AN ABSTRACT OF THE DISSERTATION OF

Daniel R. Oros for the degree of Doctor of Philosophy in Environmental Sciences presented on September 24, 1999. Title: Application of Biomarker Compounds as Tracers for Sources and Fates of Natural and Anthropogenic Organic Matter in the Environment.

Redacted for Privacy

Abstract approved: _____

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Determination of the source and fate of natural (higher plant lipids, marine lipids, etc.) and anthropogenically (e.g., petroleum, coal emissions) derived hydrocarbons and oxygenated compounds in the environment was accomplished using gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) to characterize or identify molecular biomarkers to be utilized as tracers. The distributions and abundances of biomarkers such as straight chain homologous series (e.g., *n*-alkanes, *n*-alkanoic acids, *n*-alkan-2-ones, *n*-alkanols, etc.) and cyclic terpenoid compounds (e.g., sesquiterpenoids, diterpenoids, steroids, triterpenoids) were identified in epicuticular waxes from conifers of western North America (natural emissions). These biomarkers and their thermal alteration derivatives were also identified in smoke emissions from known vegetation sources (e.g., conifers, deciduous trees and grasses) and were then applied as tracers in soils, soils that contained wildfire residues and soil/river mud washout after wildfire burning. Where possible, the reaction pathways of transformation from the parent precursor compounds to intermediate and final alteration products were determined from GC-MS data. In addition, molecular tracer analysis was applied to air, water and sediment samples collected from a lacustrine setting (Crater Lake, OR) in order to determine the identities, levels and fates of anthropogenic (i.e., petroleum hydrocarbon contamination from boating and related activities) hydrocarbons in a pristine organic matter sink. This work demonstrated that biomarker tracer analysis is a useful tool for developing environmental management and pollution mitigation strategies.

APPLICATION OF BIOMARKER COMPOUNDS AS TRACERS FOR SOURCES AND FATES OF NATURAL AND ANTHROPOGENIC ORGANIC MATTER IN THE ENVIRONMENT

By

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A DISSERTATION
submitted to
Oregon State University

in partial fulfillment of
the requirements for the
degree of

Doctor of Philosophy

Presented September 24, 1999
Commencement June 2000

Doctor of Philosophy Dissertation of Daniel R. Oros presented September 24, 1999

APPROVED:

Redacted for Privacy

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I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature authorizes release of my dissertation to any reader upon request.

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Daniel R. Oros, Author

ACKNOWLEDGMENTS

I express my gratitude to Professor Dr. Bernd R.T. Simoneit for his guidance and support throughout my graduate study at Oregon State University. I am grateful to Professors Dr. Jesse Ford, Dr. Evelyn Sherr, Dr. John Baham and Dr. James Liburdy for participating as members of my graduate committee. Thank you all very much for your advice and for making the education process a very challenging and rewarding experience. I would also like to acknowledge my family for showing endless love and patience throughout this time.

This research was funded in part by grants to Dr. Bernd R.T. Simoneit from the U.S. Environmental Protection Agency (Grant CR 823990-01-0) and the U.S. Department of the Interior, National Park Service (Grant CA-9000-8-0006). The author was awarded a graduate student fellowship by the Oregon State University Faculty Diversity Initiative - Minority Graduate Student Pipeline Support Fellowship Program for the final year of study.

CONTRIBUTION OF AUTHORS

Dr. Bernd R.T. Simoneit assisted in the conception and revision of each manuscript. Dr. Laurel J. Standley and Xiaojing Chen each assisted with the data collection for Chapter II. Dr. Laurel J. Standley and Dr. Monica A. Mazurek each assisted with the data collection for Chapter V. Dr. John E. Baham assisted in the conception and revision of Chapter V. Dr. Robert W. Collier assisted with the data collection for Chapter VI.

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APPLICATION OF BIOMARKER COMPOUNDS AS TRACERS FOR SOURCES AND FATES OF NATURAL AND ANTHROPOGENIC ORGANIC MATTER IN THE ENVIRONMENT

CHAPTER I: INTRODUCTION

Determination of the source and fate of natural (higher plant lipids, marine lipids, etc.) and anthropogenically (e.g., lubricating oil, petroleum combustion emissions, etc.) derived hydrocarbons and oxygenated compounds in the environment may be accomplished using analytical methods such as gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) which characterize or identify molecular markers (biomarkers) as tracers. Biomarkers are compounds derived from biological sources that retain some, if not all, of the structural characteristics of their parent precursor molecule after being preserved in the geological record or released into the environment. Hence, they can be traced back to their biological origin. They are present in rocks, sediments, soils, water, fossil fuels and in atmospheric emissions. A schematic showing the major pathways of biomarker cycling in the environment is given in Figure I.1.

The application of biomarkers as tracers is important for understanding earth system processes (e.g., biological degradation/diagenesis, carbon cycling, etc.) and for developing hypotheses and experiments that seek to describe the biogeochemistry occurring in environmental systems (air, soil, sediment, water) and their interfaces. Once released into the environment the lipids (e.g., hydrocarbons) and structural biopolymers (e.g., cellulose, hemicellulose, lignin), in comparison with other organic compounds (e.g., proteins, nucleic acid biopolymers, polysaccharides), are mostly refractory and undergo limited microbial degradation. Thus, they can be identified in soils and sediments where they are degraded and altered in part and preserved.

Biomarker tracer analysis has its origin in fossil fuel geochemistry where Treibs (1936) showed the link between chlorophyll-a in living photosynthetic organisms and porphyrins in petroleum and shales, thus providing the first strong evidence for an organic origin of petroleum. Many hydrocarbon biomarkers (e.g., *n*-alkanes,

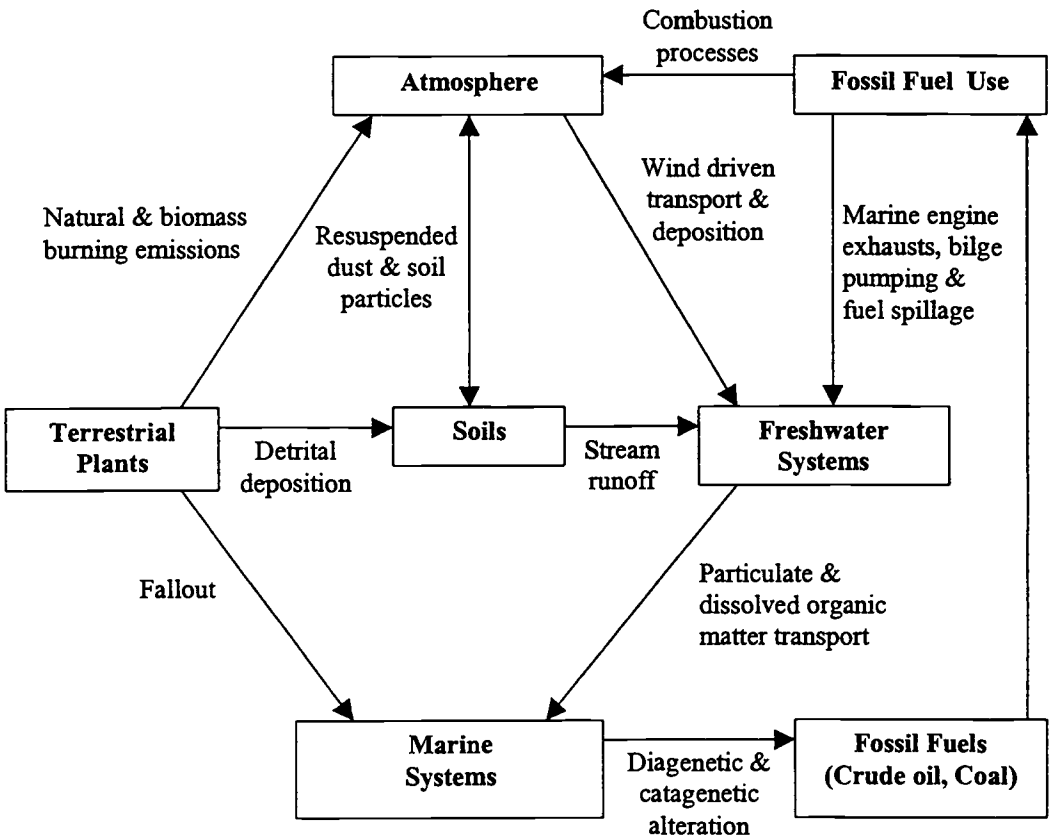

Figure I.1. Major pathways of biomarker cycling in the environment.

isoprenoids, hopanes, tricyclic terpanes, steranes, etc.) were later identified from various petroleums that provided critical information on the organic matter of source rock (source), environmental conditions during its deposition and burial (diagenesis), the degree of biodegradation, maturity and the age (Peters and Moldowan, 1993). For example, age determinations were accomplished by isolating oleanane, a triterpane biomarker characteristic of angiosperms (flowering plants) found only in Tertiary (~20-70 million years ago, m.y.a) and Cretaceous (~70-140 m.y.a.) age rocks and oils. Additionally, dinosterane, a sterane biomarker derived from marine dinoflagellates was used to distinguish Tertiary and Mezozoic (~70-250 m.y.a.) from Paleozoic (~250-600 m.y.a.) source input (Peters and Moldowan, 1993).

Biomarker tracer analysis has been used extensively in various palaeoclimate studies. For example, the changes in unsaturation within the suite of long-chain C_{37}-C_{39} *n*-alkenones biosynthesized by prymnesiophyte algae has been correlated with the sea-surface temperature at which these plants grow (Brassell *et al.*, 1986; Prahl and Wakeham, 1987). Perturbations in climate were reflected by variations in the abundance and distribution of higher plant *n*-alkanes in eastern Atlantic Ocean sediments which were deposited during cold stages due to intensified trade winds during glacial periods (Poynter *et al.*, 1989). Biomarker thermal alteration products in stratified soils and sediments might also be used as potential indicators of past biomass burning events and dry climate conditions. For example, the anhydrosaccharide 1,6-anhydro-β-D-glucopyranose (levoglucosan) derived from biomass burning of wood, specifically cellulose and retene and dehydroabietic acid derived from burning conifer resin (Ramdahl, 1983; Simoneit *et al.*, 1999). These biomass burning products, identified in this study, are also found in forest and grassland soils that have been subjected to wildfire and controlled burning.

Natural organic matter released into the environment (e.g., plant litter and detritus to soil surfaces, wildfire emissions to the atmosphere, soil organic matter washed into rivers and streams, etc.) contains the chemical fingerprint of its principal vegetation source. The distributions and abundances of the organic compounds that make up the chemical fingerprint are strongly dependent on the vegetation source and extent of degradation from microbial and thermal alteration processes. Hence, the major organic compounds which can be used as biomarker tracers in environmental samples are mainly natural products and their alteration derivatives.

Much of this work has concentrated on the Pacific Northwest ecoregion because it is relatively pristine in comparison with most areas of the northern hemisphere and so represents natural background conditions with respect to its anthropogenic pollutant levels. The major vegetation of the Pacific Northwest ecoregion is composed primarily of mixed coniferous forest. Here as elsewhere, population is increasing as are anthropogenic activities such as agricultural and industrial land development, industrial emissions, field burning and forest clearing. These activities and related practices directly and indirectly introduce significant amounts of synthetic organic compounds (e.g., organochlorine pesticides), fossil fuels (e.g., gasoline, diesel, lubricating oils, fuel additives, etc.) and their combustion products (e.g., polycyclic aromatic hydrocarbons, PAH) into the environment. The identities of the organic compounds in soils, atmospheric aerosols, combustion emissions, and riverine dissolved and particulate organic matter have not been well characterized for this region.

The primary objective of this research was to identify biomarker compounds from both natural and anthropogenic sources and to apply these as tracers to determine the fates and transport of organic matter in the environment. The predominant lipid fractions (solvent soluble organic matter) were analyzed for homologous compound series (e.g., *n*-alkanes, *n*-alkanoic acids, *n*-alkanones and *n*-alkanols) and cyclic components (e.g., diterpenoids originating from conifer resins, triterpenoids from angiosperm gums and mucilages) using GC and GC-MS. The alteration pathways and final products were also determined from GC-MS data.

Plant epicuticular waxes consist mainly of aliphatic compounds such as higher molecular weight *n*-alkanes, *n*-alkanals, *n*-alkanols, *n*-alkanoic acids and wax esters (Eglinton *et al.*, 1962; Kolattukudy, 1970, 1976). They have been identified as major components of the particulate organic matter of aerosols in urban, rural and remote areas (Simoneit and Mazurek, 1982; Simoneit *et al.*, 1988; Simoneit, 1989; Rogge *et al.*, 1993) and have been used to characterize fuel sources in biomass burning (Standley and Simoneit, 1987; Rogge *et al.*, 1994; Abas *et al.*, 1995). In Chapter II, the chemical composition of epicuticular waxes for some conifers from western North America were determined. This information provides background data which is useful for biomarker tracer analysis of environmental samples (e.g., identifying natural organic aerosol sources to the atmosphere, identifying natural organic matter sources to soils and sediments).

Natural fires and the application of biomass burning as a method for clearing vegetated areas (forest and grassland) increase the input of organic aerosol components to the atmosphere. The smoke emissions from only a limited number of biomass burning sources have been characterized for their organic components (e.g., Abas *et al.*, 1995; Hawthorne *et al.*, 1988, 1989, 1992; Oros and Simoneit, 1999; Ramdahl, 1983; Rogge *et al.*, 1998; Simoneit *et al.*, 1993, 1999; Standley and Simoneit, 1994). These studies demonstrated that biomarker tracer analysis is important for understanding the organic component contribution of combustion emissions from vegetation (e.g., natural fires) and anthropogenic (e.g., biomass burning, woodstove and fireplace burning) sources to atmospheric chemistry. The directly emitted and thermally altered biomarker tracers in smoke particles provide a chemical fingerprint which is source specific and useful for identifying emissions, their injection sources and transport in the environment (Mazurek and Simoneit, 1984, 1997; Rogge *et al.*, 1998; Schauer *et al.*, 1996; Simoneit, 1984, 1986, 1989, 1998; Simoneit *et al.*, 1988, 1991a, 1991b). Source emission data is invaluable for assessing and modeling the effects of fine particulate matter on global climate, attaining ambient air quality standards for fine particles, and preventing and remedying visibility impairment in regional airsheds and clean air corridors. Still, additional biomarker tracers of thermally-altered and directly-emitted natural products need to be characterized in order to assign input sources of organic matter from biomass combustion to aerosols. In Chapter III, potential biomarker tracers were identified in smoke samples emitted from the biomass burning of gymnosperms, mainly temperate climate conifers from western North America. In Chapter IV, biomarkers were identified in smoke samples emitted from the burning of angiosperms, mainly deciduous trees.

Vascular plants are a primary source of organic matter to soil via litter and roots (Oades, 1993). In addition, wildfires introduce organic burn residues, charcoal and ash into soils and the chemistry and fates of these thermally produced materials have not been extensively examined. Rain washing and drainage to rivers of soils are important terrestrial processes that directly influence carbon cycling. Soils subjected to these physical treatments (e.g., burning and erosion) are likely to contain organic compounds with distributions reflecting sources and both thermal and water washing processes. In Chapter V, the biomarker compositions and alteration products of the organic components were determined in litter and soil samples that were subjected to

wildfire burning, forest and grassland soils that contained ash residues from burning, and in soil and mud that was washed out after a burn by rain erosion and river transport. The different sample types allowed the determination of the organic reaction pathways from the original natural product precursors to their alteration derivatives under environmental conditions.

Petroleum hydrocarbon pollution and contamination of the environment, especially of water bodies such as estuaries and lakes, are of major regulatory concern. Boats, along with other anthropogenic as well as natural sources (e.g., terrestrial plant waxes, algal productivity, etc.) introduce hydrocarbons and other lipids into water, which have unknown effects on aquatic ecosystems. Outboard engines release their oil-enriched exhaust at and beneath the water surface. Particulate matter and volatile combustion products from inboard engine exhaust enter water directly. Although careful measures can be taken to deter all petroleum contamination in water bodies, small amounts of uncombusted lubricating oil and gasoline are unavoidably introduced into water during repairs, fueling and pumping of bilge from engine compartments. In Chapter VI, biomarker tracer analysis was used to distinguish and quantify the levels and distribution of petroleum hydrocarbons in Crater Lake water and sediments. The lake sediments represent a major environmental sink for both natural and anthropogenic organic matter.

A summary of the research is provided in Chapter VII. This work demonstrates that biomarker compounds can be applied and are of utility as tracers to determine the sources, alteration mechanisms and fate of natural and anthropogenic organic matter in the environment.

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CHAPTER II

EPICUTICULAR WAX COMPOSITIONS OF CONIFERS FROM WESTERN NORTH AMERICA

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Submitted to: ***Zeitschrift für Naturforschung***

ABSTRACT

The compositions of epicuticular waxes of conifers from western North America were determined by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). The primary components identified include alkanes, fatty acids, fatty alcohols, aldehydes, ketones, phytosterols, diterpenoids, triterpenoids and wax esters. Average chain lengths (ACL) for alkanes in Oregon conifers decreased with increasing distance away from the Coastal range which suggests an adaptation by conifers to humid climate conditions. Differences in the chemical compositions make this information useful for chemotaxonomic purposes, for identifying natural organic aerosol input sources to the atmosphere and for tracer monitoring in assessment of global climate change.

Key Words - Gymnosperms, Epicuticular Wax Composition, *n*-Alkanes, *n*-Alkanoic Acids, *n*-Alkanols, Molecular Markers

INTRODUCTION

Epicuticular plant waxes consist mainly of aliphatic compounds such as higher molecular weight *n*-alkanes, *n*-alkanals, *n*-alkanols, *n*-alkanoic acids and wax esters (Eglinton *et al.*, 1962; Kolattukudy, 1970, 1976). The identification of plant wax constituents have been of utility for chemotaxonomic purposes (Nishimoto, 1974; Tulloch, 1981; Salasoo, 1987; Zygaldo *et al.*, 1994; Maffei, 1996), as indicators for determining pollutant exposure (Lutz *et al.*, 1990; Percy and Baker, 1990; Kerfourn and Garrec, 1992; Percy *et al.*, 1993; Burkhardt *et al.*, 1995), and in studies of environmental influences on plant development (Hadley and Smith, 1990; Jagels, 1991; Cape and Percy, 1993; Pfeifhofer, 1995). Plant waxes are major components of the particulate organic matter of aerosols in urban, rural and remote areas (Simoneit and Mazurek, 1982; Simoneit *et al.*, 1988; Simoneit, 1989; Rogge *et al.*, 1993). They have been used for source reconciliation studies of urban, rural and remote aerosols (Simoneit, 1977; Gagosian *et al.*, 1982; Mazurek and Simoneit, 1984; Simoneit *et al.*, 1991a,b; Rogge, *et al.*, 1993; Chen and Simoneit, 1994; Schauer *et al.*, 1996), and for characterization of fuel sources in biomass burning (Standley and Simoneit, 1987; Rogge *et al.*, 1994; Abas *et al.*, 1995). Here we report the chemical composition of epicuticular waxes of conifers from western North America.

EXPERIMENTAL METHODS

Sampling

Samples were collected from forested areas of Oregon, USA and Durango, Mexico away from urban areas and major roads (Standley, 1987): Coastal Range, Columbia Basin, Umatilla National Forest, Willamette National Forest and a forest reserve in the Sierra Madre Occidental (Table I). The samples represent a variety of conifers from areas with different climate conditions. Conifer needles were randomly selected from individual tree canopies and composited into a single sample, thus the abundances of the chemical components reported here reflect average values. The primary components identified in the soluble lipid fractions include the alkanes, fatty

acids, fatty alcohols, aldehydes, ketones, phytosterols, diterpenoids, triterpenoids and wax esters. It is these compounds as such and their thermal alteration products which are used as tracers for tracking emissions from biomass burning (Mazurek and Simoneit, 1997).

Extraction and Fractionation

Extracts of the vegetation samples were obtained by briefly dipping (3-5 sec, 3 times each) needle fronds into chloroform ($CHCl_3$) to dissolve the external waxes. Solvent to sample contact was kept brief to minimize the extraction of significant amounts of internal cellular lipids (intra-cuticular waxes). Extracts were filtered through annealed glass wool and concentrated under aspirator vacuum to approximately 2 ml. Aliquots were taken for derivatization. Alkanoic acid and phenolic moieties were methylated using diazomethane in diethyl ether prepared from the precursor N-methyl-N'-nitro-N-nitrosoguanidine (Pierce Chemical Co.) (Schlenk and Gellerman, 1960).

The methylated extracts were separated into four fractions by preparative thin layer chromatography on silica gel plates (Analtech, Inc.) with a mobile phase mixture of hexane and chloroform (19:1). The four fractions contained the following classes of compounds: (1) *n*-alkanes and saturated and unsaturated cyclic di- and triterpenoid hydrocarbons, (2) *n*-alkanones and *n*-alkanals, (3) *n*-alkanoic acids (as methyl esters) and saturated and unsaturated di- and triterpenoid ketones, and (4) *n*-alkanols, terpenols and polar organics. The fourth fraction was then converted to trimethylsilyl derivatives by reaction with N,O-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) plus 1% trimethylchlorosilane:anhydrous pyridine (1:1) for approximately 30 minutes at 70 °C under a nitrogen atmosphere.

Instrumental Analyses

The extract fractions were analyzed by capillary gas chromatography (GC, Hewlett-Packard Model 5890A) with a 25 m x 0.20 mm i.d. fused silica capillary column coated with DB-5 (J&W Scientific) which was temperature programmed as a

hold at 65 °C for 5 min, ramped to 130 °C at 15 °C/min, then at 6 °C/min to 310 °C, with an isothermal hold at 310 °C for 60-120 min. Selected samples were also analyzed by capillary gas chromatography-mass spectrometry (GC-MS) using a Finnigan 4000 or Hewlett-Packard 6890 MSD quadrupole mass spectrometer operated in the electron impact mode at 70 eV and coupled to a GC. The GC was equipped with a 30 m x 0.25 mm i.d. capillary column coated with DB-5 (J&W Scientific) and was temperature programmed as follows: 65 °C for 6 min, to 310 °C at a rate of 4 °C/min, then held isothermal at 310 °C for 60-120 min.

Compound Identification and Quantitation

Compound identifications are based on comparisons with authentic standards, GC retention times, literature mass spectra and interpretation of mass spectrometric fragmentation patterns. The homologous compound series were quantified by comparison of the GC peak areas with that of a co-injected known standard, hexamethylbenzene. Molecular markers were quantified in the GC-MS data by comparison of peaks with the same standard.

RESULTS AND DISCUSSION

The compositions of the lipid constituents in the conifer waxes are given in Table II.1. The polar lipids for all the conifers sampled make up an overall average of 87% of the total wax extracts. The highest polar lipid content was found in Norway Spruce (94.6%) while the lowest was in Montezuma Pine (61.8%). Mountain Hemlock which has a low polar lipid content at 68% shows the highest amount of nonpolar lipids as aldehydes and ketones (24%), which is 12 times greater than the average content of aldehydes and ketones in the other wax samples. This may reflect the degree of biochemical coupling between the enzymes acyl-CoA reductase and aldehyde reductase which are required for the biosynthesis of fatty alcohols from fatty acids. Lack of a tight coupling mechanism results in the accumulation of aldehydes as are present in this conifer wax (Kolattukudy *et al.*, 1976).

Analytical data for the lipid constituents of the conifer epicuticular waxes are given in Table II.2. The carbon number range (C_{range}), carbon number maximum (C_{max}) and the carbon preference indices (CPI) (Mazurek and Simoneit, 1984) for the homologous series of *n*-alkanes, *n*-alkanoic acids and *n*-alkanols are listed. The average chain length (ACL) parameters for higher plant *n*-alkanes and *n*-alkanols are also given in Table II.2. The ACL parameter may be used as an additional indicator of source composition (Poynter and Eglinton, 1990). The ACLs were derived by using the percent composition values of individual lipid components present in conifer waxes as listed in Appendix II.1. It is important to mention, that the compositions and distributions of the solvent soluble compounds from these waxes may not exactly reflect the amounts of naturally synthesized components. Variations in lipid constituent distributions may occur, due to the fact that needle and leaf surfaces can also act as important adsorptive sinks for airborne particulate matter originating from anthropogenic as well as other plant sources (Burkhardt *et al.*, 1995).

Hydrocarbons

The conifer wax extracts exhibited *n*-alkanes ranging from C_{16} to C_{35} and C_{max} values ranging from 23 to 33. The most common C_{max} values for the *n*-alkanes were 25 and 29 each characteristic of four conifers. Brewer Spruce (WNF) and Apache Pine waxes exhibited the lowest C_{max} at 23 and three conifer waxes showed a C_{max} at 33. All C_{max} are odd carbon numbered *n*-alkanes. The CPIs for the *n*-alkanes ranged from 2.6 to 17.0 with an average of 5.8 (all >>1.0). The lowest CPI was found in the wax of California Redwood and the highest for that of Mountain Hemlock. Although the homologous series of *n*-alkanes are useful for chemotaxonomic purposes, their source information is not always definitive because of their relatively simple assemblage and the complexity of other components present in waxes (Kolattukudy, 1976). Care must be taken if the CPI is used solely for chemotaxonomic and source correlation purposes.

Table II.1. Composition of the lipid constituents in conifer epicuticular waxes.

Sample		Lipid Compositions (%)					
Common Name / Scientific Name / Region Collected	Code	*n*-Alkanes	Wax Esters	*n*-Alkanoic Acids	*n*-Alkan-ones	*n*-Alkan-ols	Polar Lipids
1 Apache Pine *Pinus engelmannii* Sierra Madre Occidental, Mexico	AP	1.4	1.8	15.3	0.1	0.5	80.9
2 Big-Cone Douglas Fir *Pseudotsuga macrocarpa* Willamette National Forest, OR	BDF	0.1	1.4	0.7	2.6	2.2	93.0
3 Brewer Spruce *Picea brewerana* Coastal Range, OR	BS(CR)	0.1	1.7	0.9	4.3	4.4	88.6
4 Brewer Spruce *Picea brewerana* Willamette National Forest, OR	BS(WNF)	1.1	0.8	1.1	2.8	4.4	89.8
5 California Redwood *Sequoia sempervirens* Jedidiah Smith State Park, CA	CR	4.4	0.5	3.3	0.1	0.3	91.4
6 Douglas Fir *Pseudotsuga menziesii* Coastal Range, OR	DF(CR)	0.1	0.9	1.1	8.3	1.4	88.2
7 Douglas Fir *Pseudotsuga menziesii* Umatilla National Forest, OR	DF(UNF)	0.1	0.4	1.2	1.5	5.4	91.4
8 Montezuma Pine *Pinus montezumae* Sierra Madre Occidental, Mexico	MP	9.8	6.5	20.3	1.2	0.4	61.8
9 Mountain Hemlock *Tsuga mertensiana* Willamette National Forest, OR	MH	3.5	3.3	0.3	23.7	1.5	67.7
10 Norway Spruce *Picea abies* Coastal Range, OR	NS	0.9	bd	0.1	2.3	2.1	94.6
11 Pacific Silver Fir *Abies amabilis* Umatilla National Forest, OR	PSF	0.1	0.3	0.8	0.6	5.8	92.4
12 Ponderosa Pine *Pinus ponderosa* Umatilla National Forest, OR	PP	1.5	3.3	2.9	4.2	4.7	83.4
13 Sitka Spruce *Picea sitchensis* Coastal Range, OR	SS	1.1	-	4.7	0.1	0.3	93.8
14 Western Juniper *Juniperus occidentalis* Columbia Basin, OR	WJ	0.1	0.1	0.1	0.5	5.6	93.6
15 White Fir *Abies procera* Umatilla National Forest, OR	WF	-	0.1	0.4	0.1	7.2	92.2

Table II.2. Analytical data of the lipid constituents in conifer epicuticular waxes.

Sample	*n*-Alkanes[1]				*n*-Alkanoic Acids[1]			*n*-Alkanols[1]			
	C_{range}	C_{max}	CPI	ACL[2]	C_{range}	C_{max}	CPI	C_{range}	C_{max}	CPI	ACL[2]
Apache Pine	16-33	23	3.2	26.8	7-34	20	7.4	14-28	24	1.5	25.1
Big-Cone Douglas Fir	22-31	25	7.4	25.8	16-28	24	7.8	16-30	26	4.0	25.3
Brewer Spruce (CR)	21-31	29	4.7	27.3	16-30	24	17.0	14-32	24	3.0	26.9
Brewer Spruce (WNF)	21-31	23	6.7	25.6	22-26	24	14.0	16-30	24	4.0	25.4
California Redwood	19-33	27	2.6	28.1	13-32	32	19.3	14-26	26	9.7	25.0
Douglas Fir (CR)	24-31	29	7.4	28.0	16-26	24	15.0	16-32	26	3.0	26.6
Douglas Fir (UNF)	21-31	25	6.0	26.5	16-26	24	10.4	16-30	26	5.6	26.5
Montezuma Pine	18-33	29	3.2	27.7	8-34	20	5.5	12-28	22	4.0	24.0
Mountain Hemlock	24-33	31	17.0	29.9	16-30	28	2.3	16-30	28	6.5	27.3
Norway Spruce	25-35	33	5.9	33.3	14-24	16	∞	16-30	26	4.0	26.5
Pacific Silver Fir	21-31	25	3.6	26.0	16-28	24	4.8	12-30	24	3.2	25.2
Ponderosa Pine	23-35	33	4.9	29.5	-	-	-	12-32	24	10.6	26.0
Sitka Spruce	18-31	29	2.8	28.0	7-32	22	5.6	18-28	20	2.9	23.0
Western Juniper	21-31	25	5.3	26.1	-	-	-	16-30	26	4.4	26.0
White Fir	21-35	33	6.0	28.4	-	-	-	16-30	22	8.2	24.1

[1]: Determined by GC/MS; C_{max} = Carbon number maximum; CPI = Carbon preference index is the sum of the odd carbon number homologs divided by the sum of the even carbon number homologs for *n*-alkanes(range at C20-C36) and the inverse for *n*-alkanoic acids (range at C15-C37) and *n*-alkanols (range at C12-C34) (Mazurek and Simoneit, 1984).

[2]: ACL = Average chain length is the average number of carbon atoms per molecule based on the abundance of the odd alkanes from C_{23}-C_{35} or the even alkanols from C_{22}-C_{34} (Poynter and Eglinton, 1990):

$$\text{n-Alkane ACL} = \frac{23 \times [C_{23}] + 25 \times [C_{25}] + 27 \times [C_{27}] + 29 \times [C_{29}] + 31 \times [C_{31}] + 33 \times [C_{33}] + 35 \times [C_{35}]}{[C_{23}] + [C_{25}] + [C_{27}] + [C_{29}] + [C_{31}] + [C_{33}] + [C_{35}]}$$

$$\textit{n}\text{-Alkanol ACL} = \frac{22 \times [C_{22}] + 24 \times [C_{24}] + 26 \times [C_{26}] + 28 \times [C_{28}] + 30 \times [C_{30}] + 32 \times [C_{32}] + 34 \times [C_{34}]}{[C_{22}] + [C_{24}] + [C_{26}] + [C_{28}] + [C_{30}] + [C_{32}] + [C_{34}]}$$

The average of the ACLs for *n*-alkanes in Oregon conifer waxes decreases by two carbon numbers with increased distance away from the coastal range. The average *n*-alkane ACL in the Coastal Range was 29.2 (n=4) while the inland region values average 27.2 (n=8). Since the mean daily temperatures of the Coastal Range and inland regions were similar during the sampling period (16.5 °C) and the regional altitudes were the same (<1 km), this observation suggests an adaptation by conifers

to a more humid climate present at the coastal range rather than a temperature dependence. This observation also occurs within species, as for example, the coastal conifers Douglas Fir and Brewer Spruce both have higher *n*-alkane ACLs than their inland relations, i.e., 28.0 to 26.5 and 27.3 to 25.6, respectively. The difference in *n*-alkane ACLs observed within species also supports the finding reported by Percy *et al.* (1993) which showed that environmental conditions, such as microclimate influences (coastal fog exposure), may influence conifer wax composition. It has also been reported that aging of conifer needles induces a shift towards longer chain length in some conifer species (Lutz *et al.*, 1990). However, since conifer needles were selected at random and composited, in order to minimize wax composition differences due to age, this should not be a factor. Further research on the observed humidity adaptation is warranted. It is further suggested that *n*-alkane ACL determinations be used as indicator tools to monitor the effects of global climate change on declining forest populations. No other regional trends are apparent from the *n*-alkane ACL data.

Alcohols

The *n*-alkanol series present in the wax extracts are listed in Appendix II.1 and displayed a C_{range} from C_{12} to C_{32} (Table II.2). The C_{max} ranged from 20 to 28 with 20 predominant in the extract of Sitka Spruce and 28 in Mountain Hemlock (all even carbon number homologs). The CPI values of the *n*-alkanols ranged from 1.5 to 10.6 with an average of 5.0 (all >>1.0 reflecting their biochemical origin). Ponderosa Pine wax had the highest CPI of 10.6 while the lowest CPI of 1.5 was found in Apache Pine wax (Table II.2). There are no apparent trends in the *n*-alkanol ACLs.

Fatty Acids

The *n*-alkanoic acids ranged from C_7 to C_{34} with C_{max} values from 16 to 28 (Appendix II.1 and Table II.2). The most common C_{max} at 24 was identified among six of the twelve species where *n*-alkanoic acids were present. All alkanoic acids had

a strong even carbon numbered predominance, characteristic of their biogenic origin. The CPIs for the *n*-alkanoic acids were high and ranged from 2.3 to 19.3 with an average of 9.9, not including the sample with a CPI of infinity. California Redwood wax displayed the highest CPI while Mountain Hemlock wax had the lowest. Since free *n*-alkanoic acids are relatively minor wax components and intermediary in the production of other wax constituents, concentrations may be influenced significantly by processes occurring in the needles and by degradation of wax esters, which can hydrolyze to alkanoic acids and alkanols (Tulloch, 1976). Thus, information from *n*-alkanoic acid and *n*-alkanol homologs must be viewed cautiously due to the variable processes which produce them.

Free ω-hydroxyalkanoic acids ranging from C_{14} to C_{16} are present in the conifer waxes (Table II.3). The C_{12}, C_{14} and C_{16} ω-hydroxyalkanoic acids are found in the estolide fraction of cuticular waxes of the *Cupressaceae* and *Pinaceae* (Herbin and Robins, 1968; Herbin and Sharma, 1969). Estolides, as neutral polyesters of 4-6 molecules of C_{12}, C_{14}, C_{16} and C_{18} ω-hydroxyalkanoic acids, have also been described for gymnosperms, which contain ω-hydroxyalkanoic acids in the cutin (Caldicott and Eglinton, 1973; Tulloch, 1976) and in epicuticular waxes (Schulten *et al.*, 1986).

Carbonyl Compounds

Homologous carbonyl compounds were identified as *n*-alkan-10-ones in the wax extracts and ranged from C_{17} to C_{31}, with an odd carbon number predominance and C_{max} at 19 and 29 (Table II.3). The *n*-alkan-10-ones in Brewer Spruce (WNF) and Norway Spruce showed the presence of only C_{29}, while Apache Pine, Montezuma Pine and Sitka Spruce had only C_{19}. Western Juniper displayed a C_{range} of C_{29} to C_{31}, while Douglas Fir (UNF) and White Fir had a C_{range} from C_{17} to C_{29}. The *n*-alkanones were not detected in the other conifer waxes.

Unsaturated aldehydes (double bond location not defined) were found as minor components in some samples with a C_{range} from C_{28} to C_{34} (Table II.3). Norway

Spruce has C_{28} and C_{29} (C_{max} at 28), while in Brewer Spruce (WNF) wax contains C_{30} to C_{34} with a C_{max} at 30. Saturated aldehydes (*n*-alkanals) were not detected in any of the wax extracts.

Wax Esters

Wax esters have been previously reported in conifer cuticular waxes (Tulloch, 1987; Sümmchen *et al.*, 1995). These compounds form crystalline zones in the cuticle that act as transport barriers to diminish the loss of water (Riederer and Schneider, 1990). Here in the epicuticular lipid extracts, the wax esters range mainly from C_{24}-C_{50} (total carbon number of compounds) and have exclusively saturated fatty acid and alcohol moieties (Table II.3). The major homolog and predominant C_{max} is C_{38} in five of the samples where wax esters are present. Acid moieties range from C_6 to C_{36} and alcohols from C_6 to C_{32}, with common combinations of acid and alcohol moieties of C_{12} to C_{14}, C_{14} to C_{14} and C_{24}, C_{16} to C_{22} and C_{26}, C_8 to C_{10} and C_{30}, and C_6 to C_{32} predominating. The compositions of the acid and alcohol moieties vary considerably from species to species, thus these compounds may be useful source indicators for plant species in environmental samples.

The averages of the wax ester ACLs of the Coastal Range conifers (38.3, n=3) are lower than that of the inland conifers (38.8, n=5) (Table II.3). This difference is especially apparent within species where the coastal conifers Douglas Fir and Brewer Spruce both exhibit significantly lower wax ester ACLs than their inland relations, 37.4 to 39.6 (difference of 2.2) and 35.6 to 37.8 (difference of 2.2), respectively. This observation suggests the presence of a plant or microbial enzymatic mechanism in the cuticle which is specific for the humidity adaptation. The proposed enzymatic reaction mechanism would include the cleavage of long chain alkyl esters into methyl esters and *n*-alkanes with two less carbon atoms. Methyl esters have been previously identified in epicuticular waxes of conifers (Tulloch, 1987) and the increase in *n*-alkane concentrations supports the increased *n*-alkane ACL observations. This finding is important and should be more thoroughly investigated by plant physiologists.

Table II.3. Analytical data for the ω-hydroxyalkanoic acids, *n*-alkan-10-ones, unsaturated aldehydes and wax esters in conifer epicuticular waxes.

Sample	ω-Hydroxy-alkanoic acids		*n*-Alkan-10-ones		Unsaturated Aldehydes		Wax Esters[1]		CPI	ACL[2]
	C_{range}	C_{max}	C_{range}	C_{max}	C_{range}	C_{max}	C_{range}	C_{max}		
Apache Pine	-	-	19	19	-	-	24-28	26	∞	26.1
Big-Cone Douglas Fir	-	-	-	-	-	-	34-41	40	43	38.5
Brewer Spruce (CR)	14-16	16	-	-	-	-	34-38	36	20	35.6
Brewer Spruce (WNF)	-	-	29	29	30-34	30	30-42	38	108	37.8
California Redwood	-	-	-	-	-	-	26-30	28	∞	27.8
Douglas Fir (CR)	14-16	14	-	-	-	-	36-38	38	16	37.4
Douglas Fir (UNF)	14-16	14	17-29	29	28-30	30	36-42	38	83	39.6
Montezuma Pine	-	-	19	19	-	-	18-30	26	∞	26.6
Mountain Hemlock	-	-	-	-	-	-	-	-	-	-
Norway Spruce	-	-	29	29	28-29	28	29-50	42	2.6	41.9
Pacific Silver Fir	14-16	16	-	-	-	-	-	-	-	-
Ponderosa Pine	14-16	14	-	-	-	-	-	-	-	-
Sitka Spruce	-	-	19	19	-	-	-	-	-	-
Western Juniper	14-16	16	29-31	29	28-32	30	28-46	38	22	39.6
White Fir	14-16	14	17-29	29	28-32	30	34-40	38	8.3	37.2

[1]: Determined by GC-MS as *n*-alkyl-*n*-alkanoate moities; Cmax = Carbon number maximum as defined by Mazurek and Simoneit (1984); CPI = Carbon preference index for wax esters is the sum of the even carbon number homologs divided by the sum of the odd carbon number homologs (Mazurek and Simoneit, 1984).

[2]: ACL = Average chain length is the average number of carbon atoms per molecule based on the abundance of the even wax esters from C_{18}-C_{50}.

$$\text{Wax Ester ACL} = \frac{< 26 \times [C_{26}] \ldots + 28 \times [C_{28}] + 30 \times [C_{30}] + 32 \times [C_{32}] + \ldots 50 \times [C_{50}]}{< [C_{26}] \ldots + [C_{28}] + [C_{30}] + [C_{32}] + \ldots [C_{50}]}$$

Molecular Biomarkers

Phytosterol (C_{28}, C_{29}) and triterpenoid (C_{30}) molecular biomarkers were detected in 10 of the 15 conifer waxes sampled and the results are given in Table II.5. Of the four phytosterols identified, the two most common were brassicasterol (present in 8 samples), followed by campesterol (present in 7). The other phytosterols present

were β-sitosterol and stigmasterol. A trace of cholesterol was found in Ponderosa Pine wax and may represent adsorption of smoke particles from meat grilling (campground) near the sampling site (Rogge *et al.*, 1991).

Table II.4. The composition and yield of phytosterol and triterpenoid molecular markers in conifer epicuticular waxes.

Compound Name	Composition	Sample (Region)* and Yield (% normalized to Cmax of *n*-alkanols) BDF (CR)	BS (WNF)	BS (UNF)	DF	MH	NS	PSF	PP	WJ	WF
Phytosterols											
Brassicasterol	$C_{28}H_{46}$	19.3	2.2	29.9	3.1	-	-	2.4	5.9	9.9	1.1
Campesterol	$C_{28}H_{48}$	-	8.8	25.0	1.5	-	-	3.1	0.8	12.5	2.2
Stigmasterol	$C_{29}H_{48}O$	8.2	9.3	40.5	-	-	-	-	-	-	-
β-Sitosterol	$C_{29}H_{50}O$	-	-	-	-	-	1.0	1.4	-	10.0	0.2
Triterpenoids											
Taraxerone	$C_{30}H_{48}O$	4.9	-	-	-	-	-	-	-	-	-
α-Amyrin	$C_{30}H_{50}O$	-	-	-	-	10.4	0.5	-	-	-	0.2
β-Amyrin	$C_{30}H_{50}O$	-	0.1	-	-	9.1	0.2	-	-	-	0.04
22-Hopanol	$C_{30}H_{52}O$	-	-	-	-	-	1.7	-	-	-	-
Ursonic acid	$C_{30}H_{46}O_3$	-	-	-	-	1.4	-	-	-	-	-
Morolic acid	$C_{30}H_{48}O_3$	-	-	-	-	0.2	-	-	-	-	-

*Sample and locale codes as in Table I (accuracy ±8%)

Diterpenoids are important biomarker constituents of many higher plants, especially of conifer resins (Riffer *et al.*, 1969; Zinkel and Clarke, 1985; Zinkel *et al.*, 1985; Simoneit, 1986; Zinkel and Magee, 1987; Barrero *et al.*, 1991; Mazurek and Simoneit, 1997). Diterpenoids in resins often bleed from conifer branches and needles and are unavoidably extracted with the epicuticular wax. Thus, the diterpenoids were determined for three examples (Apache Pine, Montezuma Pine and Sitka Spruce) and are listed in Table II.5.

