respectively. The alder leaf wax distribution was comprised of a C_{max} of C_{22} , with 70% C_{24} and 34% C_{26} . Whereas the n -alkanoic acid distribution matches that of the alder wax extract, the signature of the n -alkane fraction is different. As the aerosols are formed from a suite of vegetation types, it is apparent that ground vegetation, such as moss and Wood Fern (with C_{max} of C_{27}), had a greater influence on the n -alkane distribution. This will be discussed below. The correlations between source vegetation and regional aerosols at other, more heterogeneous sites were not as

FIGURE V.2

Gas chromatograms of n-alkanoic acid fractions (as methyl esters) collected within an alder canopy in the Oregon Coast Range

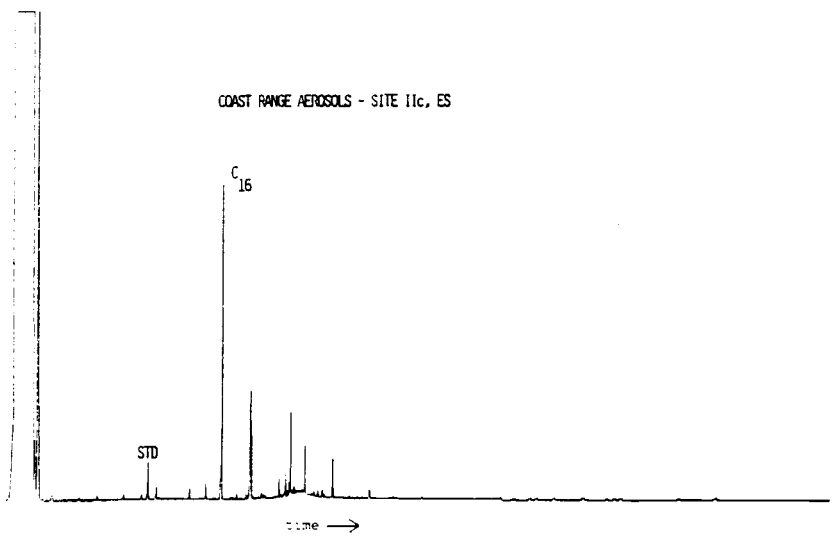
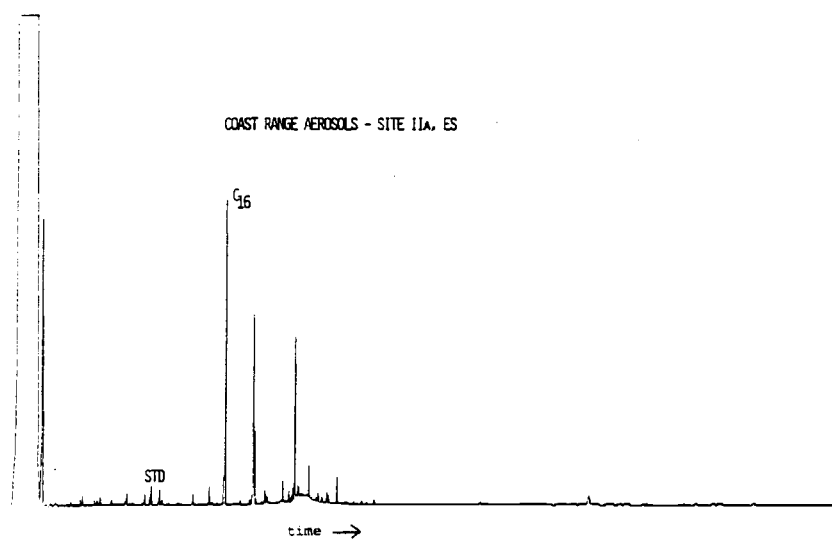
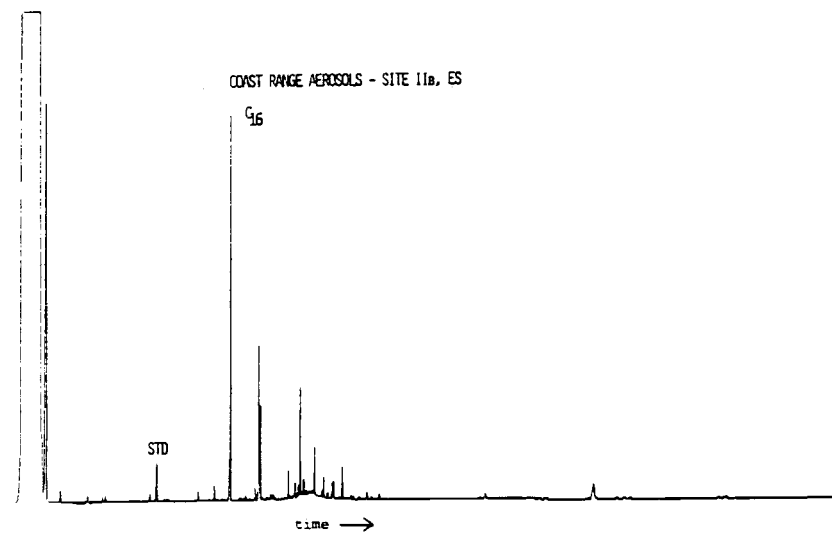


FIGURE V.2

FIGURE V.3

Distribution histograms of the n-alkanoic acid fractions of aerosols collected within an alder canopy

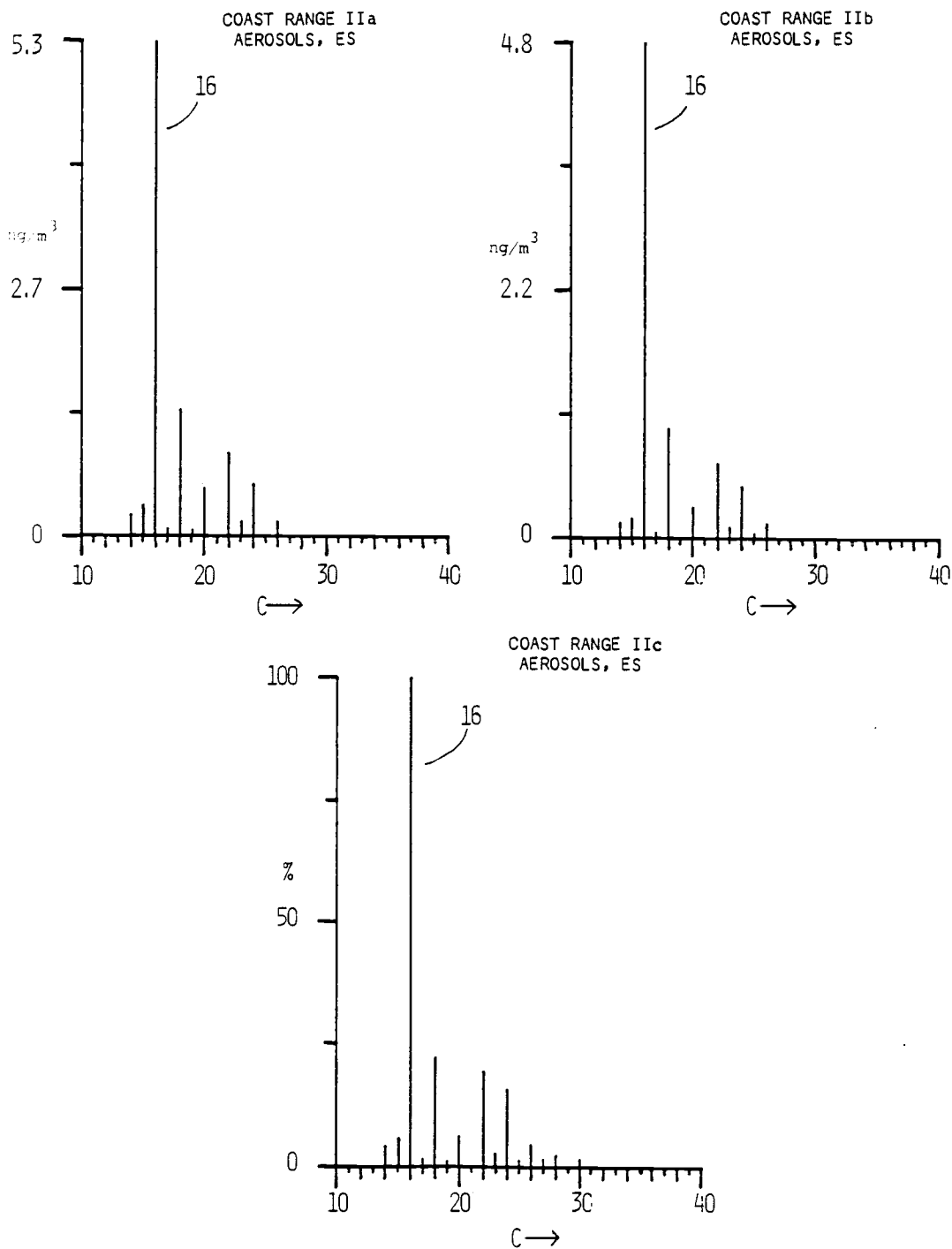


FIGURE V.3

distinct; however, some preliminary conclusions could be drawn.

In Figure V.4, histograms of aerosol n -alkanes collected on the open ridge in the Umatilla National Forest are presented. Also included, for comparison purposes, are the n -alkane distributions from the major vegetation. Recall that the region consists of clear-cut ridges where the returning growth is primarily small hardwood trees such as elm, alder and laurel, and ferns and brush. Aerosols clearly are dominated by C_{29} and C_{31} , which originate from these plant types.

Interpretations of sources must be made with caution; for example, at Wilson Ranch, n -alkane distributions consistently had a C_{max} of C_{29} . Since vegetation, though sparse, is comprised predominantly of wheat stubble and juniper (C_{max} C_{29}), this signature appeared to match that of the juniper wax. However, as will be discussed in the molecular marker section later, these aerosols have a significant component that was probably transported from the coniferous forests 100 km to the west. The n -alkane component alone was not definitive enough to distinguish the contributions from the two potential sources.

Molecular Markers: Sources and Transport

Cyclic terpenoids are produced by higher plants and are useful as chemotaxonomic tracers or molecular markers due to their relative molecular complexity. The majority of the tracers found in this study were in the class known as diterpenoids. The presence of several triterpenoid components also proved useful in tracing

FIGURE V.4

N-alkane distributions from aerosols collected on an open ridge in the Umatilla National Forest and extracts of the major vegetation in the region

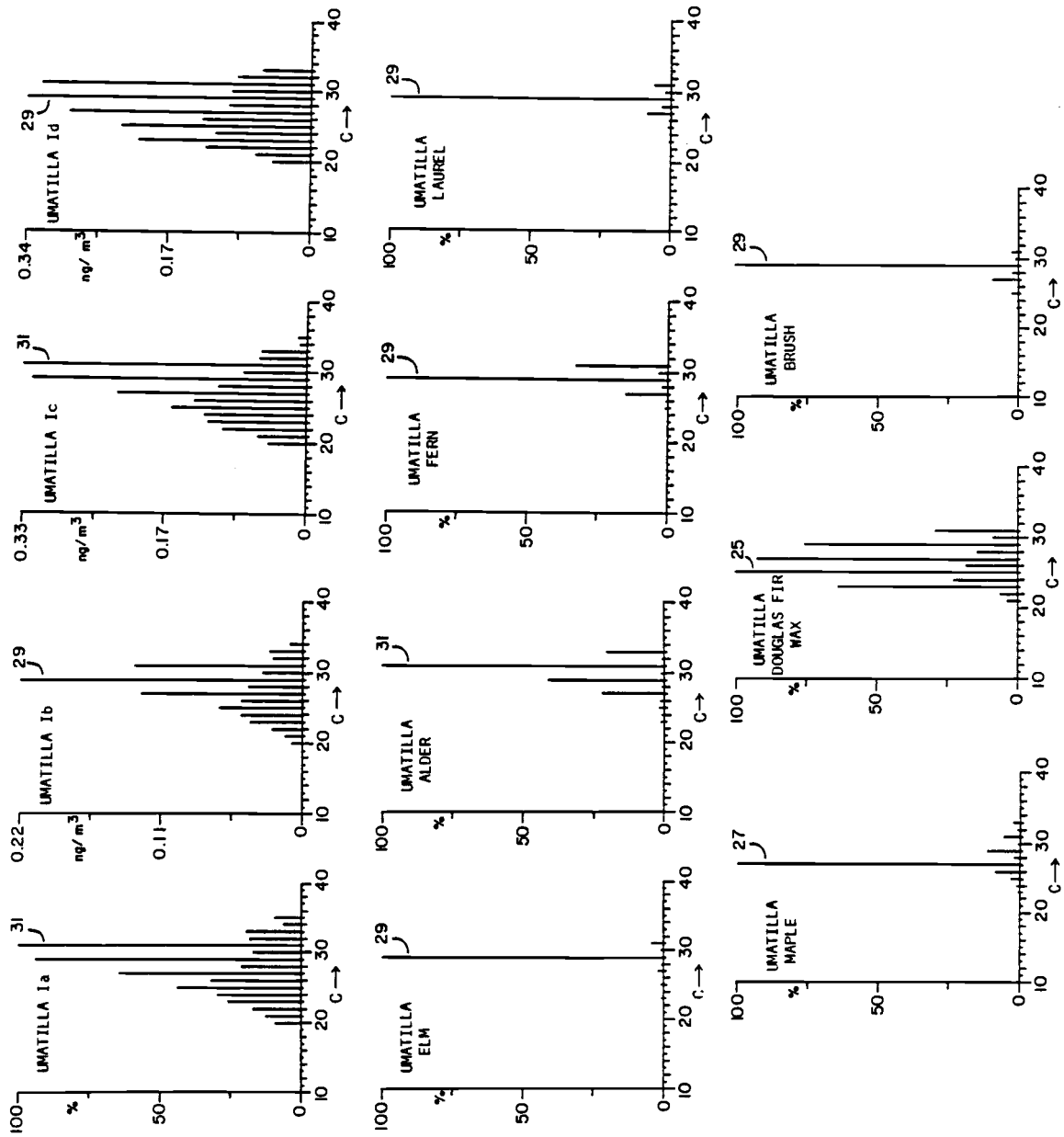


FIGURE V.4

biosphere/atmosphere interaction. Concentrations of the molecular markers present in the aerosols collected and the vegetation they are found in are presented in Tables V.5 and V.6. Mass spectra are presented in Appendix V. Also presented in Figures V.5 - V.8 are histograms of the major components and their source vegetation. A discussion of the distributions follows.

"Primary" Diterpenoids

Resinous plants produce a complex suite of diterpenoids for use as physical protection against dehydration, damage and pests (Fieser and Fieser, 1949; Thomas, 1970). The diterpenoids analyzed in these samples are the predominant components and either formed a distinct chromatographic peak or were elucidated by select-ion mass spectrometry.

Plotted in Figures V.5 and V.6 are the distributions of the predominant diterpenoids found in the plant wax extracts and aerosols. These components, except the 7-oxonorabietatrienes, were either produced directly by the source vegetation or altered slightly upon exposure after exudation to external portions of the plants. For purposes of this discussion, I will consider these "primary" components in chemotaxonomic correlations with atmospheric aerosol composition.

A clear trend stands out from these distributions. No diterpenoids were measured in the aerosols collected within the alder canopy, which demonstrates that input from adjacent mixed

TABLE V.5. MOLECULAR MARKER CONCENTRATIONS (pg/m³)

COMPOUND (M.W.)	NAME	COAST			WILLAMETTE		COLUMBIA BASIN		UMATILLA	
		I	II	III	I	II	ROWE CREEK	WILSON RANCH	I	II
1. C ₁₈ H ₁₈ (234)	retene(S)	-	-	-	-	-	present	48/14	-	9
2. C ₁₉ H ₂₆ (254)	19-norabieta-4(18)-8,11,13-tetraene(L ³)	-	-	-	-	-	-	17	-	-
3. C ₁₉ H ₂₈ α/β(256)	α: dehydroabietin (L ¹) β: 19-norabieta-8,11,13-triene (L ¹)	.5/5.0	-	.3/1.6	1.2/1.3	-	2.4/30	6.8/120	-	12/55
4. C ₁₉ H ₂₆ Oα/β(270)	α: 7-oxodehydroabietin (S) β: 7-oxo-19-norabieta-8,11,13-triene (S)	-	-	-	11/33	3.1/11	11/30	-	1.3/12	11/64
5. C ₂₀ H ₃₀ (270)	dehydroabietane (L ¹)	-	-	1.2	-	-	-	12	1.	12
6. C ₂₀ H ₂₈ O(284)	dehydroabietal (L ⁴)	9.3	-	-	44	26	4.4	23	7.4	-
7. C ₂₀ H ₃₄ a/b(290)	manoyl & epi-manoyl epoxides (L ²)	2.6/4.4	-	2.0/7	10/9.1	74/96	53/2.9	7.9/2.8	-/5.1	24/24
8. C ₂₀ H ₂₄ O ₂ (296)	e.g. 1-methyl-7-isopropyl-1,2,3,4-tetrahydrophenanthrene-1-carboxylic acid (I)	-	-	-	-	-	20	38	-	15
9. C ₂₁ H ₂₈ O ₂ (312)	13-isopropyl-5α-podocarpa-6,8,11,13-tetraen-16-oic acid (L ¹)	-	-	-	29/3.1	-	-	92/270	150	7.0
10. C ₂₁ H ₃₀ O ₂ (314)	dehydroabietic acid (S)	43	-	40	36/46	350	480	4400	59	470
11. C ₂₁ H ₃₂ O ₂ (316)	abietic acid (S)	-	-	-	-	-	8.6	440	9.3/43	-
12. T (346)		-	-	1.1	5.8/12+8.7	-	-	present	-	8.2
13. T (410)		-	-	1.0	-	-	-	-	-	-
14. C ₃₀ H ₄₆ O(422)		2.4	190	51	-	-	-	-	-	50

(I = Interpreted, L = Literature Reference and S = Standard Retention and Spectrum;
L¹ - Simoneit and Mazurek, 1982; L² - NIH/EPA Mass Spectra Library; L³ - Simoneit, 1975;
L⁴ - Enzell and Wahlberg, 1969)