Table II.5. Analytical data on the diterpenoids in epicuticular waxes of three conifers.

Compound			Yield (ng/g of needle extracted)		
Name	M.W.	Composition	Apache Pine	Montezuma Pine	Sitka Spruce
19-Norabieta-4(18),8,11,13-tetraene	254	$C_{19}H_{26}$	30	35	-
18-Norabieta-8,11,13-triene	256	$C_{19}H_{28}$	42	47	237
Dehydroabietin	256	$C_{19}H_{28}$	91	53	594
Dehydroabietane	270	$C_{20}H_{30}$	282	409	1328
Isopimaradiene	272	$C_{20}H_{32}$	43	41	572
Abietane	276	$C_{20}H_{36}$	98	-	-
Dehydroabietal	284	$C_{20}H_{28}O$	-	-	2671
Abietal	286	$C_{20}H_{30}O$	-	-	11919
13-Epi-manoyl oxide	290	$C_{20}H_{34}O$	-	256	-
Manool	290	$C_{20}H_{34}O$	-	-	52634
Manoyl oxide	290	$C_{20}H_{34}O$	-	88	-
Abieta-2,8,11,13,15-pentaenoic acid	296	$C_{20}H_{24}O_2$	42	38	194
Abieta-6,8,11,13-tetraenoic acid	298	$C_{20}H_{26}O_2$	395	111	1387
Abieta-8,11,13,15-tetraenoic acid	298	$C_{20}H_{26}O_2$	341	142	2154
Abieta-7,13,15-trienoic acid	300	$C_{20}H_{28}O_2$	1525	224	3293
Callitrisic acid	300	$C_{20}H_{28}O_2$	502	-	3608
Dehydroabietic acid	300	$C_{20}H_{28}O_2$	26833	10659	48199
Abietic acid	302	$C_{20}H_{30}O_2$	995	149	3589
Isopimaric acid	302	$C_{20}H_{30}O_2$	12452	1656	133169
Pimaric acid	302	$C_{20}H_{30}O_2$	20	72	1113
8,15-Pimaradien-18-oic acid	302	$C_{20}H_{30}O_2$	1739	252	-
Sandaracopimaric acid	302	$C_{20}H_{30}O_2$	92	29	1581
10α(H)-9,10-Secodehydroabietic acid	302	$C_{20}H_{30}O_2$	191	243	726
10β(H)-9,10-Secodehydroabietic acid	302	$C_{20}H_{30}O_2$	366	-	1509
7-Oxodehydroabietic acid	314	$C_{20}H_{26}O_3$	-	102	-
15-Hydroxydehydroabietic acid	316	$C_{20}H_{28}O_3$	45	22	449
15-Hydroxyabietic acid	318	$C_{20}H_{30}O_3$	221	70	2405
Total (μg/g)			46	15	433
% of Total Wax			39	23	52

The predominant compounds have abietane and pimarane skeletons which are the major diterpenoids produced by gymnosperms in the northern hemisphere (Thomas, 1970; LaFever *et al.*, 1994). Diterpenoids were present as major components in the three plant waxes analyzed, confirming bleed resin accumulation on needle surfaces.

In Apache and Montezuma Pines the most abundant diterpenoids were dehydroabietic acid followed by isopimaric acid. In Sitka Spruce the most abundant were isopimaric acid followed by manool, while dehydroabietic acid was also present as a major component. Dehydroabietic acid has been regarded both as a partially altered atmospheric oxidation product and pyrolysis product of resin acids, whereas pimaric acid for example is an unaltered natural product (Simoneit, 1986; Mazurek and Simoneit, 1997).

Cyclic terpenoids are produced by higher plants and are useful as chemotaxonomic tracers or molecular markers due to their molecular complexity and structural specificity (Simoneit, 1986; Hemmers and Gülz, 1989a, 1989b). For the triterpenoids, α-amyrin, accompanied by β-amyrin, was encountered most among the conifer waxes (Table II.5). Other triterpenoids in the waxes include taraxerone in Big-Cone Douglas Fir, 22-hopanol in Norway Spruce, and ursonic and morolic acids both in Mountain Hemlock waxes.

CONCLUSIONS

This work reports the lipid and molecular marker components of epicuticular waxes from predominant conifers of western North America. The average chain length (ACL) values determined for both *n*-alkanes and wax ester compositions suggests a humidity adaptation by coastal conifers which is evident by a two carbon number decrease in ACL for these compounds. The mechanism may be of plant or microbial origin and remains to be determined. Because only single samples of each vegetation type were taken at different climate locations, future work should include a more systematic analysis of the reproducibility of epicuticular plant wax signatures. However, the gross wax composition data is of utility for assessing direct particle emission signatures from biomass and secondary emission compositions from biomass fuels during burning. The data are also useful for correlating epicuticular waxes deposited into soils to their conifer source. As all the samples were collected during the late summer/early fall seasons, variations in both the homolog and terpenoid distributions are believed to be minimal, making this information useful for chemotaxonomic and source recognition studies.

ACKNOWLEDGMENTS

This work was funded in part by the U.S. Environmental Protection Agency (Grant R-823990-01).

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CHAPTER III

IDENTIFICATION AND CONCENTRATIONS OF MOLECULAR TRACERS IN ORGANIC AEROSOLS FROM BIOMASS BURNING OF TEMPERATE CLIMATE CONIFERS

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To be submitted to: ***CRC-Critical Reviews in Environmental Science and Technology***

ABSTRACT

Smoke particulate matter from conifers subjected to controlled burning, both under smoldering and flaming conditions, was sampled by high volume air filtration on precleaned quartz fiber filters. The filtered particles were extracted with dichloromethane and the crude extracts were methylated for separation by thin layer chromatography into hydrocarbon, carbonyl, carboxylic acid ester and polar fractions. Then, the total extract and individual fractions were analyzed by gas chromatography and gas chromatography-mass spectrometry. The major organic components directly emitted in smoke particles were straight chain aliphatic compounds from vegetation wax and diterpenoid acids (biomarkers) from resin. The major natural products altered by combustion included derivatives from phenolic (lignin) and monosaccharide (cellulose) biopolymers and oxygenated and aromatic products from diterpenoids. Other biomarkers present as minor components included phytosterols, both the natural and altered products, and unaltered high molecular weight wax esters. Polycyclic aromatic hydrocarbons (PAH) were also present, however, also as minor constituents. Although the concentrations of organic compounds in smoke aerosols are highly variable and dependent on combustion temperature, the biomarkers and their combustion alteration products are source specific. They are adsorbed or trapped on particulate matter and thus may be utilized as molecular tracers in the atmosphere for determining fuel type and source contributions from biomass burning.

Key Words - biomass burning, epicuticular waxes, gymnosperms, hydrocarbons, methoxyphenols, molecular biomarkers, resin acids

INTRODUCTION

The application of biomass burning as a method for clearing vegetated (forest, grassland, etc.) areas and for domestic heating, cooking, etc. significantly increases the input of organic aerosol components to the atmosphere. Biomass burning is an important primary source of soot and organic particulate matter in emissions which influence atmospheric chemical, optical and radiative properties through direct (adsorption and scattering of solar and terrestrial radiation) and indirect (modification of cloud processes) mechanisms (e.g., IPCC, 1990, 1992). Natural (unaltered) and thermally altered (pyrolysis) derivative compounds from vegetation released by biomass burning events can be utilized as specific indicators for identifying fuel source inputs, transport mechanisms and receptor fate in samples of atmospheric fine particulate matter.

The aim of this study is to report the organic chemical composition of smoke particulate matter emitted by flaming and smoldering combustion of conifers (gymnosperms) constituting the predominant species of western North America. In general, each individual plant species emits a "chemical fingerprint" of natural and thermally altered organic constituents upon burning. The incomplete thermal combustion of organic natural product precursors results in emission products which still retain structural characteristics of the precursor (molecular markers). From these products it is possible to determine precursor/product relationships and reaction pathways. These directly emitted and thermally altered molecular markers may be used as specific tracers for tracking emissions specifically from conifer (gymnosperm) burning. For example, it has been shown that the burning of conifer biomass from temperate regions yields characteristic tracers from diterpenoids as well as phenolics and other oxygenated species from lignin, which are recognizable in urban airsheds (Hawthorne *et al.*, 1992; Rogge *et al.*, 1993b, 1998; Simoneit and Mazurek, 1982; Simoneit *et al.*, 1993, 1999; Standley and Simoneit, 1994). Emission rates have only been determined for a limited number of conifer smoke samples (Rogge *et al.*, 1998). Thus, more information is necessary for modeling biomass burn emissions in air basins or air masses. Furthermore, it is important to know the organic compound composition of smoke emitted by burning of dominant biomass species in order to model mass chemical (reactions, kinetics) and physical

(radiative heat transfer) behavior of organic aerosols in the atmosphere and to determine the contribution of regional biomass burning to global climate change.

BACKGROUND

The varying temperature and aeration conditions during burning determine the molecular alteration and transformation of the organic compounds emitted from biomass fuel. The heat intensity and the duration of flaming and smoldering conditions determine the distributions and ratios of the natural versus altered compounds present in conifer smoke. The primary chemical reactions that occur under flaming conditions (temperature >300 °C) include pyrolysis, bond cleavage, fission, and tarry and volatile product formation (Shafizadeh, 1984). Under smoldering conditions (temperature <300 °C, this occurs at the start of the fire, i.e., firefront and after flaming) organic compounds and their altered products are released by a steam stripping/vaporization effect, with the extent of this process dependent on fuel moisture content. The primary chemical reactions that occur under smoldering conditions include depolymerization, water elimination, fragmentation, oxidation, and char formation (Shafizadeh, 1984).

Biomass smoke and other source emissions (e.g., petroleum, coal) introduce airborne fine particulate matter containing organic constituents (e.g., PAH and oxy-PAH) which have mutagenic and genotoxic potential (e.g., Arcos and Argus, 1975; IARC, 1989). Considering that conifer wood is a primary solid fuel source for heating of homes and cooking (e.g., fireplaces, woodstoves), besides wildfires, it is also necessary to identify the components of smoke emissions in order to make air quality assessments and to determine human exposure levels to particle bound organic compounds.

EXPERIMENTAL METHODS

Sampling

Samples were collected from temperate zone forested areas of California and Oregon, USA and Durango, Mexico away from urban areas and major roads (Table III.1). The branches (1-2 cm diameter), needles (dry and green), with bleed resin and cones of conifers were collected from various levels in the canopy of each tree (n=1 for each species sampled). All vegetation samples were placed in paper bags and allowed to dry over a two week period. Weight measurements were taken before and after burning to determine the total mass of plant material consumed. Using a controlled fire, vegetation samples were burned completely to the embers under both flaming and smoldering conditions. The emitted smoke was collected on an organically clean quartz fiber filter (annealed at 550 °C for 3 hrs; 95% particle size retention >1.0 μm) using a high volume air sampler located approximately 1.5 m diagonally above and to the side of the flames in the smoke plume. Emissions from burning biomass are primarily fine (<2 μm) particles (e.g., Rogge *et al.*, 1998; Schauer *et al.*, 1996), thus no provisions were made to remove coarse particles during sampling of these burn tests. Smoke was typically sampled for 5 minute periods at a suction flow rate of 40 ft^3/min (1.13 m^3/min). After sampling, a portion of each filter (8.8 cm^2) was cut out and set aside for volatile organic carbon and elemental carbon analysis (Birch and Cary, 1996; Johnson, *et al.*, 1981). The collection filters were then placed in precleaned 300 ml jars with Teflon lined lids to which 10 ml of chloroform was added. The jars were then stored at 4 °C until further chemical extraction was conducted.

Extraction and Fractionation

Each filter was extracted using ultrasonic agitation for three twenty-minute periods using 200 ml of dichloromethane (CH_2Cl_2). The solvent extract was filtered using a Gelman Swinney filtration unit containing an annealed glass fiber filter for the

removal of insoluble particles (Simoneit and Mazurek, 1982). The filtrate was first concentrated by use of a rotary evaporator and then a stream of filtered nitrogen gas.

Table III.1. Conifer species sampled for biomass burning in this study.

Common Name	Scientific Name	Region Collected
Apache Pine	*Pinus engelmannii*	Sierra Madre Occidental, Mexico
California Redwood	*Sequoia sempervirens*	Redwood Park, Arcata, CA
Douglas Fir	*Pseudotsuga menziesii*	McDonald Forest Arboretum, Willamette Valley, Corvallis, OR
Eastern White Pine	*Pinus strobus*	McDonald Forest Arboretum, Willamette Valley, Corvallis, OR
Lodgepole Pine	*Pinus contorta*	North Tumalo Creek, OR
Montezuma Pine	*Pinus montezumae*	Sierra Madre Occidental, Mexico
Mountain Hemlock	*Tsuga mertensiana*	McDonald Forest Arboretum, Willamette National Forest, OR
Noble Fir	*Abies procera*	Willamette Valley, Philomath, OR
Pacific Silver Fir	*Abies amabilis*	McDonald Forest Arboretum, Willamette Valley, Corvallis, OR
Ponderosa Pine	*Pinus ponderosa*	McDonald Forest Arboretum, Willamette Valley, Corvallis, OR
Port Orford Cedar	*Chamaecypris lawsonia*	McDonald Forest Arboretum, Willamette Valley, Corvallis, OR
Sitka Spruce	*Picea sitchensis*	McDonald Forest Arboretum, Willamette Valley, Corvallis, OR
Western White Pine	*Pinus monticola*	North Tumalo Creek, OR

The final volume was adjusted to exactly 4.0 ml by addition of CH_2Cl_2. Aliquots were then taken for derivatization. Alkanoic acid and phenolic moieties in the extracts were methylated using diazomethane in diethyl ether prepared from the precursor N-methyl-N'-nitro-N-nitrosoguanidine (Pierce Chemical Co.) (Schlenk and Gellerman, 1960).

The methylated extracts were separated by preparative thin layer chromatography (TLC) on silica gel plates (Analtech, Inc.) with a mobile phase eluent mixture of hexane:diethyl ether (9:1) (Simoneit and Mazurek, 1982). This procedure allows for determination of chemical information on single molecular groups or functional group series, which may not be detected due to coelution in the total extract mixture. The four fractions removed from the TLC plates contained the following classes of

compounds: (1) *n*-alkanes, *n*-alkenes, and saturated and unsaturated cyclic di- and triterpenoid hydrocarbons; (2) *n*-alkanones, *n*-alkanals and polycyclic aromatic hydrocarbons; (3) *n*-alkanoic acids (as methyl esters) and saturated and unsaturated di- and triterpenoid ketones and acids; and (4) *n*-alkanols, terpenols and polar organics. The fourth fraction and the total extract were converted prior to analysis to trimethylsilyl derivatives by reaction with N,O-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) plus 1% trimethylchlorosilane for approximately 3 hr at 70 °C.

Instrumental Analyses

The total extract and the fractions were analyzed by capillary gas chromatography (GC, Hewlett-Packard Model 5890A) with a 30 m x 0.25 mm i.d. fused silica capillary column coated with DB-5 (J&W Scientific, film thickness 0.25 μm) which was temperature programmed as follows: hold at 65 °C for 2 min, ramp to 300 °C at 6 °C/min, hold isothermal at 300 °C for 20 min. All samples were analyzed by capillary gas chromatography-mass spectrometry (GC-MS) using a Hewlett-Packard Model 5973 MSD quadrupole mass spectrometer operated in the electron impact mode at 70 eV and coupled to a Hewlett-Packard Model 6890 gas chromatograph. The GC was equipped with a 30 m x 0.25 mm i.d. fused silica capillary column coated with DB-5 (J&W Scientific, film thickness 0.25 μm) and operated using the same temperature program as described above, with helium as carrier gas.

Compound Identification and Quantitation

Compound identifications are based on comparisons with authentic standards, GC retention time, literature mass spectra and interpretation of mass spectrometric fragmentation patterns. Quantitation of the homologous compound series was conducted by comparison of the GC peak area with that of a co-injected known standard (*e.g.*, perdeuterated tetracosane, *n*-$C_{24}D_{50}$).

RESULTS AND DISCUSSION

The major organic components identified in the soluble lipid fraction of the conifer smoke samples and their concentrations (μg/kg of conifer fuel burned) are given in Appendix III.1. The distributions of the molecular classes include the following: homologous series of aliphatic compounds (*n*-alkanes, *n*-alkenes, *n*-alkanoic acids and wax esters); polycyclic aromatic hydrocarbons (PAH); monosaccharides from cellulose; phenolics from lignin; and steroid and terpenoid (mainly diterpenoid) biomarkers. The distributions and abundances of the conifer smoke constituents are strongly dependent on combustion conditions (e.g., smoldering versus flaming, duration). Thus, the values reported here should not be used as absolute but as relative chemical fingerprints for these sources. The biomarkers are source specific and may be used as confirming tracers for transport and fate studies of conifer smoke emissions in the environment.

Homologous Compound Series

Examples of the typical GC-MS TIC (total ion current) traces for the total extract and TLC fractions of four representative conifer smoke samples (Douglas Fir, Mountain Hemlock, Ponderosa Pine, and Sitka Spruce) are given in Figures III.1-III.4. The GC-MS TIC traces for the total extract and TLC fractions of the remaining conifer smoke samples are given in Appendices III.2-III.10. The TIC traces of the total extracts of the smoke samples show the distributions and relative abundances of the major organic constituents, while the TIC traces of the TLC fractions F1 through F4 show the distributions and abundances of the aliphatics, aromatics and molecular biomarkers separated according to functional group and polarity properties. The TLC separation procedure was conducted on all smoke samples in order to best identify a source specific chemical fingerprint that is representative of conifer smoke emissions. Thus, the discussion will focus on the identity and distributions (carbon number range and maxima, C_{max}, and carbon preference indices, CPI; Mazurek and Simoneit, 1984) of the major aliphatic homologs and biomarkers.

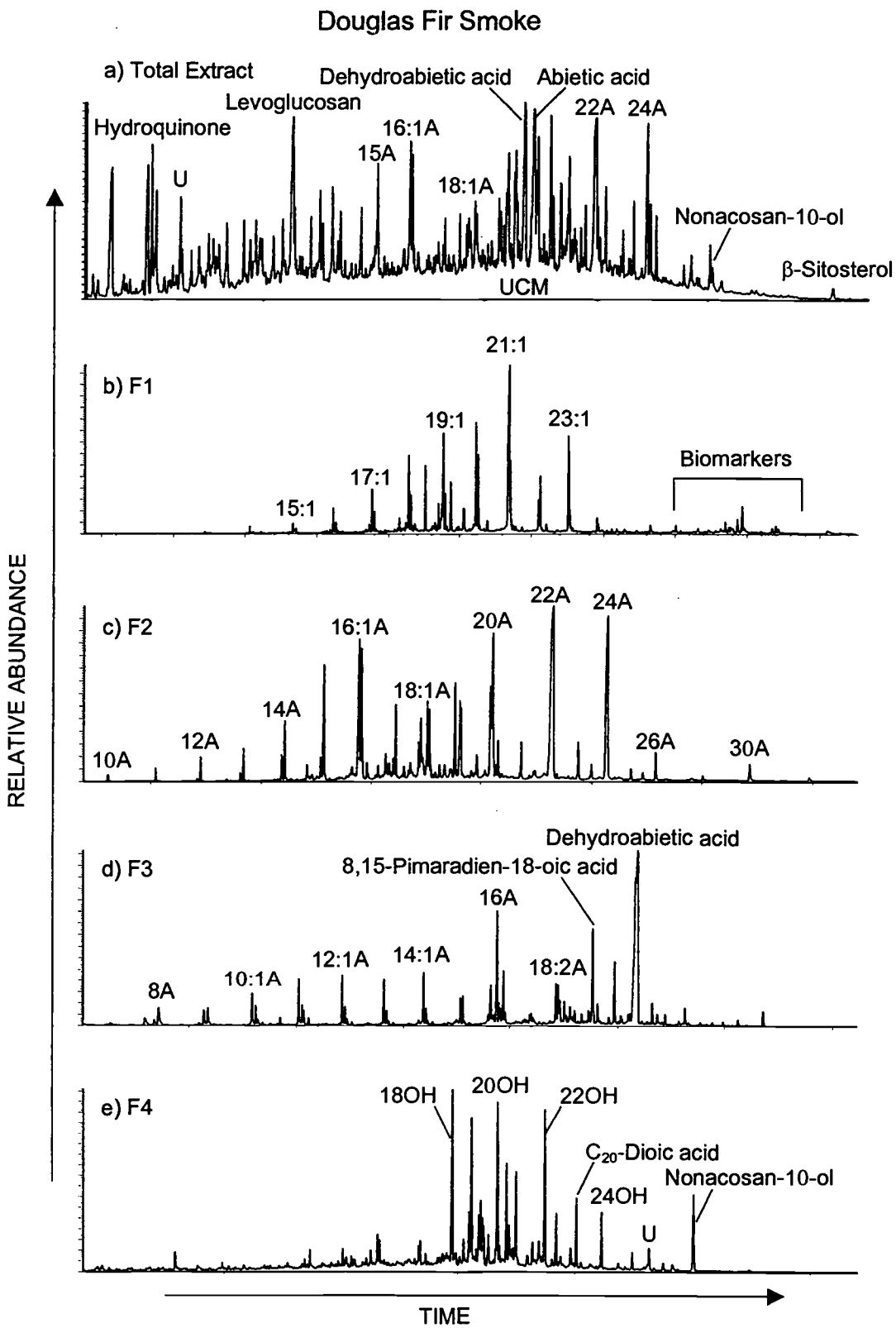

Figure III.1. GC-MS total ion current traces of Douglas Fir smoke particulate matter (numbers refer to carbon chain length of *n*-alkanes, A = *n*-alkanoic acids, OH = *n*-alkanol, U = unknown, UCM = unresolved complex mixture).

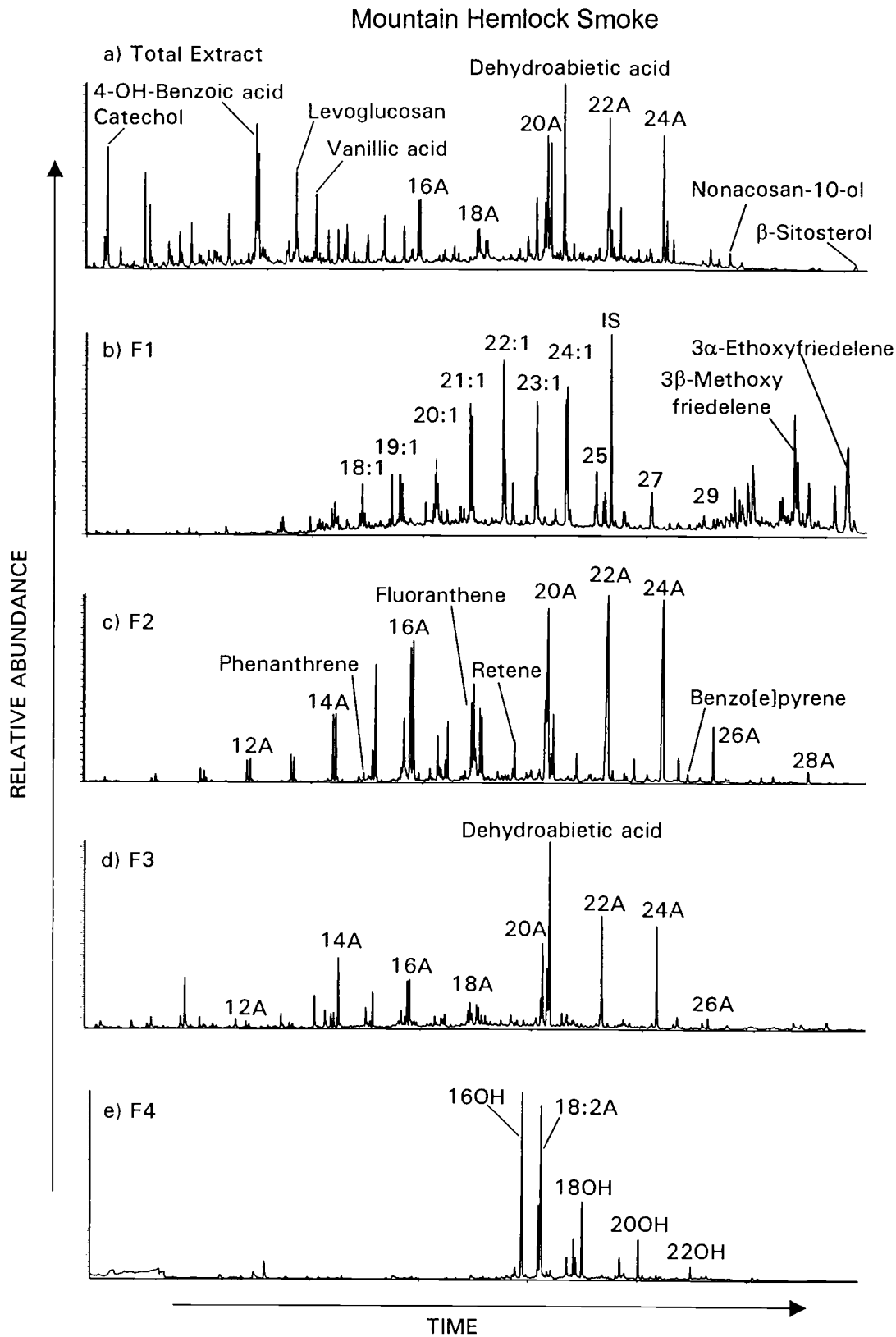

Figure III.2. GC-MS total ion current traces of Mountain Hemlock smoke particulate matter (abbreviations as in Fig. III.1 and IS = internal standard).

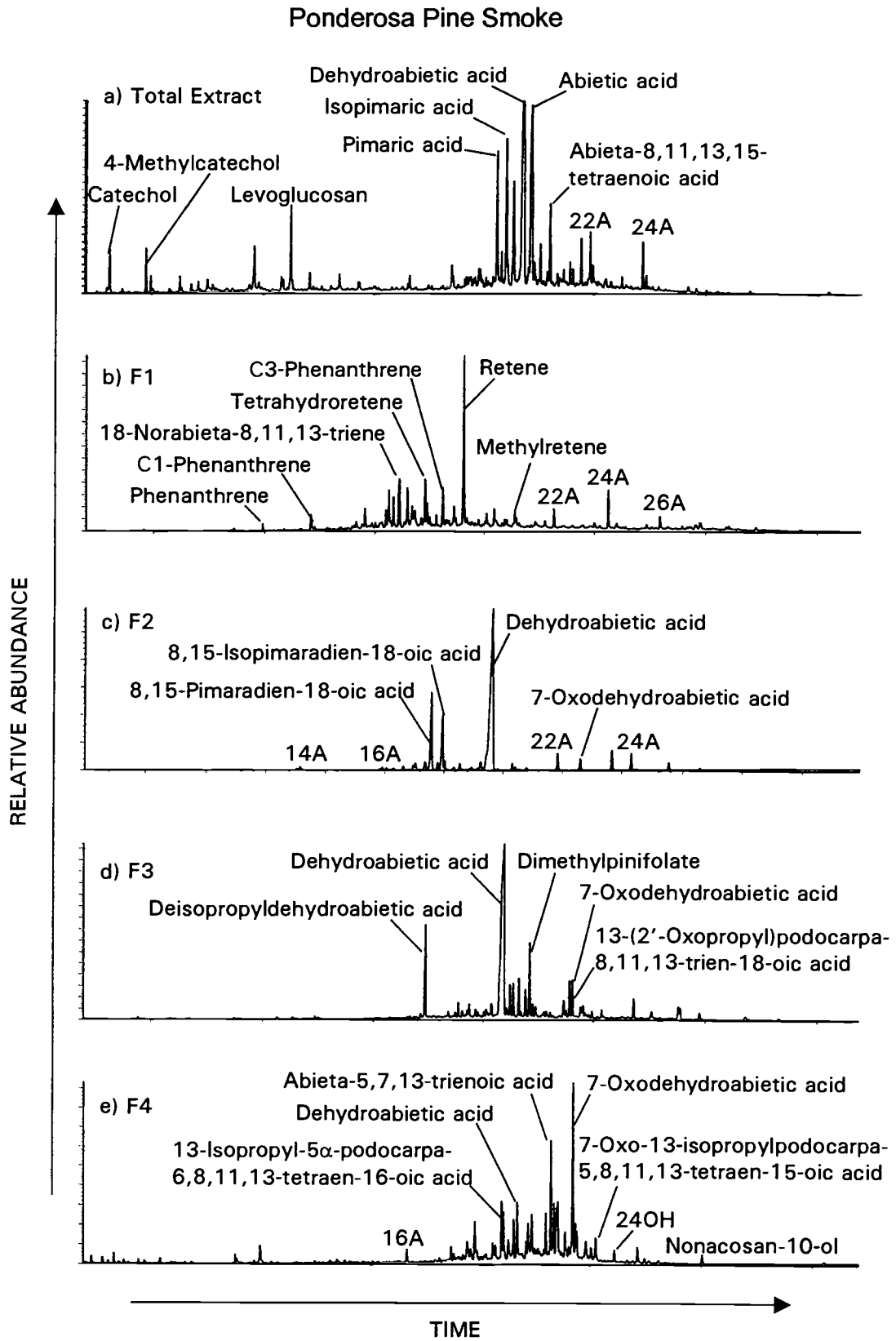

Figure III.3. GC-MS total ion current traces of Ponderosa Pine smoke particulate matter (abbreviations as in Fig. III.1).

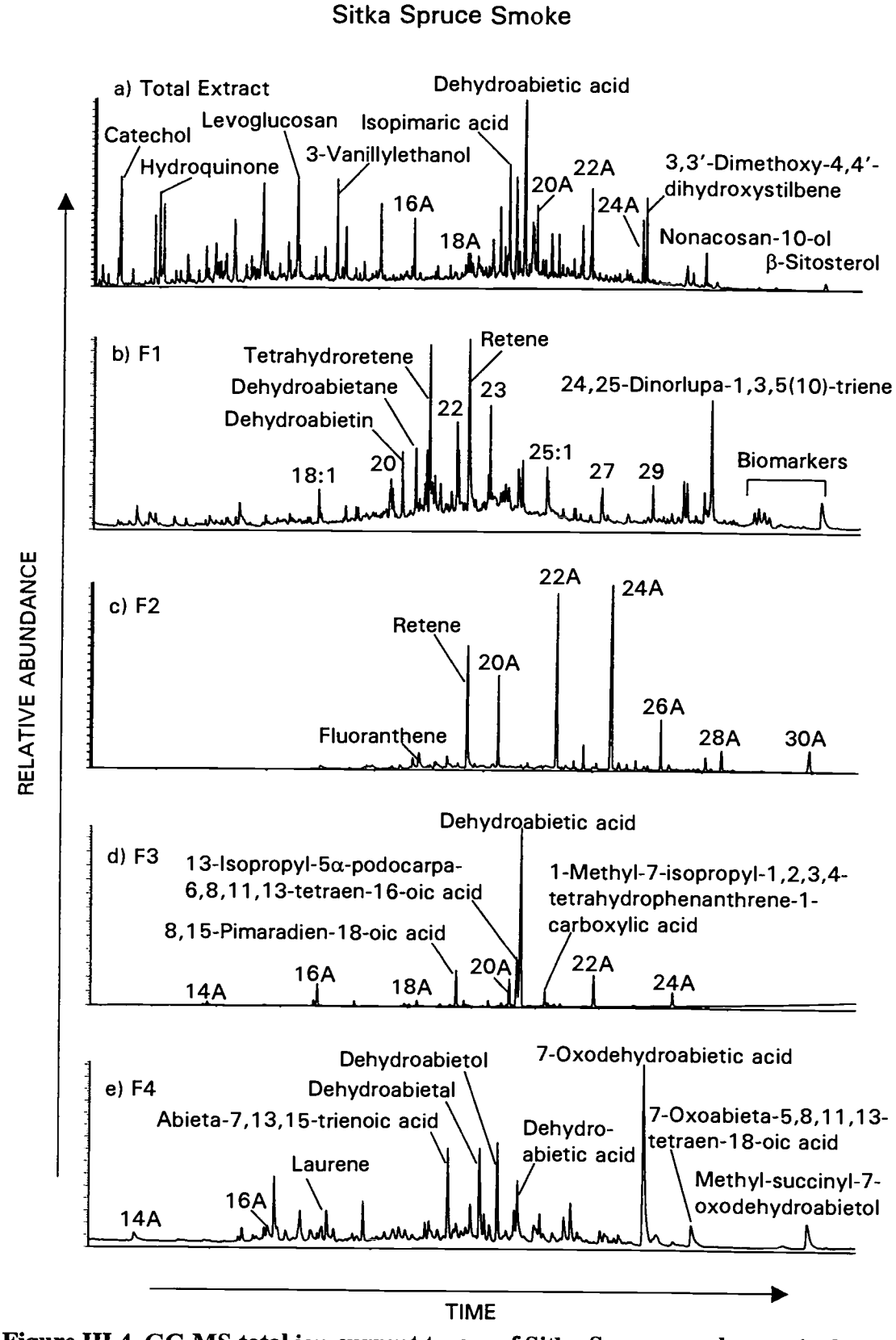

Figure III.4. GC-MS total ion current traces of Sitka Spruce smoke particulate matter (abbreviations as in Fig. III.1).

n-Alkanes

The distribution of *n*-alkanes in conifer smoke (Appendix III.1) ranges in carbon chain length from C_{14} to C_{34} and shows odd to even carbon number predominance (CPI range from 0.5 to 3.4, average = 1.5). This distribution suggests an *n*-alkane contribution from epicuticular waxes (Oros *et al.*, 1999). Vascular plants synthesize epicuticular waxes containing odd carbon number *n*-alkanes usually in the C_{25} to C_{33} range with C_{29} or C_{31} as dominant homologs which often contribute up to 90% of all paraffins found in plant waxes (Kolattukudy, 1970). The C_{max} for the *n*-alkanes are diverse and vary from 20 to 33. The *n*-alkane distributions confirm an input from epicuticular wax sources ($C_{max} \geq C_{27}$ present in 31% of all samples).

n-Alkenes

The *n*-alkenes are primarily terminal olefins (i.e., alk-1-enes). They range from C_{13} to C_{28}, with an odd to even carbon number predominance (CPI range from 0.3 to 7.3, average 1.2), and C_{max} varying from 21 to 24 and 22 predominant in 69% of all samples (Appendix III.1). Alkenes are not major components in plant waxes and their origin has been inferred to be from biomass fuel (Abas *et al.*, 1995). The *n*-alkenes are formed primarily by the thermal dehydration of *n*-alkanols (which show even carbon number predominance: Mazurek and Simoneit, 1984) and to a minor degree from the *n*-alkanes by oxidation during incomplete combustion (Abas *et al.*, 1995). The distributions of *n*-alkenes showing even carbon number predominances and C_{max} at 24, coupled with the low abundances of *n*-alkanols with C_{max} at 22 or 24 (Appendix III.1), further supports an origin from *n*-alkanols for these molecules.

n-Alkanoic Acids

The *n*-alkanoic acids range from C_7 to C_{34}, show a strong even to odd carbon number predominance (CPI range from 2.5 to 15.6, average 6.9), and C_{max} at 16, 20 or 22 (Appendix III.1). These compounds, which are basic units of plant fats, oils

and phospholipids, are identified here as a major molecular class for all conifer smoke samples. There are also minor contributions from unsaturated fatty acids, both oleic ($C_{18:1}$) and linoleic ($C_{18:2}$).

α, ω-Alkanedioic Acids

Series of α,ω-alkanedioic acids are present and range from C_9 to C_{29} (Appendix III.1). The most common α,ω-alkanedioic acid in conifer smoke is C_{20} (present in 38% of all samples). The photo-oxidation product (Stephanou and Stratigakis, 1993) of $C_{18:1}$ and $C_{18:2}$ alkenoic acids, α,ω-nonanedioic acid, is present in only a single sample. The α,ω-alkanedioic acids have been identified from a variety of sources and in the environment (Abas *et al.*, 1995; Gogou *et al.*, 1996; Hildemann *et al.*, 1994; Rogge *et al.*, 1993a; Simoneit, 1989). High molecular weight α,ω-alkanedioc acids (C_{10}-C_{24}) have been identified in rural aerosol particles and their source may be oxidation products of ω-hydroxy alkanoic acids from vegetation polyester biopolymer (Simoneit and Mazurek, 1982). The identification here of all acids confirms a source contribution from the burning of biomass.

n-Alkanones

The straight chain ketones as *n*-alkan-2-ones range from C_{16} to C_{33} and show an odd to even carbon number predominance (CPI range from 0.4 to 4.2, average 2.3). The C_{max} ranged from 21 to 27. The *n*-alkan-2-ones are mainly derived from the partial combustion of aliphatic precursors (Simoneit, 1978).

n-Alkanols

Homologous series of *n*-alkanols with even to odd carbon number predominances are present in conifer smoke (CPI = 4.1 and 5.7). The *n*-alkanols ranged from C_{18} to C_{30} with C_{max} at 22 and 24. The *n*-alkanols from C_{20} to C_{30} are predominantly of an epicuticular wax origin.

In contrast to the primary alcohols, the free secondary alcohol *n*-nonacosan-10-ol is present as a major component in most of the conifer smoke samples. This compound has been previously identified as a major component in epicuticular waxes from gymnosperm species (Tulloch, 1976, 1987; Schulten *et al.*, 1986).

Molecular Biomarkers

Molecular biomarkers (i.e., biomarkers) are organic compounds of biological origin that show little or no change in chemical structure from their parent organic molecule (i.e., natural product) found in living organisms. Such molecules are characterized by their restricted occurrence, source specificity, molecular stability and suitable concentration for analytical detection (Mazurek and Simoneit, 1984). The major biomarkers identified in the conifer smoke samples include diterpenoids, monosaccharide derivatives from cellulose, methoxyphenols from lignin, sterols and wax esters, including their thermal alteration products. It has been shown that these high molecular weight compounds are directly volatilized into smoke by an injection mechanism similar to steam volatilization/stripping. Subsequent condensation onto or entrapment into preexisting particulate matter when the smoke plume is diluted and cooled provides the means for their incorporation into the atmospheric aerosol phase (Simoneit *et al.*, 1993).

Diterpenoids

The major biomarkers present in conifer smoke are the diterpenoids and their thermal alteration products (Appendix III.1). Diterpenoids are important biomarker constituents of many higher plants, especially of conifers, in their resins (Barrero *et*

al., 1991; Erdtman *et al.*, 1968; Lorbeer and Zelman, 1988; Mazurek and Simoneit, 1997; Riffer *et al.*, 1969; Simoneit, 1986, 1998; Simoneit *et al.*, 1993, 1999; Zinkel and Clarke, 1985; Zinkel and Magee, 1987; Zinkel *et al.*, 1985). Many softwood species are prolific resin producers and have well established systems of horizontal and vertical ducts filled with resin in the wood (Parham and Gray, 1984).

The predominant biomarkers identified in conifer smoke have the abietane and pimarane skeletons which are the major diterpenoids produced by gymnosperms in the northern hemisphere (Thomas, 1970). The most common diterpenoid natural products present in the smoke samples are *iso*-pimaric acid with lesser amounts of pimaric acid, sandaracopimaric acid and abietic acid (Appendix III.1). The major thermal alteration (oxidation) products are 8,15-pimaradien-18-oic acid, dehydroabietic acid, 1-methyl-7-isopropyl-1,2,3,4-tetrahydrophenanthrene-1-carboxylic acid followed by lesser amounts of retene and 7-oxodehydroabietic acid. Dehydroabietic acid is the major organic component in smoke from Apache Pine but occurs in all samples analyzed (Appendix III.1). Dehydroabietic acid has been regarded both as a partially altered atmospheric oxidation product and a pyrolysis product of resin acids (Simoneit, 1986; Mazurek and Simoneit, 1997). Both dehydroabietic acid and retene have been proposed as candidate molecular tracer compounds for coniferous wood combustion (Ramdahl, 1983; Simoneit *et al.*, 1993; Standley and Simoneit, 1994).

The product-precursor relationship for the diterpenoids in conifer smoke may follow an alteration pathway which commences with the dehydrogenation of abietic acid to dehydroabietic acid with subsequent decarboxylation to dehydroabietin and full aromatization to retene (Simoneit, 1998) (Fig. III.5). Dehydroabietane, which is also present, may dehydrogenate to simonellite and then proceed to retene (Standley and Simoneit, 1994). The other resin acids initially rearrange to the abietane skeleton before dehydrogenation to dehydroabietic acid. They also eliminate ethylene and dehydrogenate to bisnordehydroabietic acid.

The ratios of the total natural and altered compounds that contain the abietane skeleton to the total natural and altered compounds that contain the pimarane skeleton (A/P, abietane skeletons/pimarane skeletons) range from 0.9 to 8.3 (average = 3.3) (Appendix III.1). The A/P ratios are distinct for each conifer smoke sample as is shown in Figure III.6. Thus, they may be useful indicators of source specific burn emissions.