TABLE V.6. SOURCE VEGETATION FOR MOLECULAR MARKERS IN TABLE V.5

	COAST	WILLAMETTE	COLUMBIA BASIN	UMATILLA
1.	-	-	-	-
2.	BSsap	BS wax	-	WF
3.	BSsap&wax,SF	BSwax	J	WF,DF
4.	-	-	-	-
5.	BSsap&wax,SF,M	BSwax	-	WF
6.	BSsap&wax,SF,Abark	BSwax	-	-
7.	-	BSwax	-	WF
8.	-	-	-	-
9.	BSsap	-	-	-
10.	BSsap,SF,Abark	BSwax	-	DF
11.	BSsap&wax	BSwax	-	DF
12.	-	-	-	DF
13.	NS	-	-	-
14.	M	BSwax	J	DF

Index to vegetation abbreviations:

BSsap	-	Brewer Spruce sap
BSwax	-	Brewer Spruce needle wax
WF	-	White Fir needle wax
SF	-	Sword Fern
J	-	Juniper
DF	-	Douglas-fir needle wax
M	-	Moss
Abark	-	Red Alder bark
NS	-	Norway Spruce needle wax

FIGURE V.5

Distributions of "primary" diterpenoids in aerosols plotted
against site (sites detailed in Figure V.1)

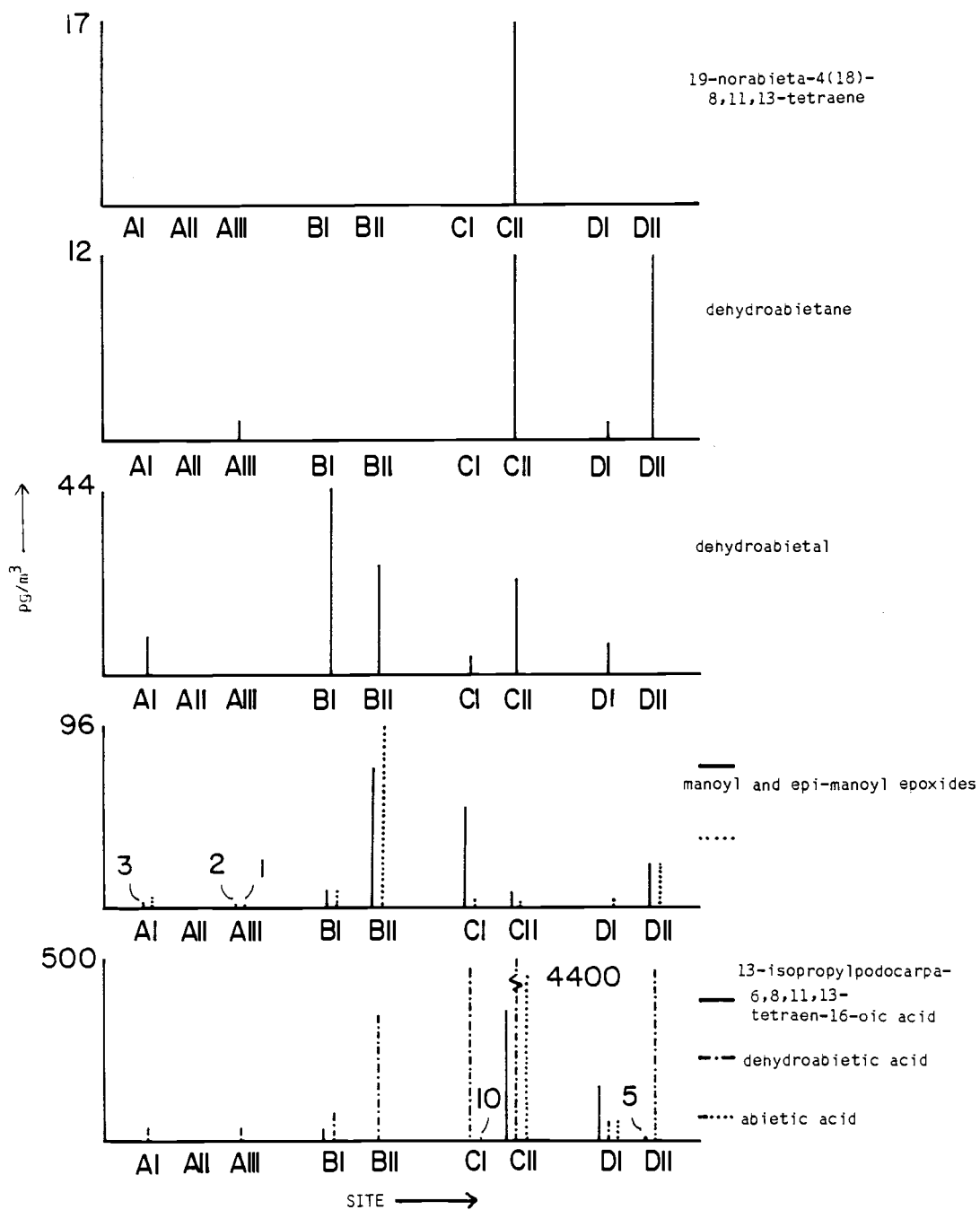
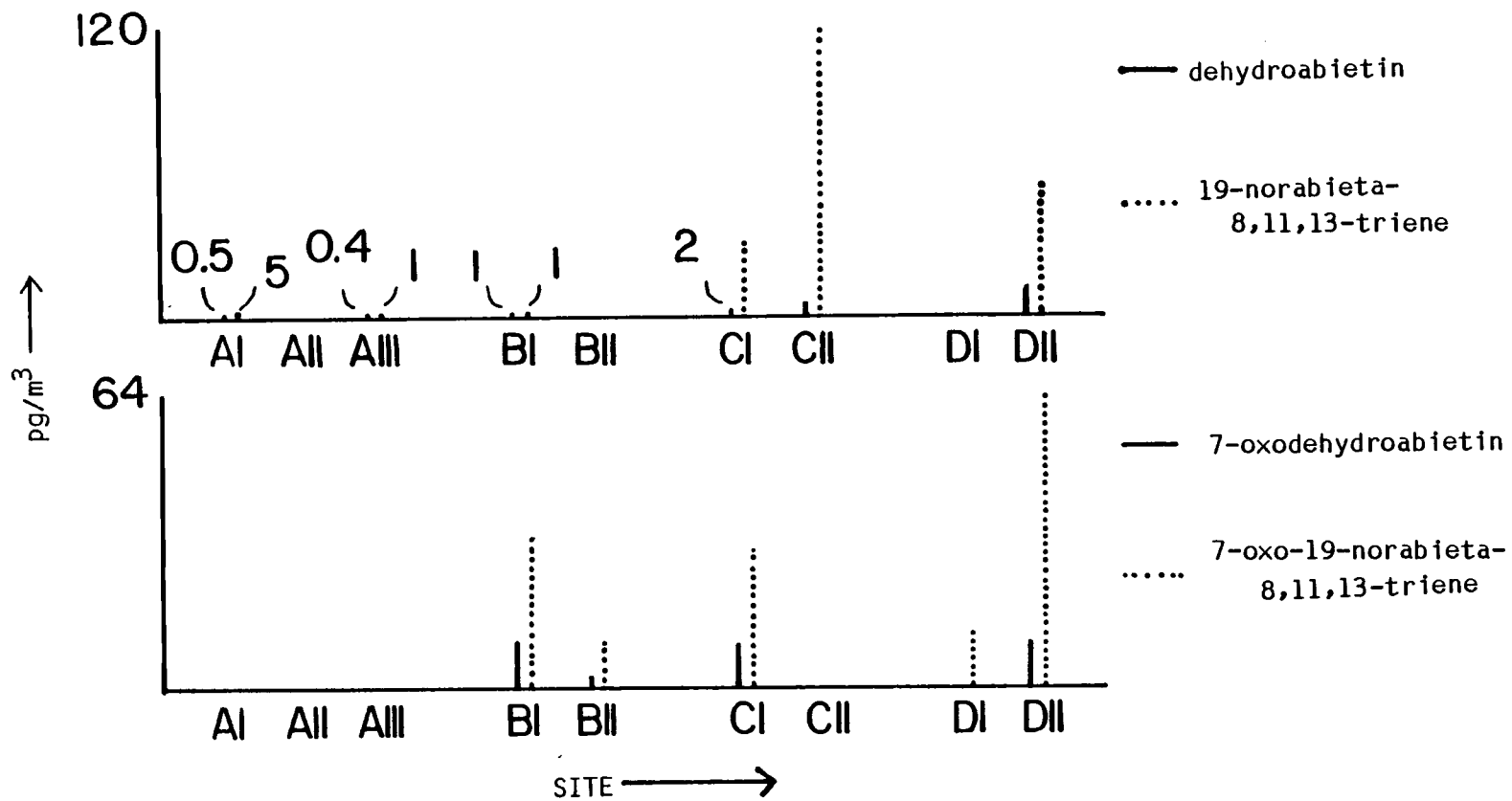


FIGURE V.5

FIGURE V.6

Distributions of dehydroabietin and its isomer and
dehydroabietone and its isomer plotted versus site (Figure V.1)

FIGURE V.6



coniferous forests into the alder canopy was minimal. The composition of the aerosols reflects the homogeneous distribution of alder and moss as was demonstrated in the discussions of the homologous series (and will be discussed in the triterpenoid section below).

Distributions of the diterpenoid components in aerosols collected at the other sites showed the following trends. Concentrations, which for the most part were in the pg/m^3 range, were lowest at the coastal sites which may reflect the fact that the air mass originating off the Pacific Ocean had just begun to accumulate material. As there was no clear upward concentration trend, either in molecular markers or in the homologous series, between the three remaining sampling regions, it would appear that a steady state between deposition and uptake of fresh wax aerosols occurs within 200 km of the continental boundary. Since particles containing plant waxes have been shown to be relatively large (Van Vaeck and Van Cauwenberghe, 1985), transport distances would be less than for smaller particles such as combustion aerosols.

Production by source vegetation present at all sites of dehydroabietin and 19-norabieta-8,11,13-triene is reflected in their wide distribution in sampled aerosols (Figure V.6). The presence of these components in the Sword Fern may be due to drippings from adjacent conifers as this has not been verified in the literature. The fact that these isomers are produced by a varied plant suite and are present in samples from all four regions means that they are not region specific and are not as useful for chemotaxonomic tracing

from any particular region as a component which has limited sources in specific regions. Note that dehydroabietin is always in higher relative concentration than 19-norabietin-8,11,13-triene. This trend has been noted and discussed in previous chapters with respect to the presence of these isomers in coniferous wood smoke (Chapter III).

Also present in the sampled aerosols (but not in source vegetation) were the ketone forms of these isomers - the 7-oxonorabietin-8,11,13-trienones. It is possible that these were produced by either photochemical or microbial degradation of the norabietatriene isomers or the same precursors (as discussed in Chapter III). Their absence in aerosols collected along the coast and the fact that they are present at concentrations comparable to or greater than the norabietatriene isomers (except the Wilson Ranch site which will be discussed later), suggests an oxidative relationship between the two. Aerosols collected at the coast would not have had time to degrade.

An interesting set of isomers, believed to be manoyl and epimanoyl oxides, which have not to my knowledge been previously reported in aerosols, were found at all sites except the alder grove. However, these isomers were only found in the extracts of White Fir and Brewer Spruce waxes collected at the second Umatilla site and the Willamette site, respectively. Since these components were common in aerosols, it is likely that there are other plant sources which were not included in this study. These compounds have

been reported in other studies of coniferous vegetation such as Pinus bandsiana, Southern Pine, and Pinus resinosa (Bower and Rowe, 1967; Conner and Rowe, 1975; Zinkel and Clarke, 1985).

Also present in most aerosol samples but not in the collected source vegetation at all sites was abietal (Figure V.5). This component has been previously reported in the soil of a coniferous forest (LaFlamme and Hites, 1978). The lack of correlation between the predominant vegetation and regional aerosols with respect to the manoyl epimers and abietal may be due to tropospheric transport from regions which contained source vegetation or as mentioned previously they may have originated in vegetation not sampled in this study.

One site which stands out clearly with respect to a lack of correlation between aerosol composition and source vegetation is the Wilson Ranch site. This site was situated 100 km east of the Willamette National Forest on a high plain devoted predominantly to agriculture. Concentrations of all of the "primary" diterpenoids except the manoyl epimers and abietal were vastly elevated over concentrations in aerosols collected at most other sites, including within coniferous canopies such as AI, BII and DII. Excepting dehydroabietin and 19-norabieta-8,11,13-triene, which were present in the extract of juniper, no correlation with source vegetation (or soil of the wheat field) was found.

The elevation in concentration was mirrored in the homologous series of n -alkanes and n -alkanoic acids. The presence and concentrations of these components in aerosols at this site may indicate long-range transport from coniferous forests to the west,

facilitated by brisk winds and pre-storm activity during the sampling period (Table V.1).

The absence of the oxidation derived 7-oxonorabieta-8,11,13-trienes in aerosols collected at Wilson Ranch is confusing in that, if transported over a distance there should have been ample time for photochemical conversion. However, conditions were stormy and thus the sky was cloudy during this sampling period which would have inhibited photochemical transformations. Further work on the photochemical oxidation of diterpenoids needs to be done to verify the processes occurring.

"Thermally Altered" Diterpenoids

Plotted in Figure V.7 are the histograms of two components, retene and 1-methyl-7-isopropyl-1,2,3,4-tetrahydrophenanthrene-1-carboxylic acid (as the methyl ester), which are thermally altered resin constituents derived from sources such as prescribed burning of coniferous forests (Chapter III), residential wood smoke (Chapter IV and Ramdahl, 1983), and campfires. As this transect was carried out in late September and early October all three of these sources are possible. Note the close correlation between relative concentrations at the various sites (except CI where generator failure prevented quantitation).

Miscellaneous Terpenoids and Triterpenoids

Presented in Figure V.8 are histograms of the distributions of a cyclic sesterterpenoid or extended diterpenoid component (C₂₅) and

FIGURE V.7

Distributions of "thermally altered" diterpenoids plotted
versus site (arrow represents present but not
quantifiable)

FIGURE V.7

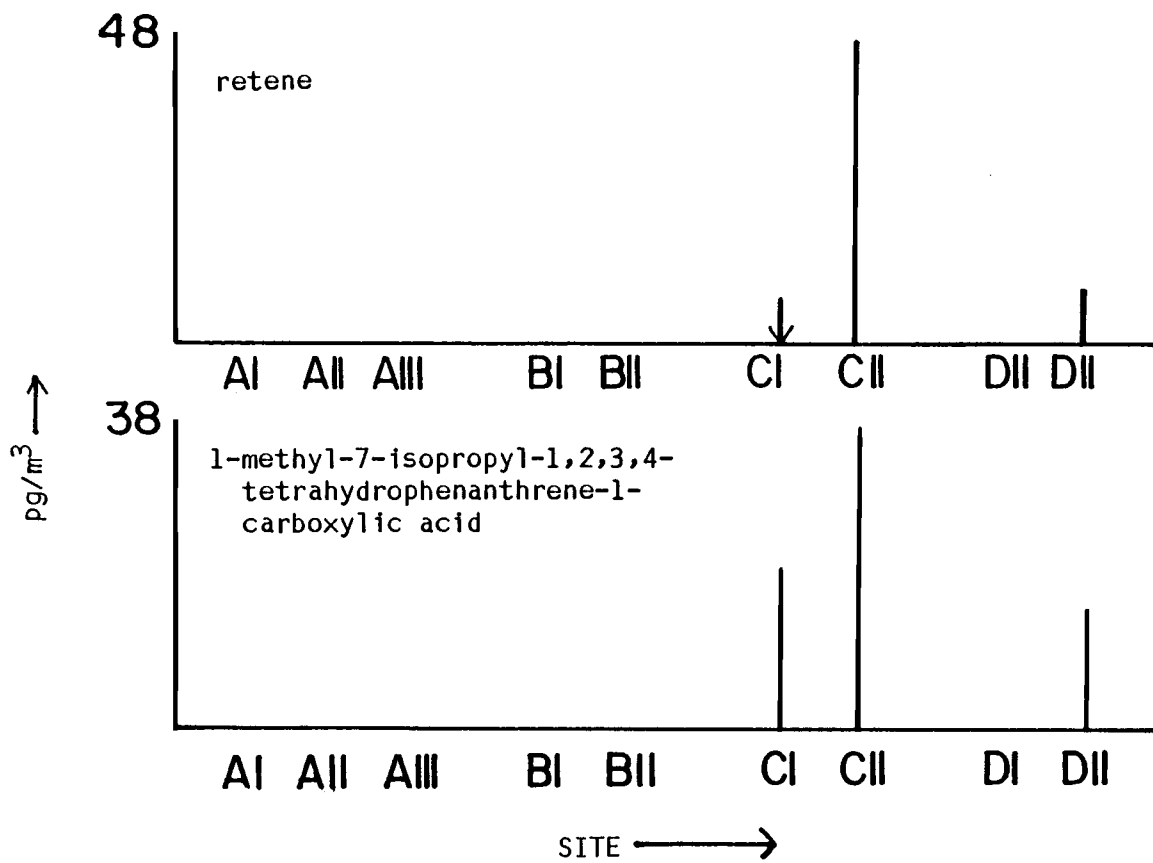
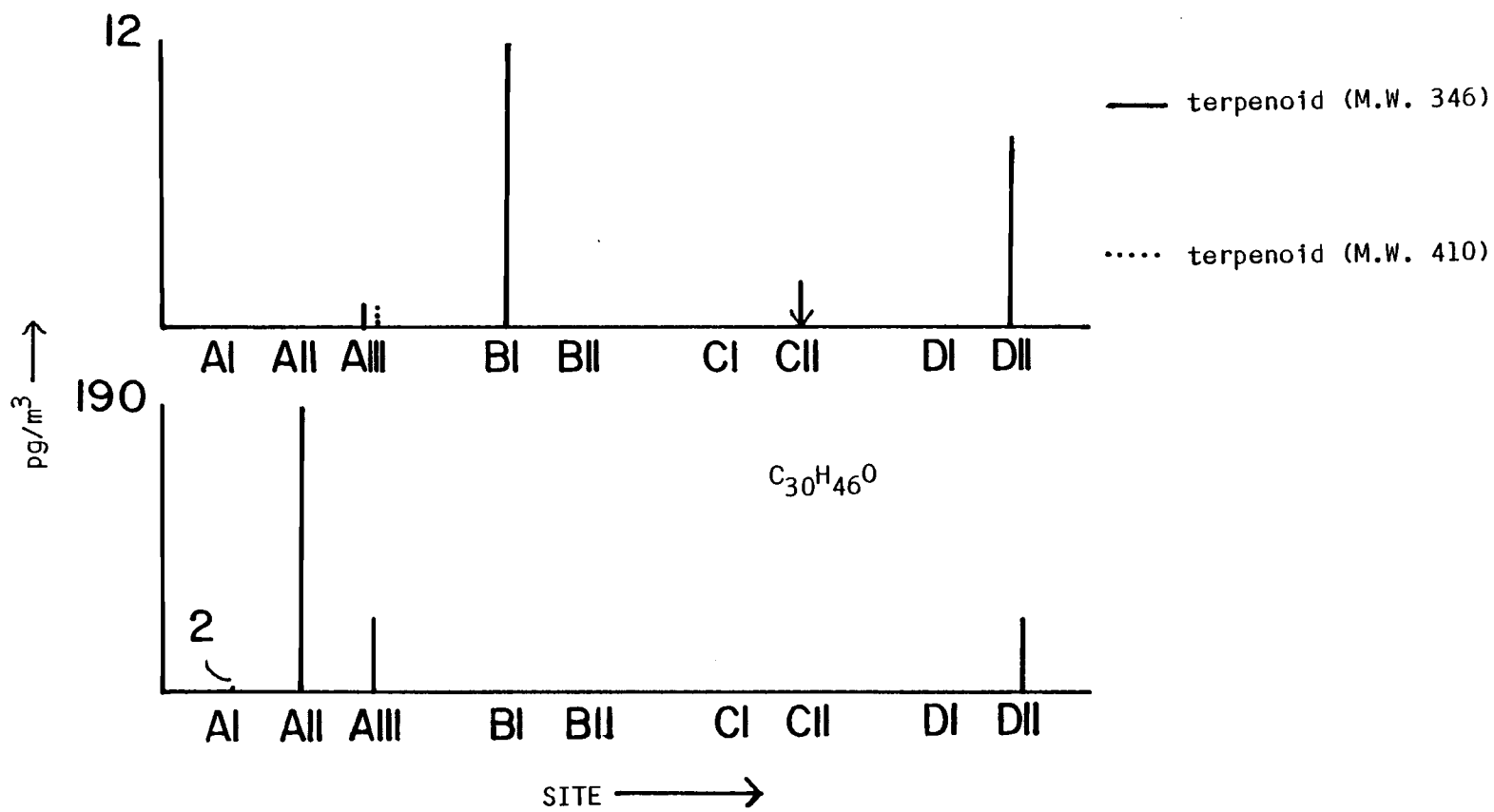


FIGURE V.8

Distributions of miscellaneous terpenoids plotted versus
site (arrow represents present but not quantifiable)

FIGURE V.3



two triterpenoids (C_{30}). The C_{25} component was present in aerosols collected within all four regions of the sampling transect but was only found in one extract of a source vegetation (Douglas-fir). This conifer is a common one in the state of Oregon, however, due in part to its utility for the wood products industry as a fast growing resource.