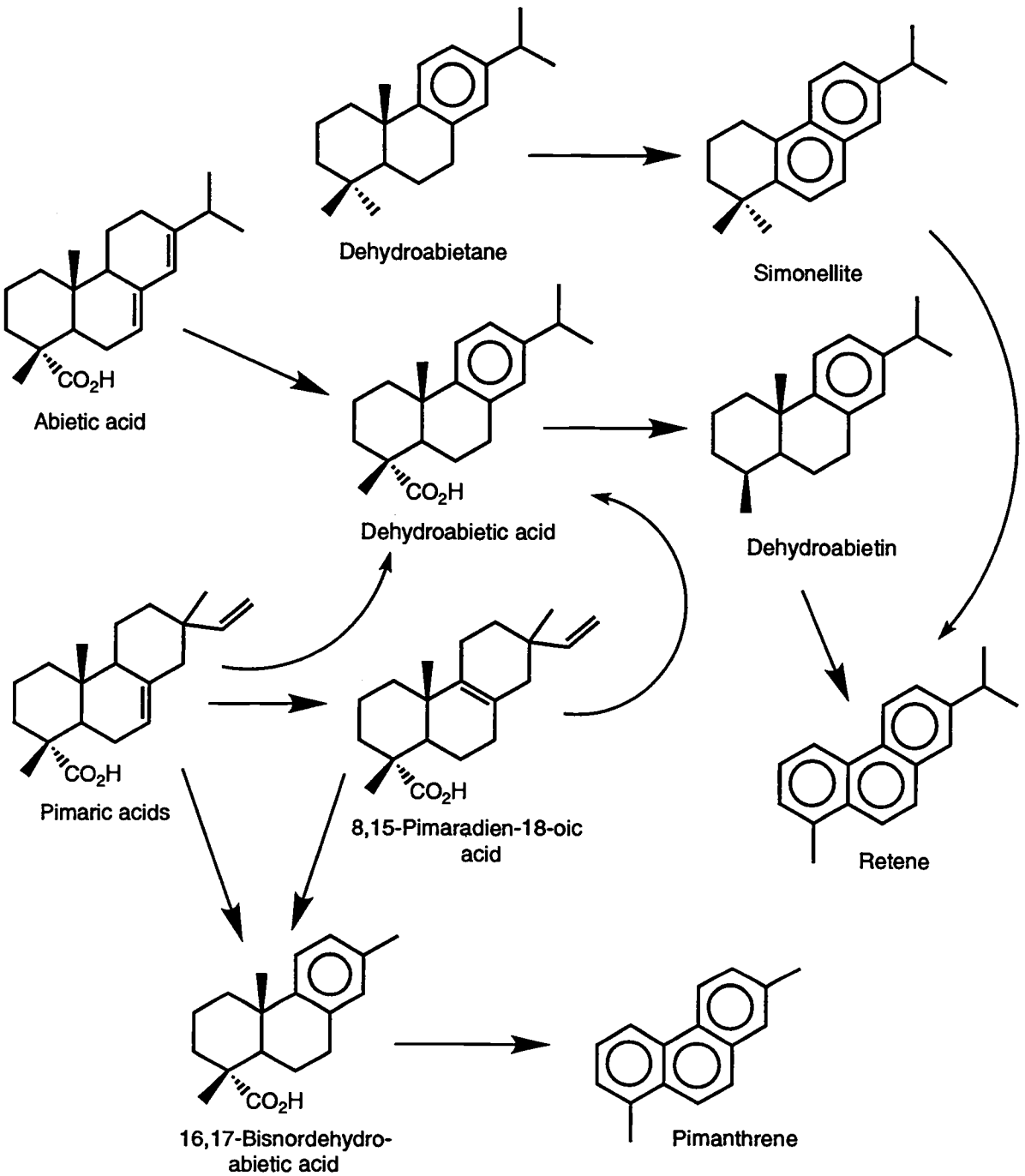

Figure III.5. Diterpenoid thermal alteration pathways.

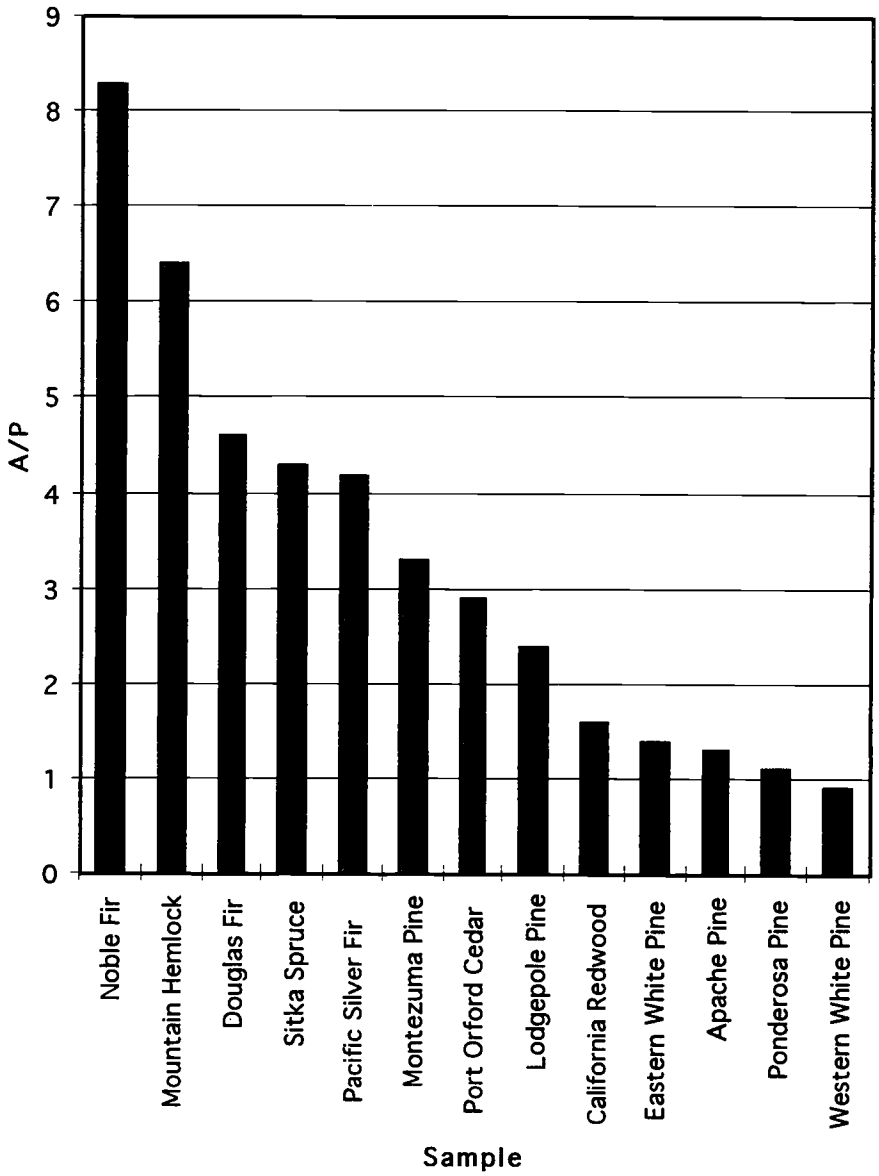

Figure III.6. Abietane to pimarane (A/P) ratios for conifer smoke samples.

Monosaccharide Derivatives

Cellulose and hemicellulose biopolymers which are mainly responsible for structural strength compose approximately 40-50% and 20-30% dry weight of wood, respectively (Petterson, 1984; Sergejewa, 1959). A cellulose molecule is a long-chain, linear polymer made up of 7,000 to 12,000 D-glucose monomers, while a hemicellulose molecule is a 100-200 sugar monomers polysaccharide mixture of glucose, mannose, galactose, xylose, arabinose, 4-O-methylglucuronic acid and galacturonic acid (Parham and Gray, 1984; Sergejewa, 1959). It is the burning of wood at temperatures > 300 °C which gives rise to the source specific molecular tracers, i.e., mainly 1,6-anhydro-β-D-glucopyranose, also called levoglucosan (Appendix III.1). Levoglucosan has been previously reported in biomass burning and atmospheric particles (Hornig *et al.*, 1985; Locker, 1988; Simoneit *et al.*, 1999). Levoglucosan is the predominant organic component in smoke from Montezuma Pine and is detectable in the smoke samples from all conifers. Levoglucosan is emitted at such high concentrations that it is detectable in aerosol particulate matter at considerable distances from the combustion sources (Simoneit *et al.*, 1999).

Methoxyphenols

Lignin biopolymer comprises approximately 20-30% of the dry weight of wood (Petterson, 1984; Sergejewa, 1959). The lignin biopolymers are derived from p-coumaryl, coniferyl and sinapyl alcohols and contain mainly anisyl, vanillyl and syringyl nuclei (Simoneit *et al.*, 1993). Gymnosperm lignin is enriched in the coniferyl alcohol precursor and on burning produces primarily vanillyl moieties. Burning (pyrolysis) of wood injects these lignin nuclei into smoke as breakdown products such as acid, aldehyde, ketone and alkyl derivatives of the methoxyphenols (Edye and Richards, 1991; Hawthorne *et al.*, 1988, 1992; Simoneit *et al.*, 1993; Mazurek and Simoneit, 1997).

The phenolics in conifer smoke are composed mainly of lignin pyrolysis products, lignans and dimers of substituted phenols. The predominant phenolic biomarkers in conifer smoke include catechol, pyrogallol, vanillin, homovanillic acid, vanillic acid, homovanillyl alcohol and acetovanillone (Appendix III.1). The phenol substitution

(i.e., 3-methoxy-4-hydroxy) pattern is consistent with an origin from gymnosperm (softwood) (Simoneit *et al.*, 1993). The phenolic compound guaiacylacetone is also present. Guaiacyl derivatives are potential biomarker tracers for both hard and softwoods (Hawthorne *et al.*, 1988). A major lignan of conifer smoke is tetrahydro-3,4-divanillylfuran (Appendix III.1). Lignans have been described previously as tracers for distinguishing between coniferous and deciduous wood smoke emissions (Simoneit *et al.*, 1993). Secondary products as dimers of substituted phenols are present and include divanillyl and 1,2-divanillylethane. Both are derived from coniferyl alcohol type precursors and have been previously identified in wood smoke (Hawthorne *et al.*, 1988; Simoneit, *et al.*, 1993). The lignin phenols, lignans and secondary dimers have mainly coniferyl alcohol type phenolic structures, thus they may be utilized as biomarker tracers for conifer combustion emissions.

Steroids

The sterols, generally comprised of the C_{28} and C_{29} phytosterol compounds, are constituents of plant lipid membranes and waxes. The sterol biomarkers are present in all conifer smoke samples (Appendix III.1). The natural product β-sitosterol is the most common sterol in conifer smoke immediately followed by campesterol and less so by stigmasterol, also the natural products. Several C_{29} thermal alteration products from the sterol precursor stigmasterol are present and include stigmasta-3,5-diene, stigmast-5-ene and stigmast-4-ene. Various aromatization products are also found, mainly as 24-ethyl-4-methyl-19-norcholesta-1,3,5(10)-triene and its structural isomers. The thermal alteration products of sterol precursors are summarized in Figure III.7 and can be used as general indicators for burning of higher plant lipids (Simoneit, 1989; Simoneit *et al.*, 1993). Pregnenes, the unsaturated C_{21} thermal cracking products from sterols by loss of the side chain, are present in Lodgepole and Ponderosa Pine smoke samples and include the isomers with double bonds at the C-5 and C-7 positions (Fig. III.7). Overall, the phytosterols and their alteration products are present only as minor constituents in conifer smoke.

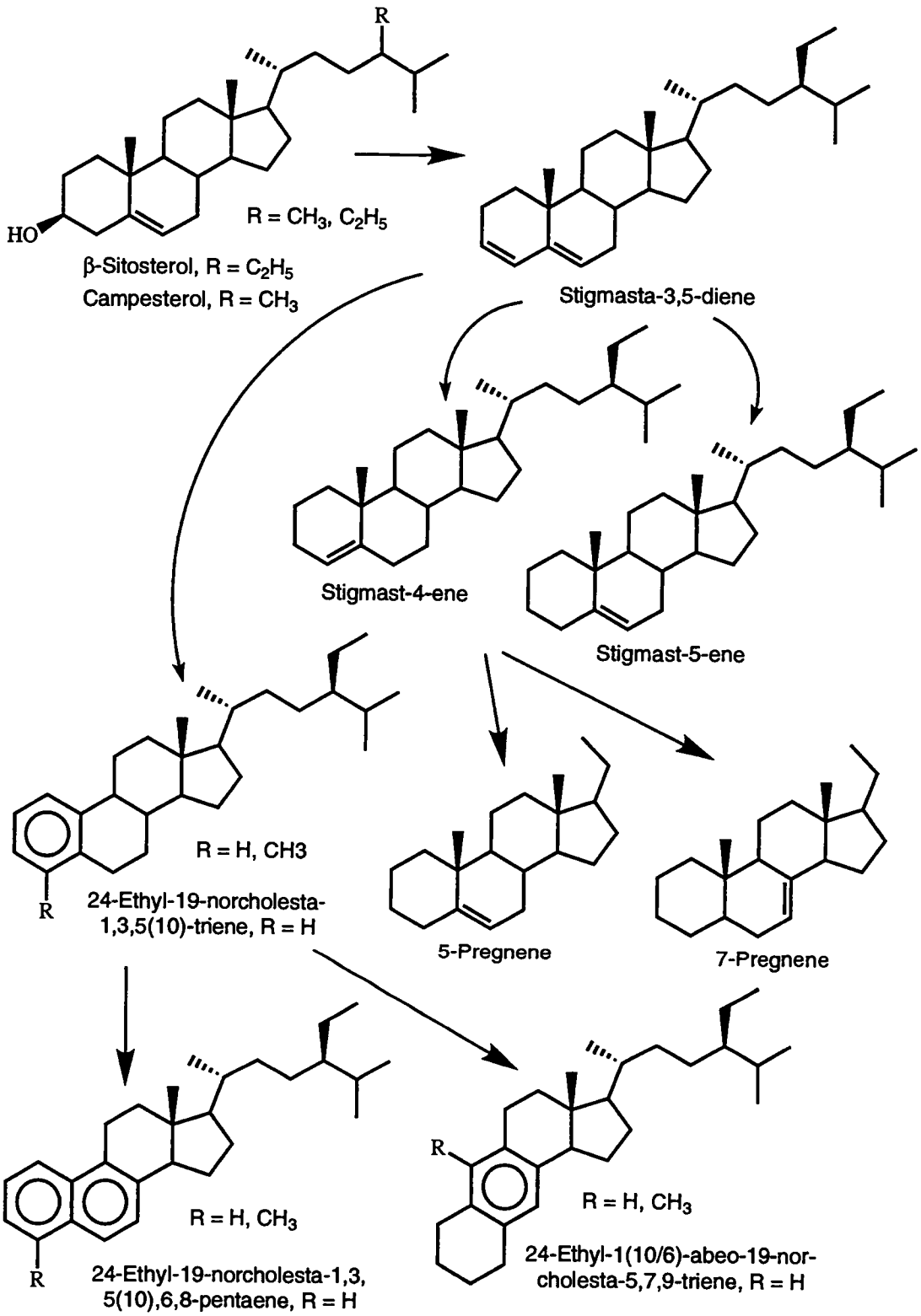

Figure III.7. Phytosterol thermal alteration pathways.

Wax Esters

Wax esters have been previously reported in conifer cuticular waxes (Oros *et al.*, 1998; Sümmchen *et al.*, 1995; Tulloch, 1987). These compounds form crystalline zones in the cuticles of needles and leaves which act as transport barriers to diminish the loss of water (Riederer and Schneider, 1990). Here, in the smoke extracts, the wax esters range mainly from C_{21} to C_{33} (total carbon number of compounds) and have exclusively saturated fatty acid and alcohol moieties (Appendix III.1). The major homolog and dominant C_{max} is 26 in seven of the samples where wax esters are present. Alkanoic acid moieties range from C_{12} to C_{16} and *n*-alkanols from C_9 to C_{21}, with common combinations of acid to alcohol moieties of C_{12} to C_{13}, C_{14} to C_{13} and C_{14} to C_{14} predominating. The combinations of the acid and alcohol moieties vary considerably from species to species, thus these compounds may be useful source indicators for conifer species in smoke samples. The presence of very high molecular weight wax esters ($>C_{40}$) would require confirmation by high temperature GC or high temperature GC-MS (Elias *et al.*, 1997, 1998).

Polycyclic Aromatic Hydrocarbons

All biomass fires are pyrolysis processes causing the formation of polycyclic aromatic hydrocarbons (PAH) from (a) the high temperature thermal alteration of natural product precursors in the source organic matter and (b) the recombination of molecular fragments in the smoke (Simoneit, 1998). The identifications and abundances of over thirty PAH compounds present in the conifer smoke samples are given in Appendix III.1. The major PAH are phenanthrene, anthracenes, C_1-phenanthrenes/anthracenes (since anthracene is a minor PAH, the alkylanthracenes are expected to be negligible, based on compound elucidation for other combustion samples, Simoneit, 1998), fluoranthene and pyrene followed by lesser amounts of C_2- and C_3- phenanthrenes, C_1-pyrenes, 11(H)-benzo[a]fluorene and chrysene. Certain PAH that exhibit mutagenic and genotoxic potential such as benz[a]anthracene, benzo[a]pyrene and cyclopenta[c,d]pyrene (Arcos and Argus, 1975; IARC, 1989), are also present, however only as minor constituents. The PAH identified here are also emitted by internal combustion engines, coal burning, and

other anthropogenic sources (Rogge *et al.*, 1993a; Oros and Simoneit, 1999; Simoneit, 1998). They are thus not exclusive markers for biomass combustion.

The ratio of methylphenanthrenes to phenanthrene (MP:P) has been previously used as an indicator of anthropogenic influences in the environment: 0.5 for atmospheric fallout (Takada *et al.*, 1991), 0.5-1.0 for combustion sources (Prahl and Carpenter, 1983), 1.0 for street and urban dusts (Takada *et al.*, 1990, 1991), 2.0-6.0 for fossil fuel (Prahl and Carpenter, 1983), and 4.0 for crankcase oil (Pruel and Quinn, 1988). The range of the MP:P ratio determined for the conifer smoke samples is 0.5 to 2.6 (average = 1.6), which is proposed here as a potential indicator for conifer burning emissions.

Unresolved Complex Mixture

An unresolved complex mixture (UCM) of structurally complex isomers and homologs of branched and cyclic hydrocarbon compounds (Eglinton *et al.*, 1975) eluting between C_{14} and C_{34} alkanes is present as a major organic component of all conifer smoke total extracts. The UCM, which has been thoroughly examined in petroleum sources, is comprised of compounds which are relatively inert to microbial degradation (Gough and Rowland, 1990; Killops and Al-Juboori, 1990). The ratio of UCM to resolved components (U:R) has been used as a parameter for the indication of petroleum contribution to aerosol particle samples (Mazurek and Simoneit, 1984). The U:R ratios for conifer smoke samples were quantified from the total extract in order to determine if this parameter is useful for distinguishing between conifer and fossil fuel (petroleum and coal) derived combustion source emissions (Appendix III.1). The conifer smoke U:R ratios range from 0.6 to 1.4 (average = 1.0). The close similarity in U:R ratios suggests that this parameter is conservative for these smoke emissions. Several U:R ratios have been determined from more mature fossil fuel derived combustion emission sources which include the following: lignite coal = 3.2 and bituminous coal = 3.3 (Oros and Simoneit, 1998); catalyst-equipped automobile engine exhaust = 5.5 and heavy-duty diesel truck engine exhaust = 9.3 (Rogge *et al.*, 1993). Thus, the lower U:R ratio of conifer smoke shows that this parameter is useful for distinguishing between conifer biomass burning and fossil fuel derived combustion source emissions. Ultimately,

the U:R ratio may be used as an indicator for identifying atmospheric transport trajectories from regional biomass burning and fossil fuel combustion emission containing air parcels. This is especially useful for determining the contributions of organic matter derived from rural versus urban emission sources.

The U:R ratios for aerosol samples collected over the western United States for rural (0.2-4.0), mixed (1.4-3.4), and urban (0.9-25.0) areas have been reported (Mazurek and Simoneit, 1984). Generally, urban aerosols were shown to contain the largest component of petroleum-derived compounds, while rural and mixed rural/urban environments showed variable contributions of anthropogenic pollutants. The average U:R ratio for conifer smoke (1.0) suggests that the UCM of rural aerosol particles from the western United States consists mainly of recent (immature) organic matter derived from conifer and perhaps other biomass combustion source emissions, such as grass smoke released from agricultural field burning, and less pronounced fossil fuel combustion emissions.

Volatile and Elemental Carbon

The concentrations of volatilizable organic carbon (VOC, equivalent to solvent extractable OC) and elemental carbon (EC, i.e., black soot) in the different conifer smoke samples are given in Appendix III.1. The volatilizable to elemental carbon ratios (VOC/EC) show a range from 3 to 78 (average = 35). The VOC/EC ratios for the conifer smoke samples are elevated in comparison to ambient air samples collected from rural sites (Crater Lake, OR = 12.4, Carus, OR = 6.5, and Sauvie, OR = 4.1) and urban areas (Los Angeles = 1.6, New York = 1.4, Santiago, Chile = 1.7, China = 1.5) (Didyk *et al.*, 1999). The low VOC/EC ratios for mainly urban and suburban areas indicate a strong influence from petroleum derived combustion emissions. The conifer smoke VOC/EC ratios are much less than that measured from an ambient air sample collected at a remote area (South Atlantic Ocean = 160, Didyk *et al.*, 1999) where influence from both petroleum combustion and biomass burning emissions is negligible. This distribution indicates that the VOC/EC ratio measured for conifer smoke may be useful in distinguishing this source from petroleum derived combustion emissions such as those found in rural and urban areas and from natural emissions (background) found in remote areas.

Major Compound Groups

The average emission rates (mg/kg) and percent abundances of the major compound groups identified in conifer smoke are given in Table III.2. Of the total resolved components the major compound groups are the diterpenoids (32%) from bleed resins, carboxylic acids (29%) from internal lipids and methoxyphenols (12.2%) derived from lignin. Other compound groups such as steroid biomarkers

Table III.2. Major compound groups identified in conifer smoke.

Major Compound Group	Total Concentration (mg/kg)	Percent* Abundance
Diterpenoids	3093±225	32.3
Carboxylic Acids	2753±167	28.6
Methoxyphenols	1172±76	12.2
Monosaccharide Derivatives	463±31	4.8
Polycyclic Aromatic Hydrocarbons	408±23	4.2
Alkenes	302±53	3.1
Alkanes	199±21	2.1
Alkanols	123±9	1.3
Steroids	90±5	0.9
Alkanones	83±10	0.9
Wax Esters	48±5	0.5
Unknowns	877±98	9.1

*Percent abundance relative to total resolved organic components.

and aliphatic homologous series are present at low abundances (<5%). Although wood is composed mostly of cellulose (40-50% of dry weight of wood, d.w.w.), with lesser amounts of hemicelluloses (20-30% of d.w.w.), and lignin (20-30% of d.w.w.) (Petterson, 1984; Sergejewa, 1959), the percent abundance of the monosaccharide derivatives (4.8%) from cellulose alteration is less than the methoxyphenols. This observation is likely due to burning of the selected plant parts (needles, cones and branches of 1-2 cm thickness) which were relatively immature in plant structural development.

Major and Unique Biomarker Tracers

The major biomarker compounds identified for conifers to be applied as potential tracers in smoke and in the atmosphere are given in Table III.3. These are the diterpenoid natural products (*iso*-pimaric acid, pimaric acid, abietic acid and sandaracopimaric acid) and their dominant combustion alteration products (8,15-pimaradien-18-oic acid, dehydroabietic acid, 1-methyl-7-isopropyl-1,2,3,4-tetrahydrophenanthrene-1-carboxylic acid, retene and 7-oxodehydroabietic acid). The major biomarker derived from combustion of cellulose biopolymer is levoglucosan, which has been previously proposed as a tracer for cellulose burning (Simoneit *et al.*, 1999). Galactosan and mannosan are also detectable as secondary cellulose derivatives. The major tracers from lignin combustion are methoxyphenolic compounds, including vanillin, vanillic acid, homovanillic acid, homovanillyl alcohol and acetovanillone, typical of the predominant coniferyl alcohol content of the precursor biopolymer. Compound series such as *n*-alkanes, *n*-alkenes, *n*-alkanoic acids, *n*-alkanones, *n*-alkanols, PAH, phytosterols, anhydrosaccharides (e.g., levoglucosan), and UCM are not source specific, because they are generally found in all biomass combustion emissions (Abas *et al.*, 1995; Simoneit, 1984, 1989; Simoneit *et al.*, 1999). However, some of these compound series are indicative of species specific biomass burning, when coupled with the directly emitted and thermally altered biomarker compounds.

Some conifer smoke samples contain unique biomarkers which may be useful as species specific tracers. For example, Mountain Hemlock smoke contains 3α-methoxyfriedelene, 3β-methoxyfriedelene, 3α-ethoxyfriedelene and 3β-ethoxyfriedelene. These triterpenoid natural products are not present in the other conifer smoke samples tested, thus they are unique tracers in smoke from this species. Port Orford Cedar smoke shows the sesquiterpenoid natural products 5-hydroxycalamanene, α-calacorene, aromadendrol, β-oplopenone and 6-deoxygeigerin along with the diterpenoids hibaene, totarol and 6,7-dehydroferruginol as unique tracers. Montezuma Pine smoke contains the diterpenoid natural products laurene, rimuene and pinifolic acid as unique markers. Laurene and rimuene are also present at lower concentrations in Sitka Spruce smoke. California Redwood smoke

Table III.3. Major and unique biomarker tracers identified in conifer smoke.

Major Biomarker Tracer	Total Concentration (mg/kg)	Percent* Abundance
Diterpenoids		
8,15-Pimaradien-18-oic acid	400±47	4.2
Dehydroabietic acid	363±36	3.8
iso-Pimaric acid	248±35	2.6
1-Methyl-7-isopropyl-1,2,3,4-tetrahydrophenanthrene-1-carboxylic acid	151±22	1.6
Retene	137±12	1.4
7-Oxodehydroabietic acid	61±7	0.6
Pimaric acid	57±7	0.6
Sandaracopimaric acid	22±2	0.2
Methoxyphenols		
Catechol	177±12	1.8
Homovanillyl alcohol	101±10	1.0
Pyrogallol	74±7	0.8
Vanillin	57±4	0.6
Vanillic acid	48±3	0.5
Homovanillic acid	44±3	0.5
Tetrahydro-3,4-divanillylfuran	42±2	0.4
Acetovanillone	25±2	0.3
Monosaccharide Derivatives		
Levoglucosan	289±18	3.0
Galactosan	89±7	0.9
Mannosan	84±6	0.9
Steroids		
β-Sitosterol	14±1	0.1
Campesterol	1±0.01	0.01

*Percent abundance relative to total resolved organic components.

has daniellic acid, polyaltic acid and 6,7-dehydroferruginol as unique diterpenoid tracers. Apache Pine smoke shows agatholic acid with lesser amounts of pinifolic acid as unique diterpenoid natural product tracers. 15-Hydroxy-dehydroabietic acid is found in Ponderosa Pine and Western White Pine smoke. Copalic acid is a unique but minor diterpenoid tracer in Western White Pine smoke. The examples of specific biomarkers may be useful as indicative tracers of species specific biomass burning.

The relative abundances (%) of key biomarkers from conifer smoke may be used to distinguish fuel type. Table III.4 shows six key biomarkers derived mostly from internal plant components (levoglucosan, dehydroabietic acid and catechol) and epicuticular wax lipids (heptacosane, palmitic acid and docosanol). The distributions of these compounds relative to one another are different and represent the unique chemical and physical characteristics between conifer species. The relative abundances of key biomarkers and homologous series compounds reported here can collectively be used as specific tracers for assessing and tracking emissions from burning of conifer fuels.

Table III.4. Abundances (% relative to maximum) of key biomarkers for identifying fuel type.

Sample	Heptacosane	Palmitic Acid	Docosanol	Levo-glucosan	Dehydroabietic Acid	Catechol
Apache Pine	0.3	74	2	36	100	33
California Redwood	1	100	0.3	81	10	37
Douglas Fir	4	25	20	100	62	59
Eastern White Pine	0.3	75	18	100	15	36
Lodgepole Pine	0.2	38	8	63	100	27
Montezuma Pine	1	59	7	100	4	39
Mountain Hemlock	3	13	6	59	100	88
Noble Fir	10	7	4	100	53	27
Pacific Silver Fir	4	81	11	100	49	79
Ponderosa Pine	0.1	3	3	7	100	3
Port Orford Cedar	2	100	2	92	2	36
Sitka Spruce	1	31	1	10	100	12
Western White Pine	1	100	9	4	5	19

CONCLUSIONS

This work reports the lipid and molecular biomarker components in smoke from burning of conifers from western North America. The data is of utility for assessing direct organic composition signatures for particle emissions from conifer fuels during biomass burning. The abundance order for the major molecular classes in conifer smoke samples was identified as the following: UCM > diterpenoids > carboxylic

acids > methoxyphenols > anhydrosaccharides > PAH > alkenes > alkanes > alkanols > steroids > alkanones > wax esters. Variations in this molecular group order exist among the conifer species burned, however, these are only minor and usually occur between close ranking molecular groups.

Although the concentrations of organic compounds in smoke aerosols are highly variable and dependent on combustion temperature, aeration, and moisture content of the source fuel, the biomarkers and their combustion alteration products are source specific. The major biomarkers identified in the smoke samples are useful as tracers for distinguishing the conifer burning component in atmospheric aerosol source attributions. The relative abundances of key biomarkers in conifer smoke may also be used to distinguish fuel type.

The range of the MP:P ratio determined for the conifer smoke samples is 0.5-2.6 (average = 1.6), which may be useful for distinguishing conifer burning emissions from fossil fuel and other combustion emissions, and from street and urban dusts. The MP:P range is proposed here as a potential indicator for identifying conifer burning emissions in atmospheric and other environmental samples. Additionally, the average U:R ratio for conifer burning emissions (1.0) may also be of utility for distinguishing this source from fossil fuel-derived combustion emissions (e.g., coal combustion, gasoline and diesel engine exhaust). The ratio also suggests that conifer and other biomass burning emissions are significant contributors of particle bound immature organic matter (UCM) present in the atmosphere of rural areas of the western United States. The VOC/EC ratios measured for conifer smoke samples range from 3 to 78 (average = 35). The distribution indicates that the VOC/EC ratios may be useful to distinguish this source from petroleum derived combustion emissions, such as those found in rural and urban areas, and from natural emissions found in remote areas.

ACKNOWLEDGMENTS

This work was funded in part by the U.S. Environmental Protection Agency (Grant CR 823990-01-0).

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CHAPTER IV

IDENTIFICATION AND CONCENTRATIONS OF MOLECULAR TRACERS IN ORGANIC AEROSOLS FROM BIOMASS BURNING OF DECIDUOUS TREES

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To be submitted to: ***CRC-Critical Reviews in Environmental Science and Technology***

ABSTRACT

Smoke particulate matter from deciduous trees (angiosperms) subjected to controlled burning, both under smoldering and flaming conditions, was sampled by high volume air filtration on precleaned quartz fiber filters. The filtered particles were extracted with dichloromethane and the crude extracts were methylated for separation by thin layer chromatography into hydrocarbon, carbonyl, carboxylic acid ester and polar fractions. Then, the total extract and individual fractions were analyzed by gas chromatography and gas chromatography-mass spectrometry. The major organic components directly emitted in smoke particles were straight chain aliphatic compounds from vegetation wax and triterpenoid acids (biomarkers) from gums and mucilages. The major natural products altered by combustion included derivatives from phenolic (lignin) and monosaccharide (cellulose) biopolymers and oxygenated and aromatic products from triterpenoids. Steroid biomarkers and polycyclic aromatic hydrocarbons (PAH) were also present, however, as minor constituents. Although the concentrations of organic compounds in smoke aerosols are highly variable and dependent on combustion temperature, the biomarkers and their combustion alteration products are source specific. They are adsorbed or trapped on particulate matter and thus may be utilized as molecular tracers in the atmosphere for determining fuel type and source contributions from biomass burning.

Key Words - biomass burning, angiosperms, hydrocarbons, methoxyphenols, molecular biomarkers

INTRODUCTION

The application of biomass burning as a method for clearing vegetated (forest, grassland, etc.) areas and for domestic heating, cooking, etc. significantly increases the input of organic aerosol components to the atmosphere. Biomass burning is an important primary source of soot and organic particulate matter in emissions which influence atmospheric chemical, optical and radiative properties through direct (adsorption and scattering of solar and terrestrial radiation) and indirect (modification of cloud processes) mechanisms (e.g., IPCC, 1990, 1992). Natural (unaltered) and thermally altered (pyrolysis) derivative compounds from vegetation released by biomass burning events can be utilized as specific indicators for identifying fuel source inputs, transport mechanisms and receptor fate in samples of atmospheric fine particulate matter.

The aim of this study is to report the organic chemical composition of smoke particulate matter emitted by flaming and smoldering combustion of deciduous trees (angiosperms). In general, each individual plant species emits a "chemical fingerprint" of natural and thermally altered organic constituents upon burning. The incomplete thermal combustion of organic natural product precursors results in emission products which still retain structural characteristics of the precursor (molecular markers). From these products it is possible to determine precursor/product relationships and reaction pathways. These directly emitted and thermally altered molecular markers may be used as specific tracers for tracking emissions specifically from angiosperm burning. For example, it has been shown that the burning of biomass from temperate regions yields characteristic tracers from terpenoids as well as phenolics and other oxygenated species from lignin, which are recognizable in urban airsheds (Hawthorne *et al.*, 1992; Rogge *et al.*, 1993b, 1998; Simoneit and Mazurek, 1982; Simoneit *et al.*, 1993, 1998a; Standley and Simoneit, 1994). Emission rates have only been determined for a limited number of biomass smoke samples (i.e., conifers; Oros and Simoneit, 1999a; Rogge *et al.*, 1998). Thus, more information on deciduous trees is necessary for modeling biomass burn emissions in air basins or air masses. Furthermore, it is important to know the organic compound composition of smoke emitted by burning of dominant biomass

species in order to model mass chemical (reaction, kinetics) and physical (radiative heat transfer) behavior of organic aerosols in the atmosphere and to determine the contribution of regional biomass burning to global climate change.

BACKGROUND

The varying temperature and aeration conditions during burning determine the molecular alteration and transformation of the organic compounds emitted from biomass fuel. The heat intensity and the duration of flaming and smoldering conditions determine the distributions and ratios of the natural versus altered compounds present in biomass smoke. The primary chemical reactions that occur under flaming conditions (temperature >300 °C) include pyrolysis, bond cleavage, fission, and tarry and volatile product formation (Shafizadeh, 1984). Under smoldering conditions (temperature <300 °C, this occurs at the start of the fire, i.e., firefront and after flaming) organic compounds and their altered products are released by a steam stripping/vaporization effect, with the extent of this process dependent on fuel moisture content. The primary chemical reactions that occur under smoldering conditions include depolymerization, water elimination, fragmentation, oxidation, and char formation (Shafizadeh, 1984).

Biomass smoke and other source emissions (e.g., petroleum, coal) introduce airborne fine particulate matter containing organic constituents (e.g., PAH and oxy-PAH) which have mutagenic and genotoxic potential (e.g., Arcos and Argus, 1975; IARC, 1989). Considering that deciduous tree wood is a primary solid fuel source for heating of homes and cooking (e.g., fireplaces, woodstoves), besides wildfires, it is also necessary to identify the components of smoke emissions in order to make air quality assessments and to determine human exposure levels to particle bound organic compounds.

EXPERIMENTAL METHODS

Sampling

Samples were collected from tropical, temperate and polar region forested zones, away from urban areas and major roads (Table IV.1). The branches (1-2 cm diameter), leaves (dry and green), with gums and mucilages were collected from various levels in the canopy of each tree (n=1 for each species sampled, except Dwarf Birch where n=2). All vegetation samples were placed in paper bags and allowed to dry over a two week period. Weight measurements were taken before and after burning in order to determine the total mass of plant material consumed. Using a controlled fire, vegetation samples were burned completely to the embers under both flaming and smoldering conditions. The emitted smoke was collected on an organically clean quartz fiber filter (annealed at 550 °C for 3 hrs; 95% particle size retention >1.0 μm) using a high volume air sampler located approximately 1.5 m diagonally above and to the side of the flames in the smoke plume. Emissions from burning biomass are primarily fine (< 2.0 μm) particles (e.g., Rogge *et al.*, 1998; Schauer *et al.*, 1996), thus no provisions were made to remove coarse particles during sampling of these burn tests. Smoke was typically sampled for 5 minute periods at a suction flow rate of 40 ft^3/min (1.13 m^3/min). After sampling, a portion of each filter (8.8 cm^2) was cut out and set aside for volatile organic carbon and

Table IV.1. Deciduous tree species sampled for biomass burning in this study.

Common Name	Scientific Name	Region Collected
Eucalyptus	*Eucalyptus dalrympleana*	Arcata, CA
Oregon Maple	*Acer macrophyllum*	Gold Beach, OR
Red Alder	*Alnus rubra*	Mary's Peak, Philomath, OR
Silver Birch	*Betula pendula*	Oregon State University, Corvallis, OR
Dwarf Birch*	*Betula glandulosa*	Shingle Point, Yukon Territory

*Composite of two Dwarf Birch samples.

elemental carbon analysis (Birch and Cary, 1996; Johnson, *et al.*, 1981). The collection filters were then placed in precleaned 300 ml jars with Teflon lined lids to which 10 ml of chloroform was added. The jars were then stored at 4 °C until further chemical extraction was conducted.

Extraction and Fractionation

Each filter was extracted using ultrasonic agitation for three twenty-minute periods using 200 ml of dichloromethane (CH_2Cl_2). The solvent extract was filtered using a Gelman Swinney filtration unit containing an annealed glass fiber filter for the removal of insoluble particles (Simoneit and Mazurek, 1982). The filtrate was first concentrated by use of a rotary evaporator and then a stream of filtered nitrogen gas. The final volume was adjusted to exactly 4.0 ml by addition of CH_2Cl_2. Aliquots were then taken for derivatization. Alkanoic acid and phenolic moieties in the extracts were methylated using diazomethane in diethyl ether prepared from the precursor N-methyl-N'-nitro-N-nitrosoguanidine (Pierce Chemical Co.) (Schlenk and Gellerman, 1960).

The methylated extracts were separated by preparative thin layer chromatography (TLC) on silica gel plates (Analtech, Inc.) with a mobile phase eluent mixture of hexane:diethyl ether (9:1) (Simoneit and Mazurek, 1982). This procedure allows for determination of chemical information on single molecular groups or functional group series, which may not be detected due to coelution in the total extract mixture. The four fractions removed from the TLC plates contained the following classes of compounds: (1) *n*-alkanes, *n*-alkenes and saturated and unsaturated cyclic di and triterpenoid hydrocarbons; (2) *n*-alkanones, *n*-alkanals and polycyclic aromatic hydrocarbons; (3) *n*-alkanoic acids (as methyl esters) and saturated and unsaturated di and triterpenoid ketones and acids; and (4) *n*-alkanols, terpenols and polar organics. The fourth fraction and the total extract were converted prior to analysis to trimethylsilyl derivatives by reaction with N,O-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) plus 1% trimethylchlorosilane for approximately 3 hr at 70 °C.

Instrumental Analyses

The total extract and the fractions were analyzed by capillary gas chromatography (GC, Hewlett-Packard Model 5890A) with a 30 m x 0.25 mm i.d. fused silica capillary column coated with DB-5 (J&W Scientific, film thickness 0.25 μm) which was temperature programmed as follows: hold at 65 °C for 2 min, ramp to 300 °C at 6 °C/min, hold isothermal at 300 °C for 20 min. All samples were analyzed by capillary gas chromatography-mass spectrometry (GC-MS) using a Hewlett-Packard Model 5973 MSD quadrupole mass spectrometer operated in the electron impact mode at 70 eV and coupled to a Hewlett-Packard Model 6890 gas chromatograph. The GC was equipped with a 30 m x 0.25 mm i.d. fused silica capillary column coated with DB-5 (J&W Scientific, film thickness 0.25 μm) and operated using the same temperature program as described above, with helium as carrier gas.

Compound Identification and Quantitation

Compound identifications are based on comparisons with authentic standards, GC retention time, literature mass spectra and interpretation of mass spectrometric fragmentation patterns. Quantitation of the homologous compound series was conducted by comparison of the GC peak area with that of a co-injected known standard (*e.g.*, perdeuterated tetracosane, n-$C_{24}D_{50}$).

RESULTS AND DISCUSSION

The major organic components identified in the soluble lipid fraction of the deciduous tree smoke samples and their concentrations (μg/kg of deciduous tree fuel burned) are given in Appendix IV.1. The distributions of the molecular classes include the following: homologous series of aliphatic compounds (n-alkanes, n-alkenes, and n-alkanoic acids); polycyclic aromatic hydrocarbons (PAH); monosaccharides from cellulose; phenolics from lignin; and steroid and terpenoid (mainly triterpenoid) biomarkers. The distributions and abundances of the

angiosperm smoke constituents are strongly dependent on combustion conditions (e.g., smoldering versus flaming, duration). Thus, the values reported here should not be used as absolute but as relative chemical fingerprints for these sources. The biomarkers are source specific and may be used as confirming tracers for transport and fate studies of deciduous tree smoke emissions in the environment.

Homologous Compound Series

Examples of the typical GC-MS TIC (total ion current) traces for the total extract and TLC fractions of deciduous tree smoke samples (Eucalyptus, Oregon Maple, Red Alder, Silver Birch and Dwarf Birch, Table 1) are given in Figures IV.1-IV.5. The TIC traces of the total extracts of the smoke samples show the distributions and relative abundances of the major organic constituents, while the TIC traces of the TLC fractions F1 through F4 show the distributions and abundances of the aliphatics, aromatics and molecular biomarkers separated according to functional group and polarity properties. The TLC separation procedure was conducted on all smoke samples in order to best identify a source specific chemical fingerprint that is representative of deciduous tree smoke emissions. Thus, the discussion will focus on the identity and distributions (carbon number range and maxima, C_{max}, and carbon preference indices, CPI; Mazurek and Simoneit, 1984) of the major aliphatic homologs and biomarkers.

n-Alkanes

The distribution of *n*-alkanes in deciduous tree smoke (Appendix IV.1) ranges in carbon chain length from C_{14} to C_{35} and shows odd to even carbon number predominance (CPI range from 2.6 to 6.8, average = 5.3). The C_{max} for the *n*-alkanes range from 25 to 29 and confirms a significant input from epicuticular wax sources. Vascular plants synthesize epicuticular waxes containing odd carbon number *n*-alkanes usually in the C_{25} to C_{33} range with C_{29} or C_{31} as dominant homologs which often contribute up to 90% of all paraffins found in plant waxes (Kolattukudy, 1970).