The triterpenoid with a molecular formula of $C_{30}H_{50}$ has a mass spectrum similar to that of a fernene and was only found (for the vegetation analyzed) in the Norway Spruce (a common species) situated in the Oregon Coast range. This coincides with its presence in coastal aerosols.

The only aerosol molecular marker traced in the alder grove was that of a triterpenoid with the interpreted formula $C_{30}H_{46}O$, (this may be an unsaturated triterpenone). Since the n -alkane signatures of the aerosols in the alder grove matched the moss signature more closely than that of the alder wax sampled, the correlation of this triterpenone marker and the closely correlated n -alkanoic acid distributions result in a reasonably well defined homogeneous canopy/aerosol system, with alder and moss waxes defining the character of the aerosols. Lupenone, a triterpenone extracted from alder wood (Chapter IV) was not found in the aerosols or the wax extract. This would reflect the fact that it is only the particulate waxes admixing into the air mass. Vegetative sources for this triterpenone were also found in the other three regions, though it was only detected in coastal aerosols and at one Umatilla site (DII). This may reflect the stability of this component.

SUMMARY AND CONCLUSIONS

Variability

Concentrations of the homologous series varied anywhere between 2% and 190% among samples collected side-by-side (CIIC and d, BIC and d, respectively) and from 3% to 160% for those collected on sequential days at the same site (AI and BI, respectively). The variation in concentration did not always correlate with the degree of variability in the signatures of the homologous series, nor did the n -alkanes necessarily match the n -alkanoic acids in variability.

Certain sites had excellent reproducibility of signatures and concentrations. Aerosols collected in a homogeneous alder grove had consistently low variability with respect to concentration and composition of both homolog distributions. On the other hand, aerosols collected within the mixed coniferous canopy in the coastal region were consistent with respect to the concentration of the n -alkanes but had a moderate degree of variability with respect to signature. The difference in concentration of n -alkanes in samples collected side-by-side ranged up to one order of magnitude, a surprisingly large variance.

In general, there was no significant difference in variability between samples collected side-by-side and those collected on a day-to-day basis at the same site. There was also just as much variability in aerosols collected on an open range as within protected canopies, excepting the alder grove. Two factors

contributed to the homogeneity of aerosols within the alder grove. The most prominent is the relative simplicity of the plant populations within the canopy. Other than some ground cover such as moss and ferns, the grove consisted of alder trees of approximately the same size and therefore age. The second factor in determining the homogeneity of the aerosols was the lack of external influence which resulted from the physical factors at the site. Being on the leeward side of the first westward mountain range, the grove was protected against the predominant wind patterns and the resulting transported aerosols.

The variation documented in this study demonstrates the importance of collecting repetitive aerosol and plant wax samples, not only within a site but on a regional scale as well. The ranges of C_{\max} among suites of vegetation and the variability within a species must be well documented in order to reduce uncertainty in interpretation. It was also apparent that samples were affected greatly by surrounding vegetation, thus it is important to collect aerosols at elevated sites when analyzing long-range transport, preferably from a platform or balloon, to minimize ground-level turbulence and heterogeneity of particles.

Correlations of Signatures

Analysis of the distributions of *n*-alkanes and *n*-alkanoic acids allowed a first approximation to be made for tracing signatures from the predominant vegetation to the ambient aerosols. Under relatively simple circumstances, i.e. - the alder grove,

correlations of aerosols to source vegetation was straightforward. However, many factors contributed to a complexity in signatures which made correlations difficult. These included: complexity of source vegetation (various component distributions); variation of signature within species; effect on samples by nearby vegetation; and meteorological parameters and terrain complexity.

Molecular markers, with a greater degree of molecular specificity than straight chain wax components, provided supportive and in some cases definitive information which aided in source correlation.

Conclusions and Suggestions for Future Work

The composition of higher weight organic matter in rural aerosols was shown to be greatly affected by regional vegetation. However, many factors contributed to the complexity of defining the source, transport and fate of the aerosols. Since there has been a recent increase of interest in the global impact of biosphere/atmosphere interaction, an increased understanding of these processes is essential. Biomarkers have been demonstrated to be definitive in source correlation. However, I would recommend further analysis of chemotaxonomic correlations between source vegetation and aerosols to determine some of the uncertainties mentioned in this chapter.

VI: Summary

Characterization of tropospheric aerosols with respect to lipid compounds (hydrocarbons, n -alkanoic acids and molecular markers) produced by biomass and the combustion of biomass revealed information on: (1) the variability of compositions and concentrations of samples collected under similar conditions; (2) the degree to which the major vegetation imparts a signature on the organic matter in rural aerosols; (3) processes involved in the thermal alteration of natural products; and (4) the use of these natural products, altered and unaltered, in source correlation and the tracing of potential input to the oceanic sedimentary record.

In general, straight chain homologous series, such as n -alkanes, provided preliminary information on processes of aerosol formation and transport. Comparison of numerous samples collected under similar circumstances revealed the extent of variability in concentration and composition. Two conclusions could be drawn from the results. It is important to take repetitive samples to minimize spurious results. Further, sampling from a platform or balloon would decrease the highly variable and significant influence from nearby vegetation.

Cyclic di- and triterpenoids provided more definitive chemotaxonomic information on correlating rural and smoke aerosols with the plants from which they were derived. Additional work needs to be done to determine the variability in signature and concentration of these components.

Two sample suites were comprised of aerosols produced by two modes of biomass combustion, namely prescribed burning and

residential wood combustion. The prescribed burns, with more extreme temperatures produced relatively lower concentrations of thermally altered products than the smoldering process (lower temperatures) of residential wood combustion. Both, however, produced ample molecular indicators of instantaneous thermal maturation.

Preliminary calculations of the relative input of altered diterpenoids to the oceans' sediments revealed the possibility that biomass combustion may contribute one to three orders of magnitude more altered diterpenoids than sedimentary diagenesis of the directly deposited unaltered diterpenoids produced by plants. Further work on the physical characteristics of particles associated with the altered diterpenoids as well as the refinement of the values used in calculating the relative inputs should be undertaken.

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APPENDICES

APPENDIX I: Relevant formulas and calculations

1. CPI (Carbon Preference Index; Bray and Evans, 1961)
i.e. for n -alkanes

$$\text{CPI} = (0.5) \left[\frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{24} + C_{26} + C_{28} + C_{30} + C_{32}} \right] +$$

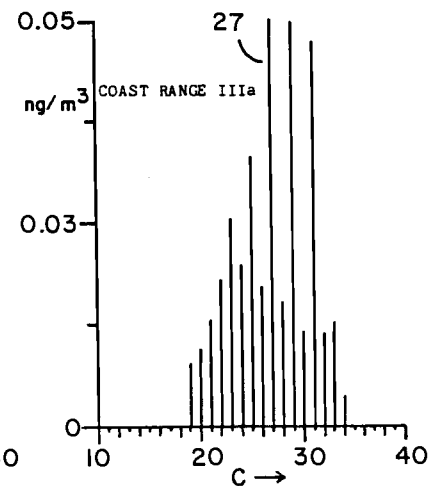
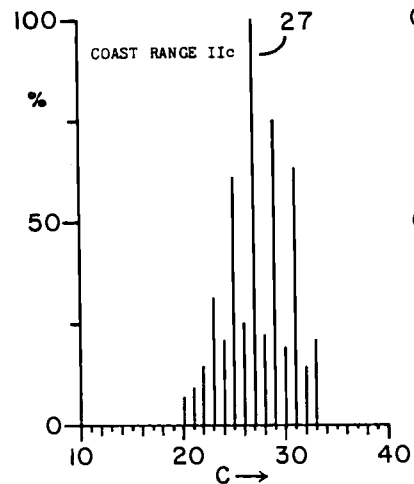
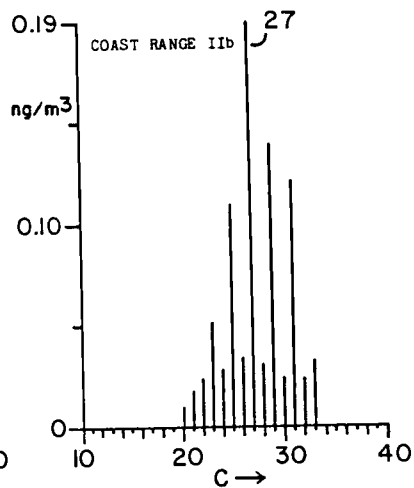
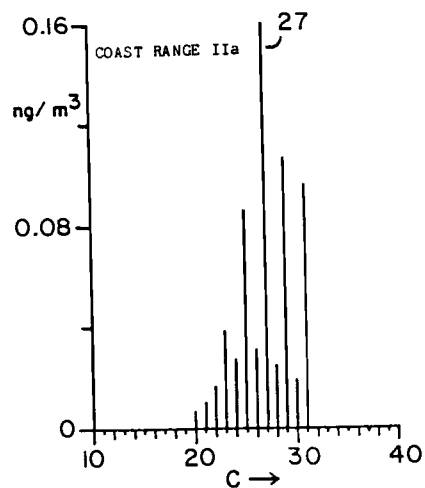
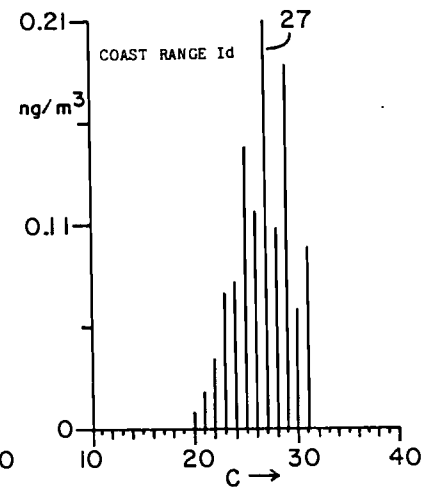
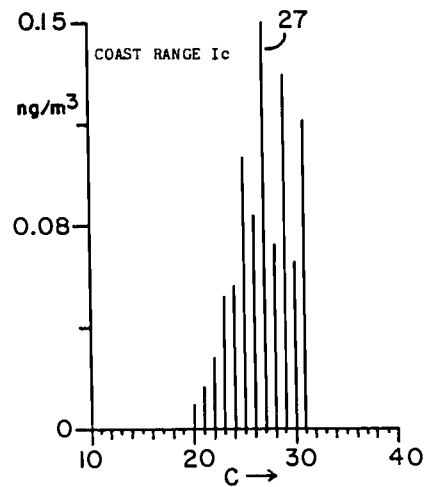
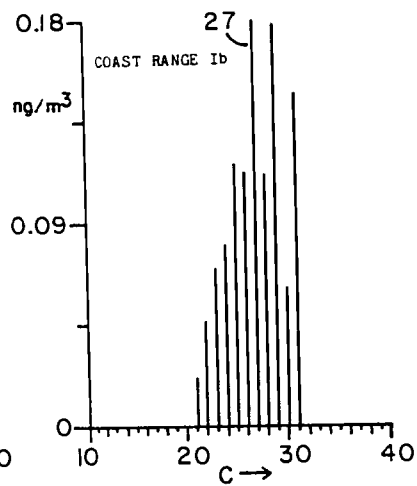
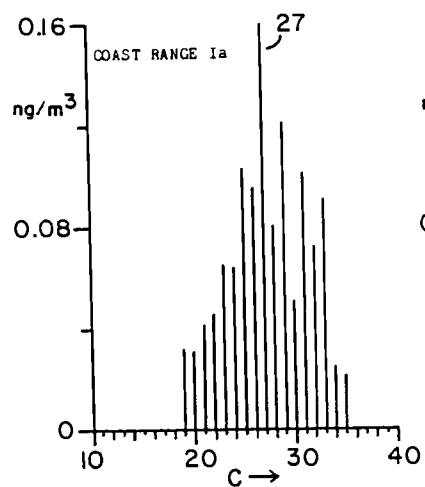
$$\left[\frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{26} + C_{28} + C_{30} + C_{32} + C_{34}} \right]$$

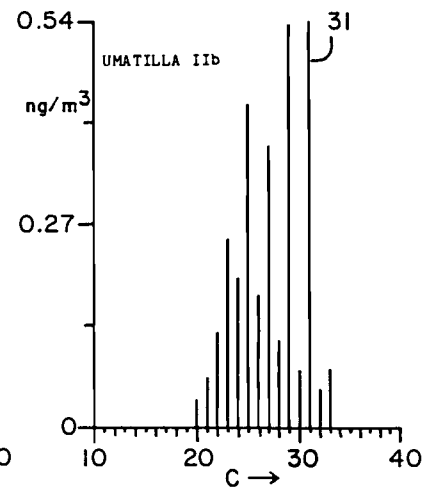
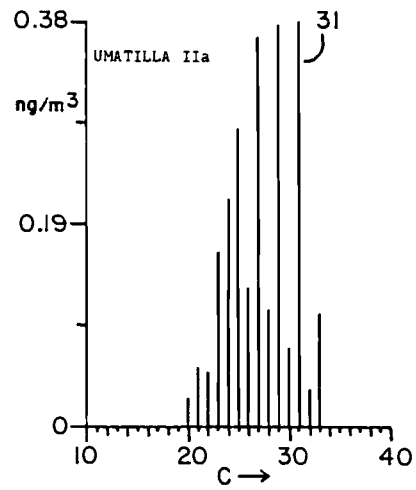
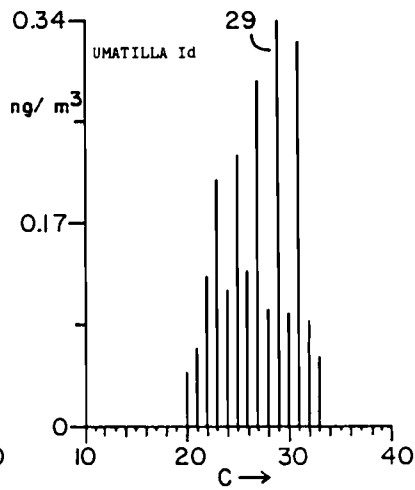
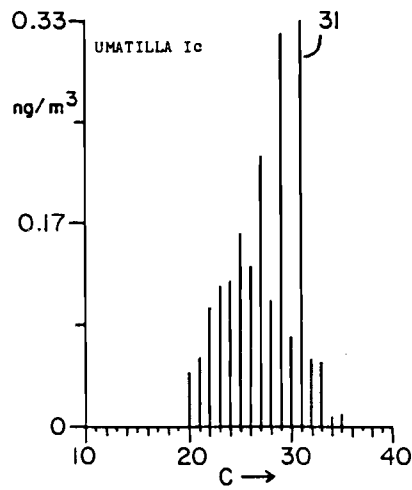
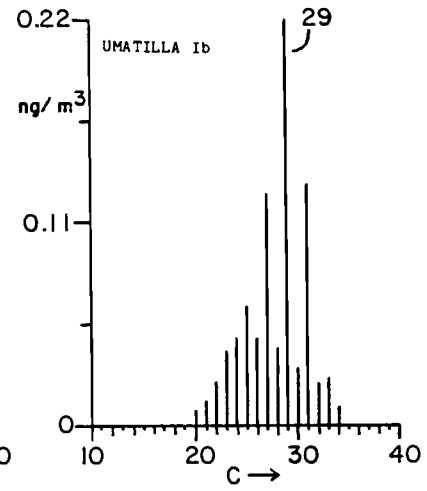
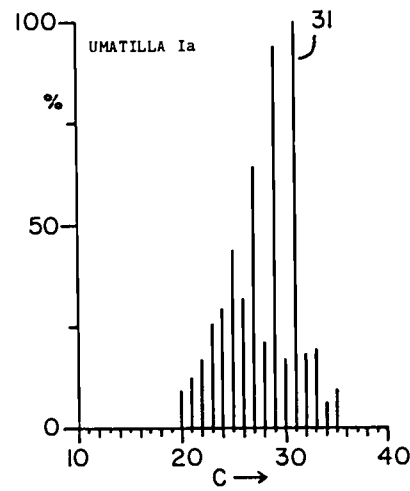
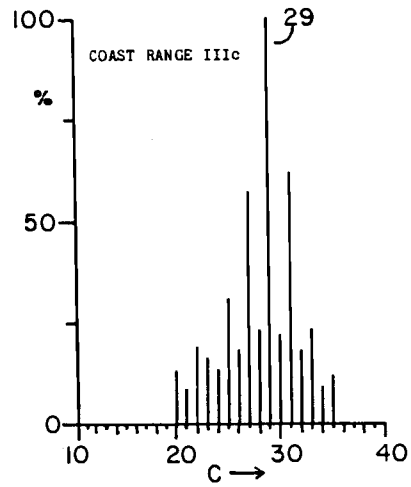
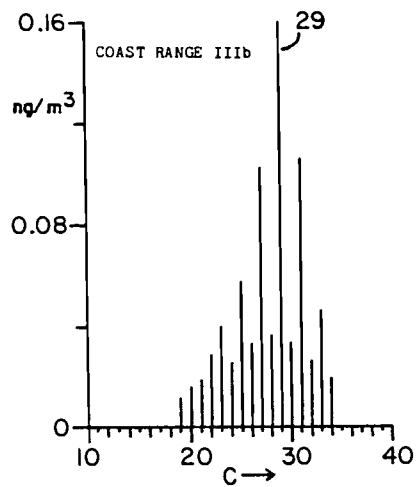
2. Calculation of the variation (V); (a - f denotes sample order in set)(from Chapter V)

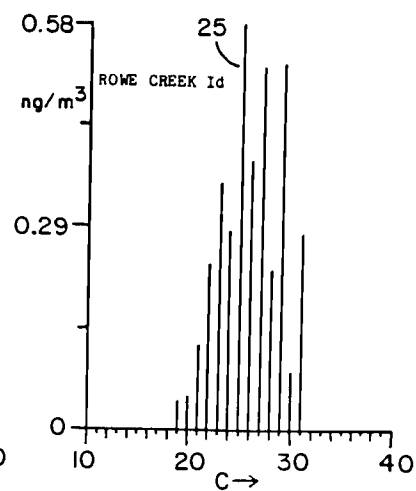
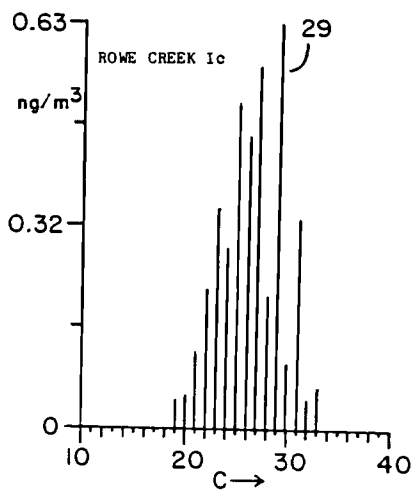
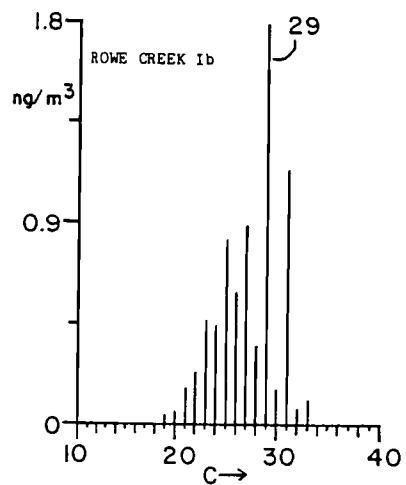
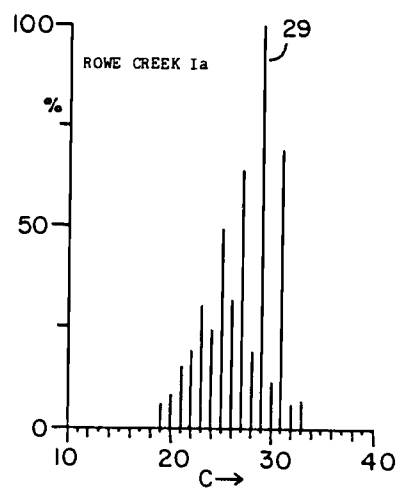
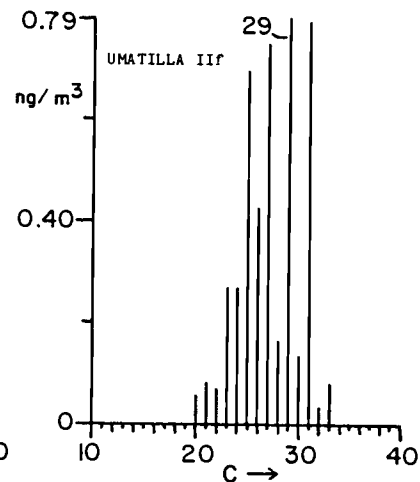
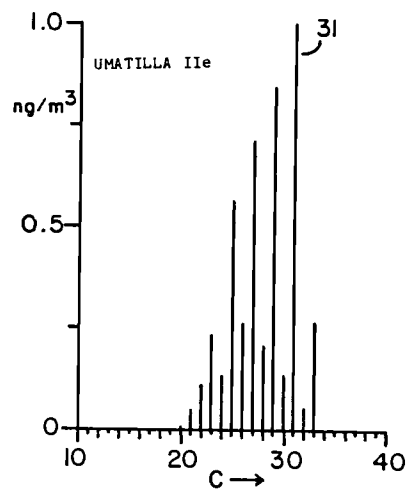
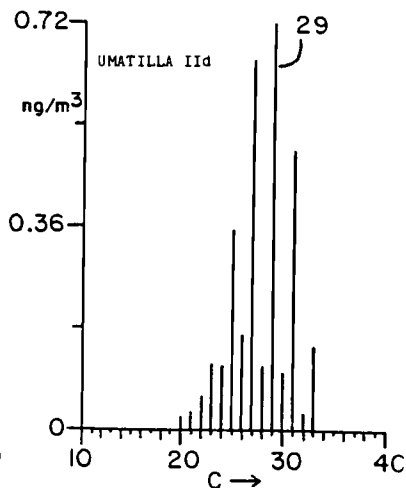
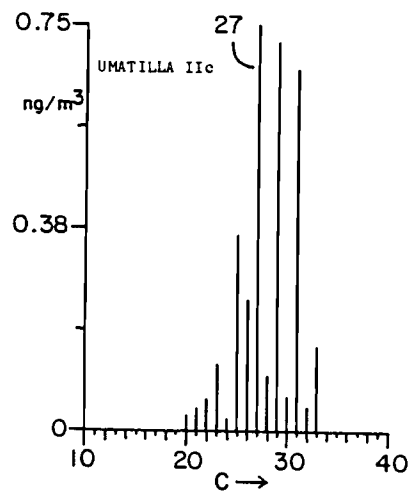
$$V_{\text{side-by-side}} = \frac{\Sigma_a - \Sigma_b}{(0.5)(\Sigma_a + \Sigma_b)}$$

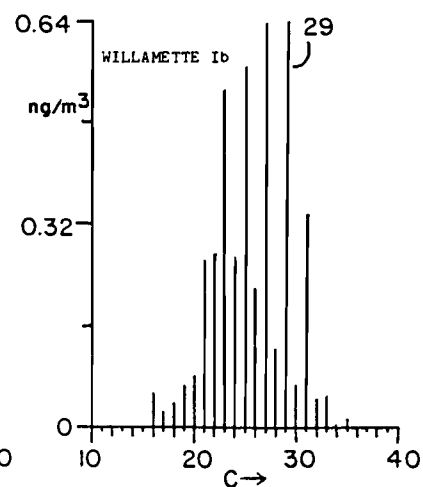
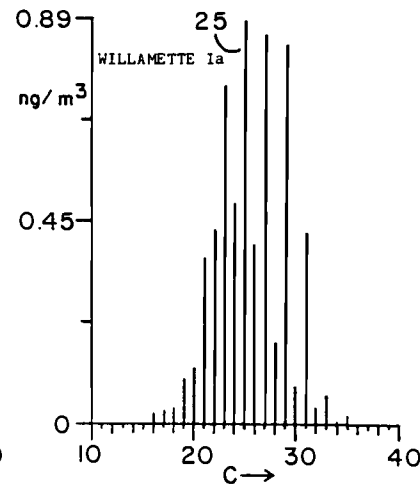
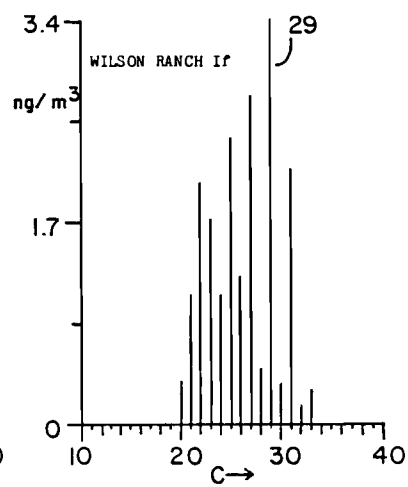
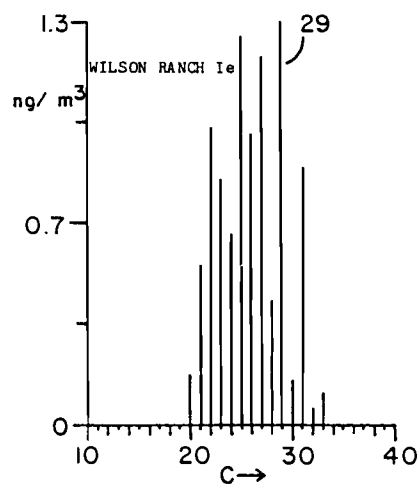
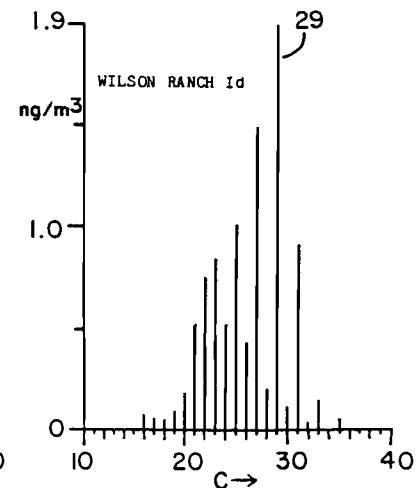
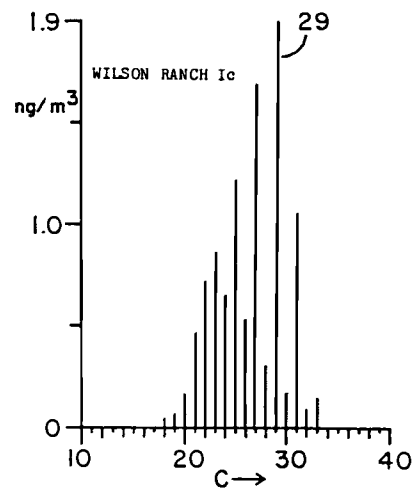
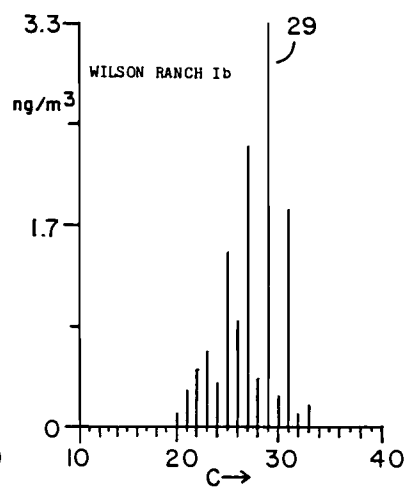
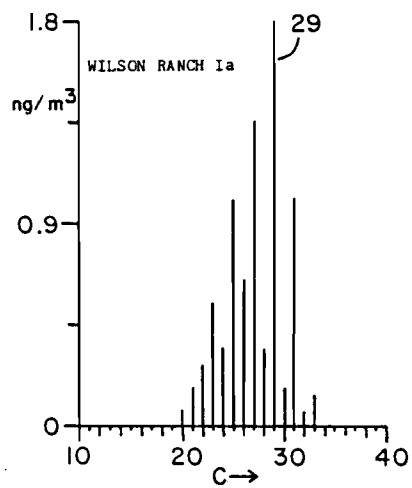
$$V_{\text{day-to-day}} = \frac{(0.5)(\Sigma_a + \Sigma_b) - (0.5)(\Sigma_c + \Sigma_d)}{(0.25)(\Sigma_a + \Sigma_b + \Sigma_c + \Sigma_d)}$$

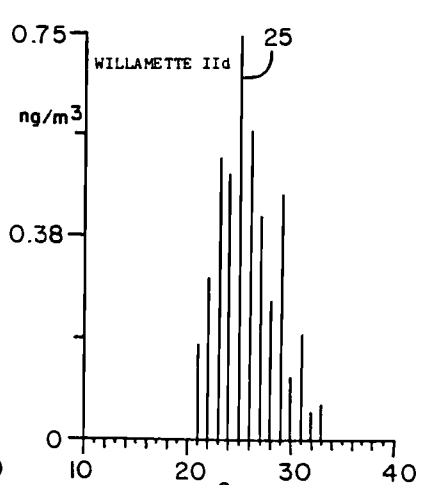
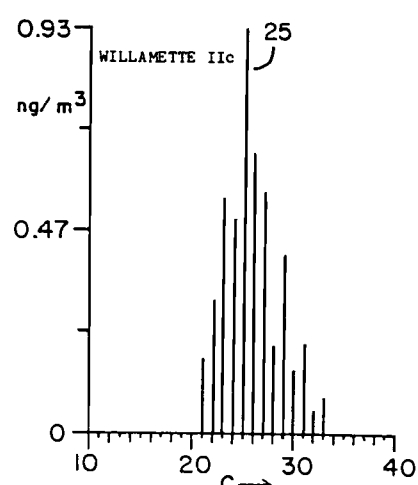
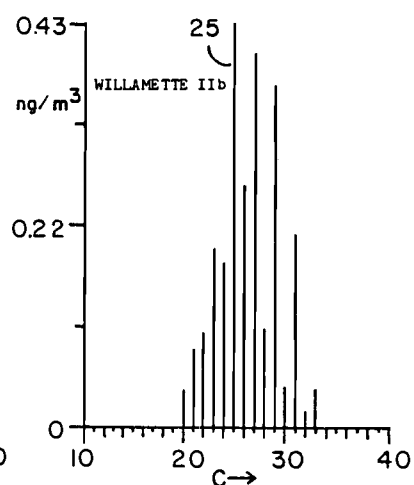
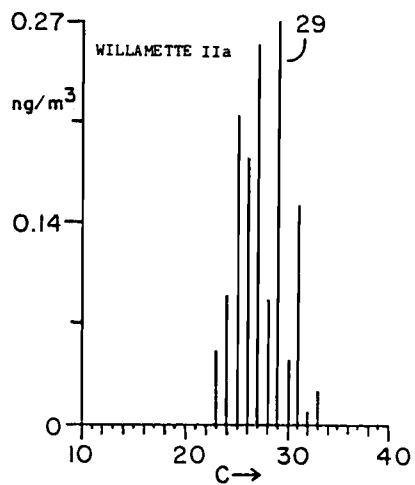
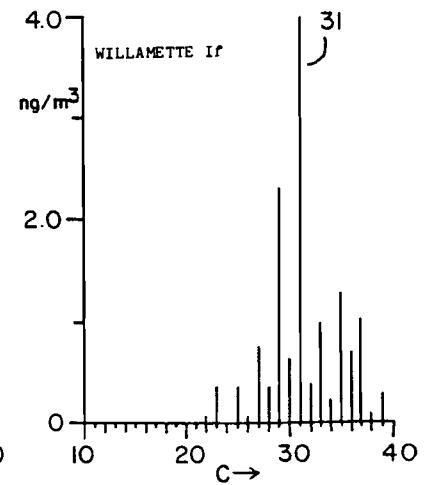
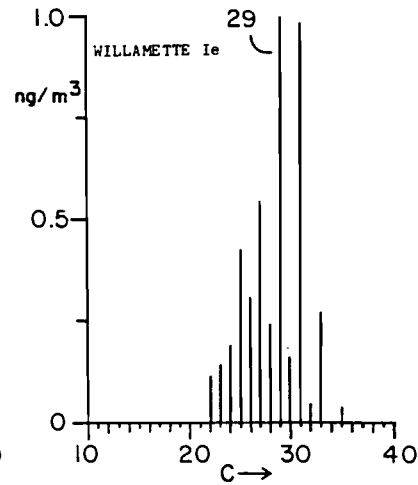
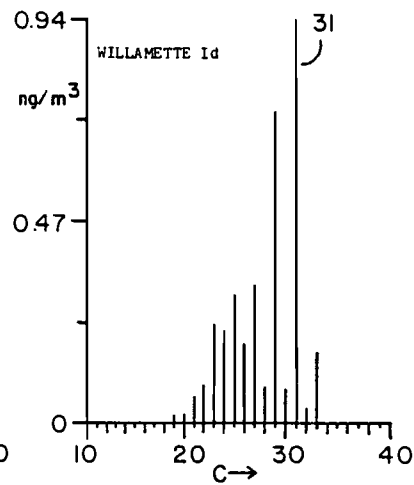
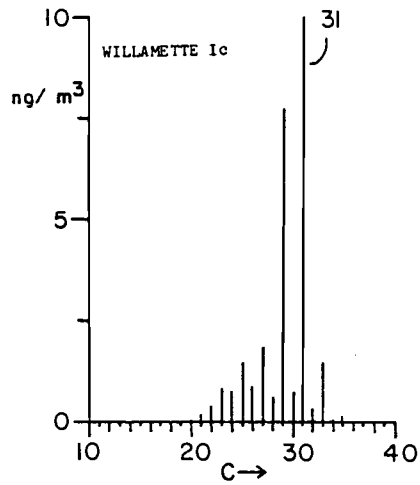
APPENDIX II: Histograms of n -alkane distributions in aerosol and vegetation extracts collected along a transect in rural Oregon