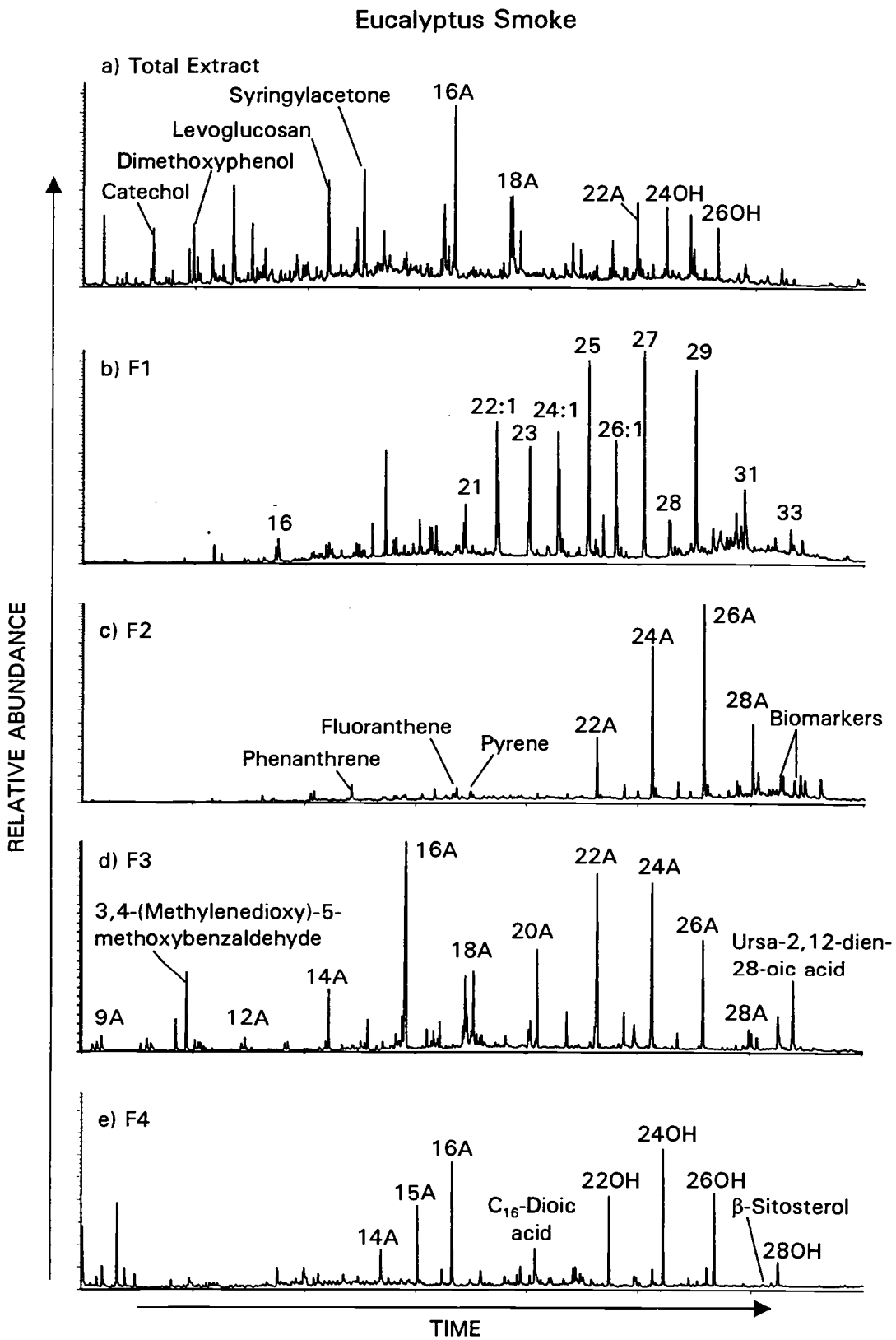

Figure IV.1. GC-MS total ion current traces of Eucalyptus smoke particulate matter (numbers refer to carbon chain length of *n*-alkanes, A = *n*-alkanoic acid, OH = *n*-alkanol).

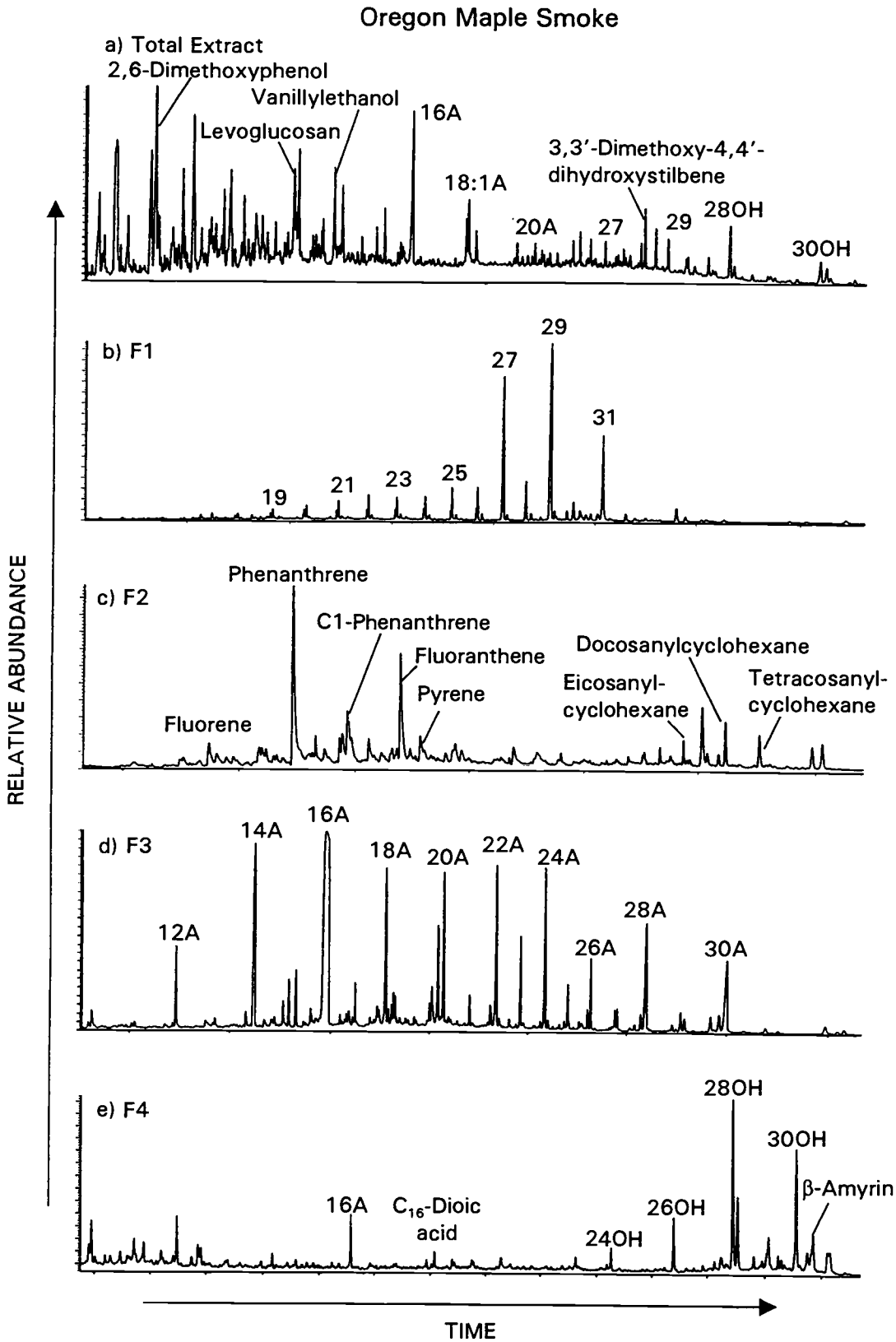

Figure IV.2. GC-MS total ion current traces of Oregon Maple smoke particulate matter (abbreviations as in Fig. IV.1).

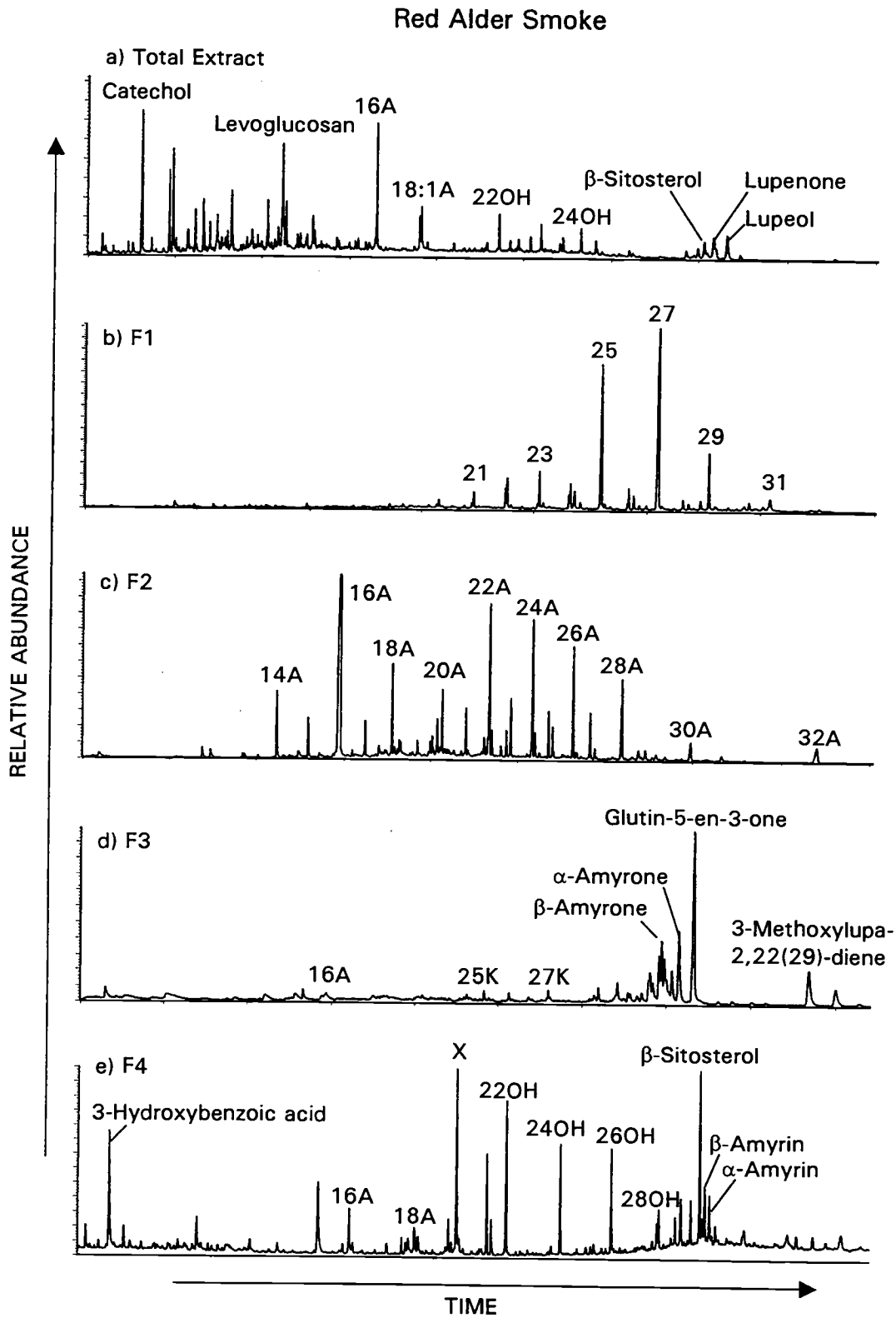

Figure IV.3. GC-MS total ion current traces of Red Alder smoke particulate matter (abbreviations as in Fig. IV.1).

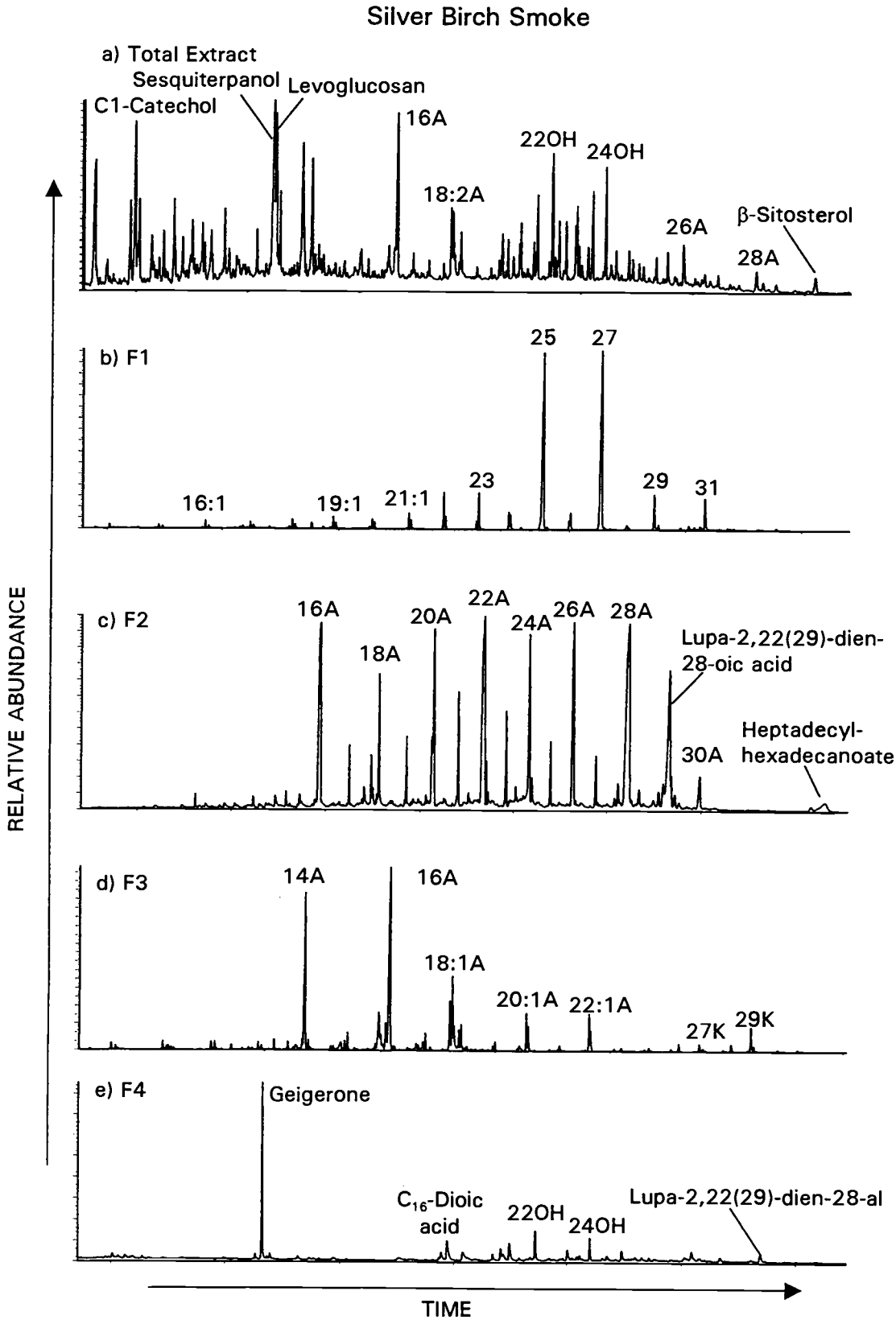

Figure IV.4. GC-MS total ion current traces of Silver Birch smoke particulate matter (abbreviations as in Fig. IV.1).

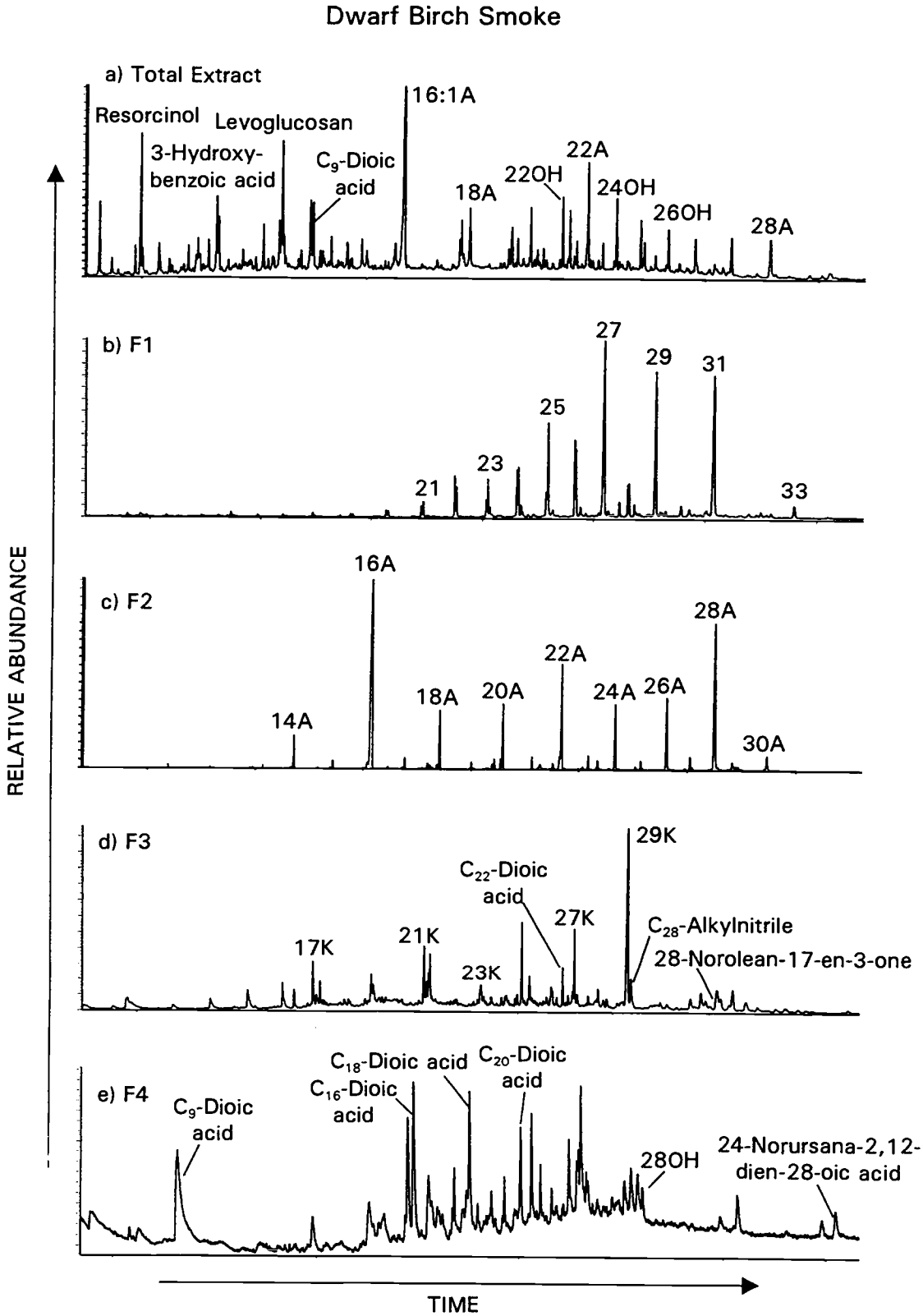

Figure IV.5. GC-MS total ion current traces of Dwarf Birch smoke particulate matter (abbreviations as in Fig. IV.1).

n-Alkenes

The *n*-alkenes are primarily terminal olefins (i.e., alk-1-enes). They range from C_{14} to C_{29}, with an even to odd carbon number predominance (CPI range from 0.2 to 0.9, average = 0.3), and C_{max} varying at 22, 25 and 26 (Appendix IV.1). Alkenes are not major components in plant waxes and their origin has been inferred to be from biomass fuel (Abas *et al.*, 1995). The *n*-alkenes are formed primarily by the thermal dehydration of *n*-alkanols (which show even carbon number predominance: Mazurek and Simoneit, 1984) and to a minor degree from the *n*-alkanes by oxidation during incomplete combustion (Abas *et al.*, 1995).

n-Alkanoic Acids

The *n*-alkanoic acids range from C_8 to C_{32}, show a strong even to odd carbon number predominance (CPI range from 5.1 to 8.7, average = 6.7), and a C_{max} at 16 (Appendix IV.1). These compounds, which are basic units of plant fats, oils and phospholipids, are identified here as the major compound class for deciduous tree smoke samples. There are also minor contributions from unsaturated fatty acids which include $C_{16:1}$, $C_{18:1}$ and $C_{18:2}$.

α, ω-Alkanedioic Acids

A series of α,ω-alkanedioic acids are present and range from C_{16} to C_{22} (Appendix IV.1). The most common α,ω-alkanedioic acid in deciduous tree smoke is C_{16}. The photo-oxidation product (Stephanou and Stratigakis, 1993) of $C_{18:1}$ and $C_{18:2}$ alkenoic acids, α,ω-nonanedioic acid, is also present, however, only in two samples. The α,ω-alkanedioic acids have been identified from a variety of sources and in the environment (Abas *et al.*, 1995; Gogou *et al.*, 1996; Hildemann *et al.*, 1994; Rogge *et al.*, 1993a; Simoneit, 1989). High molecular weight α,ω-alkanedioc acids (C_{10}-C_{24}) have been identified in rural aerosol particles and their source may be

oxidation products of ω-hydroxy alkanoic acids from vegetation polyester biopolymer (Simoneit and Mazurek, 1982). The α,ω-alkanedioc acid homologous series indicate a general origin from lipid sources and are not specific for deciduous trees. The identification here of all acids confirms a source contribution from the burning of biomass.

n-Alkanones

The straight chain ketones as *n*-alkan-2-ones range from C_{16} to C_{33} and show an odd to even carbon number predominance (CPI range from 2.5 to 5.9, average = 4.4) with C_{max} at 19, 27 and 29. The *n*-alkan-2-ones are primarily derived from the partial combustion of aliphatic precursors (Simoneit, 1978).

n-Alkylnitriles

A series of *n*-alkylnitriles ranging from C_{16} to C_{28} with a C_{max} at 16 was identified only in smoke from Dwarf Birch (Yukon Territory species). These compounds have not been reported previously in biomass burning extracts, however, they have been found in pyrolysates of kerogens (Derenne *et al.*, 1993), in urban aerosols (Abas and Simoneit, 1996), in smoke from charbroiling and meat cooking operations (Rogge *et al.*, 1991), and in smoke from burning of brown coal (Oros and Simoneit, 1998b). We propose that the *n*-alkylnitriles are formed by pyrolytic processes.

Molecular Biomarkers

Molecular biomarkers (i.e., biomarkers) are organic compounds of biological origin that show little or no change in chemical structure from their parent organic molecule (i.e., natural product) found in living organisms. Such molecules are characterized by their restricted occurrence, source specificity, molecular stability and suitable concentration for analytical detection (Mazurek and Simoneit, 1984). The

major biomarkers identified in the deciduous tree smoke samples include triterpenoids, monosaccharide derivatives from cellulose, methoxyphenols from lignin, and sterols, including their thermal alteration products. It has been shown that these high molecular weight compounds are directly volatilized into smoke by an injection mechanism similar to steam volatilization/stripping. Subsequent condensation onto or entrapment into preexisting particulate matter when the smoke plume is diluted and cooled provides the means for their incorporation into the atmospheric aerosol phase (Simoneit *et al.*, 1993).

Triterpenoids

Triterpenoids are important biomarker constituents of many higher plants, especially of angiosperms, in their gums and mucilages (Deshmane and Dev, 1971; Jain and Seshadri, 1971; Ghosh *et al.*, 1985; Hemmers *et al.*, 1989; Koops *et al.*, 1991; Rickling and Glombitza, 1992; Williams *et al.*, 1992). The predominant biomarkers identified in deciduous tree smoke are thermal alteration (oxidation) products with the lupane, oleanane and ursane skeletons. The most common triterpenoid alteration products present in the smoke samples include lupa-2,22-diene, oleana-2,12-diene, oleana-2,12-dien-18-oic acid and β-amyrone. The product-precursor relationship for the triterpenoids in these smoke samples may follow an alteration pathway which commences with the dehydrogenation of oleanolic and ursolic acid presursors, major triterpenoids found in angiosperm gums and mucilages, to dienes (Simoneit, 1998). Subsequent dehydrogenation of triterpenoid precursors results in partial aromatic hydrocarbon derivatives as intermediate products. Further dehydration of these intermediates yields the aromatic biomarkers.

Steroids

The sterols, generally comprised of the C_{28} and C_{29} phytosterol compounds, are constituents of plant lipid membranes and waxes. The sterol biomarkers are present in all deciduous tree smoke samples analyzed (Appendix IV.1). The natural product β-sitosterol is the most common sterol in deciduous tree smoke followed by

stigmasterol and campesterol, also the natural products. Several C_{29} thermal alteration products from the sterol precursor β-sitosterol are present and include stigmast-5-ene, stigmasta-4,6-diene, stigmasta-3,5-diene and stigmasta-3,5-dien-7-one. Various aromatization products are also present and compose a significant portion of the steroid content. The thermal alteration products of sterol precursors can be used as general indicators for burning of higher plant lipids (Simoneit, 1989; Simoneit *et al.*, 1993). Overall, the phytosterols and their alteration products are present only as minor constituents in these smoke samples.

Monosaccharide Derivatives

Cellulose and hemicellulose biopolymers which are mainly responsible for structural strength compose approximately 40-50% and 20-30% dry weight of wood, respectively (Petterson, 1984; Sergejewa, 1959). A cellulose molecule is a long-chain, linear polymer made up of 7,000 to 12,000 D-glucose monomers, while a hemicellulose molecule is a 100-200 sugar monomers polysaccharide mixture of glucose, mannose, galactose, xylose, arabinose, 4-O-methylglucuronic acid and galacturonic acid (Parham and Gray, 1984; Sergejewa, 1959). It is the burning of wood at temperatures > 300 °C which gives rise to the source specific molecular tracers, i.e., mainly 1,6-anhydro-β-D-glucopyranose, also called levoglucosan, with lower amounts of galactosan and mannosan (Appendix IV.1). Levoglucosan has been previously reported in biomass burning and atmospheric particles (Hornig *et al.*, 1985; Locker, 1988; Oros and Simoneit, 1999a; Simoneit *et al.*, 1999). Levoglucosan is the predominant monosaccharide in smoke and is detectable as a major component in all samples analyzed. Levoglucosan is emitted at such high concentrations that it is detectable in aerosol particulate matter at considerable distances from the combustion sources (Simoneit *et al.*, 1999).

Methoxyphenols

Lignin biopolymer comprises approximately 20-30% of the dry weight of wood (Petterson, 1984; Sergejewa, 1959). The lignin biopolymers are derived from p-coumaryl, coniferyl and sinapyl alcohols and contain mainly anisyl, vanillyl and syringyl nuclei (Simoneit *et al.*, 1993). Deciduous tree lignin is enriched in the sinapyl alcohol precursor and on burning produces primarily syringyl moieties. Burning (pyrolysis) of wood injects these lignin nuclei into smoke as breakdown products such as acid, aldehyde, ketone and alkyl derivatives of the methoxyphenols (Edye and Richards, 1991; Hawthorne *et al.*, 1988, 1992; Simoneit *et al.*, 1993; Mazurek and Simoneit, 1997).

The major biomarkers present in deciduous tree smoke are the methoxyphenols and their thermal alteration products (Appendix IV.1). The methoxyphenols are composed mainly of lignin pyrolysis products, lignans and dimers of substituted phenols. The predominant phenolic biomarkers in deciduous tree smoke include 2,6-dimethoxyphenol, pyrogallol, homovanillyl alcohol, vanillic acid, vanillin, acetovanillone, syringic acid, acetosyringone, and syringyl acetone (Appendix IV.1). The phenolic compound guaiacylacetone is also present. Guaiacyl derivatives are potential biomarker tracers for both hard and softwoods (Hawthorne *et al.*, 1988). A major lignan of deciduous tree smoke is tetrahydro-3,4-divanillylfuran (Appendix IV.1). Lignans have been described previously as tracers for distinguishing between coniferous and deciduous wood smoke emissions (Simoneit *et al.*, 1993). Secondary products as dimers of substituted phenols are present and include divanillyl and disyringyl. They are derived from coniferyl and sinapyl alcohol type precursors and have been previously identified in wood smoke (Hawthorne *et al.*, 1988; Simoneit, *et al.*, 1993). The lignin phenols, lignans and secondary dimers have mainly coniferyl and sinapyl alcohol type phenolic structures. Angiosperm lignin contains high proportions of the sinapyl as well as the coniferyl alcohol subunits, which are the precursors to the syringol and methoxyphenol degradation products from oxidation or pyrolysis (Hedges and Ertel, 1982). Hawthorne *et al.* (1989) and Simoneit *et al.* (1993) concluded that the syringyl moieties are indicators in smoke from burning of angiosperm fuels.

The ratios of the total natural and altered compounds that contain the syringyl skeleton to the total natural and altered compounds that contain the vanillyl skeleton

(S/V, syringyl skeletons/vanillyl skeletons) range from 0 to 6.1 (average = 1.7) (Appendix IV.1). The S/V ratios are distinct for each deciduous tree smoke sample. Thus, they may be useful indicators of source specific burn emissions.

Polycyclic Aromatic Hydrocarbons

All biomass fires are pyrolysis processes causing the formation of polycyclic aromatic hydrocarbons (PAH) from (a) the high temperature thermal alteration of natural product precursors in the source organic matter and (b) the recombination of molecular fragments in the smoke (Simoneit, 1998). The identifications and abundances of over twenty PAH compounds present in the deciduous tree smoke samples are given in Appendix IV.1. The major PAH are phenanthrene, anthracenes, C_1-phenanthrenes (since anthracene is a minor PAH, the alkylanthracenes are expected to be negligible, based on compound elucidation for other combustion samples, Simoneit, 1998), fluoranthene and pyrene followed by lesser amounts of C_2- and C_3- phenanthrenes, C_1-pyrenes, 11(H)-benzo[a]fluorene, and chrysene. Certain PAH that exhibit mutagenic and genotoxic potential such as benz[a]anthracene and benzo[a]pyrene (Arcos and Argus, 1975; IARC, 1989), are also present, however only as minor constituents. The PAH identified here are also emitted by internal combustion engines, coal burning, and other anthropogenic sources (Rogge *et al.*, 1993a; Oros and Simoneit, 1999a, 1999b; Simoneit, 1998). They are thus not exclusive markers for biomass combustion.

The ratio of methylphenanthrenes to phenanthrene (MP:P) has been previously used as an indicator of anthropogenic influences in the environment: 0.5 for atmospheric fallout (Takada *et al.*, 1991), 0.5-1.0 for combustion sources (Prahl and Carpenter, 1983), 1.0 for street and urban dusts (Takada *et al.*, 1990, 1991), 2.0-6.0 for fossil fuel (Prahl and Carpenter, 1983), and 4.0 for crankcase oil (Pruel and Quinn, 1988). The range of the MP:P ratio determined for the deciduous tree smoke samples is 0.5 to 1.5 (average = 1.0). This value is smaller than the M:P ratio determined previously for conifer smoke (0.5 to 2.6, average = 1.6; Oros and Simoneit, 1999a), thus it can be used to distinguish between these two biomass fuel sources in smoke emissions.

Unresolved Complex Mixture

An unresolved complex mixture (UCM) of structurally complex isomers and homologs of branched and cyclic compounds (Eglinton *et al.*, 1975) eluting as a hump between C_{14} and C_{34} alkanes is present as an organic component of all smoke sample total extracts. The UCM, which has been thoroughly examined in petroleum sources, is comprised of compounds which are relatively inert to microbial degradation (Gough and Rowland, 1990; Killops and Al-Juboori, 1990). The ratio of UCM to resolved components (U:R) has been used as a parameter for the indication of petroleum contribution to aerosol particle samples (Mazurek and Simoneit, 1984). The U:R ratios for deciduous tree smoke samples were quantified in order to determine if this parameter is useful for distinguishing between angiosperm, gymnosperm (conifer) and fossil fuel derived combustion source emissions (Appendix IV.1). The deciduous tree smoke U:R ratios range from 0.01 to 0.9 (average = 0.7). Several U:R ratios have been determined from more mature fossil fuel derived combustion emission sources which include the following: lignite coal = 3.2 and bituminous coal = 3.3 (Oros and Simoneit, 1999b); catalyst-equipped automobile engine exhaust = 5.5 and heavy-duty diesel truck engine exhaust = 9.3 (Rogge *et al.*, 1993). Conifer smoke U:R ratios range from 0.6 to 1.4 (average = 1.0) (Oros and Simoneit, 1999a). Thus, the lower U:R ratio of deciduous tree smoke shows that this parameter is useful for distinguishing between this biomass burning source and fossil fuel derived combustion source emissions. However, the close similarity in U:R ratios between deciduous tree and conifer smoke samples suggests that this parameter cannot be used to distinguish between these two biomass fuel sources in smoke emissions.

Volatile and Elemental Carbon

The concentrations of volatilizable organic carbon (VOC, equivalent to solvent extractable OC) and elemental carbon (EC, i.e., black soot) in the deciduous tree smoke samples are given in Appendix IV.1. The volatilizable to elemental carbon ratios (VOC/EC) show a range from 9 to 43 (average = 23.6). The VOC/EC ratios

for the deciduous tree smoke samples are elevated in comparison to ambient air samples collected from rural sites (Crater Lake, OR = 12.4, Carus, OR = 6.5, and Sauvie, OR = 4.1) and urban areas (Los Angeles = 1.6, New York = 1.4, Santiago Chile = 1.7, China = 1.5) (Didyk *et al.*, 1999). The low VOC/EC ratios for mainly urban and suburban areas indicate a strong influence from petroleum derived combustion emissions. The deciduous tree smoke VOC/EC ratios are much less than that measured from an ambient air sample collected at a remote area (South Atlantic Ocean = 160, Didyk *et al.*, 1999) where influence from both petroleum combustion and biomass burning emissions is negligible. This distribution indicates that the VOC/EC ratio measured for deciduous tree smoke may be useful in distinguishing this source from petroleum derived combustion emissions such as those found in rural and urban areas. However, the deciduous tree smoke VOC/EC ratio is similar to the ratio determined previously for conifer smoke (3 to 78, average = 35; Oros and Simoneit, 1999a), thus it can not be used to distinguish between these two biomass fuel sources in smoke emissions.

Major Compound Groups

The average emission rates (mg/kg) and percent abundances of the major compound groups identified in conifer smoke are given in Table IV.2. Of the total resolved components the major compound groups are the carboxylic acids (56.4%) from internal lipids, n-alkanes (15.1%) from waxes and methoxyphenols (8.4%) derived from lignin. Other compound groups such as triterpenoid and steroid biomarkers and aliphatic homologous series are present at low abundances (<5%). Although wood is composed mostly of cellulose (40-50% of dry weight of wood, d.w.w.), with lesser amounts of hemicelluloses (20-30% of d.w.w.), and lignin (20-30% of d.w.w.) (Petterson, 1984; Sergejewa, 1959), the percent abundance of the monosaccharide derivatives (1.5%) from cellulose alteration is less than the methoxyphenols. This observation is likely due to burning of the selected plant parts (leaves and branches of 1-2 cm thickness) which were relatively immature in plant structural development.

Table IV.2. Major compound groups identified in deciduous tree smoke.

Major Compound Group	Total Concentration (mg/kg)	Percent* Abundance
Carboxylic acids	1589±258	56.4
n-Alkanes	425±73	15.1
Methoxyphenols	237±50	8.4
n-Alkenes	129±35	4.6
Triterpenoids	118±13	4.2
Alkanones	116±23	4.1
PAH	66±12	2.3
Monosaccharide Derivatives	41±5	1.5
Steroids	31±6	1.1
Alkylcyclohexanes	13±4	0.5
n-Alkanols	8±2	0.3
Unknowns	43±19	1.5

*Percent abundance relative to total resolved organic components.

Major and Unique Biomarker Tracers

The major biomarker compounds identified for deciduous trees to be applied as potential tracers in smoke and in the atmosphere are given in Table IV.3. These are the methoxyphenolic compounds derived from lignin combustion which contain both coniferyl and sinapyl alcohol precursors. The methoxyphenolic biomarker tracers include catechol, homovanillyl alcohol, vanillic acid, vanillin, acetovanillone, pyrogallol, homovanillic acid, syringic acid, syringyl acetone, acetosyringone and disyringyl. The syringyl moieties, typical of the sinapyl alcohol precursor biopolymer, are useful biomarker indicators for deciduous tree smoke emissions.

The major triterpenoid biomarker tracers are combustion alteration products which include oleana-2,12-dien-18-oic acid, lupa-2,22-diene, lupenone, oleana-2,12-diene, lupa-2,22(29)-dien-3-ol and β-amyrone. The natural product β-amyrin is also present as a major biomarker tracer. The major biomarker derived from combustion of cellulose biopolymer is levoglucosan, which has been previously proposed as a tracer for cellulose burning. Galactosan and mannosan are also detectable as

Table IV.3. Major and unique biomarker tracers identified in deciduous tree smoke.

Major Biomarker Tracer	Total Concentration (mg/kg)	Percent* Abundance
Methoxyphenols		
Catechol	37±11	1.3
Homovanillyl alcohol	24±6	0.8
Vanillic acid	11±2	0.4
Vanillin	9±4	0.3
Acetosyringone	8±2	0.3
Acetovanillone	7±2	0.2
Pyrogallol	6±2	0.2
Tetrahydro-3,4-divanillylfuran	5±1	0.2
Syringylacetone	5±1	0.2
Homovanillic acid	4±2	0.1
Syringic acid	3±1	0.1
Disyringyl	1±0.3	0.1
Triterpenoids		
Olean-2,12-dien-18-oic acid	9±2	0.3
Lupa-2,22-diene	6±2	0.2
Lupenone	2±0.5	0.1
Oleana-2,12-diene	2±0.4	0.1
β-Amyrin	2±0.5	0.1
Lupa-2,22(29)-dien-3-ol	2±0.5	0.1
β-Amyrone	0.6±0.1	0.1
Monosaccharide Derivatives		
Levoglucosan	75±11	2.6
Galactosan	27±4	0.9
Mannosan	14±2	0.5
Steroids		
β-Sitosterol	10±1	0.4
Campesterol	0.3±0.1	0.1

*Percent abundance relative to total resolved organic components.

secondary cellulose derivatives. The major steroid biomarker tracers are the natural products β-sitosterol and campesterol. Compound series such as *n*-alkanes, *n*-alkenes, *n*-alkanoic acids, *n*- alkanones, *n*-alkanols, PAH, phytosterols, anhydrosaccharides (e.g., levoglucosan), and UCM are not source specific, because they are generally found in all biomass combustionemissions (Abas *et al.*, 1995;

Simoneit, 1984, 1989; Simoneit *et al.*, 1999). However, some of these compound series are indicative of species specific biomass burning, when coupled with the directly emitted and thermally altered biomarker compounds. They can collectively be used as specific tracers for assessing and tracking emissions from burning of deciduous tree fuel.

Some deciduous tree smoke samples contain unique biomarkers which may be useful as species specific tracers. For example, Eucalyptus smoke contains lupa-2,22(29)-dien-28-al, 24-norolean-2,12-en-28-oic acid, oleana-2,12-dien-28-oic acid and ursa-2,12-dien-28-oic acid. These triterpenoid natural products are not present in other deciduous tree smoke samples, thus they are unique tracers in smoke from this species. Oregon Maple smoke shows the triterpenoids α-amyrin, ursa-2,20-diene and lupa-1,22(29)-dien-3-one as unique tracers. Red Alder smoke shows 3α-lupeol, 3β-lupeol, glutin-5-en-3-one, olean-13(18)-en-3-one, taraxerone, isomultifluorenone, 3-methoxylupa-2,22(29)-diene, dihydrohyctanthanoic acid, olean-13(18)-en-3-one-28-oic acid and 29-chlorolup-1-en-3-one as unique tracers. Silver Birch smoke shows sesquiterpenoids which include caryophylla-2(12),5-dien-13-aldehyde, sesquiterpanol and geigerone as unique tracers. It also shows the triterpenoids allobetul-2-ene and lupa-2,22(29)-dien-28-oic acid as unique tracers. The steroid alteration products stigmasta-3,5-diene, stigmasta-4,6-diene and 24-ethylcholesta-4,22-diene are also unique tracers in Silver Birch smoke. Dwarf Birch smoke shows the triterpenoids des-A-allobetulin, nortriterpene, triterpadiene, nortriterpenone, 24-norursana-2,12-dien-28-oic acid and the steroid stigmasta-3,5-dien-7-one as unique tracers. The unique biomarkers are useful as indicative tracers of species specific biomass burning.

The relative abundances (%) of key biomarkers from deciduous tree smoke may be used to distinguish fuel type. Table IV.4 shows six key biomarkers derived mostly from internal plant components (levoglucosan, β-sitosterol, vanillic acid and syringic acid) and epicuticular wax lipids (heptacosane and docosanoic acid). The distributions of these compounds relative to one another are different and represent the unique chemical and physical characteristics between deciduous tree species. The relative abundances of key biomarkers and homologous series compounds reported here can collectively be used as specific tracers for assessing and tracking emissions from burning of deciduous tree fuels.

Table IV.4. Abundances (% relative to maximum) of key biomarkers for identifying fuel type.

Sample	Heptacosane	Docasanoic Acid	Levoglucosan	β-Sitosterol	Vanillic Acid	Syringic Acid
Eucalyptus	23	100	0.2	1.9	0.4	0.7
Oregon Maple	71	100	98	18	24	11
Red Alder	100	95	51	9	6	4
Silver Birch	100	12	36	4	3	0
Dwarf Birch	30	100	27	3	4	0

CONCLUSIONS

This work reports the lipid and molecular biomarker components in smoke from burning of six deciduous trees (angiosperms). The data is of utility for assessing direct organic composition signatures for particle emissions from deciduous tree fuel types during biomass burning. The abundance order for the major compound classes in deciduous tree smoke samples was identified as the following: UCM > carboxylic acids > *n*-alkanes > methoxyphenols > *n*-alkenes > triterpenoids > n-alkanones > PAH > anhydrosaccharides > steroids > alkylcyclohexanes > *n*-alkanols. Variations in this molecular group order exist among the deciduous tree species burned, however, these are only minor and usually occur between close ranking molecular groups. Although the concentrations of organic compounds in smoke aerosols are highly variable and dependent on combustion temperature, aeration, and moisture content of the source fuel, the biomarkers and their combustion alteration products are source specific. The major biomarkers identified in the smoke samples are useful as tracers for distinguishing the deciduous tree burning component in atmospheric aerosol source attributions.

The range of the MP:P ratio determined for the deciduous tree smoke samples is 0.5-1.5 (average = 1.0), which may be useful for distinguishing deciduous tree burning emissions from fossil fuel and other combustion emissions, and from street and urban dusts. The MP:P range is proposed here as a potential indicator for identifying deciduous tree burning emissions in atmospheric and other environmental

samples. Additionally, the average U:R ratio for deciduous tree burning emissions (0.7) may also be of utility for distinguishing this source from fossil fuel-derived combustion emissions (e.g., coal combustion, gasoline and diesel engine exhaust). The ratio also suggests that deciduous tree and other biomass burning emissions are significant contributors of particle bound immature organic matter (UCM) present in the atmosphere of rural areas of the western United States. The VOC/EC ratios measured for deciduous tree smoke samples range from 9 to 43 (average = 23.6). The distribution indicates that the VOC/EC ratios may be useful to distinguish this source from petroleum derived combustion emissions, such as those found in rural and urban areas, and from natural emissions found in remote areas.