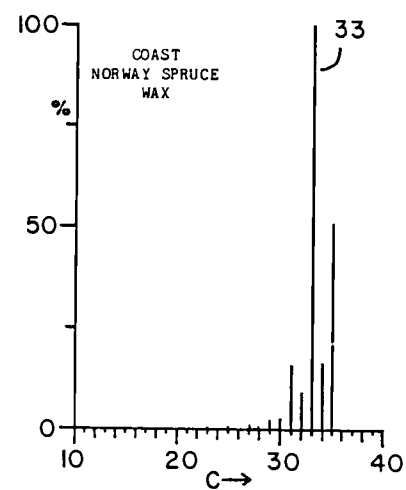
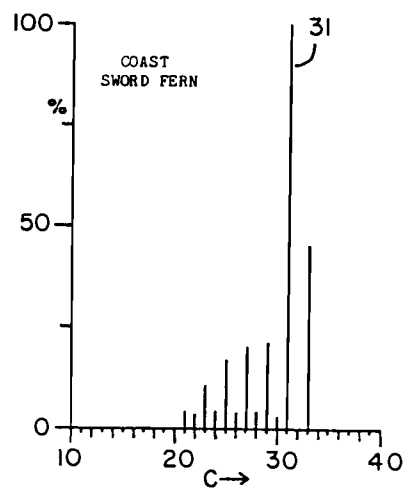
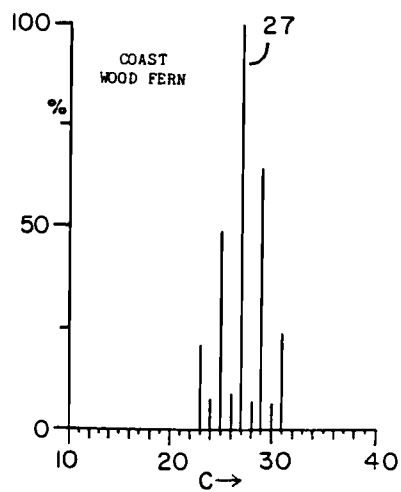
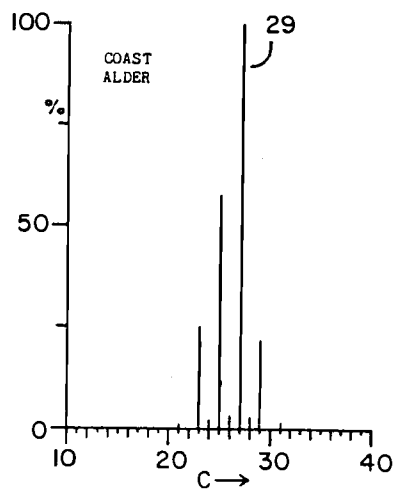
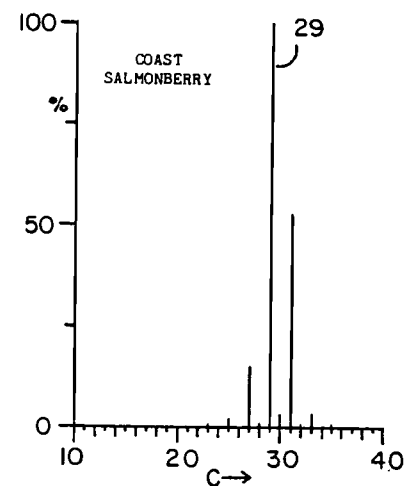
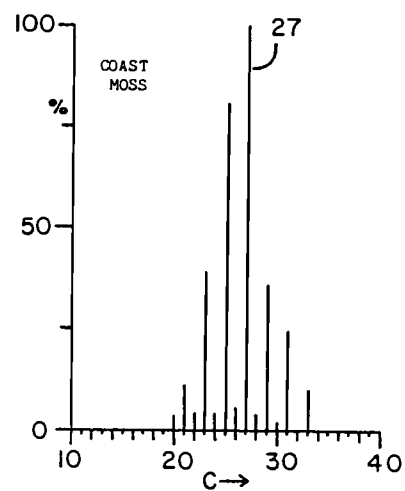
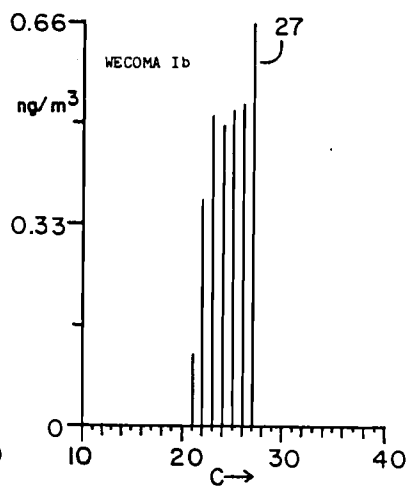
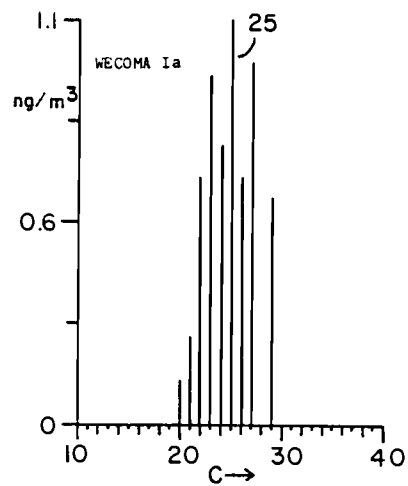


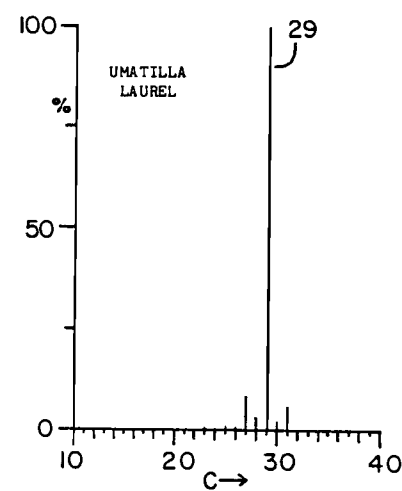
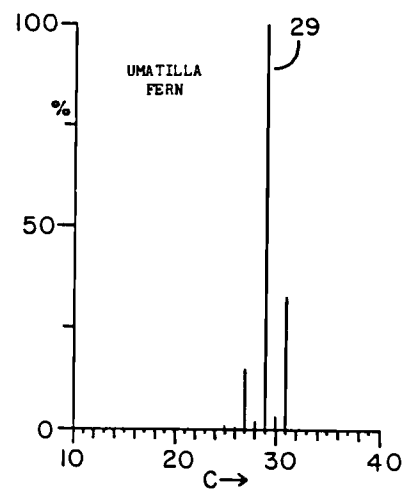
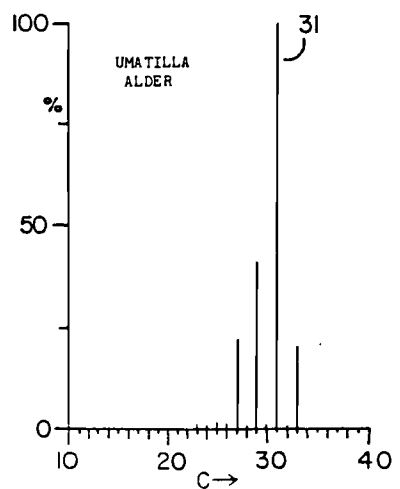
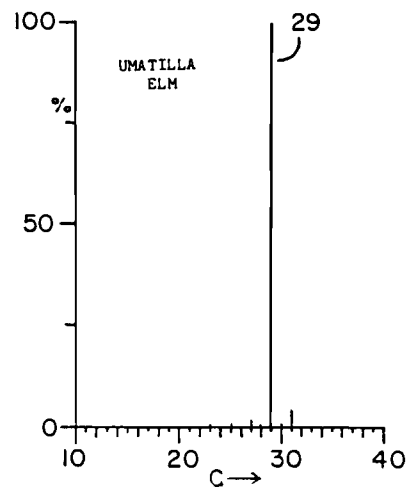
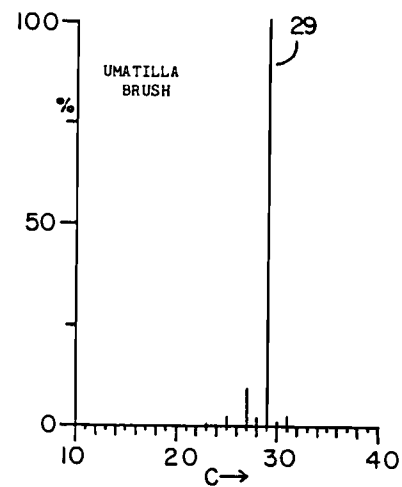
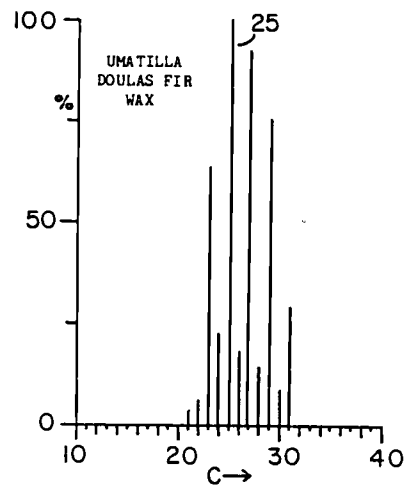
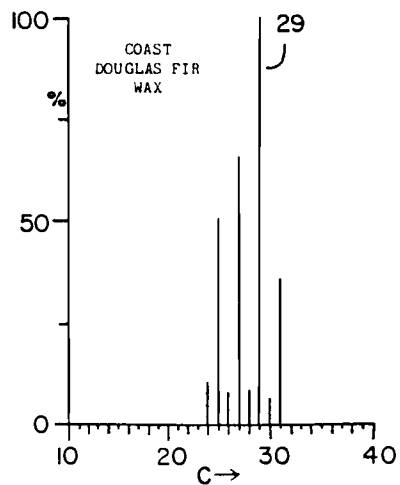
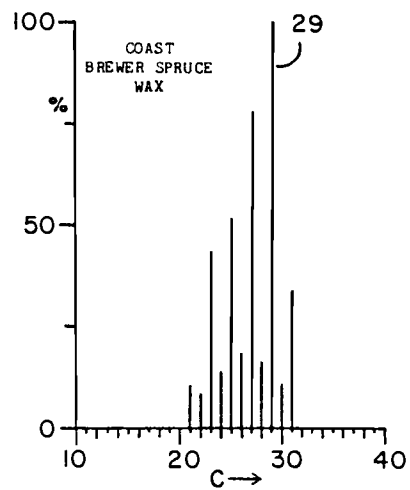


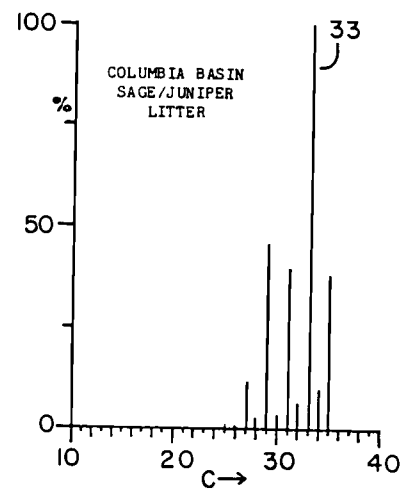
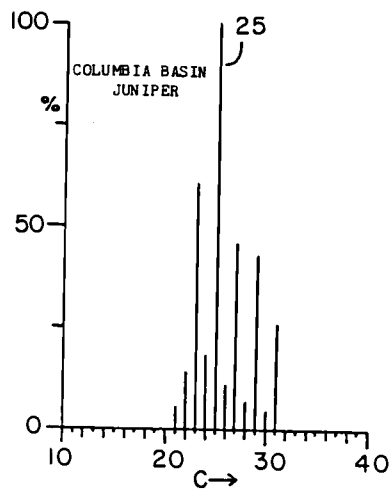
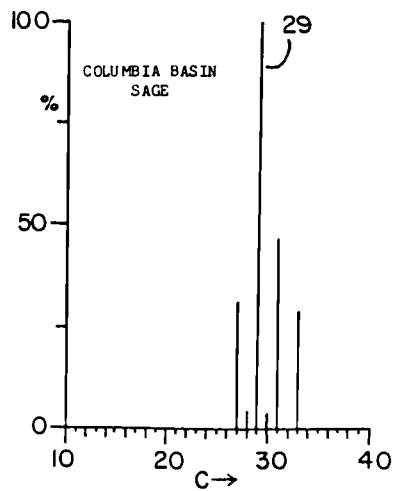
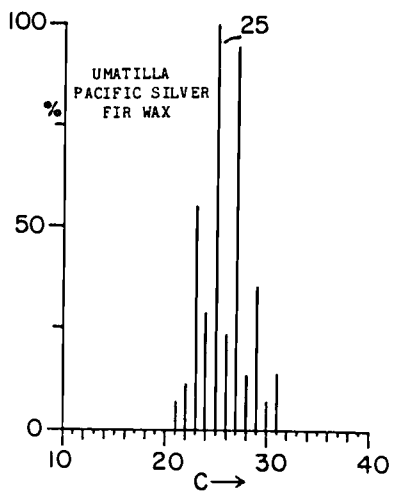
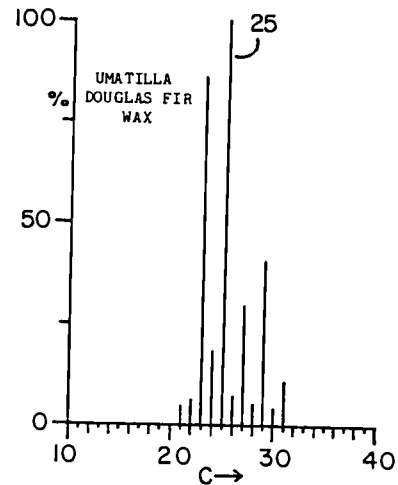
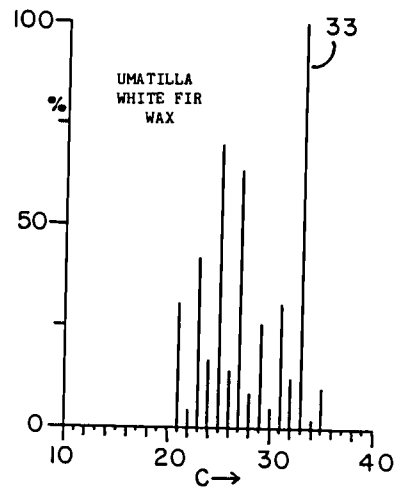
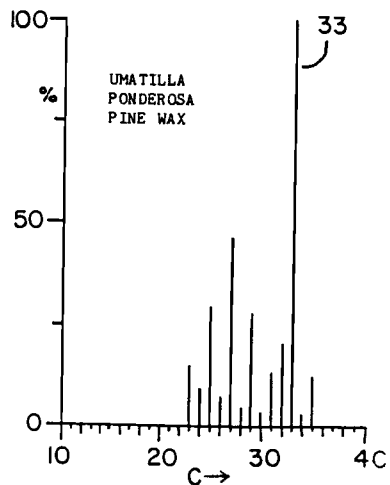
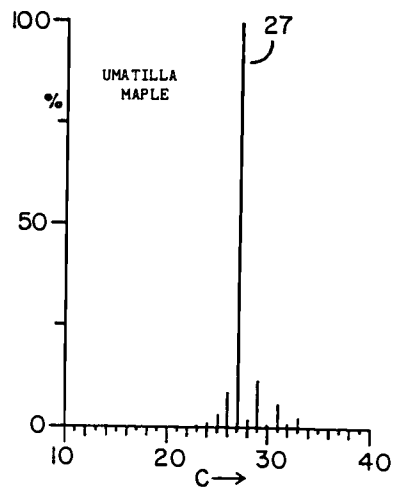


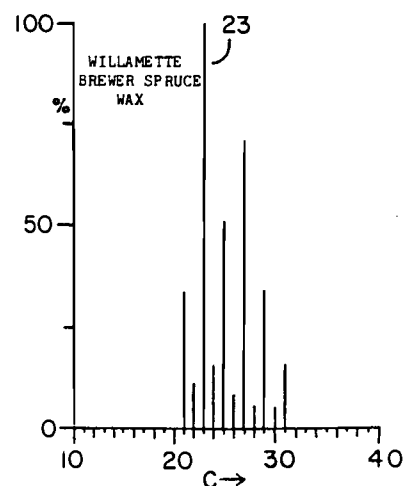
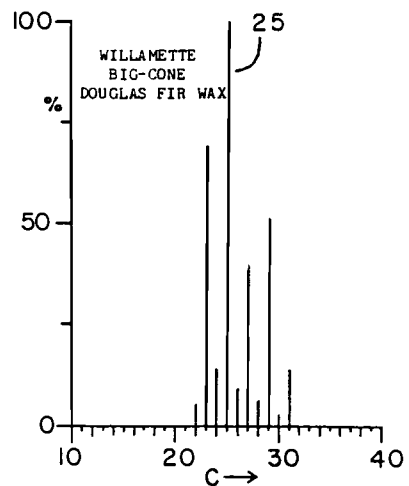
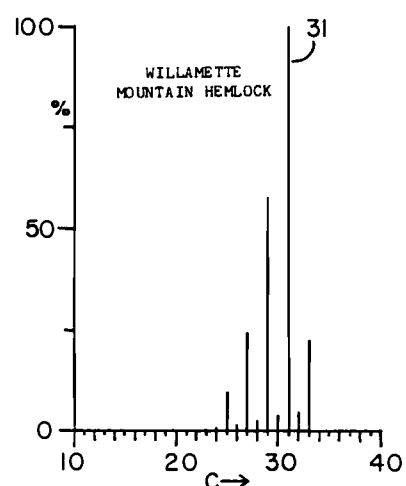
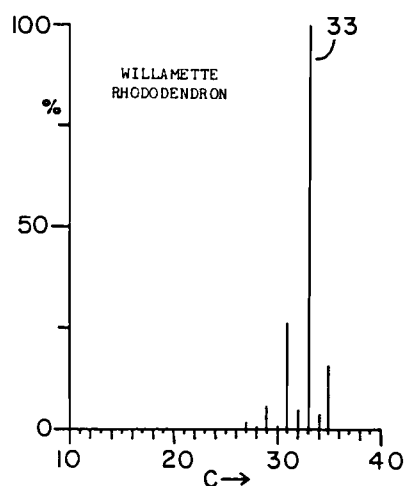
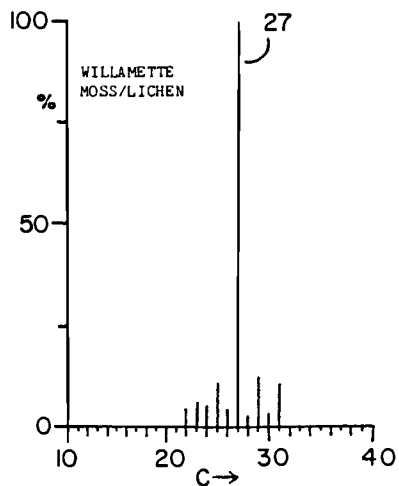
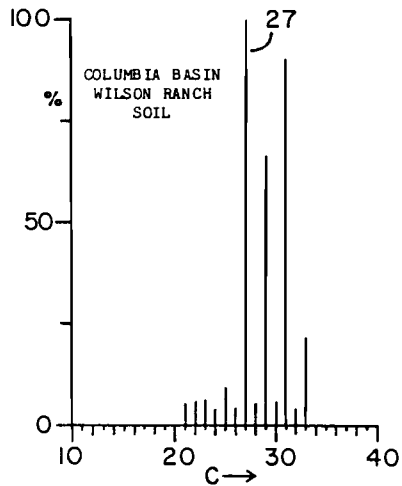




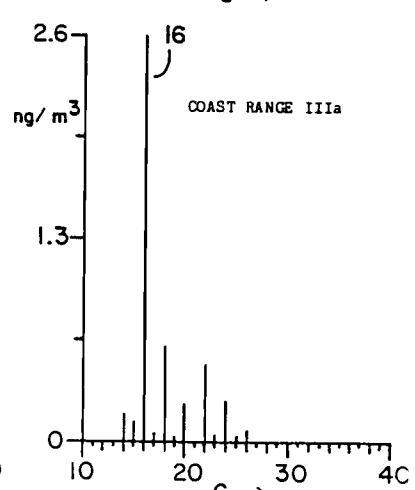
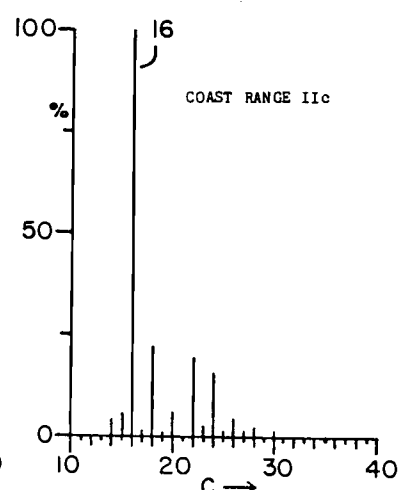
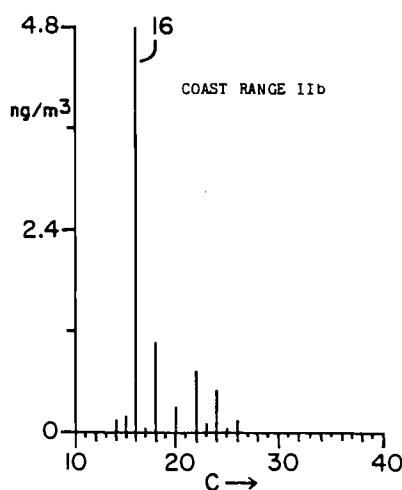
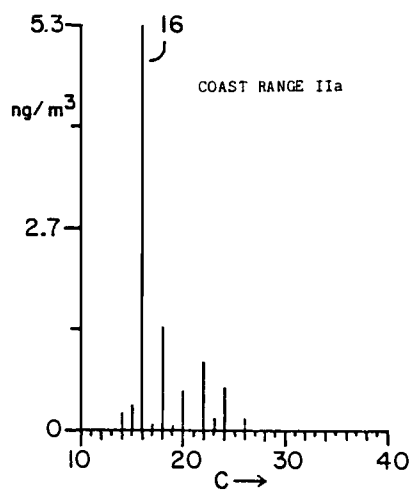
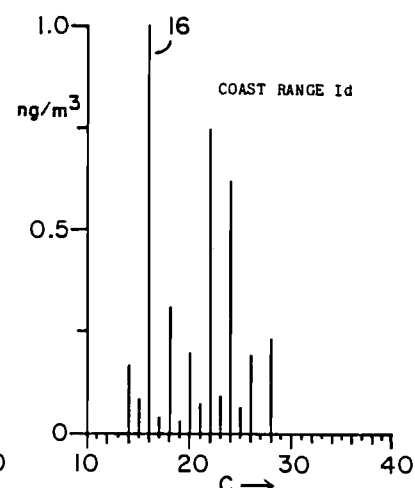
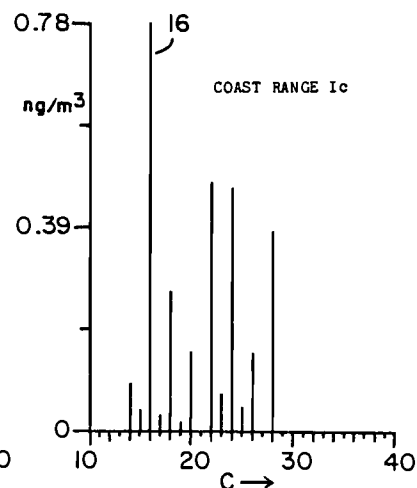
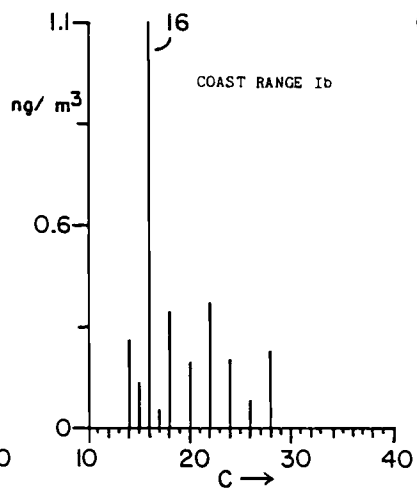
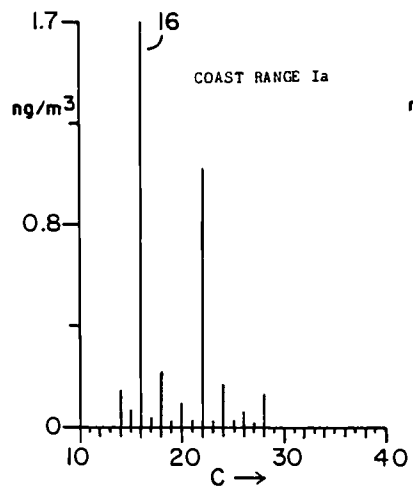


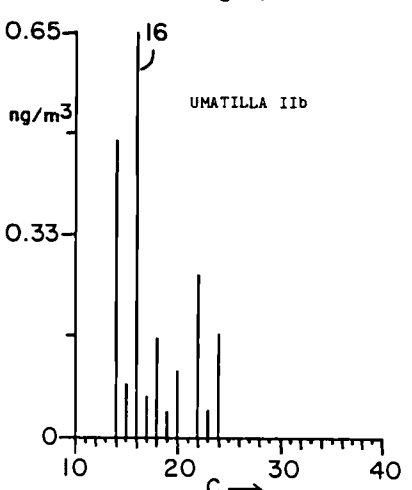
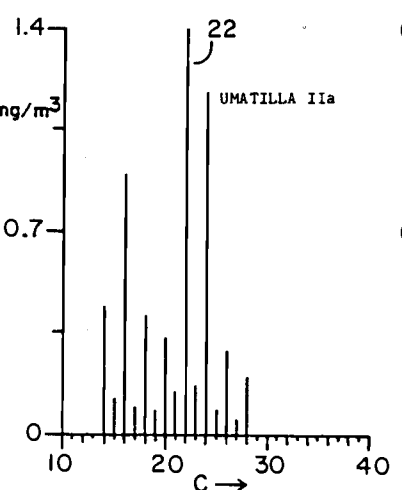
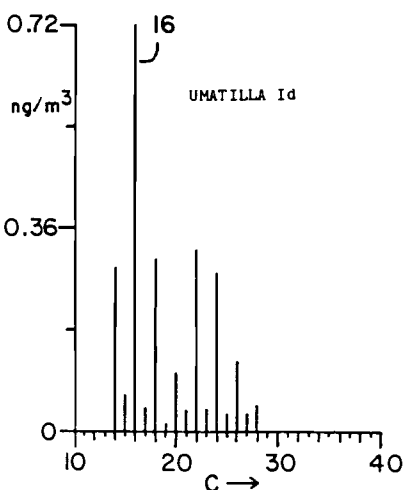
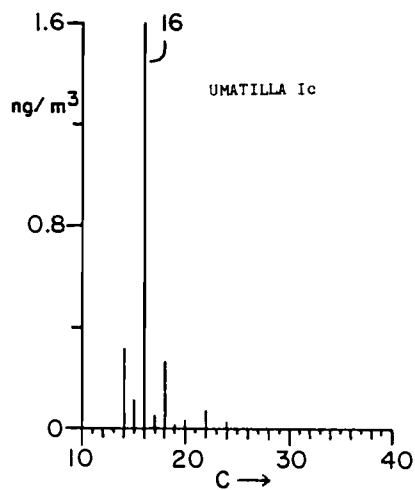
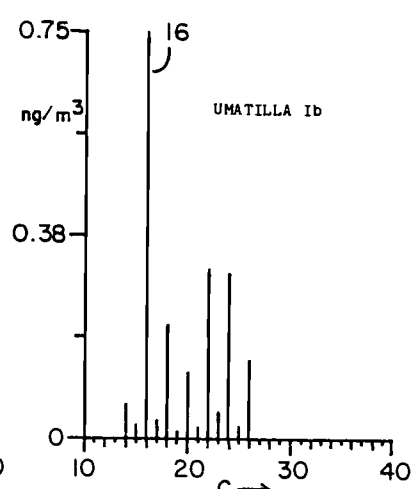
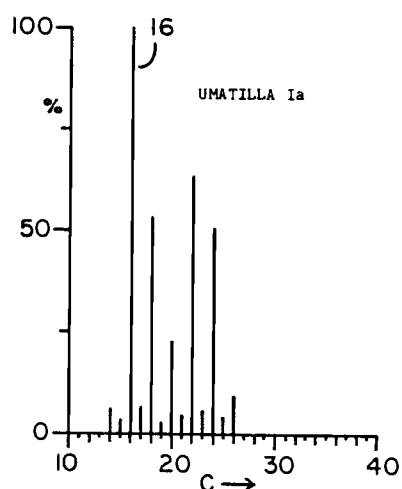
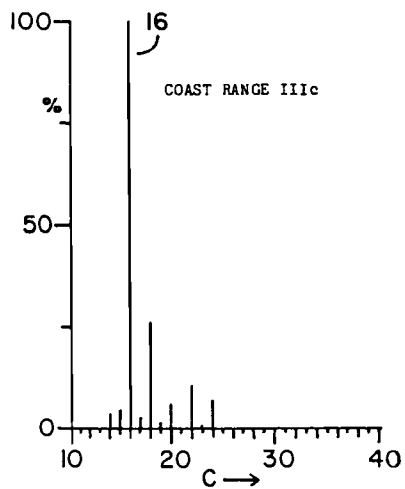
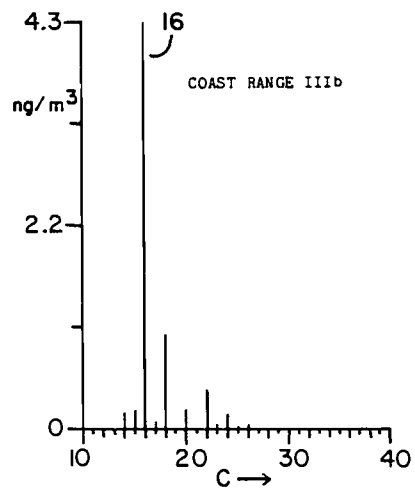


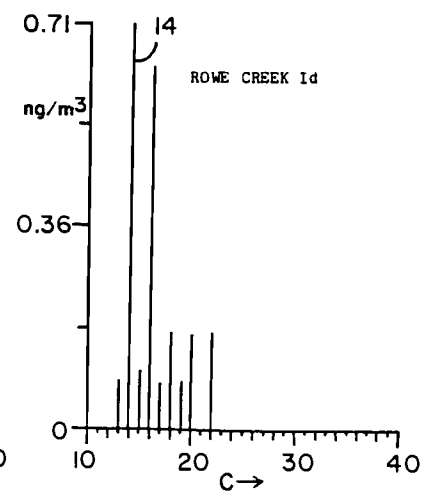
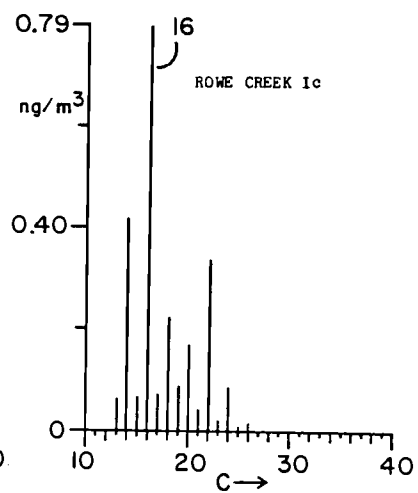
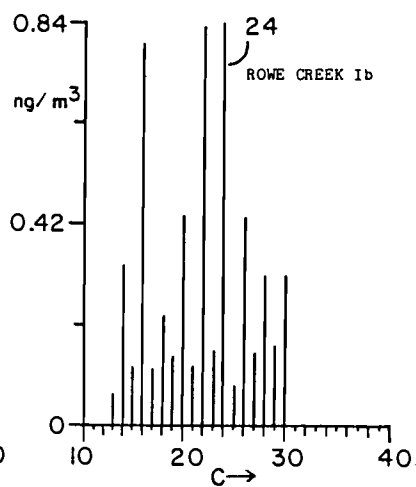
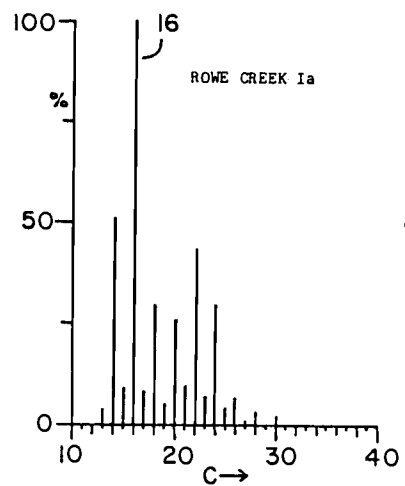
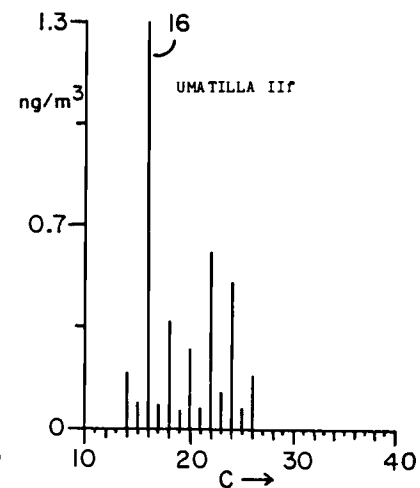
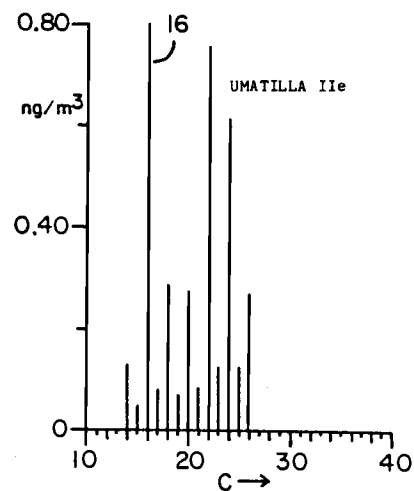
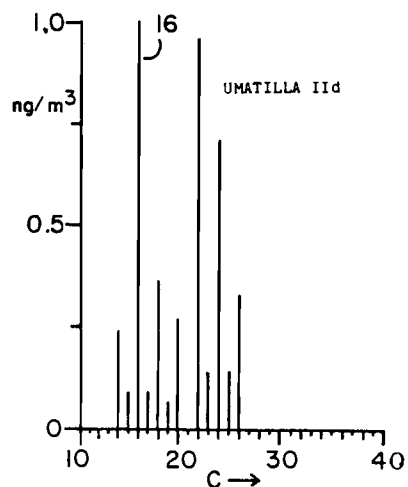
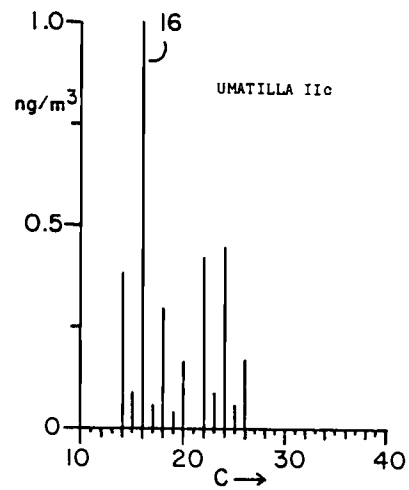