ACKNOWLEDGMENTS

This work was funded in part by the U.S. Environmental Protection Agency (Grant CR 823990-01-0).

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CHAPTER V

ORGANIC TRACERS FROM WILD FIRE RESIDUES IN SOILS AND RAIN/RIVER WASH-OUT

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To be submitted to: ***Water, Air and Soil Pollution***

ABSTRACT

The molecular compositions and alteration products of the major organic components in soils and litter subjected to controlled or wildfire burning, and subsequent erosion by rain and river transport have been determined by GC-MS. The representative chemical fingerprint imparted to soils by biomass burning shows *n*-alkanoic acids > *n*-alkanes > *n*-alkanols > phytosterols > other terpenoids. Biomarker tracer analysis indicates that organic compounds remain as internal lipid components of char and heavy particles and are deposited onto soil during wildfire and prescribed burning. The process of rain erosion and river transport releases some of these internal components into the surroundings where they are further subjected to biological alteration. The distributions and abundances of homologous compound series in soils coupled with biomarker tracer analysis provides a chemical fingerprint which is useful for identifying the single or multiple plant species contributing organic matter by both thermal (burning) and biological processes. Such fingerprints are useful for tracking soils which are transported in the atmosphere by wind as suspended particles in dust storms and on land by rain erosion to rivers.

Key Words - *n*-Alkanes, *n*-Alkanoic Acids, *n*-Alkanols, Molecular Markers

INTRODUCTION

Wildfires and the application of biomass burning as a method for clearing vegetated (forest and grassland) areas, as well as disposing of slash, significantly increase the input of organic particulate matter to the atmosphere and indirectly by rain erosion to river systems. Both of these problems of environmental degradation are of global concern (e.g., Levine, 1991, 1996). In order to apportion the impact of biomass burning, the source-receptor model has been applied mainly to urban areas and needs to be extended to rural and remote regions (e.g., Schauer *et al.*, 1996; Rogge *et al.*, 1993a). Soil resuspension both before and after burning of vegetation cover has not been considered in any source-receptor study. Also, erosional transport of soil and ash to rivers has not been studied in this context. Thus there is a need to determine the composition of soil organic matter in terms of natural components and additional products from burning of associated biomass.

Vascular plants are a primary source of organic matter to soil via litter and roots (Oades, 1993). Fresh plant material is often mixed into soil by earthworms and other animals where it is degraded by heterotrophic microorganisms such as bacteria, actinomycetes and fungi (Metting, 1993). Organic matter degradation can also be influenced by heterogeneous reactions which occur at interfaces of mineral solids (Miltner and Zech, 1998). Thus, soil organic matter is diverse with respect to its source material and subsequent degradational influences.

Wildfire and controlled burn events introduce organic burn residues, charcoal and ash into soils and the fates of these materials have not been extensively examined. Rain washing and drainage to rivers of soils are important terrestrial processes that directly influence carbon cycling. Soils subjected to these physical treatments (e.g., burning and erosion) are likely to contain organic compounds with distributions reflecting sources and both thermal and water washing processes. The aim of this study is to investigate the molecular compositions and alteration products of the organic components in soil and litter samples before and after they have been subjected to burning (wildfire/prescribed) and to subsequent erosion by rain and water transport. This is an initial demonstration of the organic geochemistry tracer approach for fingerprinting the molecular composition of soil lipids and for defining their sources.

EXPERIMENTAL METHODS

Sampling

Soil and litter samples were collected from temperate zone forest, grassland and chaparral landscapes of California and Oregon, USA away from urban areas before and after burning (both controlled and wildfires). The samples were of various types: 1) litter under forest trees and chaparral, 2) surficial soils after wildfire burning of conifer forest and grassland, 3) eroded soil after wildfire burning and washing into a creek, and 4) other source vegetation materials (Table V.1). Only the top layer (0-3 cm depth) of soil and surface litter was sampled. After collection, all samples were placed in precleaned 300 ml jars with Teflon lined lids. Wet samples were freeze dried and other samples were preserved by addition of 10 ml of chloroform ($CHCl_3$) for sterilization. The jars were then stored at 4 °C until further chemical extraction was conducted.

Extraction and Fractionation

Each sample was extracted by ultrasonic agitation for three twenty-minute periods using 200 ml of dichloromethane (CH_2Cl_2) and methanol mixture (3:1 v/v). These extracts represent the solvent-soluble organic matter called lipids. The wax from ryegrass was extracted by briefly dipping (3-5 sec, 3 times each) stems into $CHCl_3$ to dissolve the external wax. All solvent extracts were filtered using a Gelman Swinney filtration unit containing an annealed glass fiber filter for the removal of insoluble particles (Simoneit and Mazurek, 1982). The filtrates were first concentrated by use of a rotary evaporator and then a stream of filtered nitrogen gas. The final volumes were adjusted to 5-10 ml by addition of CH_2Cl_2 depending on concentration based on total extract gas chromatographic (GC) analysis. All extracts were treated with 14% boron trifluoride (BF_3) in methanol or with diazomethane (CH_2N_2) in diethyl ether to esterify carboxylic acids. This step was carried out in 5 ml conical vials which contained an aliquot of 1.0 to 1.5 ml of concentrated lipid extract plus 0.5 to 1.0 ml esterification reagent. For the BF_3 method, the vials were tightly capped and placed in an 80-85 °C water bath for 15 minutes, then the reaction mixture was quenched

Table V.1. Sample descriptions and homologous compound series distributions.

No.	Description	Total Extract Yield (mg/g)	n-Alkanes[1]			n-Alkanoic Acids[1]			n-Alkanols[1]		
			CPI	C_{range}	C_{max}	CPI	C_{range}	C_{max}	CPI	C_{range}	C_{max}
1	Ryegrass field soil (before burn), Dayton soil series, Philomath, OR (Collected 4/99)	93	6.8	15-31	27	15	16-24	16	11	16-30	26
2	Ryegrass field soil (after burn), Philomath, OR (Collected 4/99)	235	13	15-33	31	5	14-32	16	12	20-30	26
3	Soil with litter, collected on 8/78, 2 months after Firebough, CA grassland fire of 6/78 (Nees Avenue)	8330	10.3	25-35	31	11	14-30	16	nd	15-28	28
4	Ryegrass wax (*Lolium perenne*), Philomath, OR (Collected 4/99)	65	27	25-33	31	nd	16-32	16	nd	22-28	26
5	Soil with litter from burn area, Whitmore, CA forest fire of 1975 (Collected 8/78)	1440	2.5	15-35	29	4	12-32	16	nd	10-28	22
6	Litter from Douglas fir, 100m from Sierra Ski Ranch Rd, Echo Summit, CA (Collected 7/78)	10,300	6.1	21-33	29	12	14-32	22	nd	12-24	22
7	Douglas fir wax, Coastal Mountain Range of western Oregon (Collected 7/83)	nd	7.4	24-31	29	15	16-26	24	3	16-32	26
8	Mud in arroyo after rain, Agoura, CA fire of 10/78, 500m from Kanan Road (Collected 11/78)	810	5.2	13-33	29	20	14-30	16	nd	18-26	22
9	Silt/detritus washout in Trancas Creek, Agoura, CA fire of 10/78, Paseo Canyon, 5km from mouth, (Collected 11/78)	22,100	8	13-33	29	13	12-30	16	nd	16-30	24

[1]: Determined by GC-MS; C_{max} = carbon number maximum as defined by Mazurek and Simoneit (1984); CPI for n-alkanes: [CPI = ΣC_{13}-$C_{35}/\Sigma C_{12}$-C_{34}] from Mazurek and Simoneit (1984); CPI for n-alkanoic acids and n-alkanols: [CPI = ΣC_{12}-$C_{34}/\Sigma C_{13}$-C_{35}] from Mazurek and Simoneit (1984); nd: not determined (for lipids only even carbon numbered homologs were present).

with about 1 ml of doubly-distilled, chloroform-extracted water. The CH_2N_2 reaction mixture was allowed to vent to the atmosphere. The organic phase, containing the methylated filter extract, was concentrated to ~100 ml.

The extracts were subjected to thin layer chromatography (TLC) using silica-gel plates (0.25 mm SiO_2 thickness) and elution with a mixture of hexane and diethyl ether (9:1). The TLC plates had been cleaned prior to use by repetitive elutions with methanol and CH_2Cl_2. After each washing, the top centimeter of silica-gel was scraped off in order to remove contaminants. Prior to sample application, the TLC plates were activated in an oven at 120 °C for 45 minutes. The TLC elution regions corresponding to hydrocarbons, esters, ketones (and aldehydes), alcohols and origin were visualized by UV light and iodine vapor in conjunction with the coelution of a standard compound mixture (Simoneit and Mazurek, 1982). The bands corresponding to these fractions were scraped off the TLC plate, eluted with CH_2Cl_2 or ethyl acetate, concentrated and transferred to 2 ml vials. These fractions were then subjected to GC and gas chromatography-mass spectrometric (GC-MS) analyses. The total extracts and polar fractions were also converted prior to analysis to trimethylsilyl derivatives by reaction with N,O-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) plus 1% trimethylchlorosilane and a trace of pyridine for approximately 3 hr at 70 °C.

Instrumental Analyses

The GC analyses were conducted on a Hewlett-Packard Model 5840A gas chromatograph using a 25 m x 0.20 mm i.d. fused silica capillary column coated with DB-5 (J&W Scientific, film thickness 0.25 μm). The GC-MS analyses were conducted using a Hewlett-Packard Model 5973 MSD quadrupole mass spectrometer operated in the electron impact mode at 70 eV and coupled to a Hewlett-Packard Model 6890 gas chromatograph. The GC of the MS system was equipped with a 30 m x 0.25 mm i.d. fused silica capillary column coated with DB-5 (J&W Scientific, film thickness 0.25 μm). Both GCs were temperature programmed as follows: hold at 65 °C for 2 min, ramp to 300 °C at 6 °C/min, and then hold isothermal at 300 °C for 20 min. Helium was used as carrier gas.

Compound identifications are based on comparisons with authentic standards, GC retention time, literature mass spectra and interpretation of mass spectrometric fragmentation patterns.

RESULTS AND DISCUSSION

Examples of the typical GC-MS total ion current (TIC) traces (equivalent to GC traces) for the samples are shown in Figures V.1-V.6. The total extracts show the distributions and relative abundances of all the major organic constituents which consist primarily of aliphatic homologues and molecular biomarkers. The fractions were analyzed to determine the distributions of homologous aliphatic series and biomarkers separated according to functional group and polarity properties. Analytical data for the lipid characteristics of the soil samples include the carbon number range (C_{range}), carbon number maxima (C_{max}), and carbon preference indices (CPI) (Mazurek and Simoneit, 1984) for the homologous series of *n*-alkanes, *n*-alkanoic acids and *n*-alkanols (Table V.1). The abundances (% relative to total GC response) of the major compound groups for each sample are given in Table V.2 and the corresponding biomarkers are summarized in Table V.3. The discussion focuses on the homologous series distributions and characteristic biomarkers identified for each sample. Precursor to product reaction pathways were also determined where possible for the major biomarker groups.

Grass Field and Prairie Burning

Total Extract

Analytical data on the homologous series distributions (CPI, C_{range} and C_{max}) are shown in Table V.1. The GC-MS TIC traces for the extracts of the soils before and after a prescribed burn of a Ryegrass (*Lolium perenne*) field are shown in Figures V.1 and V.2, respectively. The GC-MS TIC traces of Ryegrass wax are given in Figure V.3. The total extract of the soil before burning shows saturated and unsaturated *n*-alkanoic acids, *n*-alkanols, and phytosterol biomarkers as the

predominant compound groups. The total extract of the soil after burning shows saturated and unsaturated *n*-alkanoic acids, *n*-alkanols, *n*-alkanes and phytosterol biomarkers as the predominant compound groups. These distributions are similar to that from Ryegrass wax suggesting that plant wax lipids make up a significant portion of the extractable soil organic component.

Hydrocarbons

The *n*-alkanes in the grass soil before burning show a C_{range} from 15 to 31, with C_{max} at 27 and an odd carbon number predominance (CPI=6.8). The presence of *n*-alkanes indicates a significant input from epicuticular wax sources. Vascular plants synthesize epicuticular waxes containing odd carbon number *n*-alkanes, usually in the C_{range} from 25 to 33 with 29 or 31 as dominant homologs, which often contribute up to 90% of all paraffins found in plant waxes (Kolattukudy, 1970). This is evident in the distribution of the *n*-alkanes isolated from Ryegrass wax which show a C_{range} from 25 to 33, with C_{max} at 31 and a strong odd carbon number predominance (CPI=27)(Figure V.3). The lower CPI in the grass soil indicates that this compound group has undergone mild degradation.

The *n*-alkanes in the grass soil after burning show a C_{range} from 15 to 33, with C_{max} at 31 and a strong odd carbon number predominance (CPI=13). The *n*-alkanes are the predominant compound group in comparison with others in the total extract. From this distribution it can be inferred that during prescribed burning plant waxes are melted/vaporized and deposited on the soil surface. Thus, prescribed burning or wildfires may increase the hydrophobic nature of the soil, which in turn can alter the hydrologic regime of a landscape and increase surface runoff/erosion.

A series of *n*-alkenes primarily as terminal olefins (*n*-alk-1-enes) are present in the soil after burning and show a C_{range} from 17:1 to 23:1. The *n*-alkenes are not major components of plant waxes and are likely derived from the thermal dehydration of *n*-alkanols (which exhibit an even carbon number predominance; Mazurek and Simoneit, 1984) and to a minor degree from *n*-alkanes by oxidation during incomplete combustion (Abas *et al.*, 1995).

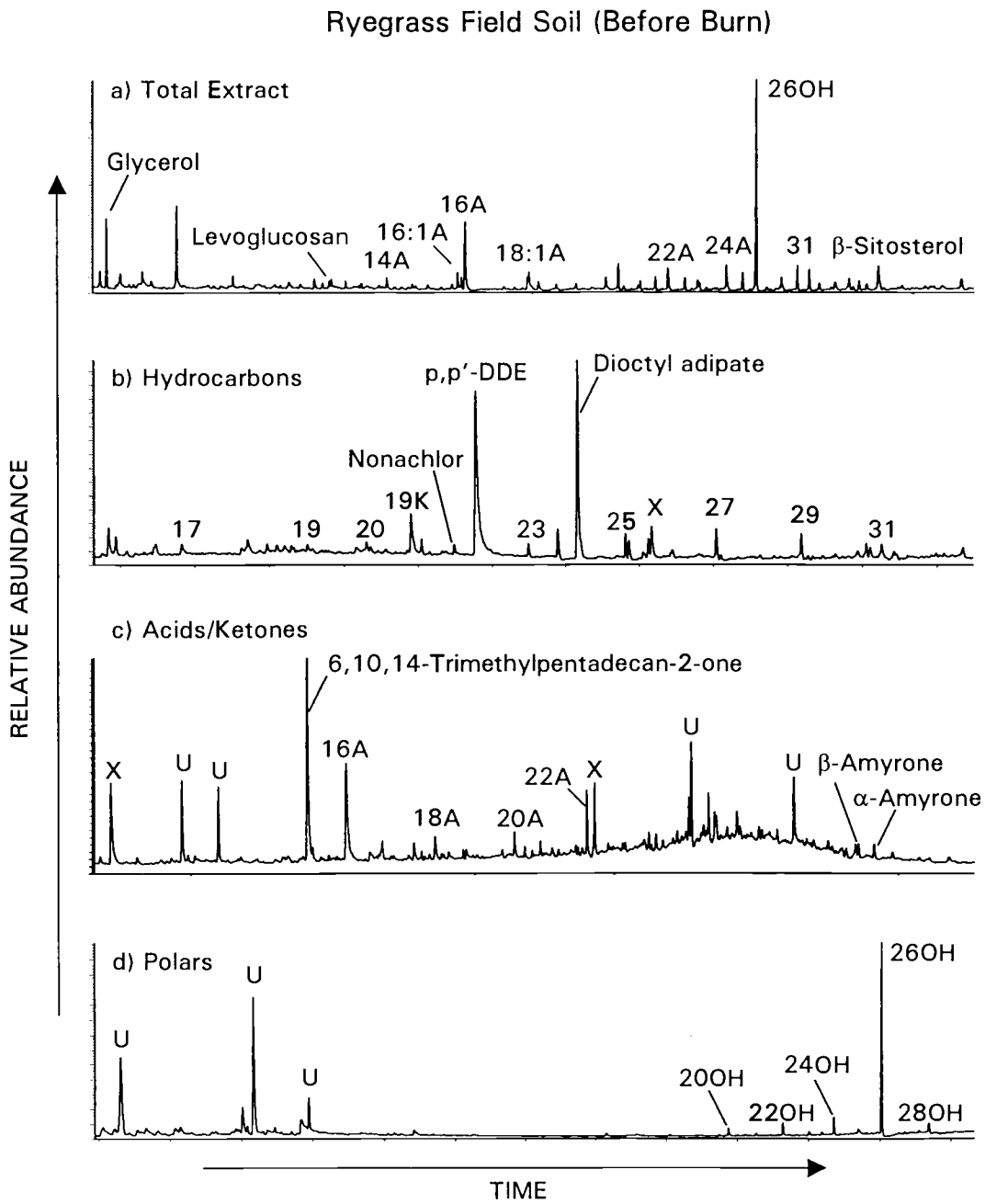

Figure V.1. GC-MS total ion current traces of Ryegrass Field Soil before prescribed burning (numbers refer to carbon chain length of *n*-alkanes, A = *n*-alkanoic acid, OH = *n*-alkanol, K = *n*-alkanone, X = contaminant and U = unknown).

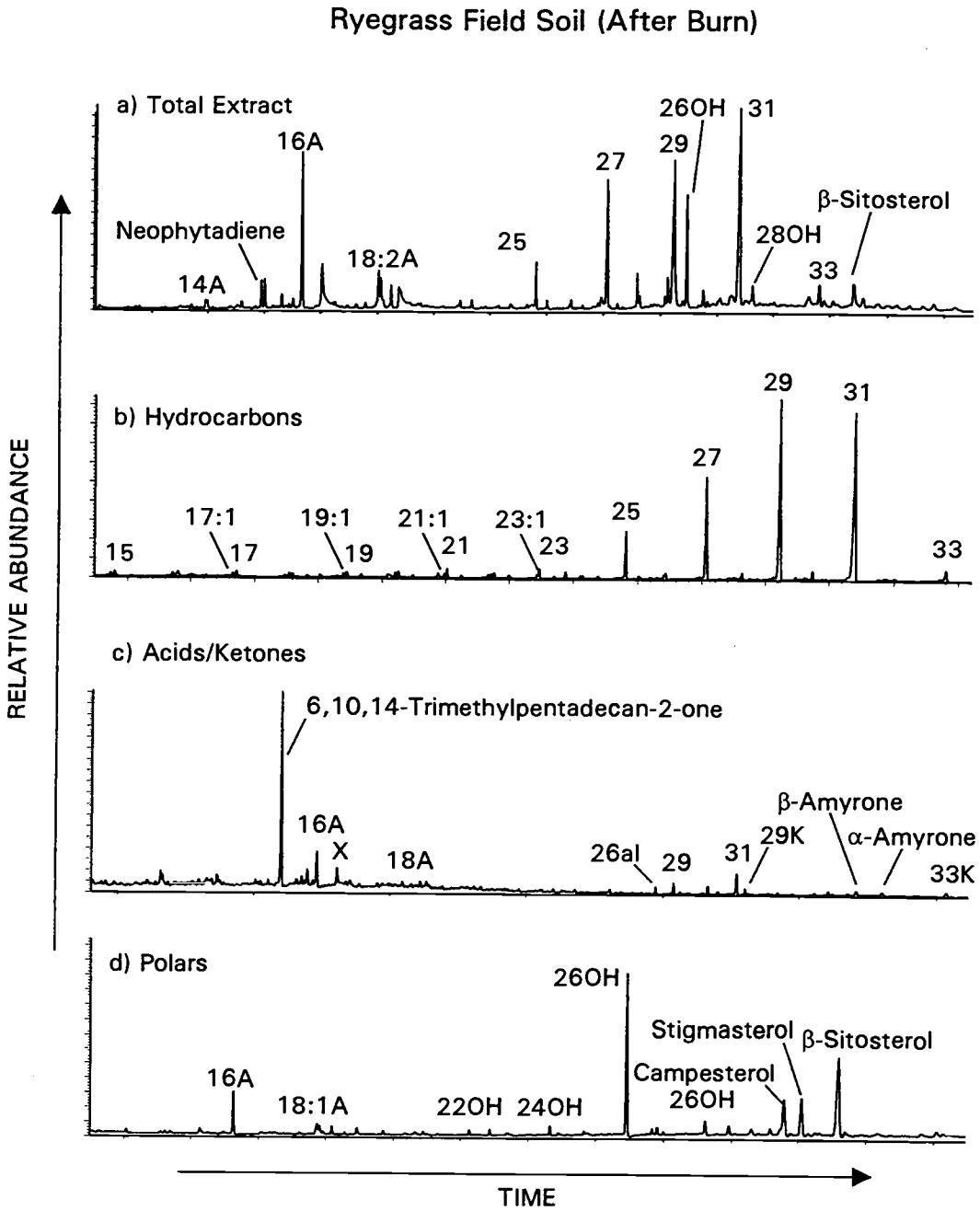

Figure V.2. GC-MS total ion current traces of Ryegrass Field Soil after prescribed field burning (abbreviations as in Fig. V.1).

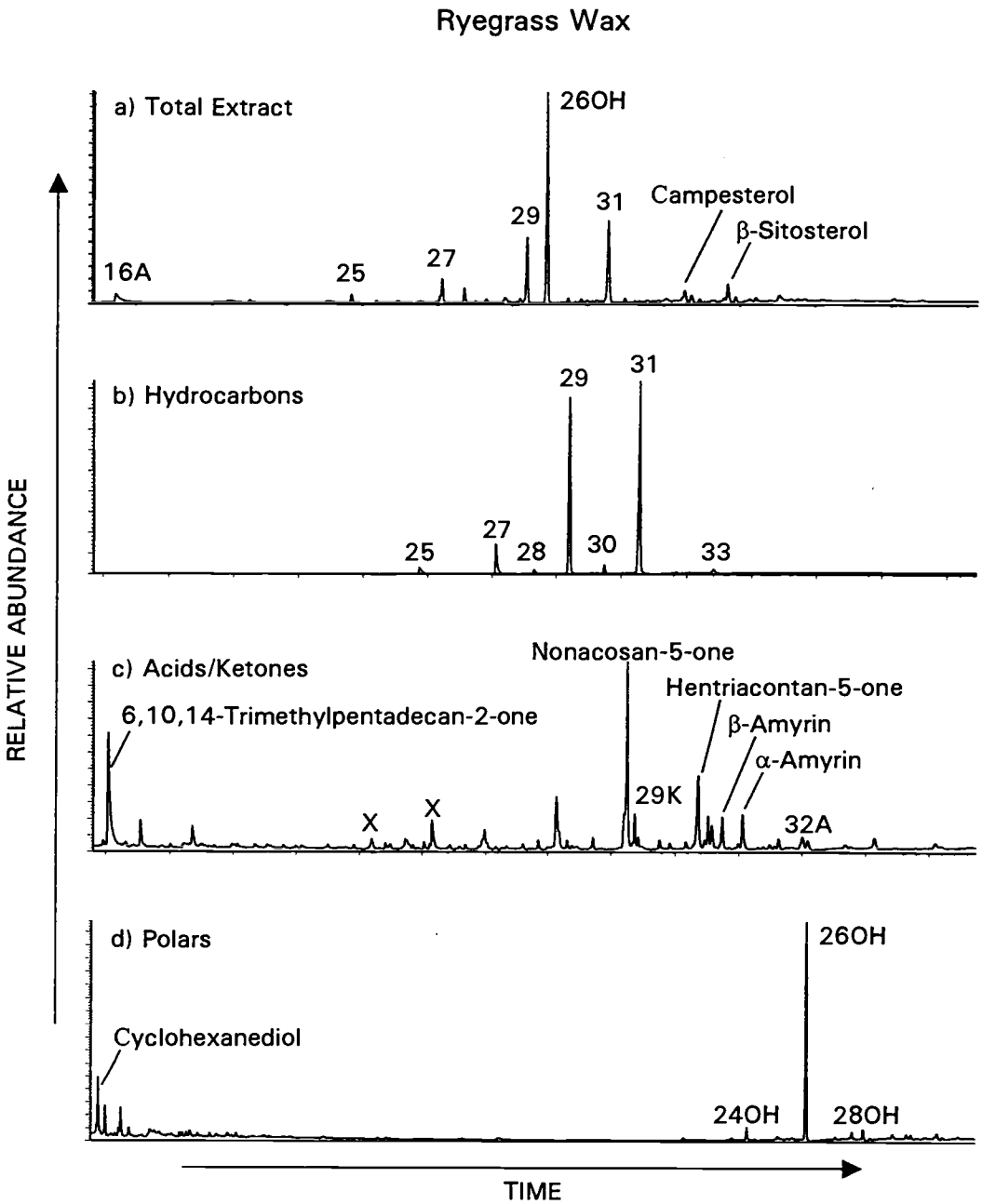

Figure V.3. GC-MS total ion current traces of Ryegrass Wax (abbreviations as in Fig. V.1).

Fatty Acids

The *n*-alkanoic acids exhibit a C_{range} from 16 to 24, with C_{max} at 16 and a strong even carbon number predominance (CPI=15) in the grass soil before burning. The *n*-alkanoic acids are the predominant compound group in comparison with others in the total extract. The strong CPI is characteristic of their biogenic origin as these compounds are basic units of plant fats, oils and phospholipids. Since free *n*-alkanoic acids are relatively minor plant wax components and intermediary in the production of other wax constituents, their concentrations in soils may be influenced significantly by biochemical processes occurring in plant sources and by the degradation of wax esters, which can hydrolyze to alkanoic acids and alkanols (Tulloch, 1976). In comparison, the *n*-alkanoic acids in the grass soil after burning show a C_{range} from 14 to 32, with a C_{max} at 16 and an even carbon number predominance (CPI=4.8). This is similar to the *n*-alkanoic acid distribution for Ryegrass wax. The low CPI of the fatty acids in the soil after burning shows significant *n*-alkanoic acid degradation from burning.

Carbonyls

The grass soil before the burn shows 6,10,14-trimethylpentadecan-2-one as a major component and nonadecan-2-one as a minor component. The isoprenoid 6,10,14-trimethylpentadecan-2-one has been described to derive by both bacterial and photochemical oxidation of phytol, the isoprenoidyl side chain of chlorophyll a (Brooks and Maxwell, 1974; Rontani and Giusti, 1988). In comparison, Ryegrass wax also contains 6,10,14-trimethylpentadecan-2-one as a major component while noncosan-5-one and hentriacontan-5-one are minor components. Additionally, the grass soil after the burn contains 6,10,14-trimethylpentadecan-2-one, nonacosan-2-one, tritriacontan-2-one and hexacosanal all as minor components. The *n*-alkanones are mainly derived from thermal alteration processes. The hexacosanal is a naturally occurring fatty aldehyde from plant wax, which often has the same chain length as the fatty alcohols of the same wax (Kolattukudy *et al.*, 1976).

n-Alkanols

The *n*-alkanols show a C_{range} from 16 to 30, with a C_{max} at 26 and an even carbon number predominance (CPI=11) in the grass soil before burning. In the soil after the burn the *n*-alkanols show a C_{range} from 20 to 30, with a C_{max} at 26 and also an even carbon number predominance (CPI=12). Both of these distributions are similar and likely derived from Ryegrass wax which shows *n*-alkanols as the predominant compound group (Figure V.3). In addition, the *n*-alkanol distribution can be influenced by the degradation of wax esters which can hydrolyze to *n*-alkanols and *n*-alkanoic acids (Tulloch, 1976).

Biomarkers

Molecular biomarkers (i.e., biomarkers) are polycyclic organic compounds which have altered or original chemical structures that can be related to their parent molecule of a biological origin (i.e., natural product, generally terpenoids and steroids). Such molecules are characterized by their restricted occurrence, source specificity, molecular stability and suitable concentration for analytical detection (Mazurek and Simoneit, 1984).

Triterpenoids

Triterpenoids are major biomarker components of gums and mucilages from angiosperms and gramineae. In both soils the major triterpene biomarkers are α-amyrone (I, R = O, for structures cited see Appendix V.I) and β-amyrone (II, R = O), which are present as minor components in comparison with other compound groups. They are derived from the oxidation of the natural products α-amyrin (I, R = OH) and β-amyrin (II, R = OH), respectively, which are also major components in

Ryegrass wax. Ryegrass wax also contains the related triterpenes 18α(H)-oleana-2,12-diene, 18β(H)-oleana-2,12-diene, ursana-2,12-diene and ursana-2,6,12-triene (Table V.2) as minor components.

Phytosterols

The phytosterols are generally comprised of C_{28} and C_{29} compounds and are constituents of plant lipid membranes and waxes (Goad, 1977). The grass field soil before the burn contains β-sitosterol (III) as a major biomarker, with campesterol and stigmasterol (IV) as minor components. These compounds are also significant components in Ryegrass wax, which supports this input to the soil. However, soil algae and fungi also produce these compounds (Weete, 1974, 1976). This soil also contains minor amounts of oxidation derivatives which include cholest-4-en-3-one (V), stigmasta-3,5-diene-7-one (VI) and the aromatization product 24-ethyl-4-methyl-19-norcholesta-1,3,5(10)-triene (VII). In comparison, the grass field soil after the burn contains β-sitosterol (III) as a major component, with stigmasterol (IV), campesterol, stigmast-4-en-3-one (VIII), and stigmasta-3,5-dien-7-one (VI) present as minor components. It appears that burning does not significantly alter the phytosterol composition in soils. They are mostly unchanged natural products or are only minimally altered by thermal processes which suggests that they tend to remain as internal lipid components of wildfire ash residues.

Monosaccharides

The thermal degradation of cellulose biopolymer produces the 1,6-anhydride of glucose called levoglucosan (IX) as a major product (Shafizadeh, 1984). Levoglucosan has been previously reported in biomass burning and atmospheric particles (Hornig *et al.*, 1985; Locker, 1988; Simoneit *et al.*, 1999). It is present as a minor component in the grass field soil before the burn and appears to be preserved from previous (~5 years) prescribed burning of the grass straw and stubble. Open

field burning of grass straw and stubble after the grass seed harvest has been a common agricultural practice in the Willamette Valley, Oregon since the late 1940s and is used for control of disease and disposal of residue (Young *et al.*, 1994). Levoglucosan is also present as a minor component in the soil after burning, but not in grass wax.

Chlorinated Compounds

Synthetic chlorinated compounds are common constituents in agricultural soils due to their widespread application as pesticides and strong ability to persist in the environment. The major chlorinated compounds identified as minor components in the grass field soil before burning include chlordane ($C_{10}H_6Cl_8$), nonachlor ($C_{10}H_5Cl_9$), methoxychlor ($C_{16}H_{15}Cl_3O_2$), and 1,1-dichloro-2,2-di(4'-chlorophenyl)ethylene or p,p'-DDE ($C_{14}H_8Cl_4$). DDE is derived from the dehydrochlorination of DDT, an agricultural insecticide once widely applied in the United States. Various other alteration derivatives were also present as minor components, however, their exact identifications were not made. Chlorinated compounds were not detected in the soil after burning which is likely due to their loss by thermal degradation and direct volatilization to the atmosphere during open field burning. The plowing of the field after the final grass seed harvest (~5 year grass stands) is the principal mechanism by which chlorinated compounds, specifically DDT and DDE, are reintroduced into the upper layer of soil, where they are later vaporized to the atmosphere by field burning.

Prairie Soil After Wildfire

The GC-MS TIC traces of the extract of a prairie soil after a wildfire is shown in Figure V.4. The total extract shows saturated and unsaturated *n*-alkanoic acids, *n*-alkanols and phytosterols as the predominant compound groups. The *n*-alkanes, levoglucosan (IX) and phytosterols are also present, however, as minor compounds.

The *n*-alkanes show a C_{range} from 25 to 35, with C_{max} at 31 and a strong odd carbon number predominance (CPI=10.3). In comparison with Ryegrass wax, the *n*-

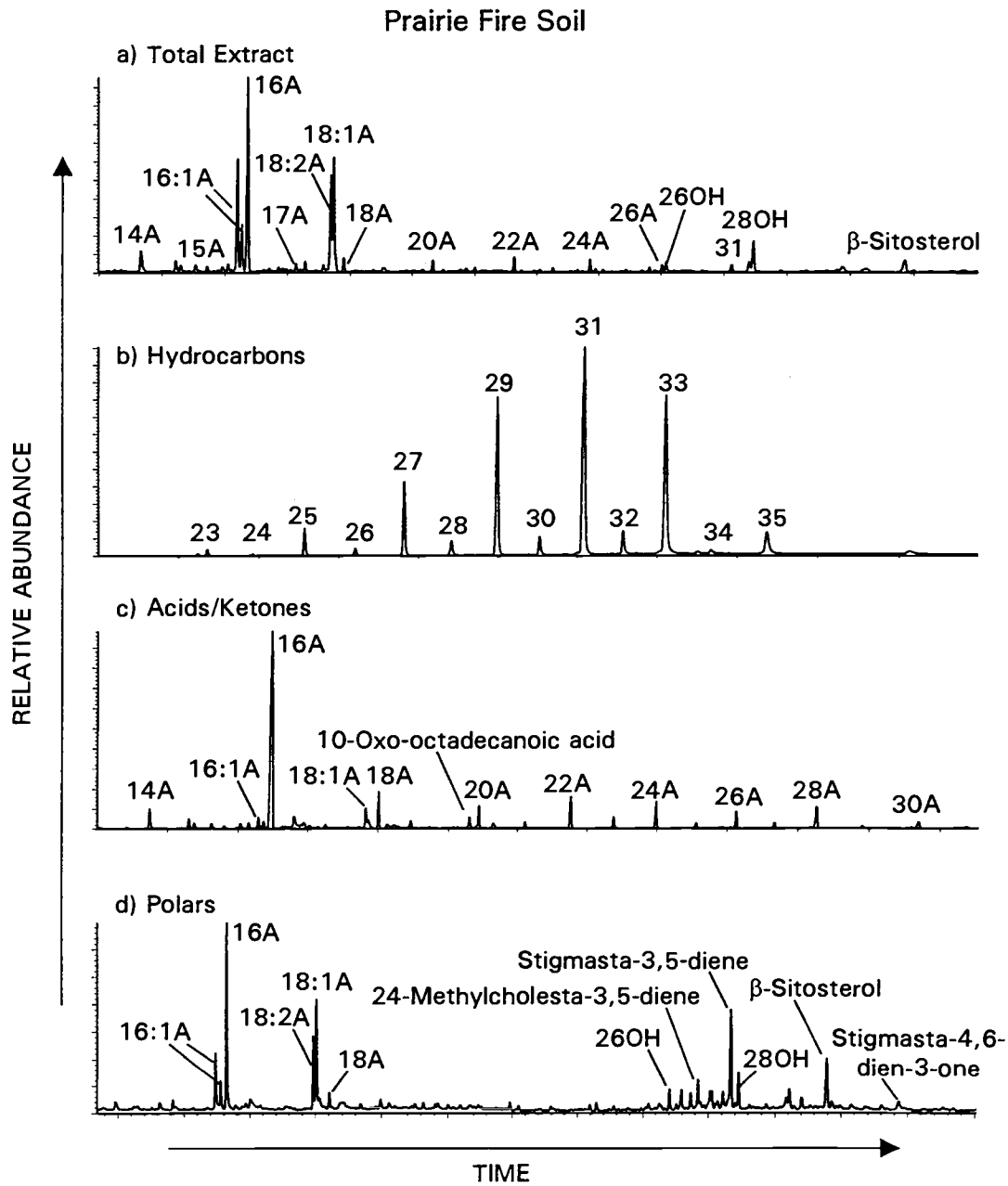

Figure V.4. GC-MS total ion current traces of Prairie Fire Soil (abbreviations as in Fig. V.1).

alkane distribution indicates a strong contribution from grass waxes. This prairie area has accumulated grass litter for numerous years prior to the fire, thus resulting in higher concentrations of lipid tracers.

The *n*-alkanoic acids show a C_{range} from 14 to 30, with C_{max} at 16 and an even carbon number predominance (CPI=11.3). The strong CPI reflects the high level of organic matter that is produced and preserved in grassland soils. The unsaturated *n*-alkenoic acids, $C_{16:1}$, $C_{18:1}$ and $C_{18:2}$, are also present as major components and represent primary unweathered lipids.

The *n*-alkanols range from C_{15} to C_{28} with a C_{max} at 28. Pentadecanol is likely derived from lower plants, fungi, spore waxes or wax esters (Jaffé *et al.*, 1996). The prairie soil contains β-sitosterol as a major component and campesterol and stigmasterol as minor components, as is the case for the prior soil samples. Several thermal alteration derivatives from phytosterol are present and include stigmasta-3,5-diene as a significant component and minor stigmasta-4,6-dien-3-one, 24-ethylcholest-5-ene, 24-methylcholesta-3,5-diene and 24-ethylcholesta-3,22-diene.Levoglucosan is present as a minor component derived from the thermal alteration of cellulose and is deposited on the soil during wildfire burning (Simoneit *et al.*, 1999). The distributions and abundances of homologous series, biomarkers and their alteration products are similar to those observed for both Ryegrass field soils and Ryegrass wax. This shows that grasses impart their chemical fingerprint to soils by their high rate of primary production. Additionally, the physical nature of the Dayton type soils, which are poorly drained, further contribute to organic matter concentration and preservation.

The major tracers identified for the grass and prairie soils after burning include C_{16} and C_{18} *n*-alkanoic acids, C_{25} to C_{33} *n*-alkanes and the C_{26} *n*-alkanol. The major biomarker tracers include the triterpenoids α-amyrone and β-amyrone, the phytosterols β-sitosterol and stigmasterol, and levoglucosan. These tracers represent the characteristic background signature from burning of grasses. They also comprise the bulk of the organic components in grassland soils where both natural and burned organic matter is deposited.

Mixed Forest/Chaparral Soil After Wildfire Burning and Forest Litter

Soil and Douglas fir litter were collected from a mixed forest/chaparral biome in Whitmore, CA. Three years before sampling a wildfire burned the area, thus the soil should contain both natural components derived primarily from the overlaying vegetation and thermal alteration derivatives from the wildfire.

Total Extracts

The GC-MS TIC traces for the extracts of Whitmore fire soil and Douglas fir litter are shown in Figures V.5 and V.6, respectively. Analytical data for the homologous series distributions (CPI, C_{range} and C_{max}) are given in Table V.1. The total extract of Whitmore fire soil contains saturated and unsaturated *n*-alkanoic acids, ω-hydroxyalkanoic acids, *n*-alkanols, diterpenoids and phytosterols as the predominant compound groups. There are minor amounts of sesquiterpenes, methoxyphenols derived from lignin alteration, levoglucosan from cellulose, and a series of alkylthiophenes which are likely derived from soil microbial processes. The total extract of Douglas fir litter contains *n*-alkanoic acids, ω-hydroxyalkanoic acids, *n*-alkanols, diterpenoids and phytosterols as the predominant compound groups. The similarity in total extract compositions and comparison with the Douglas fir wax composition show that conifers are the principal source of organic tracers in forest soils.

The *n*-alkanes in forest soil show a C_{range} from 15 to 35, with a C_{max} at 29 and a low odd carbon number predominance (CPI=2.5), which reflects an input from epicuticular wax sources and subsequent alteration. The low CPI indicates that both *n*-alkane alteration by burning and biodegradation have occurred in this soil. In the Douglas fir litter the *n*-alkanes show a C_{range} from 21 to 33, with a C_{max} at 29 and a strong odd carbon number predominance (CPI=6.1). This distribution is in agreement with the *n*-alkanes isolated from Douglas fir epicuticular waxes which have a C_{max} at 29 and CPI=7.4 (Oros *et al.*, 1999). The *n*-alkanoic acids in the forest

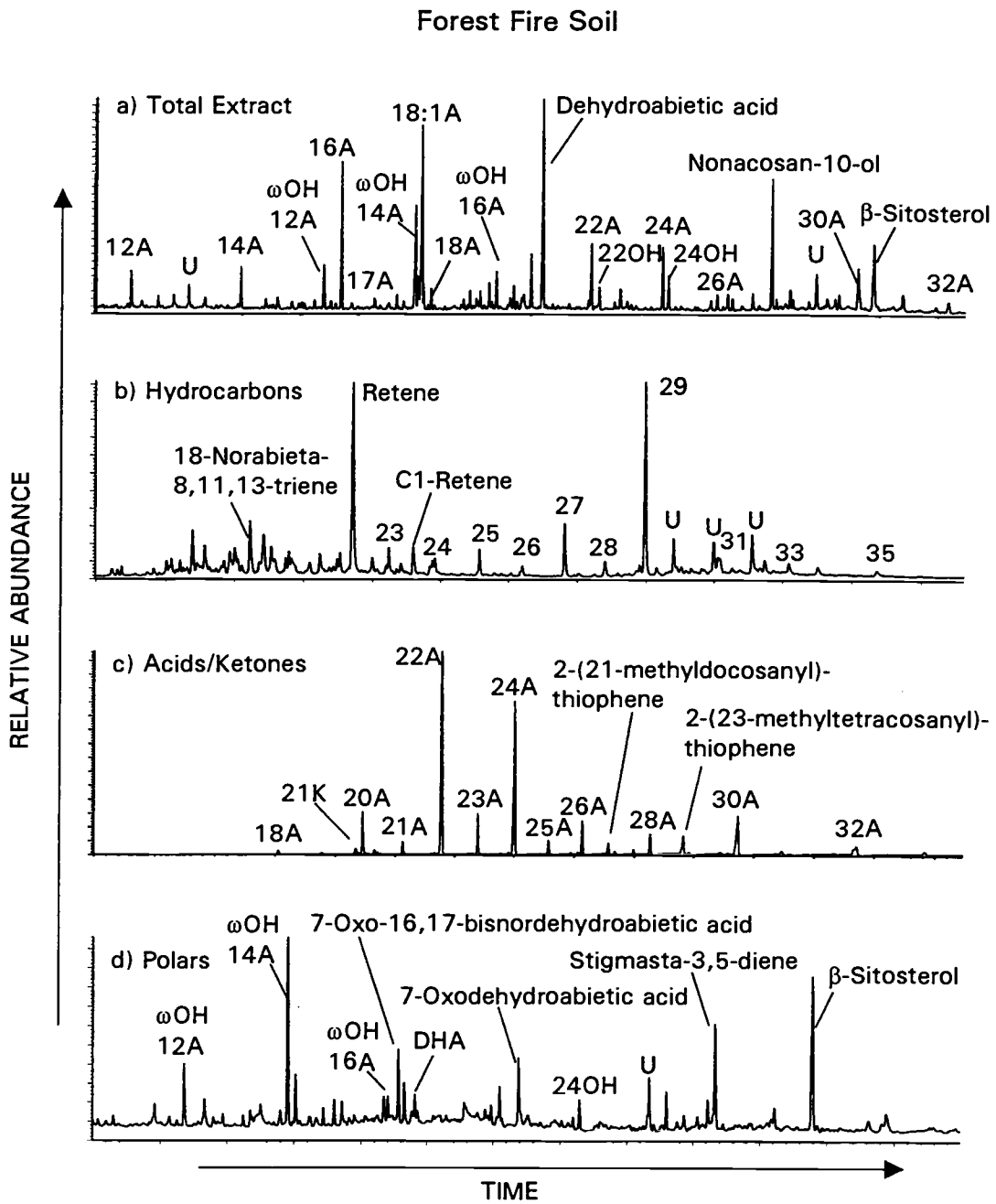

Figure V.5. GC-MS total ion current traces of Forest Fire Soil (abbreviations as in Fig. V.1).