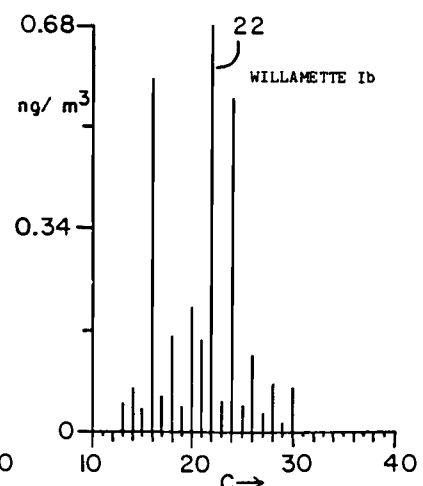
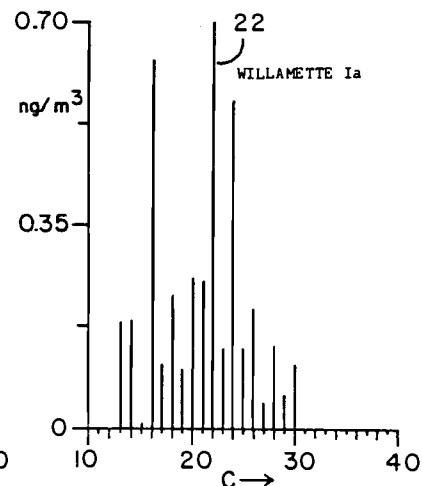
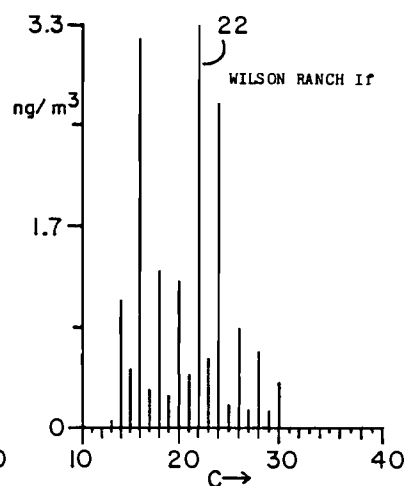
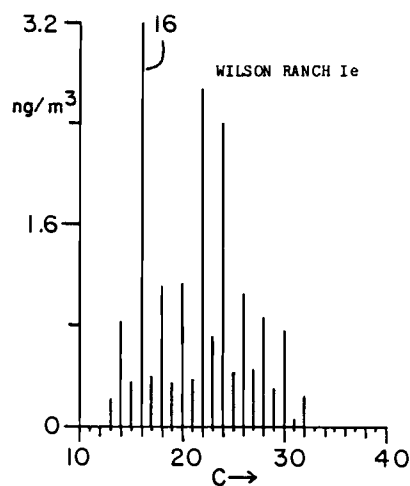
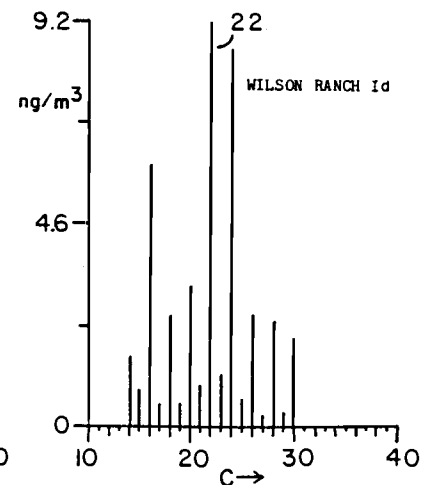
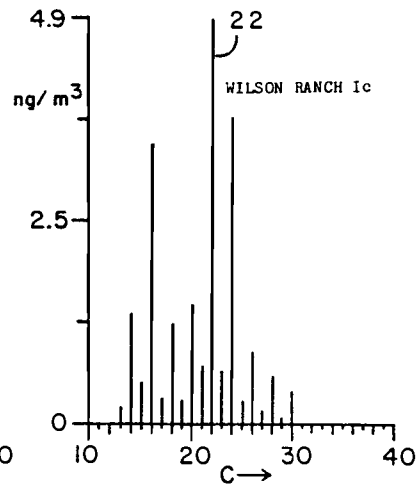
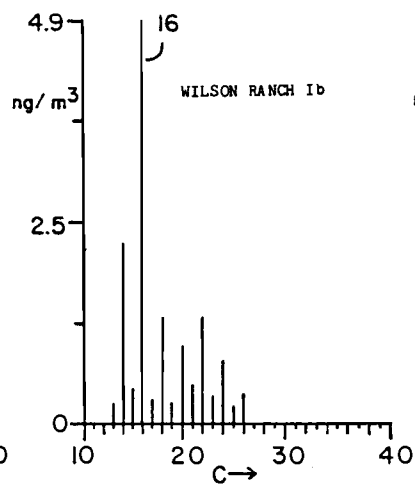
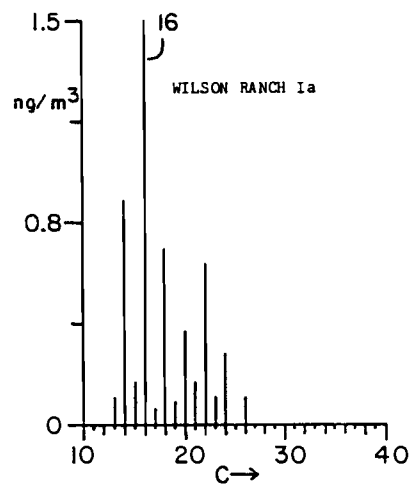


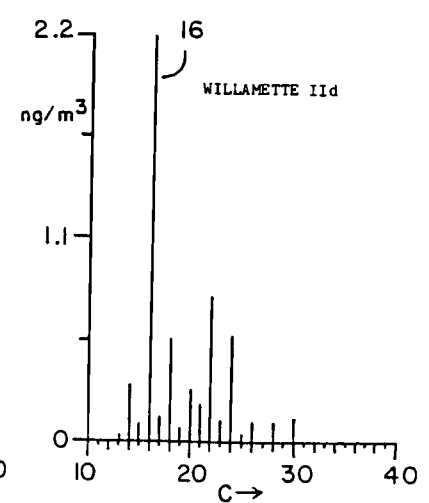
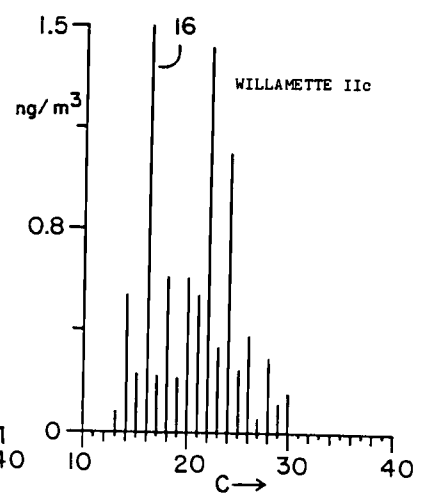
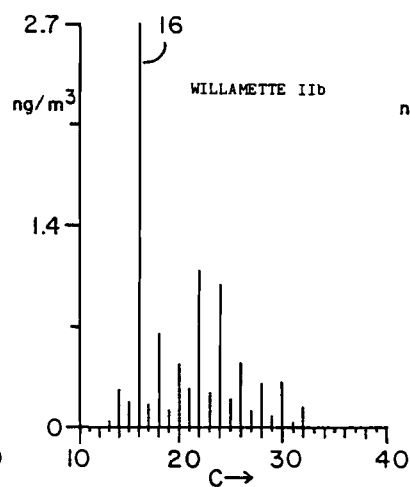
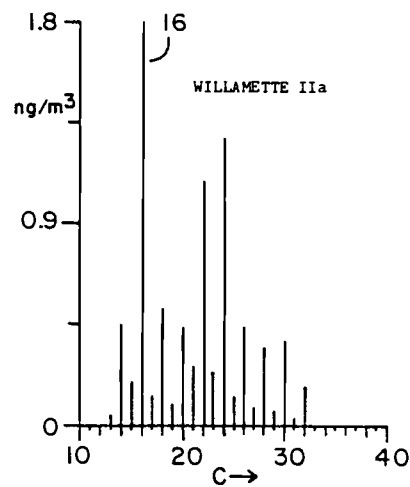
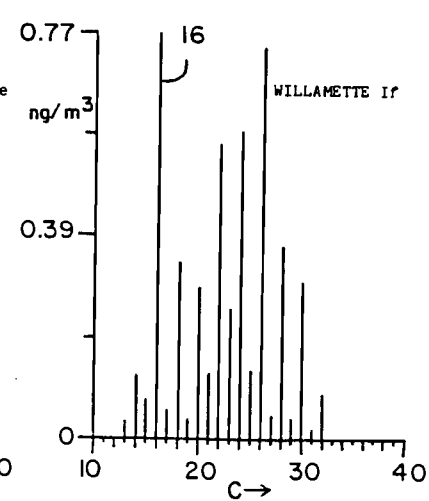
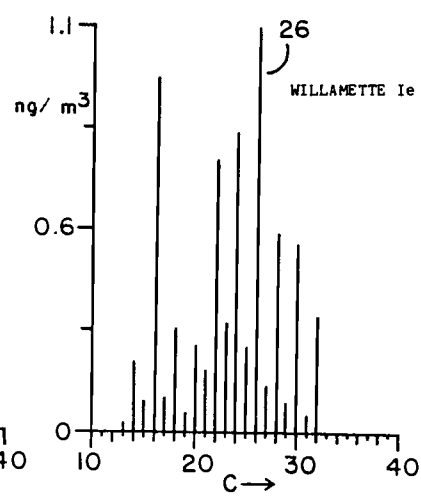
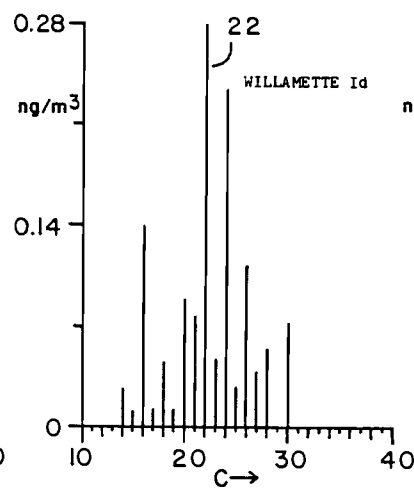
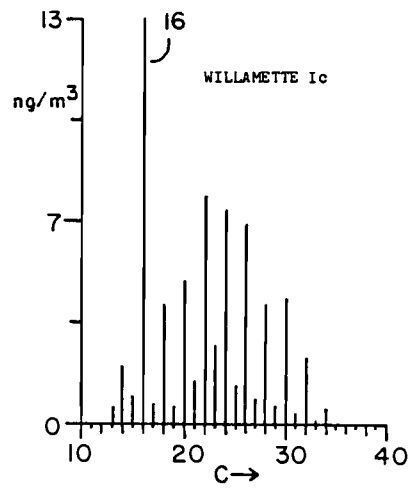
APPENDIX III: Histograms of n-alkanoic acid distributions
in aerosol and vegetation extracts
collected along a transect in rural Oregon

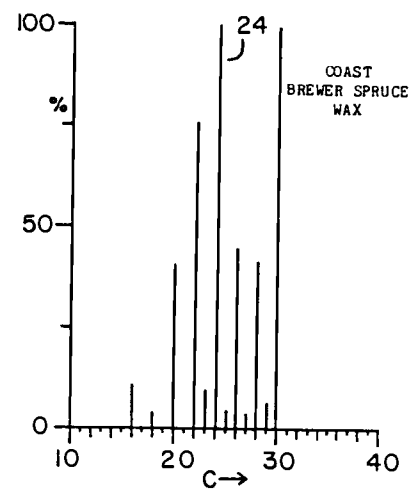
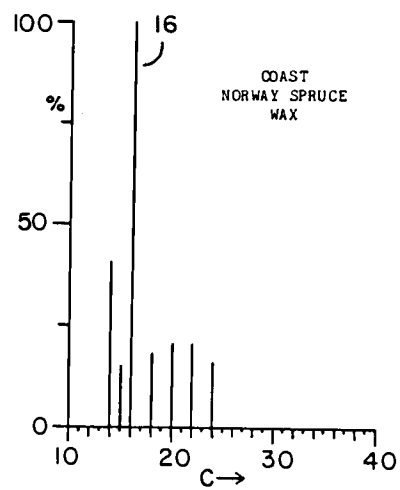
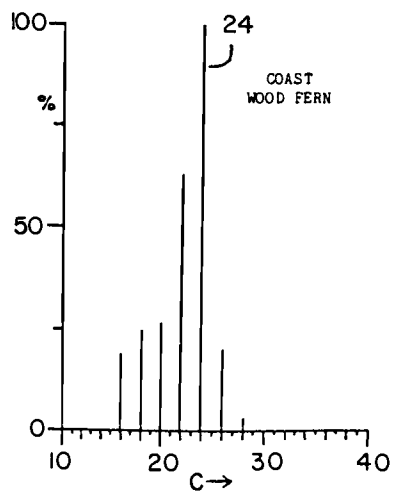
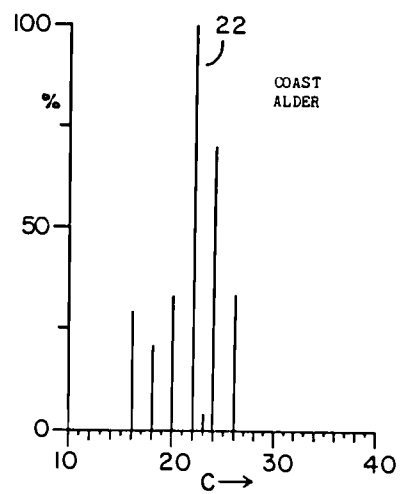
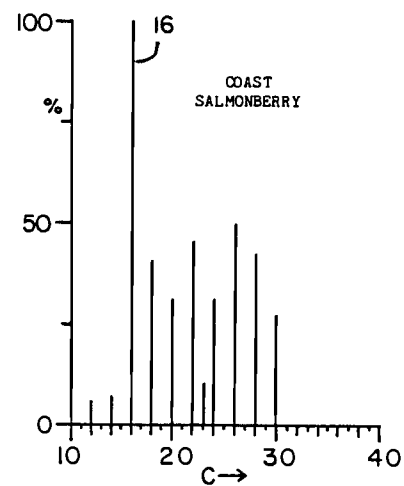
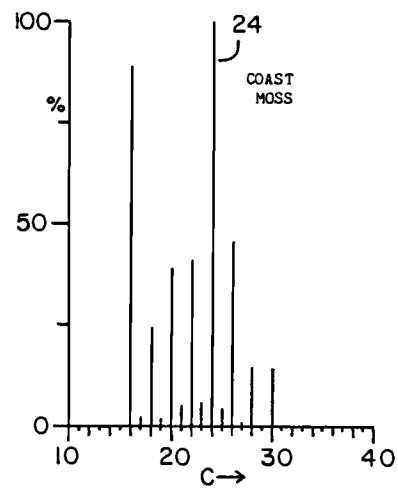
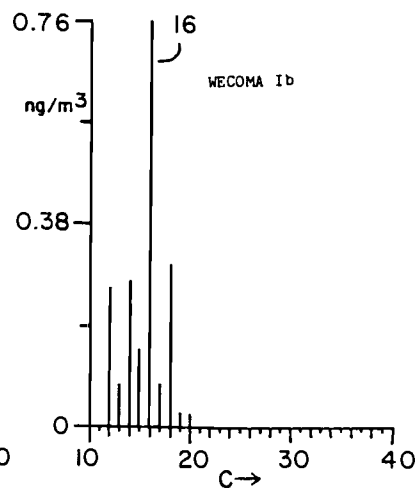
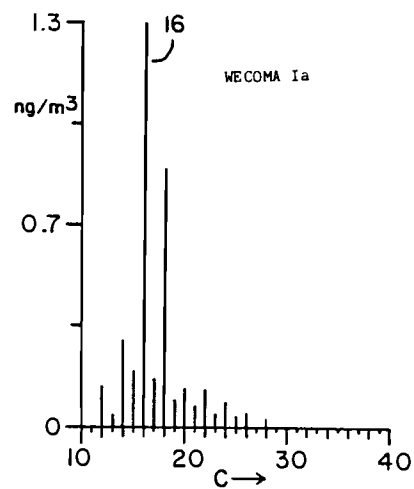


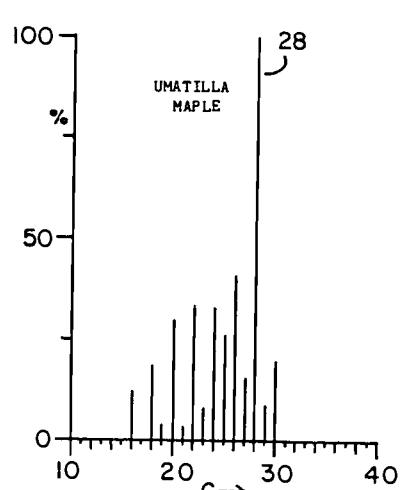
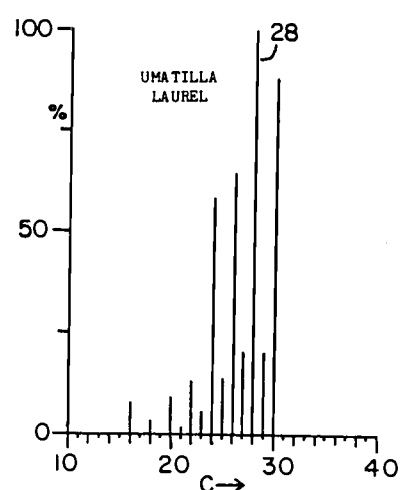
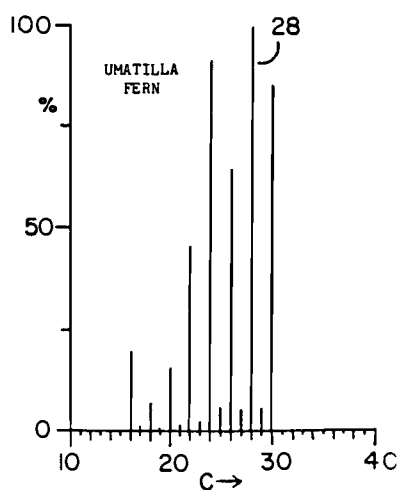
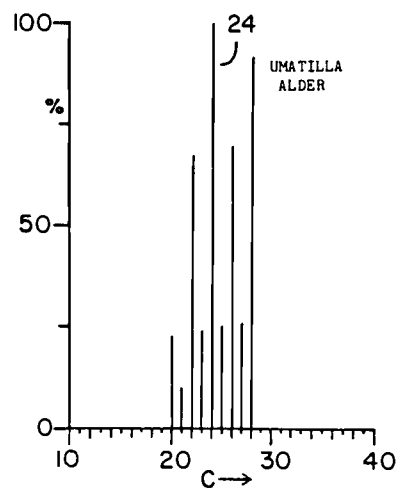
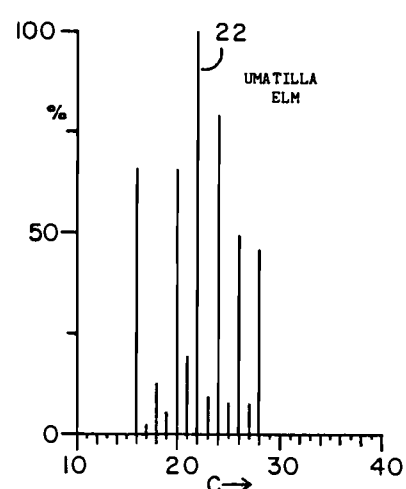
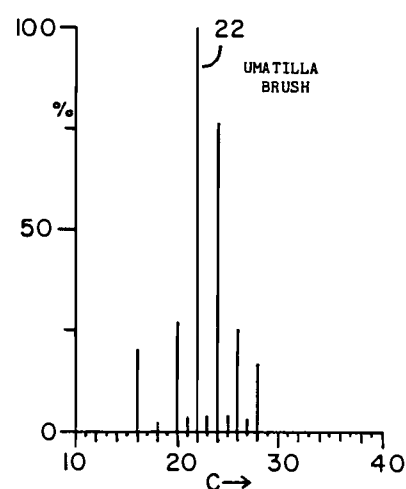
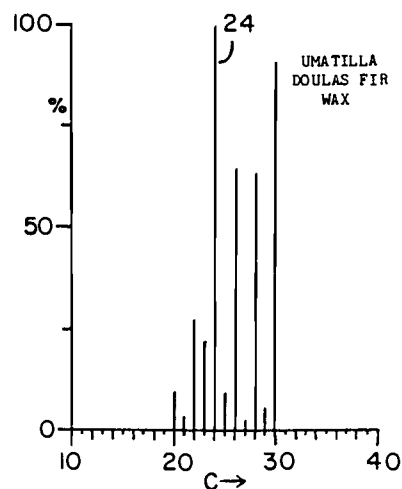
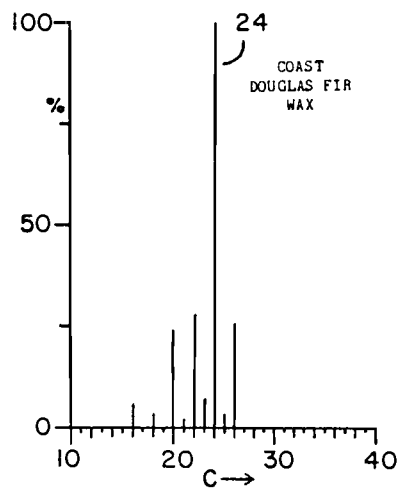