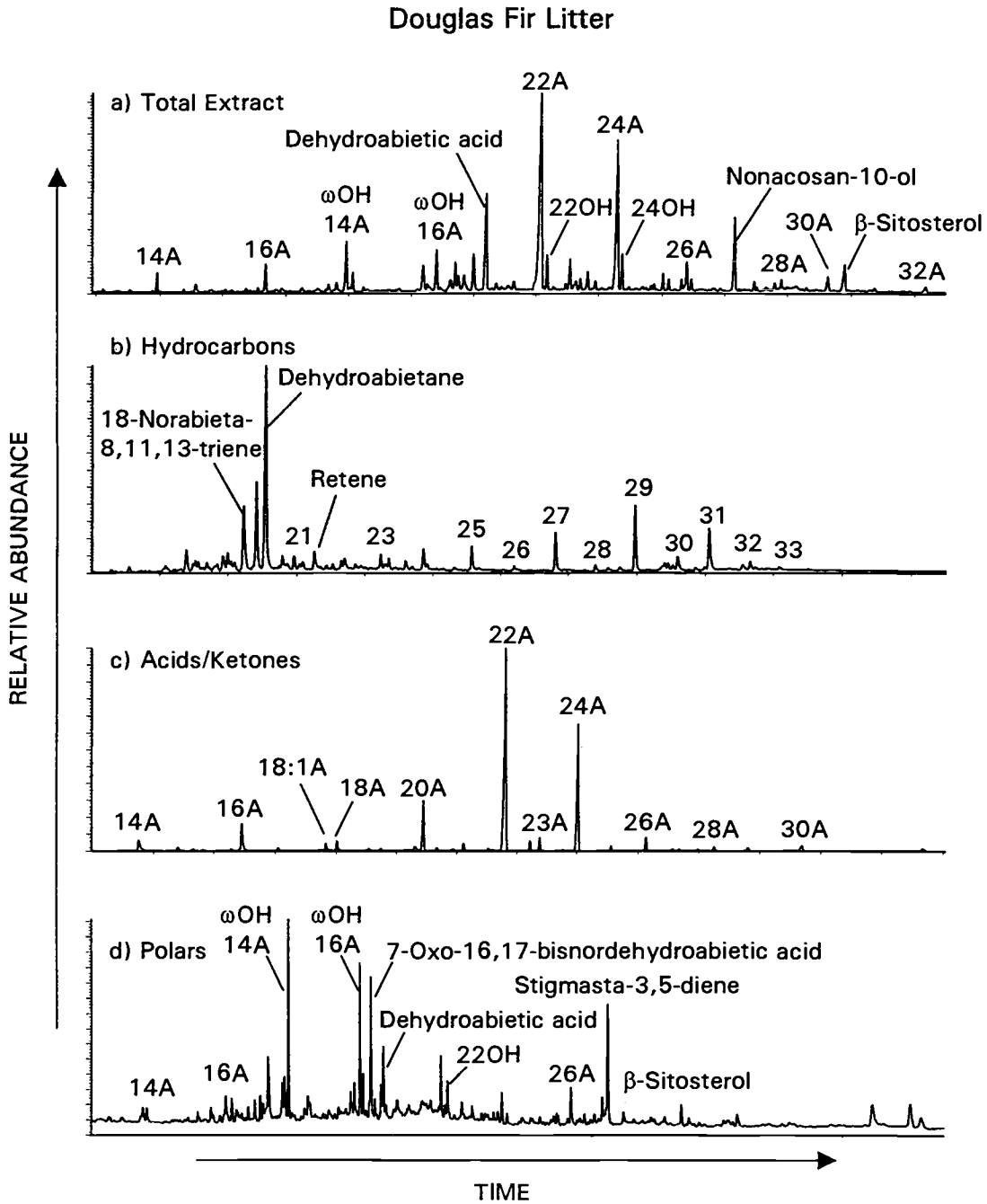

Figure V.6. GC-MS total ion current traces of Douglas Fir Litter (abbreviations as in Fig. V.1).

soil have a C_{range} from 12 to 32, with a C_{max} at 16 and an even carbon number predominance (CPI=4.3). In comparison, the *n*-alkanoic acids in Douglas Fir litter range from C_{14} to C_{32}, with a C_{max} at 22 and a stronger even carbon number predominance (CPI=12). The *n*-alkanoic acids are the predominant compound group for both samples. Both samples also contain a series of ω-hydroxyalkanoic acids as major components, which range from C_{12} to C_{22} with a C_{max} at 14, and are derived from structural polyester biopolymers of vegetation (Simoneit and Mazurek, 1982). They have been identified previously in gymnosperm cutin (Caldicott and Eglinton, 1973; Tulloch, 1976) and more recently in Douglas fir epicuticular waxes where they show a similar distribution (Oros *et al.*, 1999).

A series of *n*-alkan-2-ones ranging from C_{21} to C_{31} with a C_{max} at 21 and an odd carbon number predominance (CPI=10.1) is present as minor components in the forest fire soil. The *n*-alkan-2-ones have been identified previously in a garden soil (C_{range} from 19 to 35, with C_{max} at 25 and 33) and a peat (C_{range} from 17 to 33, with C_{max} at 25 and 27) where they showed similar distribution patterns (Morrison and Bick, 1966). This suggests that the *n*-alkan-2-ones are possibly oxidation products derived from microbial metabolic processes. The *n*-alkan-2-ones have also been shown to derive from the combustive alteration of aliphatic moieties and/or alkanes (Lief *et al.*, 1992). They are not present in the Douglas fir litter or in the wax of Douglas fir.

Both samples contain major amounts of *n*-alkanols which range mainly from C_{12} to C_{24} as even carbon number homologs with a C_{max} at 22. Alkanols are common constituents of conifer epicuticular waxes (Oros *et al.*, 1999). Minor low molecular weight *n*-alkanols ($<C_{16}$) are present, which suggests that lower plant, mycorrizhal fungi, spore waxes and wax esters from bacterial hydrolysis may be their potential sources (Jaffé *et al.*, 1996). In contrast to the primary alcohols, the free secondary alcohol *n*-nonacosan-10-ol is found as a major component in both Douglas fir litter and the forest fire soil. This compound has been identified previously as a major component in epicuticular waxes from both gymnosperms (Tulloch, 1976, 1987; Schulten *et al.*, 1986) and angiosperms (Gülz *et al.*, 1992).

Biomarkers

The major biomarkers identified in the forest fire soil and Douglas fir litter are diterpenoid and phytosterol natural products and their thermal alteration derivatives (Table 3). The forest fire soil also contains minor sesquiterpenes and a triterpene derivative.

Cadalene, calamenene and eudalene, derivatives from sesquiterpenoid natural products, are present as minor components in the forest fire soil. Sesquiterpenoids are major constituents of resins and essential oils and have been characterized for many higher plants (Simonsen and Barton, 1961; Hanson, 1977 to 1982). Their presence in the soil may indicate a thermal origin and entrapment with other fire detritus.

Diterpenoids are important biomarker constituents of many higher plants, especially in conifer resins (Barrero *et al.*, 1991; Erdtman *et al.*, 1968; Mazurek and Simoneit, 1997; Riffer *et al.*, 1969; Simoneit, 1986, 1998; Simoneit *et al.*, 1993, 1998; Zinkel and Magee, 1987). The forest fire soil contains diterpenoid biomarkers as major components. They are primarily oxygenated and aromatic products with the major compound identified as dehydroabietic acid (X). Dehydroabietic acid has been proposed previously as a candidate tracer compound for coniferous wood combustion (Rogge *et al.*, 1998; Simoneit *et al.*, 1993; Standley and Simoneit, 1994). In addition, minor amounts of retene, C_1-retene, 18-norabieta-8,11,13-triene (XI), 18-norabieta-4,8,11,13-tetraene, 19-norabieta-4(18),8,11,13-tetraene, 7-oxo-16,17-bisnordehydroabietic acid, 7-oxodehydroabietic acid (XII) and dehydroabietane (XIII) are found. All are thermal alteration derivatives of the natural product precursor abietic acid. Dehydroabietane and 7-oxo-dehydroabietic acid may also be derived from biodegradation of resin acids (Biellmann and Wennig, 1971). Several thermal alteration derivatives from the pimarane natural product skeleton (e.g., from pimaric acid) are present as minor components and include pimanthrene, pimara-8,15-diene (XIV) and isopimara-7,15-diene (XV). The abundances of the diterpenoids indicate a major input from conifers and the thermal alteration derivatives of diterpenoids confirm a residue from burning of conifers. The diterpenoid composition for the Douglas fir litter is similar, however, it has low concentrations of thermally altered products and enhanced amounts of

oxidation/microbial alteration products, including abieta-6,8,11,13-tetraenoic acid, 7-oxo-16,17-bisnordehydroabietic acid, pimaric acid, and isopimaric acid.

An alteration pathway from precursor to final product may be achieved through either biological and/or thermal processes. Diterpenoids with the abietane skeleton can follow a pathway which commences with the dehydrogenation of abietic acid to dehydroabietic acid followed by decarboxylation to dehydroabietin and full aromatization to retene (Simoneit, 1998). In addition, a previously determined precursor to product reaction pathway under thermal conditions shows that dehydroabietane may dehydrogenate to simonellite and then to retene (Standley and Simoneit, 1994). Retene has previously been proposed as a tracer for conifer combustion sources (Ramdahl, 1983). Microbial alteration also oxidizes the precursors to aromatic and 7-oxo derivatives (Biellmann and Wennig, 1971; Tavendale *et al.*, 1997).

The triterpenoid biomarker A-neoursa-3(5),12-diene (XVI) is present as a minor component in forest soil. It is a thermal alteration derivative from the triterpenoid natural product α-amyrin and its presence indicates a minor organic matter contribution from an angiosperm source.

The forest soil contains β-sitosterol (III) as the major phytosterol biomarker and campesterol as a minor component. Of the thermal alteration derivatives, stigmasta-3,5-diene is the major component while stigmasta-4,6-diene, stigmast-4-en-3-one (V), stigmasta-3,5-dien-7-one (VI), 5α(H)-24-ethylcholest-2-ene and 24-ethyl-4-methyl-19-norcholesta-1,3,5(10)-triene (VII) are minor components. Stigmasta-3,5-dien-7-one (VI), may be a thermal or microbial oxidation derivative from the natural product β-sitosterol. The phytosterol thermal alteration derivatives can be used as general indicators and tracers for burning of higher plant biomass (Simoneit, 1989, 1998; Simoneit *et al.*, 1993).

The major phytosterols in Douglas fir litter are β-sitosterol (III) and stigmasta-3,5-diene. The phytosterol thermal aromatization product 24-ethyl-4-methyl-19-norcholesta-1,3,5(10)-triene (VII) is present as a trace component.

Levoglucosan is found as a minor component in both the forest fire soil and the Douglas fir litter. It is a specific tracer for burning of vegetation cellulose and was deposited with ash from wildfire burning.

Methoxyphenolic compounds are present as minor components in the forest fire soil but not in the Douglas fir litter. The methoxyphenols identified are vanillin (XVII), isovanillic acid, vanillic acid (XVII, R = OH) and acetosyringone (XVIII). These compounds are primarily pyrolysis products derived from the thermal degradation of lignin biopolymer in plants. The phenol substitution (i.e., 3-methoxy-4-hydroxy) pattern is consistent with an origin from gymnosperms (Simoneit *et al.*, 1993). The acetosyringone indicates a minor input from angiosperm lignin (Simoneit *et al.*, 1993). These methoxyphenols have previously been proposed as biomarker tracers for burning of wood (Hawthorne *et al.*, 1988; Simoneit *et al.*, 1993).

The forest fire soil contains a series of branched alkylthiophenes (XIX) which include 2-(21-methyldocosanyl)thiophene, 2-(23-methyltetracosanyl)thiophene, 2-(25-methylhexacosanyl)thiophene and 2-(27-methyloctacosanyl)thiophene. The alkylthiophenes are likely derived from the selective intermolecular incorporation of inorganic sulfur species into functionalized lipids such as fatty acids or alkenes by soil bacteria or fungi (Sinninghe Damsté *et al.*, 1989).

Soil Erosion After Wildfire

Total Extracts

The GC-MS TIC traces extracts from Kanan Canyon (mud) and Paseo Canyon (silt) soils both containing wildfire residues which were subjected to rain and subsequent erosion transport, respectively, are shown in Figures V.7 and V.8, respectively. Analytical data for the homologous series distributions (CPI, C_{range} and C_{max}) are given in Table V.1. The total extract of the Kanan Canyon soil shows saturated and unsaturated *n*-alkanoic acids and *n*-alkanes as the predominant compound groups, with *n*-alkanols and phytosterols as minor components. The total extract of the Paseo Canyon soil shows *n*-alkanes, *n*-alkanoic acids, *n*-alkanols, phytosterols and triterpenoids as the predominant compound groups. Both distributions indicate a significant input of plant organic matter to these soils.

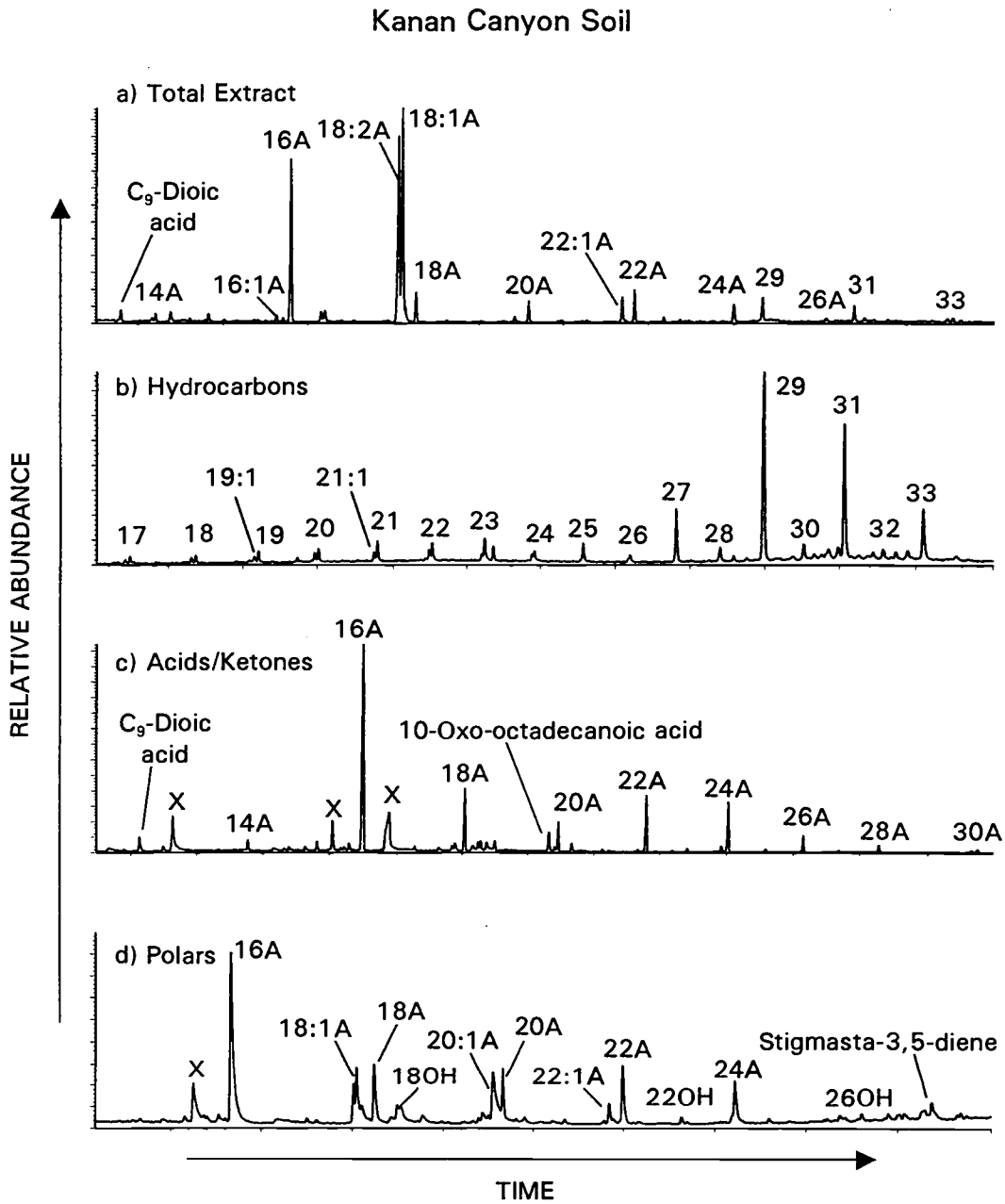

Figure V.7. GC-MS total ion current traces of Kanan Canyon Soil (abbreviations as in Fig. V.1).

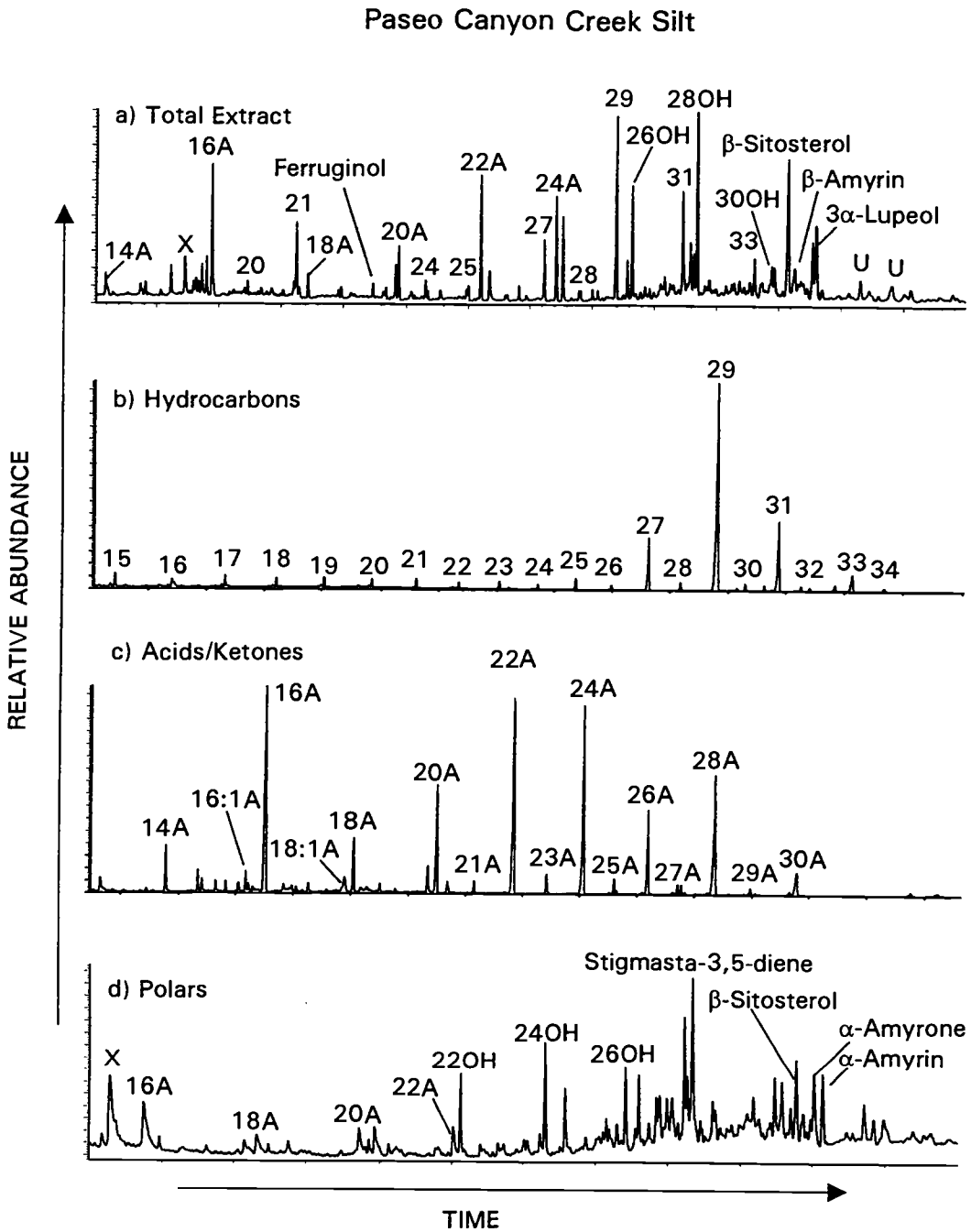

Figure V.8. GC-MS total ion current traces of Paseo Canyon Creek Silt (abbreviations as in Fig. V.1).

Aliphatic Compounds

The *n*-alkanes in both samples range from C_{13} to C_{33}, with a C_{max} at 29. The alkanes of the Kanan Canyon soil have a CPI=5.2 while those for the Paseo Canyon soil have a CPI=8.0. The distributions indicate that the *n*-alkanes are derived from a mixed plant source. In comparison, the lower CPI in Kanan Canyon soil indicates that the *n*-alkanes have been selectively degraded by thermal or microbial processes.

The *n*-alkanoic acids of the Kanan Canyon soil have a C_{range} from 14 to 30, with a C_{max} at 16 and a strong even carbon number predominance (CPI=20). In Paseo Canyon soil the *n*-alkanoic acids have a similar range and the same C_{max} with even carbon number predominance (CPI=13). The *n*-alkenoic acids $C_{18:1}$ and $C_{18:2}$ are present as major components in Kanan Canyon soil while $C_{16:1}$ *n*-alkenoic acid is minor. Paseo Canyon soil contains no $C_{18:2}$ and both $C_{16:1}$ and $C_{18:1}$ *n*-alkenoic acids are minor components. On comparison, the similarity in distributions suggest that the *n*-alkanoic acids and *n*-alkenoic acids have similar biological sources and the lower alkenoic acid content of the Paseo Canyon sample reflects oxidation during longer distance transport from the source.

Kanan Canyon soil contains α,ω-nonanedioic acid as a minor component. The α,ω-alkanedioic acids have been identified from a variety of sources and in the environment (Abas *et al.*, 1995; Rogge *et al.*, 1993b; Simoneit, 1989; Simoneit and Mazurek, 1982; Stephanou and Stratigakis, 1993) and have previously been proposed as thermal oxidation products of ω-hydroxyalkanoic acids from polyester biopolymers of vegetation (Simoneit and Mazurek, 1982). The α,ω-nonanedioic acid may also be an oxidation product from $C_{18:1}$ alkenoic acids (Kawamura and Gagosian, 1987; Stephanou, 1992). The α,ω-nonanedioic acid is probably not retained in the Paseo Canyon sample because of its water solubility during erosional transport.

The *n*-alkanols of Kanan Canyon soil range from C_{18} to C_{26}, with C_{max} at 22, while Paseo Canyon soil has a range from C_{16} to C_{30}, with C_{max} at 24. Low molecular weight *n*-alkanols ($<C_{16}$) were not detected in these samples which suggests that lower plants, fungi, spore waxes, and wax esters are not major contributors of organic matter.

Biomarkers

Triterpenoid biomarkers are present as major components in Paseo Canyon soil and minor in Kanan Canyon soil. The triterpenoids present in both samples include α-amyrin (I, R=OH), β-amyrin (II, R=OH), α-amyrone (I, R=O), β-amyrone (II, R=O) and 3α-lupeol (XX). In addition, Kanan Canyon soil contains lupa-2,22-diene (XXI).

Stigmasta-3,5-diene is the major component derived from phytosterols in Kanan Canyon soil, while β-sitosterol (III), stigmasta-3,5-dien-7-one (VI), 3-methoxystigmast-22-ene, stigmasta-4,6-diene, β-sitoster-2-ene and 24-ethyl-4-methyl-19-norcholesta-1,3,5(10)-triene (VII) are all minor components. The Paseo Canyon soil contains β-sitosterol and stigmasta-3,5-diene as major components, while cholesterol, stigmasta-3,5-diene-7-one and 24-ethyl-4-methyl-19-norcholesta-1,3,5(10)-triene are minor. The presence of cholesterol (C_{27}) indicates a contribution from animal or aquatic plant organic matter to this sample. The C_{27} structures (e.g., cholesterol) generally dominate the sterol composition of aquatic plants (algae), whereas the C_{29} compounds (e.g., sitosterols) constitute the majority of the sterols in land plants (Volkman, 1986).

Comparisons of Natural, Burn and Water Washed Soil Compositions

Homologous Compounds

The distributions and abundances of homologous compound series and biomarkers in litter and soil samples are dependent on origin, extent of thermal alteration, oxidative degradation, and microbial and fungal metabolism. The abundances (% relative to total GC signal, equivalent to lipids) of the major compound groups are shown in Table V.2 for all samples. The mean distribution for

the major compound groups is as follows: *n*-alkanoic acids (48%) > *n*-alkanes (18%) > *n*-alkanols (15%) > phytosterols (6%). All other compound groups are minor (<5%).

The mean of the abundances (%) of the four major compound groups for natural (n=3), burned (n=3) and rain/river washed (n=2) burn samples are shown in Figure V.9. The mean distribution for natural samples is as follows: *n*-alkanoic acids (36%) > *n*-alkanols (26%) > *n*-alkanes (16%) > phytosterols (7%). This distribution reflects the biochemically determined ratio from fresh and/or only mildly degraded plant organic matter. The abundances of the major compound groups in both burned and rain and river washed burn samples are lower than the natural sample distributions, and thus reflect the degree of organic matter alteration imparted from both thermal and biological processes.

Table V.2. Abundances (% relative to total GC response) of the major compound groups.

Compound Group	Ryegrass field soil (before burn)	Ryegrass field soil (after burn)	Rye-grass wax	Grassland fire soil	Whitmore fire soil	Douglas Fir litter	Kanan Canyon soil	Paseo Canyon soil
n-Alkanoic Acids	40.8	22.2	6.4	90.1	50.1	61.9	90.5	23.6
n-Alkanes	7.6	61.5	40.1	1.9	1.0	1.0	5.20	25.2
n-Alkanols	30.5	9.9	41.2	7.2	6.9	6.3	0.8	20.5
Phytosterols	8.8	1.5	9.8	0.7	9.8	2.9	1.30	13.6
Diterpenoids	bd	bd	bd	bd	14.4	17.2	bd	0.5
ω-OH-Alkanoic Acids	bd	bd	bd	bd	13.9	9.9	bd	bd
Triterpenoids	bd	0.9	2.5	bd	bd	bd	1.2	15.0
Methoxyphenols	11.1	bd	bd	bd	2.7	0.7	0.8	bd
Carbonyls	0.2	3.2	bd	bd	0.8	bd	bd	1.4
Monosaccharides	1.0	0.1	bd	0.1	0.4	0.1	bd	bd
n-Alkenes	bd	0.7	bd	bd	bd	bd	0.2	bd
Wax Esters	bd	bd	bd	bd	bd	bd	bd	0.2
PAH	bd	bd	bd	bd	bd	bd	bd	bd
Total	100	100	100	100	100	100	100	100

bd: below minimum detection limit (10ng/μl)

Alternatively, the abundances above the natural sample distributions can derive from the release or decomposition of other organic compounds, which are deposited to soil surfaces as components of char and heavy particulate matter during wildfire and prescribed burning. The mean distribution for the burn samples is as follows: *n*-alkanoic acids (54%) > *n*-alkanes (28%) > *n*-alkanols (8%) > phytosterols (4%). In comparison with the natural samples, the *n*-alkanoic acids and *n*-alkane abundances increase in soil after burning which is likely due to their release and formation from heavy organic matter. The *n*-alkanol abundance decreases which can be ascribed to both selective thermal dehydration and microbial degradation. The phytosterol biomarker abundances also decrease due to thermal degradation processes.

The distribution of the four major compound groups in rain and river washed burn samples is as follows: *n*-alkanoic acids (57%) > *n*-alkanes (15%) > *n*-alkanols (11%) > phytosterols (8%). These samples contain characteristics of both natural (e.g., similar *n*-alkane and phytosterol abundances) and burn (e.g., similar *n*-alkanoic acid and *n*-alkanol abundances) samples. In comparison with the burn samples, the *n*-alkanoic acids, *n*-alkanols and phytosterols all increase in abundance. This may be due to enhanced concentration effects based on aqueous solubility. The *n*-alkanes decrease in abundance which is possibly due to selective microbial degradation and physical removal based on their lower aqueous solubility, because of their hydrophobic nature.

Major Biomarker Tracers

The major biomarkers to be applied as potential tracers for soil organic matter are primarily natural products and their alteration derivatives (Table V.3). The phytosterols which are proposed as tracers for soil containing vascular plant organic matter include β-sitosterol, campesterol and stigmasterol, which are constituents of plant lipid membranes and waxes. Cholesterol may be useful for soils with algal and faunal detritus. Of the phytosterol alteration derivatives the proposed tracers for soil are 24-ethyl-4-methyl-19-norcholesta-1,3,5(10)-triene, stigmasta-3,5-diene and stigmasta-4,6-diene. Their presence suggests that alteration is mediated primarily by thermal processes. Stigmasta-3,5-dien-7-one may be an oxidative or microbially altered product in soils.

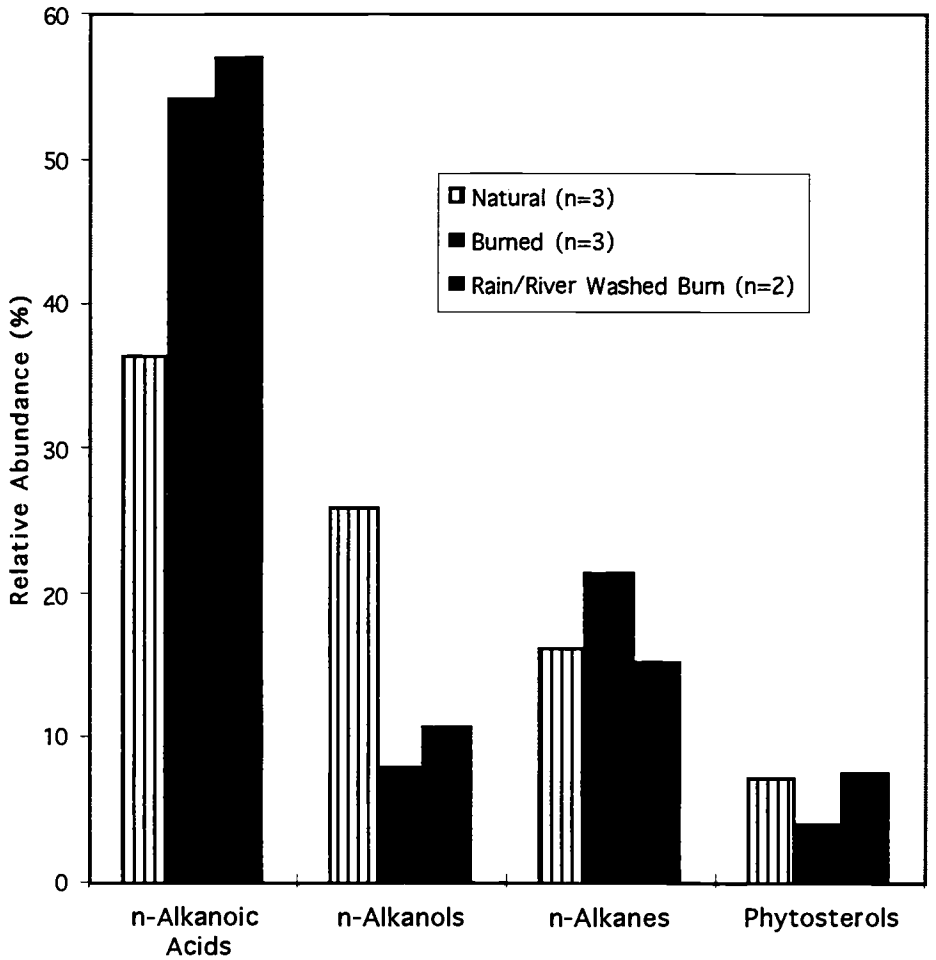

Figure V.9. Bar plot showing the distributions and relative abundances (mean %) of the four major compound groups for natural, burned and rain/river washed burn samples.

Table V.3. Biomarkers identified in natural, burned and rain/river washed samples.

Compound Group	Compound Name	Source[1]
Phytosterols	β-Sitosterol	1,2,3,4,5,6,7,8
	24-Ethyl-4-methyl-19-norcholesta-1,3,5(10)-triene	1,5,6,7,8
	Stigmasta-3,5-diene	4,5,6,7,8
	Campesterol	1,2,3,4,5
	Stigmasta-3,5-dien-7-one	1,5,7,8
	Stigmasterol	1,2,3,4
	Stigmasta-4,6-diene	4,5,7
	Stigmasta-4-en-3-one	2,5
	Cholesterol	2,8
	Stigmasta-4,6-dien-3-one	2,4
	24-Ethylcholest-5-ene, 24-Ethylcholesta-3,22-diene, 24-Methylcholesta-3,5-diene	4
	24-Methylcholestan-3β-ol, Stigmastanol	2
	Cholest-7-en-3-ol, Neoergosterol	2
	3-Methoxystigmast-22-ene, β-Sitoster-2-ene	7
	5α(H)-24-Ethylcholest-2-ene	5
	Cholest-4-en-3-one	1
Triterpenoids	α-Amyrin, β-Amyrin	1,2,3,7,8
	α-Amyrone, β-Amyrone	1,2,7,8
	3α-Lupeol	7,8
	18α(H)-Oleana-2,12-diene, 18β(H)-Oleana-2,12-diene	3
	Ursana-2,12-diene, Ursana-2,6,12-triene	3
	Lup-2,22-diene	7
	A-Neoursa-3(5),12-diene	5
Diterpenoids	Dehydroabietane, Isopimara-7,15-diene, Dehydroabietic acid	5,6
	Abieta-6,8,11,13-tetraenoic acid, 18-Norabieta-8,11,13-triene	5,6
	18-Norabieta-4,8,11,13-tetraene, 7-Oxo-16,17-bisnordehydroabietic acid	5,6
	Pimaric acid, Isopimaric acid, Pimara-8,15-diene	6
	Retene, C_1-Retene, 19-Norabieta-4(18),8,11,13-tetraene	5
	7-Oxodehydroabietic acid, Pimanthrene	5
	Ferruginol	8
Monosaccharide	Levoglucosan	1,2,4,5,6
Methoxyphenols	Vanillin, Isovanillic acid	5
	Vanillic acid, Acetosyringone	5
Sesquiterpenes	Cadalene, Calamenene, Eudalene	5
Alkylthiophenes	2-(21-Methyldocosanyl)thiophene, 2-(23-Methyltetracosanyl)thiophene, 2-(25-Methylhexacosanyl)thiophene	5
Other	α-Tocopherol	2

[1]: 1=Ryegrass field soil (before burn); 2=Ryegrass field soil (after burn); 3=Ryegrass wax; 4=Grassland fire soil; 5=Whitmore fire soil; 6=Douglas fir litter; 7=Kanan Canyon soil; 8=Paseo Canyon creek silt.

The triterpenoids which are proposed as potential biomarker tracers for soil include α-amyrin, β-amyrin and 3α-lupeol. They are major constituents of angiosperms. The triterpenoid derivatives from thermal alteration (burning) and proposed as tracers are mainly α-amyrone and β-amyrone.

The diterpenoid tracers proposed for soil from conifer forests are alteration derivatives from resin components which include dehydroabietic acid, dehydroabietane, 18-norabieta-8,11,13-triene, 18-norabieta-4,8,11,13-tetraene, 7-oxodehydroabietic acid, 7-oxo-16,17-bisnordehydroabietic acid and isopimara-7,15-diene. The diterpenoids are major constituents of gymnosperm resins and the alteration products described here are derived from oxidative and thermal degradation processes.

CONCLUSIONS

The distributions and abundances of homologous compound series and biomarkers in soils are influenced by origin, extent of thermal alteration and bioavailability. The
representative chemical fingerprints imparted to soils show *n*-alkanoic acids > *n*-alkanes > *n*-alkanols > phytosterols > other terpenoids. This distribution may vary slightly between landscapes and biomes depending on the origin (vegetation cover) and physical/chemical characteristics of the soil.

Under wildfire and prescribed burning conditions, the heat intensity, aeration, and duration of smoldering and flaming conditions determine the distributions and ratios of the emitted homologous compound series that are imparted to ash and deposited to soil surfaces. Although the biomarkers are higher molecular weight components, their loss by direct volatilization and sequestration to fine smoke particles during biomass burning is significant (Simoneit *et al.*, 1993, 1999). Such compounds are also shown here to remain as internal lipid components of char and heavy particles which are deposited onto soil during wildfire and prescribed burning. The process of rain erosion and river transport releases some of these internal components into the surroundings where they are further subjected to biological alteration.

The distributions and abundances of homologous compound series coupled with biomarker tracer analysis provides a chemical fingerprint which is useful for identifying the single or multiple plant species contributing organic matter to soils by both thermal (burning) or biological processes. Such a fingerprint is useful for tracking soils that are transported in the atmosphere by wind as suspended particles in dust storms and on land by rain erosion to rivers.

ACKNOWLEDGMENTS

Partial funding of this work by the U.S. Environmental Protection Agency (Grant CR 823990-01-0) is gratefully acknowledged.

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CHAPTER VI

INVESTIGATION OF THE EXTENT AND SIGNIFICANCE OF PETROLEUM HYDROCARBON CONTAMINATION IN CRATER LAKE, CRATER LAKE NATIONAL PARK, OREGON, U.S.A.

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ABSTRACT

In order to evaluate hydrocarbon inputs from anthropogenic and natural sources to Crater Lake water, surface slick and sediment samples were collected and analyzed by gas chromatography-mass spectrometry for determination of their aliphatic and aromatic hydrocarbon concentrations and compositions. Results show that hydrocarbons originate from both natural (terrestrial plant waxes and algae) and anthropogenic (petroleum use) sources and are entering the lake through direct input and atmospheric transport. The distributions and abundances of *n*-alkanes, polycyclic aromatic hydrocarbons (PAH) and unresolved complex mixture from petroleum are similar for all surface slick sampling sites. The levels of PAH in surface slicks range from 7.2-8.5 pg/cm^2 which are low. Transport of hydrocarbons from the lake surface to the sediments has resulted in an accumulation at background levels (petroleum <1440 μg/kg, dry wt.). A comparison of PAH in shallow (40 μg/kg at 5 m depth) and deep (15 μg/kg at 616 m depth) sediments shows that concentrations are lower at depth. In shallow sediments, especially around the boat mooring area, the concentrations of *n*-alkanes (<1440 μg/kg at 5 m depth) exceed the petroleum and natural *n*-alkane concentrations at the other sites which shows that boating activities leave a detectable level of petroleum in lake sediments. The presence of biomarkers such as the tricyclic terpanes, hopanes and steranes further confirms petroleum input to these sediments.

INTRODUCTION

Crater Lake is the deepest lake in the United States and the primary resource feature of Crater Lake National Park. It is one of the clearest bodies of water in the world and attracts tourists and research scientists worldwide. National concern about the clarity of Crater Lake was demonstrated in September 1982 when Congress approved Public Law 97-250 authorizing and directing the Secretary of the Interior to conduct a 10-year limnological study of Crater Lake and to immediately implement such actions as may be necessary to retain the lake's natural pristine water quality.

Because Crater Lake has no surface outlet, it may be particularly susceptible to anthropogenic pollution inputs. The Park Service and its concessionaire currently operate four tour boats, two research boats and three skiffs on Crater Lake. These boats, along with other anthropogenic as well as natural sources, introduce unknown quantities of hydrocarbons into the water, which have unknown effects on the lake ecosystem. Outboard engines release their oil-enriched exhaust at and beneath the water surface. Particulate matter and volatile combustion products from inboard engine exhaust enter the water directly. Although careful measures are taken to deter all petroleum contamination, small amounts of uncombusted lubricating oil and gasoline are unavoidably introduced into the lake during repairs, fueling and pumping of bilge from engine compartments.

The environmental effects of using marine engines for visitor tours and park operations is an ongoing concern that has not been fully evaluated. Qualitatively, hydrocarbon contamination is not apparent in the lake; limited visible fuel slicks are generally localized around operating boat exhausts. However, research on the levels of hydrocarbons is needed in order to make informed decisions on current and future boat use on Crater Lake. The current concession contract, including the authority to conduct commercial boat tours on Crater Lake, expired in 1997. The level of commercial boat tours will be one issue in developing a new concession prospectus for the next contract.

Petroleum hydrocarbon pollution and contamination of the environment, especially of water bodies such as estuaries and lakes, are of major regulatory concern. Petroleum pollution can be an obvious phenomenon (e.g., crude oil spill), whereas in low-level chronic cases it is not as clearly obvious. For this report, pollution is defined as a consequence of the anthropogenic introduction of substances

in excess of their natural concentrations which results in a detrimental and detectable impact on the environmental system. Contamination is defined as merely an excess of a substance above its natural concentration without a detrimental effect. This distinction is generally evaluated on a case-by-case basis. It is proposed that the present status of Crater Lake should be discussed in terms of minor contamination from petroleum hydrocarbons.

Nevertheless, the concern with petroleum hydrocarbon contamination of water bodies is important. Petroleum is a complex mixture of tens of thousands or more compounds, including low concentrations of the polycyclic aromatic hydrocarbons which impart the carcinogenic and mutagenic properties to the total mixture (Farrington and Meyers, 1975; Farrington, 1980). In addition, the volatile and more water soluble petroleum components cause detrimental effects on fish reproduction and behavior, and on water quality (e.g., Cranwell, 1975). Furthermore, during quantitative analyses for total petroleum hydrocarbon concentrations it is critical to delete the concentrations of the recently biosynthesized or natural hydrocarbons (usually *n*-alkanes from vegetation waxes) which are nondetrimental to the aquatic environment. It should also be emphasized that the polycyclic aromatic hydrocarbons (PAH), which are the primary health concern, can be derived from other thermal combustive processes as major products, besides being present at trace levels in petroleum.

The objective of this investigation is to conduct the first comprehensive assessment of the levels and distribution of petroleum hydrocarbons in Crater Lake water and sediments. Hydrocarbons in the lake can originate from a variety of natural (terrestrial plant waxes, algal productivity, etc.) and anthropogenic (petroleum combustion, biomass burning, etc.) sources and can enter the lake through a variety of pathways (direct input, runoff, long range atmospheric transport, etc.). Samples representative of the different inputs were taken to assess hydrocarbon concentrations and compositions. Below, we present background information summarizing features of the lake which are particularly significant to the hydrocarbon study. More information on the physics, chemistry and biology of the system can be found in Drake *et al.* (1990), Larson *et al.* (1993) and a series of articles recently published in the Journal of Lake and Reservoir Management (Vol. 12, Issue 2, 1996).

BACKGROUND

Crater Lake

Crater Lake National Park

The park entrance at Annie Spring is 76 miles from Medford and 56 miles from Klamath Falls and can be reached by Oregon Highway 62, which is kept open year-round. The park can also be reached from the north by Oregon Highway 138 during the summer season. Park roads lead from the boundaries into the park where they meet the 33-mile Rim Drive encircling the lake. Winter access is maintained only from the south and west on Oregon Highway 62 through the Munson Valley headquarters area and up to the Rim Village area. Road closures, particularly between headquarters and the rim, are common during the winter. Snowmobile use is permitted on the north entrance road between Oregon Highway 138 and the junction with the Rim Drive (NPS, 1984).

The major concentration of visitor facilities are located in the Rim Village on the south rim of the caldera. These include the main interpretive facility, Sinnot Memorial, and most of the service facilities including a cafeteria, lodge and store. The Park Service provides 400 vehicle parking spaces adjacent to Rim Village facilities and near the rim walkways.

Crater Lake National Park is principally a day-use area. Visitation occurs mainly in the summer (June, July, August) with 75% of the people arriving between Memorial Day and Labor Day. Visitation to the park peaks during the month of August and in 1992 the park recorded approximately 140,000 visitors in that month. Winter use, particularly on weekends, consists mainly of regional residents sightseeing. Cross-country skiing and snowshoeing is largely concentrated around park headquarters and the Rim Village, while snowmobiling is restricted to the park road from the north entrance to the caldera rim. Studies have shown that 85% of the visitors remain in the park less than eight hours, 65% less than four hours and that 75% of this visitation occurs during the five-hour period between 10:00 am and 3:00 pm. It is concentrated in the Rim Village facilities each day during the summer (NPS, 1984; 1987). Further update information on the number of vehicles entering the park

has not been provided by the Park Service and was also not found in any public information bulletins or reports on park use.

Climate

Crater Lake National Park is located near the midpoint of the Sierra Cascade Mountain province of the Pacific mountain system. The region is influenced by the Pacific Ocean weather and the majority of the storm fronts that pass the north Pacific Coast each winter (NPS, 1987; Redmond, 1990). Hourly meteorological measurements have been recorded on the caldera rim and on a lake buoy since 1993. During the two year period (Dec. '93-'95), the minimum air temperature on the rim was -14.6°C (5.7°F) and the maximum was 25.8°C (78.4°F), with a mean of 3.2°C (37.7°F). The wind direction is primarily from the SSE (from Medford, OR) with a significant diurnal reversal. Approximately 70% of the annual precipitation falls from November through March as snow, with less than 6% from June through August. Summer rain is usually associated with thunderstorms and can carry significant sediments from the caldera wall into the lake. Annual snowfalls can total over 600 inches (15.2 m) and long-lasting snow depths of 100 to 200 inches (2.5-5.0 m) occur.

Limnology

Crater Lake fills the caldera of Mt. Mazama and has a total surface area of 53.2 km^2 and a volume of 17.3 km^3 (Phillips, 1968). It is situated at an elevation of 1882 m above sea level and is the deepest lake in the United States with two semi-enclosed basins, one in the northeastern portion of the lake (North Basin, 590 m) and the second in the southwestern section of the lake (South Basin, 485m) (Fig. VI.1). It has no surface outlets and water loss is primarily through surface evaporation and seepage, 49% and 51%, respectively (Redmond, 1990). Precipitation input to the lake (247 cm/yr) occurs primarily as snow deposited directly on the lake surface (Redmond, 1990). The residence time of water with respect to precipitation input into

the lake has been estimated at 132 years and the residence time of solutes dissolved in the lake with respect to seepage is 256 years (Collier *et al.*, 1990).

An in depth report on the mixing processes in Crater Lake is given in McManus *et al.* (1993). Thermal stratification of the upper lake begins in the late spring and the seasonal thermocline reaches its maximum gradient from mid-August to late September (Larson, *et al.*, 1993; McManus *et al.*, 1993). The seasonal thermocline presents a temporary barrier to mixing between the surface water layers and the deep lake, however, the overall rate of vertical mixing is remarkably fast for this deep system --2 to 4 years (Crawford and Collier, 1997; McManus *et al.*, 1993; McManus *et al.*, 1996).

Surface water temperatures in late June through September range from 8.8 to 19.2°C, decrease to a minimum value of 3.5°C at a depth of about 300 m, and thereafter temperatures increase slightly with increased depth to a value as high as 3.7°C due to geothermal inputs at the bottom (Collier *et al.*, 1991; Drake *et al.*, 1990). Surface water temperatures in the winter often drop to ~2.5°C as the upper 200 m become well-mixed and reverse stratified.

The concentration of total dissolved solids is ~104 mg/liter and the major ions are well mixed vertically with a slight (3-5%) increase towards the bottom due to hydrothermal inputs (Larson *et al.*, 1996; McManus *et al.*, 1993). The water column is well oxygenated due to rapid vertical mixing coupled with the relatively low flux of organic carbon through the water column (McManus *et al.*, 1996).

Water clarity, as measured by Secchi disk depth, varies seasonally and interannually due to changes in both biotic and lithogenic particles (Larson *et al.*, 1996). The values are among the highest reported for oligotrophic lakes in the world. Clarity appears to be low during periods of rapid snow melt and avalanches (late winter and early spring) as well as after large thunderstorm rainfall. The clearest periods are usually in the early summer. As the seasonal thermocline strengthens, the clarity again decreases due to particle trapping and phytoplankton growth in the epilimnion. The deepest readings reported for the lake were observed recently in 1988 – 34.8 m, 1994 – 40.8 m, 1996 – 40 m, and 1997 – 43.3 and 40.8 m. Although many of the data collected before 1978 report relatively deep observations (Dahm *et al.*, 1990), it is difficult to fully evaluate if there has been a long-term change in lake clarity. This is due to both the limited data collected before 1978 and

the high frequency natural variations which have subsequently been demonstrated by more recent studies (Larson *et al.*, 1996).

Nutrients and Primary Production

The concentrations of nitrate-N are near or below detection limits (1 μg/l) in the upper 200 m of the lake while below these depths the concentrations increase and are typically highest at 550 m (11-17 μg/l). Orthophosphate-P is relatively well mixed vertically, with a slight depletion in the upper lake. Concentrations increase from ~12 μg-P/l at the surface to ~15 μg-P/l in the deep lake. Chlorophyll is found throughout the euphotic zone (0-200 m) with maximum concentrations occurring at depths between 100 and 140 m between late June and the end of September (McIntire *et al.*, 1996). Euphotic zone inventories range from 30-140 mg/m^2 with a mean near 80 mg/m^2. Primary production in this system is nitrogen limited (Larson *et al.*, 1993) and very sensitive to the introduction of new nitrogen from exogenous sources and from exchange with the deep lake reservoir of regenerated nitrate (Collier *et al.*, 1990). Integrated total production ranges from 5-60 mg C/m^2/hr with a mean value near 35 mg C/m^2/hr.

Natural Hydrocarbon Sources

Terrestrial

Crater Lake is an ultra-oligotrophic lake, thus natural hydrocarbon contributions to the water column and surface are mainly from atmospheric input of detritus from higher plants. The primary hydrocarbons contributed by terrestrial vascular plants can include high molecular weight epicuticular waxes (i.e., lipids, on leaves and needles), terpenes (bark and tree resins) and other particles containing lipids (spores, pollen, etc.). Lipids derived from higher plants may be characterized by a number of features as follows (Hatcher *et al.*, 1982; Simoneit, 1978; Simoneit *et al.*, 1980). The *n*-alkanes in the range from *n*-C_{20} to *n*-C_{40} show a strong predominance of odd-

carbon numbered over even-numbered homologous compounds. This predominance is especially apparent from *n*-C_{25} to *n*-C_{35}, with a strong preference of the *n*-C_{27}, *n*-C_{29}, and *n*-C_{31} alkanes. Even carbon numbered aliphatic alcohols with 24 to 36 carbon atoms are also relatively common, especially in plant waxes. The most prominent fatty acids generally are palmitic (C_{16}), C_{18} monounsaturated acids and stearic acid (C_{18}).

Aquatic

Natural hydrocarbons in the lake may originate from aquatic sources such as phytoplankton, zooplankton, bacteria, macrophytes, zoobenthos and fish. Phytoplankton are the most important producers of organic matter in the aquatic environment. Within the water column algae (e.g., diatoms and dinoflagellates) may contribute saturated and unsaturated hydrocarbons having both straight and branched chains. Algae synthesize *n*-alkanes in the range from *n*-C_{14} to *n*-C_{32}, where often *n*-C_{15} or *n*-C_{17}, or both are the predominating alkanes (Simoneit *et al.*, 1980; Tissot and Welte, 1984). Zooplankton and other micronekton also contribute hydrocarbons to the water column, primarily by reproduction, excretion, feeding activities and by the decomposition of detrital organic matter. Lipids from zooplankton include wax esters (consisting of long-chain alcohols, C_{12}-C_{18}, and fatty acid, C_{12}-C_{18}, constituents) and pristane (2,6,10,14-tetramethylpentadecane). Pristane, but not phytane, is a major component found in marine zooplankton body fat and may be used for maintaining buoyancy in the water column (Blumer *et al.*, 1963). Bacteria in the water column and in the sediments can contribute functionalized hopanoid biomarkers (e.g., hopanols, hopenes) which are pentacyclic terpenoids derived primarily from their membranes (Simoneit, 1978; Peters and Moldowan, 1993).

Recent research utilizing manned submersibles showed that there are inputs of hydrothermal fluids into the bottom of Crater Lake (Collier *et al.*, 1991). Sublacustrine hydrothermal springs and concomitant organic matter alteration by a magmatic intrusion heating source can contribute hydrothermally derived hydrocarbons to the water column (Tiercelin *et al.*, 1993). However, measurements by Collier *et al.* (1991) showed no evidence of hydrothermally-generated hydrocarbons seeping into the lake.

Atmospheric Input

Crater Lake is subject to aerosol fallout from pollen, natural particles and charcoal. Natural aerosols are normally composed of particles with adsorbed organic compounds from vegetation sources such as high molecular weight epicuticular plant waxes, fatty acids (C_{12}-C_{30}, higher plants) and biomarkers such as terpenes (conifer resins) (Simoneit, 1989). The pollen fallout during early summer represents a significant organic matter input to the lake surface. Most of this organic matter is degraded and only traces are preserved in the lake sediments.

Anthropogenic Hydrocarbon Sources

Environmental Effects

The major environmental concerns with regards to petroleum hydrocarbon contamination of water bodies such as lakes and estuaries are the detrimental effects on fish reproduction and behavior. Lower chronic levels result in increased turbidity by particulate matter from biodegradation of petroleum hydrocarbons on the water surface and in the water column, with concomitant micronekton productivity (e.g., Bidleman *et al.*, 1990; Edgerton *et al.*, 1987; Jackivicz and Kuzminski, 1973; Marcus *et al.*, 1988). Chronic petroleum contamination is preserved in the environment due to incomplete degradation, bioconcentration and bioaccumulation. The cosolubility of petroleum hydrocarbons in natural lipids (fats) aids this preservation. Descending biowaste and other particulate matter (e.g. pollen) in the water column ultimately result in an overall incremental build-up of petroleum hydrocarbons in the sedimentary sinks. Once buried in sediments the petroleum hydrocarbons, including the polycyclic aromatic hydrocarbons, are preserved.

The interaction of hydrocarbon fuel dispersion from marine engine use with the aquatic environment has been amply reviewed (e.g., Edgerton *et al.*, 1987; English *et al.*, 1963a, 1967b; Jackivicz and Kuzminski, 1973). A more recent report has

confirmed the presence of gasoline compounds in Lake Tahoe (Boughton and Lico, 1998). Mainly the gasoline anti-knock additive methyl *tert*-butyl ether (MTBE) was found as deep as 30 m below the lake surface during the summer boating season.

Marine Engine Use (Tours and Research)

The Park Service and its concessionaire currently operate four tour boats, two research boats and three skiffs on Crater Lake. Boat operation facilities are located at Cleetwood Cove and on Wizard Island. The lake shore terminal at Cleetwood Cove contains floating docks, a small ticket sales counter, a manually operated gasoline storage tank and a restroom facility. During the summer, approximately 700 people a day hike down the 1.1 mile long Cleetwood Trail to view the lake and/or take a guided boat tour around the lake. The estimated number of boat tours for the 1995 summer season was 656 trips.

The concessionaire owns and operates four, 60-passenger, boats which provide two-hour tours around the lake, and a skiff with a small outboard motor. The tour boats are powered by unleaded gasoline (Texaco: Road Valley Fuels, Klamath Falls, OR) using inboard engines (2 boats: Ford Redline 460 $inch^3$ = 7.5 liter; 1 boat: Ford Redline 351 $inch^3$ = 5.7 liter; 1 boat: Chevrolet Crusader 350 $inch^3$ = 5.7 liter). Each tour boat contains two gasoline tanks with a maximum capacity of 65 gallons (246 liters) per tank. Engine exhaust for these boats exits below the water line. At the end of every tour operation day, excess water (possibly containing lubricating oil) from the boat engine compartment is released into the lake through bilge pumping.

The Park Service's primary research vessel was replaced in 1994. The new vessel is equipped with inboard engines rather than outboard engines to minimize release of unburned fuel and lubricating oils into the lake. The research vessel, "Neuston" is equipped with two inboard engines (2 X 5.0 liter V8 Volvo). Two smaller boats equipped with outboard engines are also used: the "Whaler" (70 HP Johnson outboard); and the "Livingston" (9.9 HP Johnson outboard). The two-cycle outboard engines use a premixed 16:1 unleaded gasoline to lubricating oil mixture for operation.

A 2000 gallon (7570 liters) tank storing the gasoline to fuel all boats operating on Crater Lake is located about 0.25 miles west of the Cleetwood Cove parking area,

adjacent to Rim Drive. The gasoline is gravity fed to a 300 gallon (1136 liters) tank located close to the Cleetwood Cove boat dock. The gasoline from the 300 gallon tank is transferred using a hand operated pump to a fuel dispenser located at the boat dock. The total amount of gasoline delivered to Cleetwood Cove for boat use in 1995 was 7629 gallons (28,876 liters); 93% of the total was used for tour boat operations. This fuel delivery system is currently being analyzed and redesigned to reduce the risk of fuel spills.

Wizard Island has two boat landings, two concession-owned boat houses and one Park Service boat house. The boat houses, which are on the south side of the island, are used primarily for storage of boats during the winter season, for maintenance, and for scientific research purposes during summer lake operations (July through early September). Hazardous chemical storage lockers containing various petroleum products (e.g., lube oil, gasoline, grease) are located in both boat houses. Approximately 50 gallons (190 liters) of gasoline are stored at the Park Service facility to support research operations from the island. Other materials (rags, paper towels, etc.) which may have come into contact with petroleum products are stored in aluminum containers with lids.

Atmospheric Input

Crater Lake is subject to aerosol fallout from urban particles and charcoal besides the natural particles and pollen. Natural aerosols are normally composed of particles with adsorbed organic compounds from vegetation sources as mentioned earlier (Simoneit, 1989). Organic aerosols derived from anthropogenic sources in urban areas by combustion processes and vehicular emissions (petroleum, heating and cooking oils, etc.) and charcoal also from biomass burning (e.g., wild fires), are composed mainly of petroleum hydrocarbons and minor amounts of polycyclic aromatic hydrocarbons (PAH) (Simoneit, 1984). Some PAH are of environmental concern because they are genotoxic and carcinogenic to many organisms (Cerniglia, 1984; Heitcamp and Cerniglia, 1987).

Crater Lake has been designated a Class I area under the Clean Air Act, as amended in 1977. This classification allows the least incremental increase for sulfur dioxide (petroleum refining, power plants, and smelting sources) and particulate

matter above ambient levels. The Clean Air Act also states that visibility and other air quality related values within the park shall be protected (NPS, 1987). Information regarding the ambient air quality in Crater Lake National Park has been released under the National Visibility Monitoring Program (1995). The Inter-Agency Monitoring of Protected Visual Environments (IMPROVE) program began collecting data on visual air quality for selected EPA mandated Class I areas in 1988. Sixty seven sites participated in the program including a site located at Crater Lake. The goals of the program were: 1) to determine existing visual air quality in federal Class I areas, 2) to identify sources of existing man-made impairment, and 3) to document long-term trends for tracking progress towards the long-term goal of no man-made impairment of protected areas.

The results of monitoring aerosols at Crater Lake during the period of March 1993 through February 1994, show that atmospheric particle composition is fairly evenly split between sulfates (urban output, coal/oil fired power plants, refining and smelting activities), organics (biogenic natural emissions, smoke, industrial and urban emissions) and soot (vehicular exhaust, smoke) (NVMP, 1995). Dirty days (dirtiest 20% of total observations) in spring, autumn and winter show increased nitrate concentrations (automobiles, any combustion source) which are virtually absent from median (median 20%) and clean (cleanest 20%) days. Visibility conditions at Crater Lake are relatively uniform throughout the year with a visibility decrease during the autumn season. According to the IMPROVE results for site visibility, Crater Lake ranks as the 6th cleanest site out of 42 total sites nationally (NVMP, 1995).

Atmospheric transport and deposition of metals, such as iron associated with fine dust particles, has been suggested by Collier *et al.* (1990). The vertical profiles for iron, manganese and lead collected during the summer of 1984 show the existence of a surface maximum, trapped in the seasonal thermocline, which decreases rapidly below 75 m. Collier *et al.* (1990) hypothesized that the primary source of the surface maxima is atmospheric deposition and further showed the presence of a significant lead maximum at the surface which suggested an anthropogenic input from local sources (e.g., leaded gasoline combustion) or from the long-range transport of aerosols. The atmospheric transport and deposition of metals associated with particulate matter to the lake surface water may enhance primary production if the

deposited metals are essential for phytoplankton growth and metabolism (e.g., Fe or Mn for photosynthesis).

The atmospheric transport and deposition of pollen into Crater Lake occurs annually during the months of June and July. Pollen particles tends to accumulate along the shoreline at Cleetwood Cove and other protected embayments forming "pudding" masses alongside and underneath rocks. Pollen contributes natural hydrocarbons (waxes) as it degrades in the environment.

Acute Hydrocarbon Input Events

Helicopter Crash

On September 23, 1995 a single-engine helicopter (Aerospatiale AS-350 B-1 Astar) crashed into Crater Lake. Park service officials estimated that the helicopter was carrying approximately 70-90 gallons (265-340 liters) of fuel, 2-3 gallons (~10 liters) of lubricating oil, and 2 quarts (~2 liters) of hydraulic fluid at the time of impact. Rescue and surface water clean-up operations were begun within hours after the crash. A boom was deployed to skim off petroleum hydrocarbons on the lake surface. Surface water samples and miscellaneous debris were also collected at the crash site. The vehicle was not recovered.

Road Maintenance

The park service is responsible for maintaining road accessibility within the National Park. During the winter season, the northern park entrance remains closed to all automobile traffic. Vehicle access to the park during this period is through the south entrance along Oregon State Highway 62. During periods of heavy snowfall, two diesel powered push plows and one diesel operated rotary snow plow are usually operating on a daily basis to keep park roads open.

At the end of the 1995 summer season, a chip seal (tar-oil type CSS-1) was applied to Rim Village road which failed to hold due to unexpected environmental conditions. The continuous snowfall events through the winter followed by the

subsequent snow clearing activities resulted in the relocation of snow containing chip seal material alongside Rim Village Road and on the caldera rim. After the snow melt the chip seal material was highly visible along the asphalt walkways, above the wall barrier and on the caldera rim. A maintenance crew was dispatched to remove the chip seal material along the road side; however, no material was removed from the caldera rim because of the existing hazardous working conditions to park employees. The impact of the chip seal relocation is not yet known, however, this event might contribute petroleum hydrocarbon to the lake in runoff from snow melt and surface soil erosion.

While both of these input events represent 'unique' circumstances, they characterize a class of uncontrolled/accidental inputs that occur in association with human uses of the Park. The use and maintenance of roadways in the Park will always contribute some amount of hydrocarbons to the local particulate matter in the atmosphere and caldera rim runoff. The design and operation of these facilities needs to include an element considering these hydrocarbons. Potential vehicle accidents (including boats on the lake, automobiles, aircraft) are rare due to appropriate regulation of their use. The helicopter crash probably represents the nature of the pollutant impacts that might be expected from other worse-case accidents (such as grounding/break-up of a tour boat).

EXPERIMENTAL METHODS

Sample Collection and Treatment

The analytical techniques of organic geochemistry are ideally suited to examine the character of fossil fuel hydrocarbons as well as natural sources of hydrocarbons in surface water and sediments in terms of their structural and compositional makeup (Bidleman *et al.*, 1990; Dimock *et al.*, 1980; Eglinton *et al.*, 1975; Marcus *et al.*, 1988; Simoneit and Aboul-Kassim, 1994; Voudrais and Smith, 1986). In order to evaluate hydrocarbon inputs from boating (anthropogenic) and natural (biogenic) sources to Crater Lake, a preliminary baseline sampling survey and a final analytical sampling survey of various lake environments were conducted. Surface slick

(surface microlayer), water column and sediment samples were collected for the determination of their aliphatic and aromatic hydrocarbon concentrations and compositions. Air samples were also collected on the caldera rim to determine the characteristics of atmospheric hydrocarbon inputs to the lake. A map showing the hydrocarbon sampling sites is given in Figure V1.1.

Chemical analyses of samples for hydrocarbons were conducted after suitable extraction and fractionation by using gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) instrumentation at Oregon State University (OSU) and at the Geochemical and Environmental Research Group (GERG) laboratory at Texas A&M University. A list of the environmental samples collected in Crater Lake for hydrocarbon analyses is given in Table VI.1. This report discusses the characterization of petroleum hydrocarbons present in selected samples of air, surface water and sediments collected at Crater Lake. Most of the total extracts consist primarily of natural lipid components with traces of petroleum hydrocarbons.

Gasoline and lubricating oil (Napa SAE 30) used primarily for tour boats were obtained from the concessionaire at the Cleetwood Cove boating facility. The premixed fuel for the two-cycle motor boats was also sampled. The hydrocarbon fluid samples were collected in preheated (<350°C) 10.0 ml vials with teflon lined caps. Immediately following collection the samples were stored at 4°C and then transported to OSU and GERG for the determination of source hydrocarbons by GC and GC-MS analyses.

At GERG, fluid samples for hydrocarbon analysis were first subsampled by diluting an aliquot with a known amount of methanol. An aliquot of the diluted sample (<5.0 ml) was then taken and spiked with internal standard in 5.0 ml of water. The spiked sample was then analyzed by GC and GC-MS for BTEX (benzene, toluene, ethylbenzene and xylenes) volatiles which were determined by purge and trap procedures based on EPA Method 8020 (EPA, 1986). Polycyclic aromatic hydrocarbons (PAH) were extracted using the procedure outlined in GERG Standard Operating Procedure (SOP) 8902 Rev 4 and analyzed according to protocol in GERG SOP 9406 Rev 1. The following parent and alkylated PAH compounds were analyzed: C_0, C_1, C_2, C_3, C_4-naphthalenes; biphenyl; acenaphthylene; acenaphthene; C_1, C_2, C_3-fluorenes; C_0, C_1, C_2, C_3, C_4-phenanthrenes; C_0, C_1, C_2, C_3, C_4-anthracenes; C_0, C_1, C_2, C_3-dibenzothiophenes; C_1-fluoranthenes; C_0, C_1-pyrenes; benz(a)anthracene; C_0, C_1, C_2, C_3, C_4-chrysenes; benzofluoranthenes;

Crater Lake Sampling Sites

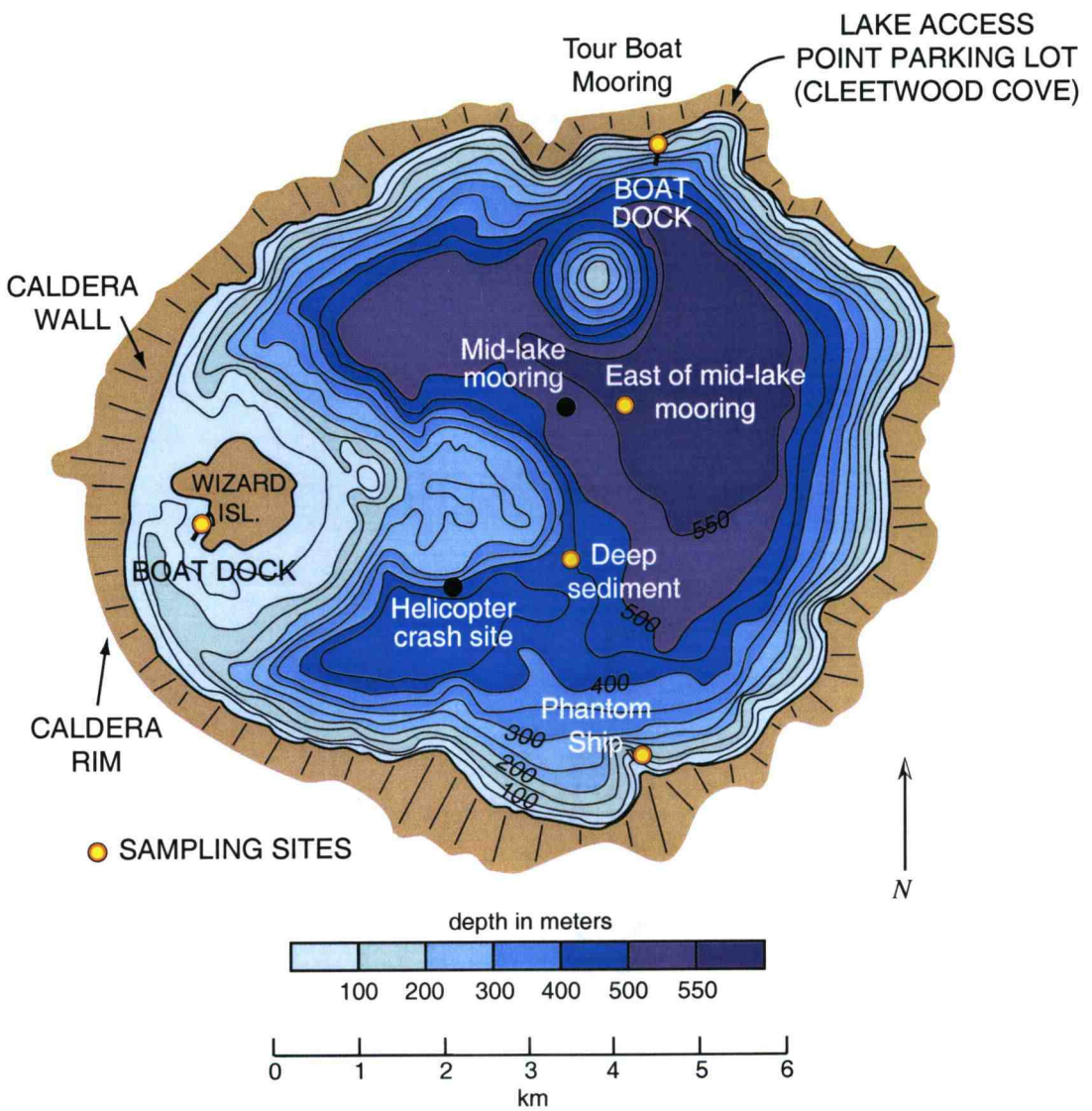

Figure V1.1 Crater Lake sampling sites.

benzopyrenes; perylene; indenopyrene; dibenzanthracene; and benzoperylene. Data was also reviewed for accuracy and met the quality assurance (QA) criteria as specified in the SOP for BTEX and PAH products based on the methods above.

Table VI.1. Environmental samples collected in Crater Lake.

Sample Category	Quantity Collected	Analysis Applied[1]
Preliminary Sampling Survey		
A. Surface Slicks	9	HC/PAH
B. Sediment and Soil	14	HC/PAH
C. Helicopter Crash Site	8	HC/PAH
D. Petroleum Products	3	HC/PAH
E. Air	3	HC/PAH
Final Sampling Survey		
A. Surface Slicks	4	HC/PAH
1) Cleetwood Cove-Boat Mooring		
2) East of Mid-Lake Mooring		
3) Phanthom Ship-North Side		
4) Wizard Island-South Bay		
B. Water Column	4	BTEX/HC
1) Cleetwood Cove-Boat Mooring		
2) East of Mid-Lake Mooring		
3) Phanthom Ship-North Side		
4) Wizard Island-South Bay		
C. Sediment	2	HC/PAH
1) Cleetwood Cove-Boat Mooring (5 m water depth)		
2) North Basin (590 m water depth)		
D. Petroleum Products	2	BTEX/HC/PAH
1) Gasoline		
2) Lubricating Oil		

[1] HC: Hydrocarbons as *n*-alkanes and UCM; BTEX: Naphthenic petroleum products includes benzene, toluene, ethylbenzene, xylenes and their derivatives; PAH: Polycyclic aromatic hydrocarbons.

Water column samples were collected at approximately 1.0 m below the surface using pre-heated (<350°C) 500 ml narrow mouth glass bottles (amber with teflon

lined lids). Immediately following collection, the unfiltered water samples were stored at 4°C and then transported to GERG for chemical analysis of BTEX compounds by EPA Method 8020.

Samples of water surfaces impacted by fuel residues and with natural slicks were acquired using 20 x 26 cm pre-cleaned quartz fiber filter sheets (annealed at 350°C for a minimum of 4 hours) (Simoneit and Aboul-Kassim, 1994). Each filter was used to blot the surface film six times by alternating sides during collection. This assumes that the area blotted (0.31 m^2/filter) adsorbed the surface slick or surface microlayer, typically 100 μm thickness, uniformly from that area. Sample filters were then placed in pre-heated (<350°C) "Qorpak" wide-mouth jars (with teflon lined caps), spiked with approximately 15 ml of a chloroform/methanol (2:1) solvent mixture to stop microbial alteration and degradation, then stored at 4°C for transport to OSU and GERG. At OSU, the sample filters were solvent extracted four times each with 50.0 ml aliquots of methylene chloride (CH_2Cl_2). The CH_2Cl_2 fraction containing the hydrocarbons was then separated from water in a separatory funnel, filtered and evaporated under aspirator vacuum to approximately 1 ml. The crude extracts were fractionated by liquid chromatography into aliphatic and aromatic hydrocarbons using a column of silica gel and alumina with gradient solvents as eluent. Total extract and sample fractions (positives and blanks) were concentrated using a rotary evaporator and then under a stream of filtered N_2 gas to a final volume (<100 ml) necessary for hydrocarbon detection by GC. Surface slick samples were also submitted to GERG for chemical analysis using the GERG SOP for chemical extraction and determination of PAH.

Lake sediments were collected using a Soutar box corer and by SCUBA diver. Samples were taken from mid-lake at approximately 590 m depth and at various locations and depths in Cleetwood Cove. For hydrocarbon analysis only the top 2.0 cm of undisturbed surface sediment was sampled. All sediment samples were placed in Kapak bags, sealed and then stored on dry ice. At the OSU laboratory, the wet sediments were extracted using ultrasonic agitation for three periods of 15 minutes each in 200 ml of 3:1 CH_2Cl_2/MeOH solvent mixture. The extractions were carried out in organically clean 500 ml pyrex beakers. The solvent extract was filtered using a Gelman Swinney filtration unit containing an annealed glass fiber filter for the removal of insoluble particles then followed by isolation of the CH_2Cl_2 soluble organic fraction from water using a separatory funnel. The filtrate was first

concentrated on a rotary evaporator and then using a stream of filtered N_2 gas to an extract volume of approximately 4 ml. The volume was then adjusted to 4.0 ml exactly by addition of CH_2Cl_2 then analyzed for hydrocarbons by GC and GC-MS. Sediment samples were also submitted to GERG for chemical analysis using the GERG SOP for chemical extraction and determination of PAH.

Air sampling at Crater Lake rim during the winter (May) and summer seasons (July) was done over 48 hour periods to collect ambient aerosol particulate matter. A standard high volume air sampler (GCA/Precision Scientific) with a flow rate of 40 ft^3/min (1.13 m^3/min) was positioned in an open meadow (snow field in winter) approximately 300 m south of Crater Lake lodge. After sample collection, a small portion of the sampling filter (2.5 x 3.5 cm) was removed for total carbon analysis (as volatilizable and black soot carbon) and the remainder placed in organically clean "Qorpak" wide mouth jars (with teflon lined caps), preserved with 5.0 ml of chloroform and then stored at 4°C until chemical analysis. In the laboratory, the air sample filters were extracted three times using ultrasonic agitation for 15 minutes each in 200 ml of CH_2Cl_2. The extractions were carried out within the filter storage jars. The solvent extract was filtered using a Gelman Swinney filtration unit containing an annealed glass fiber filter for the removal of insoluble particles. The filtrate was first concentrated on a rotary evaporator and then using a stream of filtered nitrogen gas to an extract volume of approximately 4.0 ml. The volume was then adjusted to 4.0 ml exactly by addition of CH_2Cl_2. An aliquot of the total extract was then subjected to GC and GC-MS analyses.

The organic carbon analysis of the particulate matter on the aerosol filters consists of a two-step laser combustion method (Johnson *et al.*, 1981; Birch and Cary, 1996). The CO_2 generated first from the volatilizable organic matter is quantified and then that from the black carbon (soot).

GC and GC-MS Analyses

In gas chromatography (GC), organic compounds are partitioned between a moving gas phase and a stationary high-molecular-weight liquid phase on the column wall. The compounds separate according to their molecular weights and are detected as they emerge from the column. The data are plotted as relative response versus

time. One detection method for GC is mass spectrometry (MS), i.e., GC-MS. The GC column effluent is introduced into the MS and mass spectra are continuously scanned (one spectrum per second). Thus, mass spectra of individual compounds can be obtained after suitable background subtraction. Plots of relative intensity versus time for the total ion current resemble GC traces and individual ions can also be monitored (mass fragmentograms).

Samples were fingerprinted by maintaining the same conditions with high resolution gas chromatography on a Hewlett-Packard (HP) Model 5890A GC, equipped with a split/splitless injector and a flame ionization detector (FID). The samples were analyzed in the split or splitless modes using a fused capillary column (30 m x 0.25 mm i.d., 0.25 μm film thickness, DB-5, J & W Scientific) with helium as carrier gas and operating conditions as follows: FID 300 °C, injector 300°C, the oven temperature was programmed from 45 to 300°C at 4°C/min after 15 minutes and held isothermal at 300°C for 20 minutes. The analog signal was monitored with an HP 3393A integrator or with an HP Chemstation Software program. The data is presented as plots of relative response versus time. Identification was based on comparison of the retention times with standard reference compounds. The following standard mixtures were injected on GC: (1) Wisconsin diesel range hydrocarbons (AccuStandard Inc.); (2) a series of *n*-alkanes ranging from C_{10} to C_{36}; and (3) pristane and phytane.

The GC-MS analyses were conducted on an HP 5973 MSD mass spectrometer interfaced directly with a HP Model 6890 GC and equipped with a 30 m x 0.25 mm i.d. fused silica capillary column. The operating conditions were as the same as given above. The GC-MS data were acquired and processed with HP Chemstation Software equipped with a GC-MS Data Library. The data is presented as plots of relative intensity of the total ion counts or individual fragment ions (called mass fragmentograms) versus time. Compound assignments were made from individual mass spectra and GC retention times and with comparison to authentic standards where possible. Blank and positive samples were analyzed as controls for this method.

Hydrocarbon Parameters

The following organic geochemical parameters are used for interpreting the data:

1. Makeup of natural and anthropogenic organic components (homologous alkane series, Simoneit, 1978) present in Crater Lake.

2. Carbon Preference Index (CPI) is a single value to express the ratio of odd-carbon-numbered to even-carbon-numbered *n*-alkane peaks in a given sample (Simoneit, 1978). The CPI helps in differentiating biogenic from petrogenic *n*-alkanes in organic environmental samples. In particular, it is useful for making estimates of terrestrial plant wax contribution versus fossil fuel contamination. Vascular plants synthesize epicuticular waxes as odd number *n*-alkane hydrocarbons usually in the C_{25}-C_{33} range (CPI >>1). In crude oils, the high molecular weight *n*-alkanes inherited from terrestrial plants are normally diluted by hydrocarbons from kerogen degradation which increases the even number *n*-alkane concentrations, resulting in a CPI of around 1.0. An even-over-odd *n*-alkane predominance, although much less common, is associated with organisms such as bacteria and diatoms.

The *n*-alkanes were detected in the total extract or separated hydrocarbon fractions by the GC retention index or in GC-MS data by the mass fragmentogram plot of the m/z 85 key ion.

3. Isoprenoid hydrocarbons: The isoprenoid hydrocarbons pristane (Pr) and phytane (Ph) can be used together as specific indicators for the presence of petroleum residues (Peters and Moldowan, 1993). They are mature biomarkers found in generally all crude oils and are stable in the environment. Pr and Ph have specific chemical structures which are unique to their source and together they are not synthesized by contemporary biota. However, a high concentration of pristane alone (> *n*-heptadecane) can be derived from zooplankton.

4. Unresolved Complex Mixture (UCM): The broad "hump" seen associated with the heavier compounds in petroleum and lubricating oils results from an unresolved "complex" mixture of branched and cyclic hydrocarbons which generally indicates a

petrogenic hydrocarbon input from heavier hydrocarbon fractions of petroleum. The UCM is always present in unburned petroleum emissions, however, its chemical components cannot be fully determined. Its major input vector into environmental systems is from engine lubricating oils.

5. Petroleum Biomarkers: Biomarkers or molecular markers are indicator compounds that can be used for defining the sources of organic matter in the environment (e.g., Simoneit, 1978, 1986). As applied here, biomarkers characteristic of petroleum products are characterized to confirm such an origin for extractable organic matter. The petroleum biomarkers are triterpenoid hydrocarbons (17α(H)-hopanes) and steroid hydrocarbons (steranes and diasteranes) which are minor but unique components in petroleum products such as lubricating oils (Bieger *et al.*, 1996; Peters and Moldowan, 1993; Rogge *et al.*, 1993a). The chemical structures of representative biomarkers are shown in Appendix VI.1.

The hopanes were detected in the GC-MS data by the mass fragmentogram plot of the m/z 191 key ion and similarly the steranes and diasteranes are found in the key ion plots of m/z 217 and 218.

6. Polycyclic Aromatic Hydrocarbons: Polycyclic aromatic hydrocarbons (PAH) can be derived from three sources in an environment such as Crater Lake. First, combustion emissions from vehicles using petroleum-derived fuels and lubricants contain PAH with a relatively high amount of alkyl substituents (e.g., Marcus *et al.*, 1988). The typical indicators used are the phenanthrene/anthracene series. This signature is distinguishable from the PAH emitted by the second source, biomass burning, where the phenanthrene/anthracene (P/A) series would show an enriched content of C_2 and C_4 homologs (i.e., pimanthrene and retene, alteration products from conifer resin compounds). The third source is high temperature combustion which emits the higher molecular weight PAH as described for many urban areas (Neff, 1979). These PAH (e.g., pyrene, chrysene, etc.) were detectable in some of the samples analyzed from Crater Lake. However, the source emission for this third category overlaps with the first.

7. BTEX: These are the volatile aromatic ($<C_{12}$) petroleum products which include benzene, toluene, ethylbenzene and xylenes and other derivatives. BTEX products

are generally found in gasoline as additive hydrocarbons to improve fuel efficiency and are extremely volatile once released in the environment.

Quality Assurance/Quality Control (QA/QC)

In order to insure acceptable performance of analytical results, quality control (QC) data was generated to assess the accuracy and precision of test data. Quality control measurements may include data on calibration standards, performance evaluation samples, blind standards, known standards, duplicate samples, blanks, spiked samples and limits for quality control spiked samples, reference standards, duplicate and detection limits. Although this project would benefit greatly by applying all the above, the actual types and quantity of necessary QC data is limited to cost, analytical methods and sampling program design. Therefore, in order to insure acceptable performance levels, a special sampling QA data program was designed to meet a set of specific analytical objectives:

1. To initially screen (qualitative and quantitative analysis) for the presence of petroleum hydrocarbons (e.g., gasoline, diesel, lubricating oil) in multiple environmental samples (air, water, soil and sediment) using gas chromatography.

2. To confirm the presence of petroleum hydrocarbons by gas chromatography-mass spectrometry in select environmental samples.

3. To determine the abundances (quantitative analysis by GERG/Texas A&M) of specific petroleum molecular classes (e.g., BTEX, PAH) in select environmental samples (surface slick, water, sediments, gasoline and lubricating oil) using EPA Method 8020.

Based on these objectives, the following list of QC data were identified and applied to the GC and GC-MS chemical analyses. Corrections were applied, when necessary, for making quantitative determinations.

1. Solvent Blanks: All organic solvents (Reagent Grade, redistilled in glass CH_2Cl_2) used to solubilize hydrocarbons were analyzed for the presence of analyte(s). No analytes were found, thus no further action was taken.

2. Calibration Standards: Organic compounds of known concentrations which were the same or similar to the target analyte(s) were used as calibration standards and included perdeuterotetracosane (n-$C_{24}D_{50}$), a standard mixture of BTEX (benzene, toluene, ethylbenzene, xylene) and a standard mixture of polycyclic aromatic hydrocarbons.

3. Performance Standards: A homologous series of n-alkanes (C_{10} to C_{33}) including the isoprenoids pristane and phytane were used periodically to monitor retention times and detector response as compounds eluted from the GC capillary column.