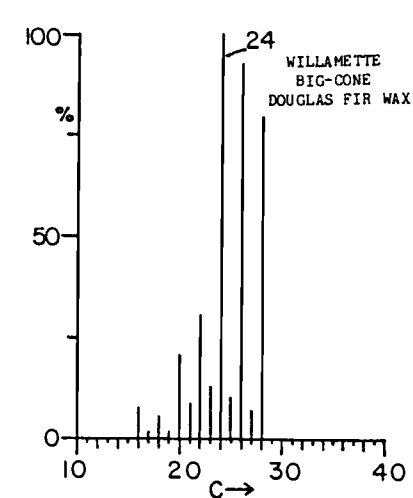
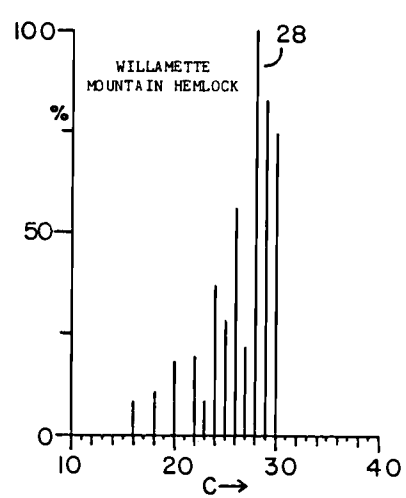
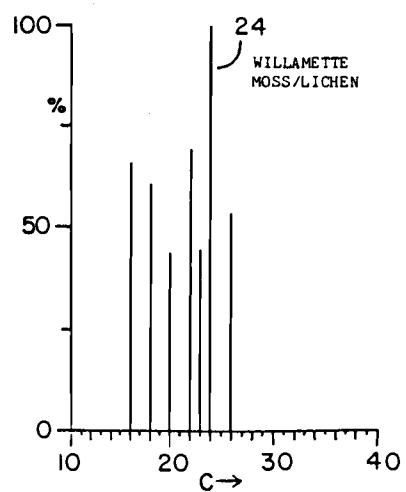
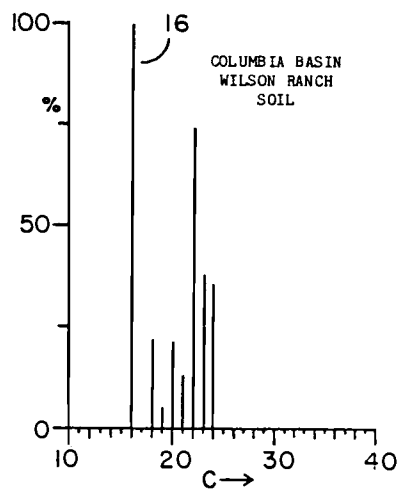
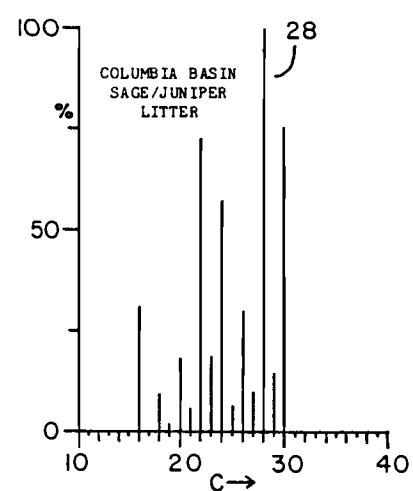
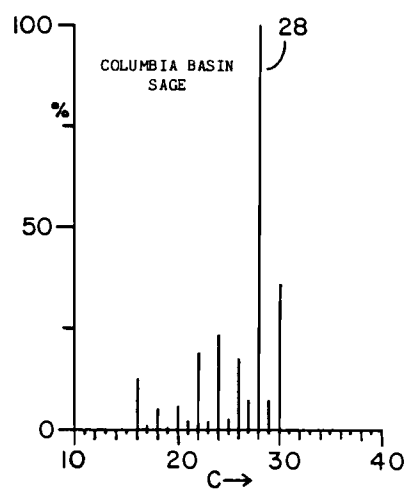
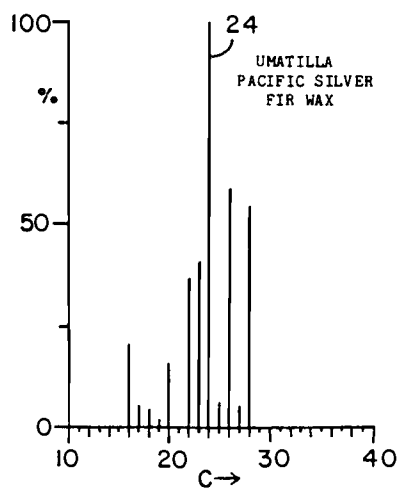
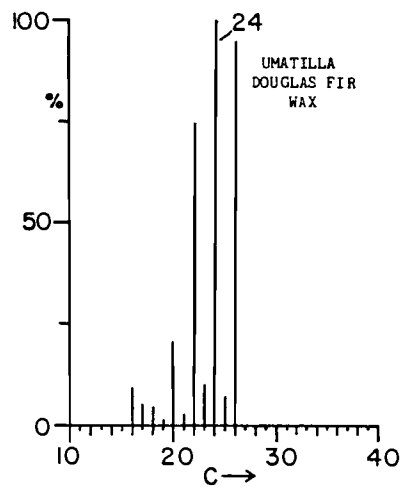


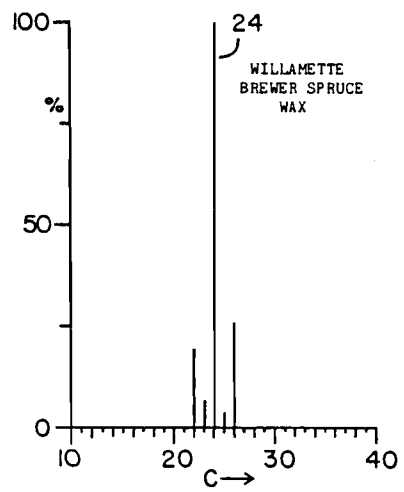




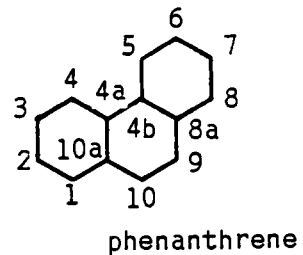
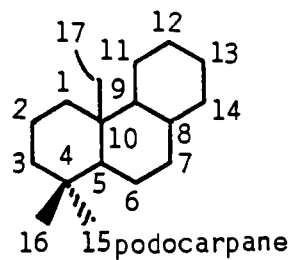
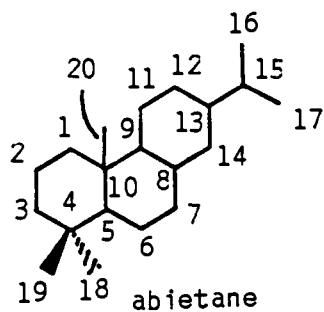




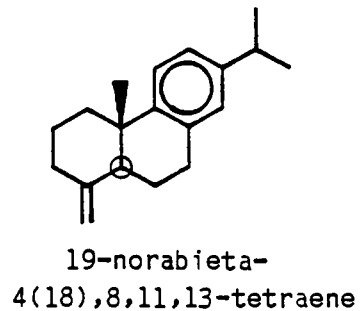
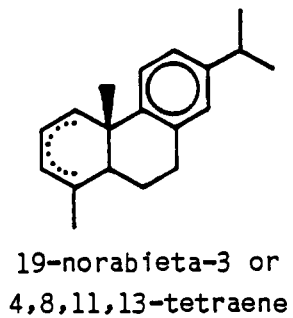
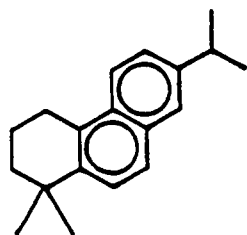
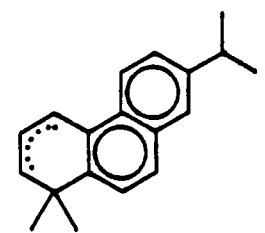
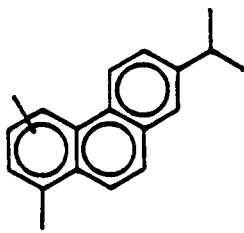
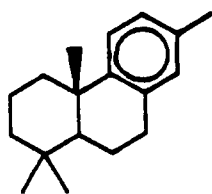
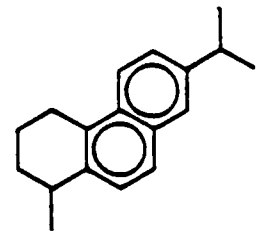
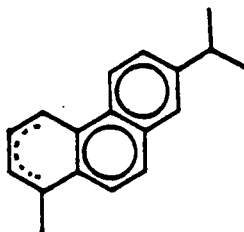
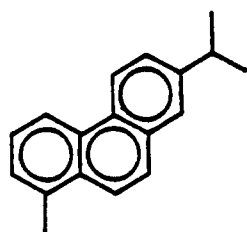


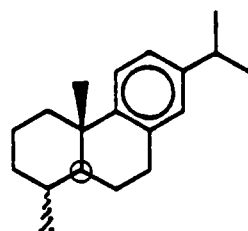


APPENDIX IV: Structures of diterpenoids and triterpenoids

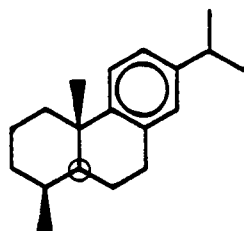


Numbering convention of various diterpenoid skeletons

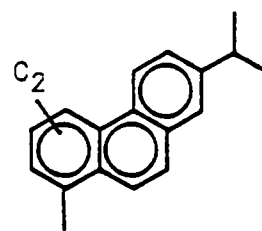




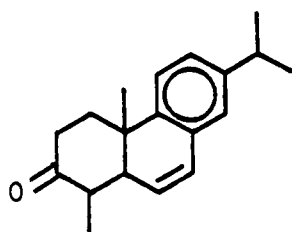
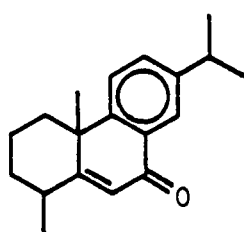
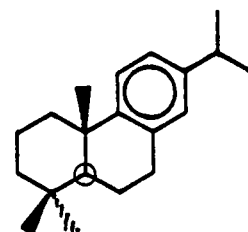
dehydroabietin



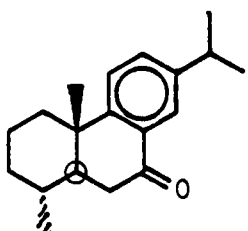
19-norabietane-8,11,13-triene



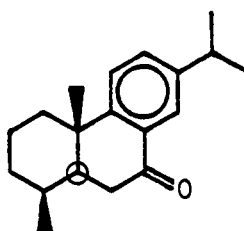
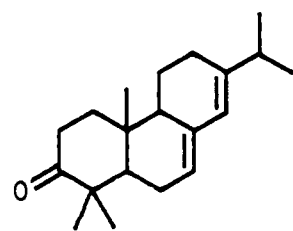
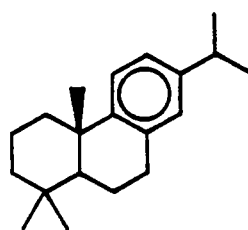
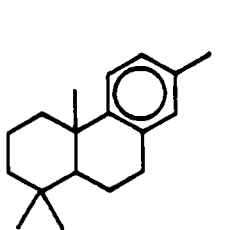
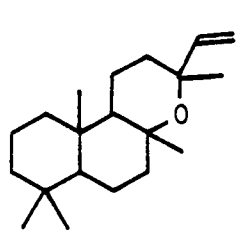
dimethylretenes

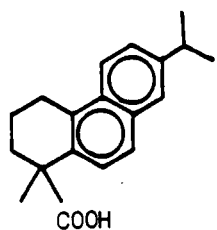
e.g. 3-oxonorabieta-
6,8,11,13-tetraenee.g. 7-oxonorabieta-
5,8,11,13-tetraene

dehydroabietane

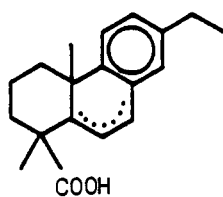


7-oxodehydroabietin

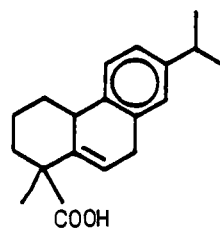
7-oxo-19-norabieta-
8,11,13-trienee.g. 3-oxonorabieta-
7,14-dieneCHO
dehydroabietaCOOH
16,17-bisnordehydro-
abietic acidmanoyl &
epi-manoyl epoxides



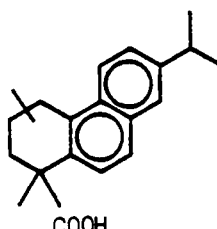
e.g. 1-methyl-7-isopropyl-1,2,3,4-tetrahydrophenanthrene-1-carboxylic acid



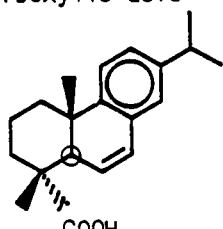
e.g. 1,4a-dimethyl-7-ethyl-1,2,3,4,4a,9 or 10a-hexahydrophenanthrene-1-carboxylic acid



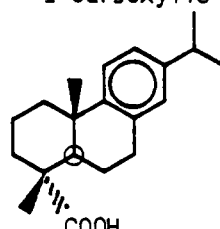
e.g. 1-methyl-7-isopropyl-1,2,3,4,9,10-hexahydrophenanthrene-1-carboxylic acid



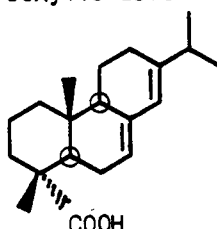
e.g. 1A-dimethyl-7-isopropyl-1,2,3,4-tetrahydrophenanthrene-1-carboxylic acid



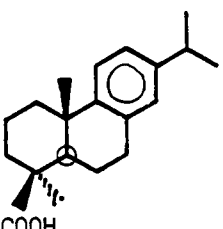
13-isopropyl-5 α -podocarpa-6,8,11,13-tetraen-16-oic acid



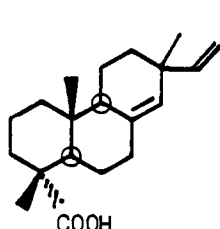
dehydroabietic acid



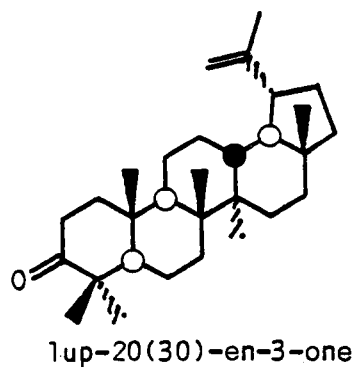
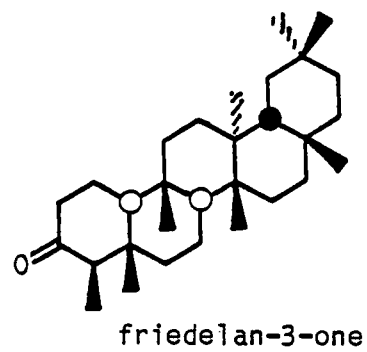
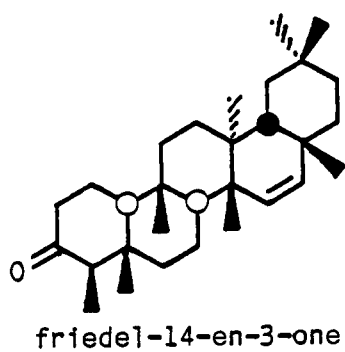
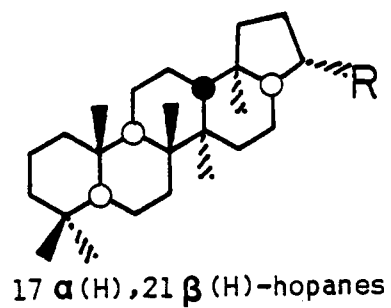
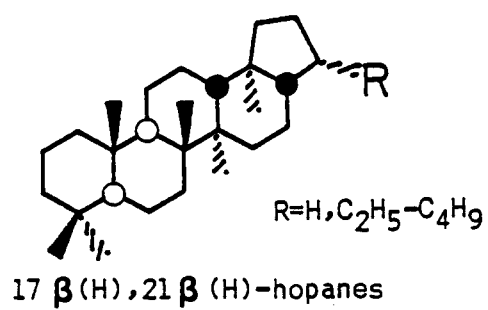
abietic acid



callitrisic acid



pimaric acids



APPENDIX V: Mass spectral reference file (mass spectra of
carboxylic acids as methyl esters)