4. Matrix Spikes and Matrix Spike Duplicates: An intralaboratory split sample was spiked with a known concentration of target analyte(s). The spiking was done prior to sample preparation and analysis. The matrix spike was used to document the bias of a method in a given sample matrix.

5. Surrogate Recovery Standards: Organic compounds were used to spike samples, which were similar to the target analyte(s) in chemical composition and behavior in the analytical process. Surrogates are compounds not normally found in environmental samples and are used to determine the levels of analyte recovered after sample treatment and analysis.

6. Field Blanks: Trip blank, ambient blanks, bottle blanks and equipment rinse blanks were not collected since hydrocarbon contamination from these sources was not expected. Preventative actions were taken prior, during and after sampling in order to minimize hydrocarbon contamination.

7. Minimum Detection Limits: The amount of calibration standard observed (concentration) divided by its signal to noise ratio.

RESULTS AND DISCUSSION

Petroleum Hydrocarbon Use

The major petroleum hydrocarbon use categories and the total petroleum amounts used during 1995 are given in Table VI.2. The primary petroleum products used in the park include gasoline, diesel, heating and lubricating oils. Diesel and heating oil are the main petroleum products used in Munson Valley, especially during the winter season. On the lake, gasoline is used to fuel watercraft (tour and research boats,

Table VI.2. The major petroleum hydrocarbon use categories and annual hydrocarbon budget for Crater Lake National Park in 1995.

Use Category	Petroleum Product	Amount (gallons)	Amount ($m^3 = 10^3$ liters)
Cleetwood Cove Boat Operations	Gasoline	7629	29
Park Service	Gasoline	453	2
	2 Cycle Lube Oil	2	$8x10^{-3}$
Concessions	Gasoline	7176	27
Munson Valley	Gasoline	20788	79
	Diesel	36692	139
	Heating Oil	40127	152

skiffs) and lubricating oil is used for boat engines and for making up the fuel-oil mixture (50:1 to 100:1) necessary to operate outboard motors. Boat fueling and tour and research operations unavoidably introduce petroleum hydrocarbons and their combustion residues to the lake.

Sampling Sites and Analyses Conducted

The sampling sites for the preliminary and final chemical surveys and the hydrocarbon analyses applied to each sample are given in Table VI.1. Various sampling sites were chosen to best represent the distributions and concentrations of hydrocarbons, BTEX and PAH products in Crater Lake. All samples were subjected to hydrocarbon and PAH analyses while water column samples and petroleum fluids were further tested for BTEX products. The concentrations and distributions of petroleum hydrocarbons present in Crater Lake from gasoline (BTEX) and engine emissions and other combustive processes (PAH) are reported in Table VI.3. Analytical data for the *n*-alkane, UCM and isoprenoid hydrocarbon constituents for all the samples collected are reported in Appendix VI.2. The parameters used to interpret the analytical results are presented below and a discussion of the hydrocarbon distributions and concentrations found in the various samples is included.

Water Column Hydrocarbons

Crater Lake water column samples were subjected to BTEX analysis for determination of petroleum input from gasoline spillage and boat exhaust (Table VI.3). The BTEX products were not found at concentrations above the procedural blanks used for this analysis (<5.0 μg/ml). Thus, the BTEX product concentrations in the water column are not a significant component or contributor of hydrocarbons. BTEX products, once applied to a water surface from a gasoline spill or from boat exhaust, are very volatile and have limited solubility in cold water. Therefore, they are not likely to concentrate significantly in the water column. Analyses for heavier petroleum hydrocarbons dissolved in the water column were not conducted because their solubilites are low and their concentrations in surface slicks were found to be low reflecting background levels. Petroleum hydrocarbons in the water column are adsorbed to particulate material which ultimately sinks to the lake sediments.

Table VI.3. The concentrations and distributions of total PAH and BTEX compounds detected in Crater Lake samples.

	Total PAH[1]	BTEX[2]			
		Benzene	Toluene	Ethylbenzene	Xylene
Surface Slicks	ng/m^2				
Cleetwood Cove-Boat Mooring	8.50				
East of Mid-Lake Mooring	7.56				
Phantom Ship-North Side	7.63				
Wizard Island-South Bay	7.16				
Water Column		µg/L	µg/L	µg/L	µg/L
Cleetwood Cove-Boat Mooring		<5.0	<5.0	<5.0	<5.0
East of Mid-Lake Mooring		<5.0	<5.0	<5.0	<5.0
Phantom Ship-North Side		<5.0	<5.0	<5.0	<5.0
Wizard Island-South Bay		<5.0	<5.0	<5.0	<5.0
Sediments	µg/kg				
Cleetwood Cove (5 m water depth)	39.9				
North Basin (616 m water depth)	15.4				
Petroleum Fluids	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Lubricating Oil	158.7	<6250	<6250	<6250	<6250
Gasoline	13497	22325	86450	18063	62501

[1] PAH analysis consists of the following compounds: C_0, C_1, C_2, C_3, C_4-naphthalenes; biphenyl, acenaphthylene; acenaphthene; C_0, C_1, C_2, C_3-fluorenes; C_0, C_1, C_2, C_3, C_4-phenanthrenes; C_0, C_1, C_2, C_3, C_4-anthracenes; C_0, C_1, C_2, C_3-dibenzothiophenes; C_0, C_1-fluoranthenes; C_0, C_1-pyrenes; benz(a)anthracene; C_0, C_1, C_2, C_3, C_4-chrysenes; benzofluoranthenes; benzopyrenes; perylene; indenopyrene; dibenzanthracene; and benzoperylene (data from GERG).

[2] BTEX analysis follows EPA Method 8020 (data from GERG).

Surface Slick Hydrocarbons

Aliphatic and higher molecular weight hydrocarbons (C_{10}-C_{30}) are hydrophobic and therefore concentrate at the water-air interface forming a slick (film) with the natural lipids which also accumulate there. The larger-chain surface active molecules tend to concentrate at the water-air interface and compression of the water surface by wind and currents displaces the shorter-chain, more hydrophilic compounds downward. Thus, the more water soluble and volatile petroleum components (e.g.,

BTEX) partition into the water column or evaporate and are therefore depleted in the water-air interface slick. These surface films (also termed surface microlayer, upper 100 μm) are important for concentrating lipophilic higher molecular weight compounds such as petroleum hydrocarbons and natural lipids (Morris and Culkin, 1975). Therefore, sampling of surface slicks is a way to analyze an enriched upper limit in concentration of hydrophobic hydrocarbons like the petroleum hydrocarbons superimposed on the natural background lipids.

The primary petroleum hydrocarbons found in Crater Lake surface slicks have been identified as exhaust products and motor lubricating oil residues from internal combustion engines. The results of the chemical analyses show that normal and isoprenoid alkanes and an envelope (UCM, hump) of unresolved branched and cyclic hydrocarbons, typical of petroleum products, were detected in surface slicks at different sites of Crater Lake. Gasoline hydrocarbons can be identified by their characteristic GC fingerprint which contains a peak pattern for naphthenic compounds in the low molecular weight ($<C_{12}$) range, while lubricating oil can be identified by its pronounced UCM. Both fingerprints are used as indicators for direct input (unburned) of petroleum products. The characteristic GC fingerprint for the gasoline and lubricating oil mixture (16:1 ratio) used for outboard motors contains both the naphthenic compounds from gasoline and the UCM from lubricating oil. The presence of *n*-alkanes ranging from C_{17} to C_{26} (with CPI=1) is also used as an indicator of petroleum derived hydrocarbons.

Slick samples were collected at various sites to best represent the overall spatial distribution of hydrocarbons on the lake surface. Analytical data of the hydrocarbons collected from sampling sites with high impact from tour boating activities (Cleetwood Cove, Wizard Island), sites along or near the boat touring route (The Palisades, Phanthom Ship, Spring 42) and a background site (East of Midlake Mooring) are shown in Appendix VI.2 (also see Fig. VI.1). For comparison purposes, the hydrocarbon data from surface slicks collected within days after the helicopter crash are used both to determine the impact of the crash on surface hydrocarbon levels and as a temporal indicator showing rapid dispersal and evaporative loss of hydrocarbons at the water surface.

Comparisons of the Crater Lake surface slick GC-MS traces (Fig. VI.2- VI.3) show *n*-alkanes present as a homologous series ranging in chain length from C_{14} - C_{36} with C_{max} at *n*-C_{21} and odd carbon number predominance $>C_{25}$, which indicates

a minor contribution from natural sources (higher plant wax). The presence of an UCM and *n*-alkanes with a CPI=1.0 (from C_{14}-C_{24}) confirms that these samples also contain lube oil and engine exhaust products. The occurrence of both pristane and phytane support the petroleum related origin of most of the *n*-alkanes and the UCM.

Within several days after the helicopter crash in Crater Lake, surface slick samples and crash debris were collected for analysis. The hydrocarbons extracted from the recovered log book page, which had a characteristic fuel odor, contained a fingerprint for petroleum components typical of kerosene or Jet A fuel (Mayfield and Henley, 1991). Hydrocarbons were also present in natural foam samples collected near Phantom Ship after the crash, however, they are not necessarily derived from the aircraft fuels (as opposed to the rescue/collection activity). The presence of *n*-alkanes, C_{14} and C_{15}, indicated that a trace of helicopter jet fuel was present in this surface slick. The absence of alkanes $<C_{14}$ was likely due to evaporative losses which began immediately after hydrocarbon exposure at the air-water interface or from losses that occurred during sample handling and preparation. However, much care was taken in the latter to avoid this occurrence. Thus, the helicopter crash introduced petroleum hydrocarbons (*n*-alkanes and minor UCM) to the lake surface and water column from fuel, lubricating oil and hydraulic fluid leakage. However, the measured level of total surface slick petroleum hydrocarbons as *n*-alkanes (840 $\mu g/m^2$) does not differ significantly from a site sampled during the same period as a background reference (Mid-lake near mooring: 830 $\mu g/m^2$) or from a surface slick collected two months earlier at a nearby site (Spring 42: 1060 $\mu g/m^2$). Thus, the impact of the helicopter crash did not appear to contribute significantly to the petroleum hydrocarbon concentrations in the surface slicks several days after the crash.

The plant wax concentrations measured as *n*-alkanes in surface slicks increased greatly during the summer months of July, 1995 (average at 270 $\mu g/m^2$, n=5) through September (average at 4310 $\mu g/m^2$, n=4). This increase reflects the seasonal release of pollen from the surrounding forests and new plant growth, with deposition

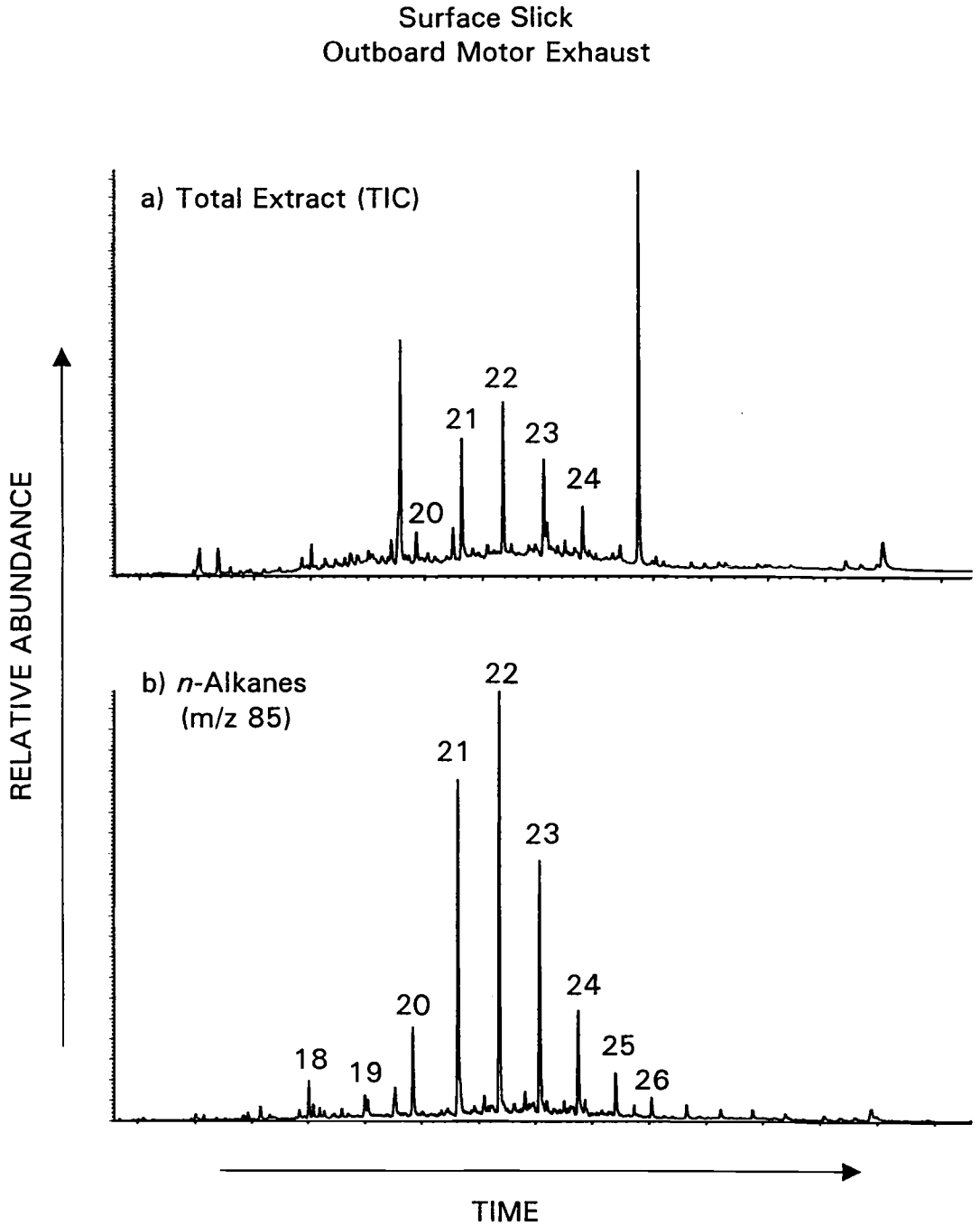

Figure VI.2. GC-MS data of fractionated surface slick extract collected at interior section of Cleetwood Cove boat dock: a) total ion current trace of the total hydrocarbon fraction; b) *n*-alkane hydrocarbons (detected in data of a by the key fragment ion m/z 85).

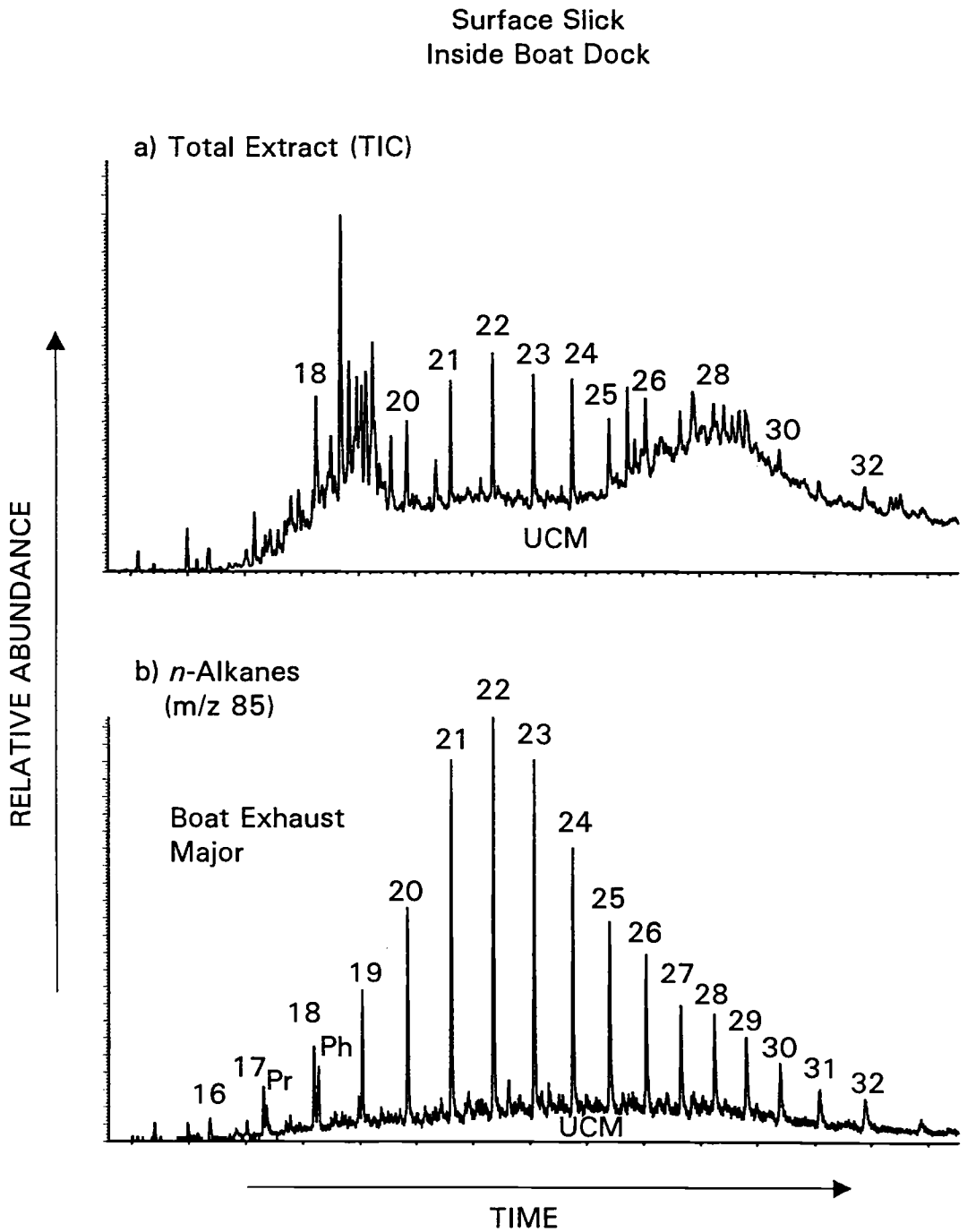

Figure VI.3. GC-MS data of surface slick samples immediately behind the outboard engine exhaust: a) total ion current trace of the hydrocarbon fraction; b) *n*-alkane hydrocarbons (detected in data of a by key fragment ion m/z 85).

of detritus to the lake surface by atmospheric transport. The accumulation of pollen is very noticeable along the shoreline of Cleetwood Cove and Wizard Island during the months of July through September. A visual observation of the shorelines and surface waters conducted in October showed a decrease in the abundance of pollen at these sites.

The PAH concentrations measured in surface slicks range from 72 to 85 ng/m^2 (Table VI.4). The absence of the C_2 and C_4 products corresponding to pimanthrene and retene, respectively, indicates that these PAH are derived from engine exhaust and not from wood smoke in aerosol particle fallout.

The concentrations and distributions of total PAH products on the lake surface as a thin film are essentially constant (72 ng/m^2 measured at Wizard Island and 85 ng/m^2 at Cleetwood Cove). The slightly higher PAH concentration evident in surface slick from Cleetwood Cove is possibly due to increased tour boat activities at this location.

A comparison of the concentrations and distributions of the total petroleum hydrocarbons (PAH, petroleum *n*-alkanes and UCM) for the surface slick sampling sites is given in Table VI.4. A bar plot showing the total petroleum hydrocarbon concentrations and distributions in the surface slicks are presented as an overview in Figure VI.4. The petroleum *n*-alkane concentrations range from 630 to 1610 μg/m^2 and have the highest concentration at Wizard Island in the wake of a tour boat. At the other sampling sites the petroleum *n*-alkane concentrations have similar values.

The total PAH concentrations were determined by summing the individual PAH concentrations reported by GERG. A list of the PAH compounds identified by GERG and their concentrations in the Crater Lake environmental samples is given in Appendix VI.3. The PAH concentrations and distributions for all sampling sites have background values (ng/m^2) as discussed earlier, with naphthalene concentrations exceeding the higher molecular weight pyrolytic PAH. Naphthalene is a major component of gasoline and thus may represent primarily unburned fuel. The UCM and *n*-alkane concentrations at Wizard Island in the boat wake, however, are higher than measurements taken at other surface slick sampling sites which are similar (Appendix VI.2, Fig. VI.4). The Wizard Island sample reflects the tour boat activity of docking, idling and launching in this more confined area which contributes more engine exhaust products to the water surface. An additional contributing factor to the higher UCM and petroleum *n*-alkane concentrations may be the physical geography

of Wizard Island's natural harbor, which can accumulate hydrocarbons by the different wind conditions resulting in decreased surface slick dispersal away from the area.

Table VI.4. The concentrations and distributions of petroleum hydrocarbon constituents[1] in Crater Lake surface slicks.

Sampling Site	PAH ($\mu g/m^2$)	*n*-Alkanes ($\mu g/m^2$)	UCM ($\mu g/m^2$)	Total HC ($\mu g/m^2$)
Cleetwood Cove	0.085	630	3440	4070
East of Mid-Lake	0.076	830	4870	5700
Phanthom Ship	0.076	710	4330	5041
Wizard Island[2]	0.072	1610	7140	8750

[1]Total HC: Total hydrocarbon as sum of PAH, *n*-alkanes and UCM. PAH determined by GC-MS, *n*-alkanes and UCM determined by GC.

[2]Sample collected in wake of tour boat.

Sediment Hydrocarbons

Mass fragmentograms showing the concentrations and distributions of petroleum hydrocarbons in diver collected sediments from the tour boat mooring area in Cleetwood Cove are shown in Figures VI.5-VI.6. Figure VI.5 shows that the total hydrocarbon fraction from the extract of the 5 meter deep sediments contains both natural and anthropogenic hydrocarbons. The major peaks in the total ion current trace are natural lipid compounds. The odd carbon number *n*-alkanes from C_{27}-C_{33} are present which indicate a contribution from plant waxes. Also present are the isoprenoids pristane and phytane and the UCM which are derived from petroleum products. The relative concentrations of the *n*-alkanes are better resolved by the m/z 85 fragmentogram (Fig. VI.5b) and the specific key fragment ions of the petroleum biomarkers (e.g., tricyclic terpanes and hopanes which are minor cyclic hydrocarbons in petroleum that are used to confirm the petroleum source) are plotted over the more limited elution range shown (Fig. VI.5c) for detection.

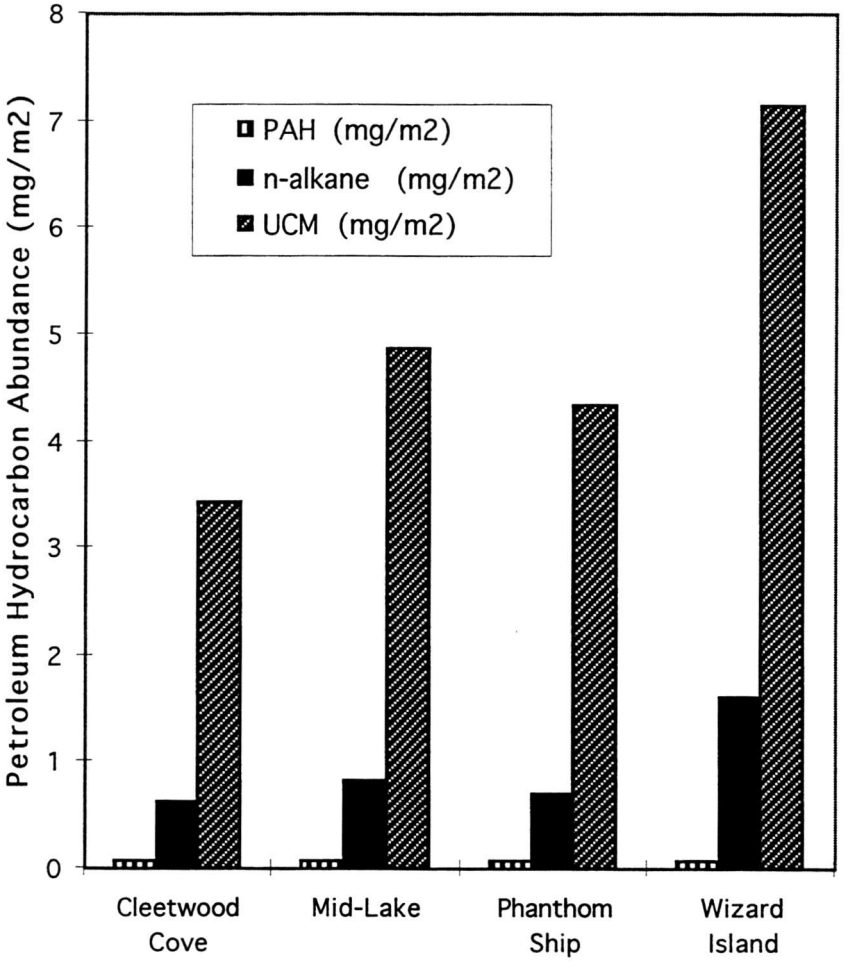

Figure VI.4. Bar plot summarizing the concentrations and distributions of petroleum hydrocarbons in various Crater Lake surface slicks (the Wizard Island sample was taken in the wake after departure of a tour boat about 50 m from the dock).

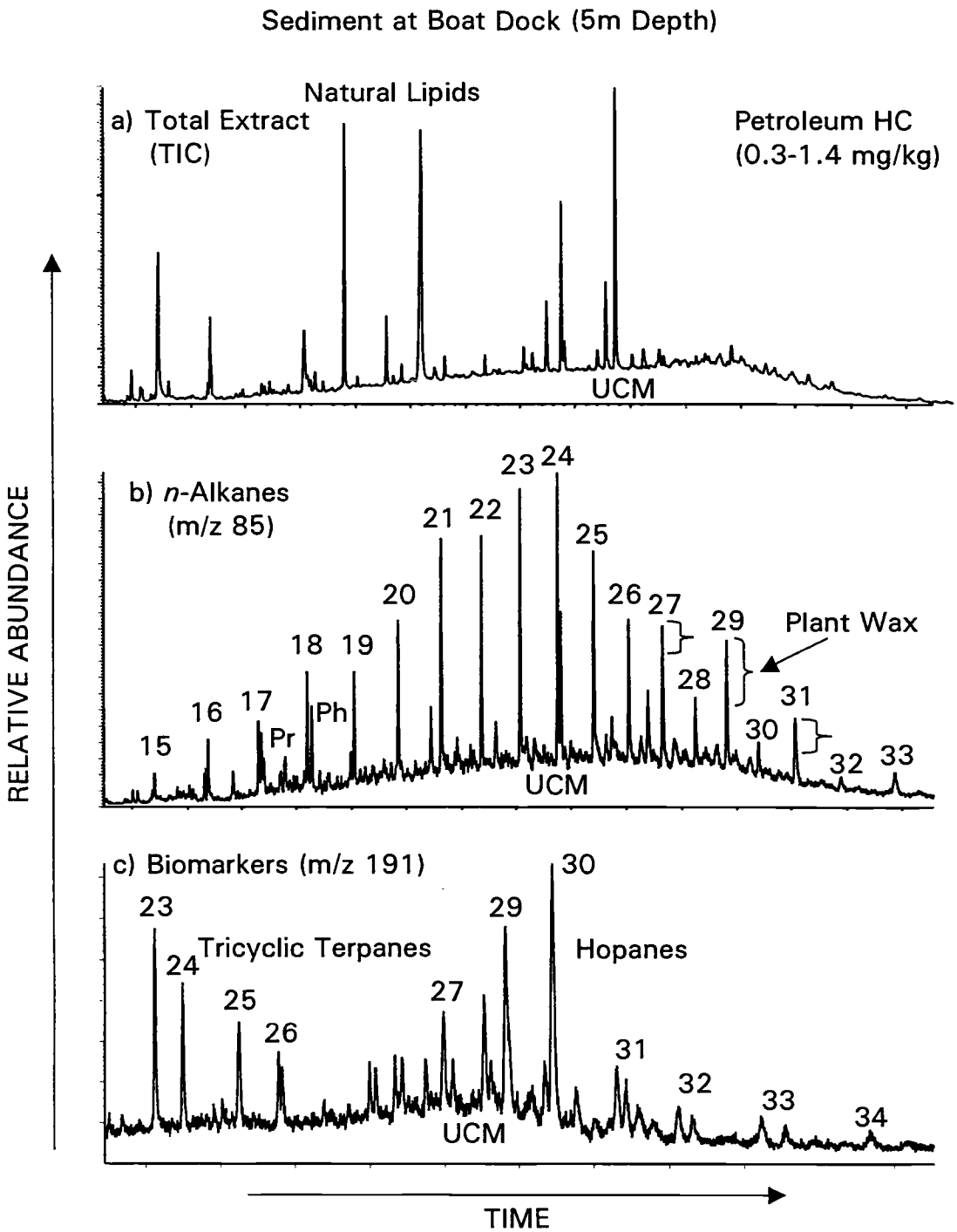

Figure VI.5. Salient features of the GC-MS analysis of a total hydrocarbon fraction from the extract of sediment collected at Cleetwoood Cove boat mooring in 5 m water depth: a) total ion current trace; b) m/z 85 key ion for *n*-alkanes, Pr = pristane, Ph = phytane; c) m/z 191 key ion for tricyclic terpane and hopane biomarkers from petroleum, carbon numbers are indicated.

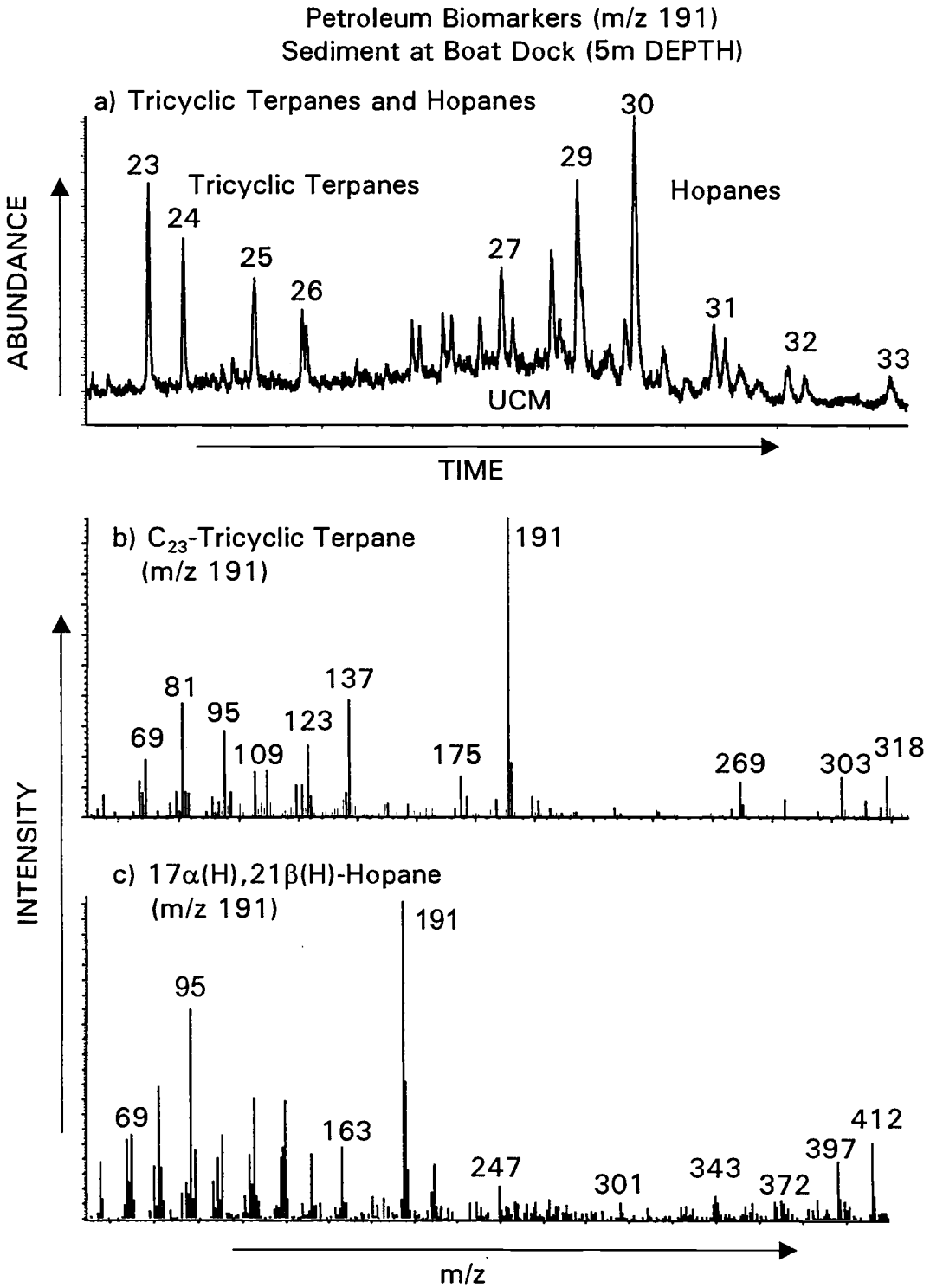

Figure VI.6. Mass fragmentograms (m/z 191) of petroleum biomarkers in sediments from Cleetwood Cove Boat Dock (5 m water depth): a) petroleum tricyclic terpane and hopane biomarker signatures; b) mass fragmentogram of C_{23}-tricyclic terpane; c) mass fragmentogram of 17α(H),21β(H)-hopane.

The *n*-alkanes for all sediment samples range from C_{15}-C_{33}, with a C_{max} at C_{29}, which are both indicators for some input of natural plant wax. The relatively high content of even carbon numbered *n*-alkanes versus the odd, i.e., low carbon number predominance, indicates the presence of petroleum residues from vehicle exhaust. The *n*-alkane contribution from natural sources was calculated as the excess superimposed odd carbon numbered alkanes present above the smooth petroleum alkane envelope (Simoneit *et al.*, 1991). Two examples of biomarker signatures used to confirm the petroleum source in sediments are given in Figure VI.6. The 17α(H),21β(H)-hopanes and the extended tricyclic terpanes (m/z 191 mass fragmentograms, example structures are given in Appendix VI.1) are present at low levels decreasing in concentration to the deeper sediment samples. The biomarker distribution matches with that reported for sediment samples from other geographic areas (e.g., Simoneit and Kaplan, 1980) confirming the petroleum product source. The steranes and diasteranes, another petroleum biomarker group, of the same sediment samples provide secondary confirmation of a petroleum source. These compounds occur at trace levels and are only detectable in the shallow sediments.

A sediment sample from the deepest part of the lake was extracted and analyzed for hydrocarbon content. The total extract was methylated and analyzed by GC-MS (Fig. VI.7). The major peaks in the total ion current trace are natural fatty acids (as methyl esters and confirmed by the m/z key ion plot, Fig. VI.7b) and elemental sulfur (S_8). Hydrocarbons are minor constituents (Fig. VI.7c) and are of a natural origin from plant wax (>C_{25}) and degraded algal (plankton) lipids (<C_{25}). There is no UCM present and the hopane and sterane biomarkers from petroleum are not detectable. The deep lake sediments are pristine. The total hydrocarbons attributable to petroleum amount to <0.02 mg/kg (background level, Table VI.5). Significant petroleum residues from motor exhaust are detectable in the sediments of Cleetwood Cove, but the values are low compared to other areas (Table VI.5). It should be

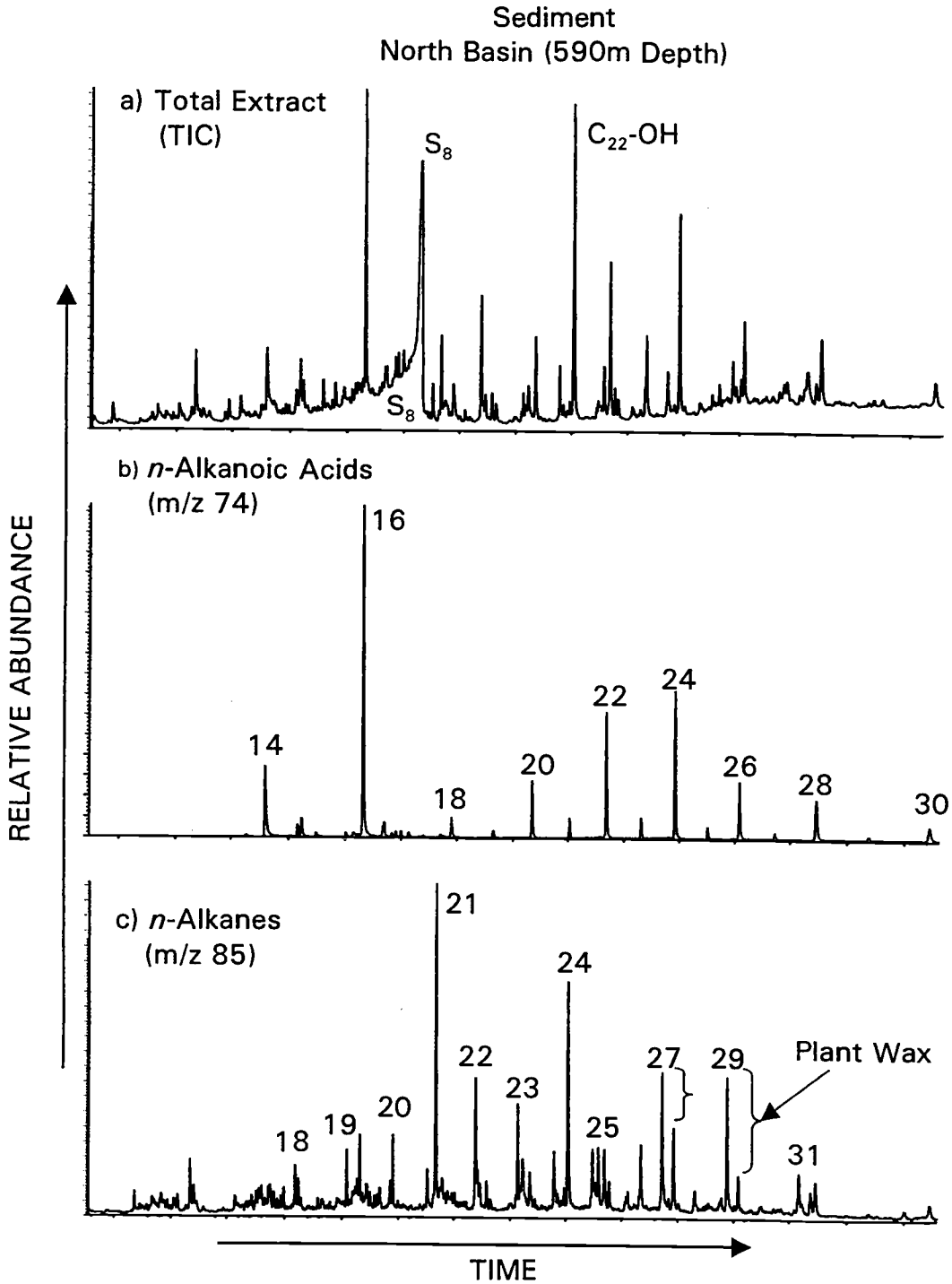

Figure VI.7. Salient features of the GC-MS data for sediment from North Basin in Crater Lake (590 m water depth): a) total extract; b) m/z 74 fragmentogram showing the *n*-alkanoic acids; c) m/z 85 fragmentogram showing the *n*-alkanes. Numbers refer to carbon chain length of components, S_8 = elemental sulfur.

pointed out that the guideline cutoff for non-polluted (by oil and grease, assumed equivalent to petroleum residues) harbor sediment is <1000 mg/kg and moderate pollution is from 1000-2000 mg/kg (EPA, 1977).

Analysis of the total petroleum hydrocarbon concentrations and distributions in sediments shows that the UCM was minor or not found at levels above the instrument detection limits. Both plant wax and petroleum *n*-alkane concentrations decrease with depth possibly due to biodegradation during the sedimentation process or variability in the sediment particle sizes. Petroleum *n*-alkanes are found at greater concentrations than plant wax *n*-alkanes at each sampling depth. This was especially obvious in Cleetwood Cove boat mooring sediments (5 m depth) where the petroleum *n*-alkanes are six times more concentrated than plant wax *n*-alkanes.

Table VI.5. The concentrations of total petroleum hydrocarbons and PAH in Recent sediments of Crater Lake and various other locations for comparison.

Sampling Site	Petroleum HC (mg/kg, dry wt. of sediment)	PAH (mg/kg, dry wt. (of sediment)
Crater Lake, Cleetwood Cove, 5 m Water Depth	0.3-1.4	0.04
Crater Lake, North Basin, 590 m Water Depth	0.016	
Crater Lake, SE Deep, 416 m Water Depth		0.015
Rhone River Estuary, Mediterranean Sea[1]	167	3
Mediterranean Sea, 100 m Water Depth[1]	21	3
Coburn Mountain Pond, ME[2]	20	
South Orkney Island, Antarctica[3]	0.4	0.04

[1]Bouloubassi and Saliot (1993), moderately polluted.

[2]Ho *et al.* (1991), contaminated from regional atmospheric deposition.

[3]Cripps (1994), low impacted region, typical background.

The results of PAH analyses for surface sediments collected with a box corer nearshore at Cleetwood Cove (5 m depth) and at North Basin (616 m depth) show PAH concentration levels at 39.9 μg/kg and 15.4 μg/kg, respectively. Total PAH concentrations in the shallow water sediments are higher than in the deep lake

sediments (Table VI.5). A comparison of selected PAH compounds in sediments at Crater Lake and other areas in the western United States and Alaska is given in Table VI.6. Crater Lake has very low concentrations of PAH in sediments. These compounds tend to accumulate once deposited in sediments due to slower degradation compared to the water column and lake surface.

Table VI.6. Range of some PAH compounds in sediments at Crater Lake and other areas for comparison.

PAH	Crater Lake N. Basin (1) (µg/kg)	Crater Lake Cl. Cove (1) (µg/kg)	Mono Lake CA (2) (µg/kg)	Coastal WA (3) (µg/kg)	Lake Washington WA (4) (µg/kg)	Hitchenbrook Island AK (2) (µg/kg)
Phenanthrene	0.4	2.3	110		400	2.5
Anthracene	0.4	0.4			40	
Fluorene	0.2	0.5		43	150	0.6
Pyrene	0.5	3.1	65	39	1000	0.6
Benz(a)anthracene	0.2	0.8		43	90	1.4
Chrysene/Triphenylene	0.2	1.8	94		300	
Benzo(b)fluoranthene	0.2	3		88	60	6
Benzo(k)fluoranthene	0.1	0.9			500	
Benzo(e)pyrene	0.6	1.7			300	
Benzo(a)pyrene	0.5	1.5			100	
Perylene	0.3	0.6			40	
Indeno(1,2,3-cd)pyrene	0.3	4.2			500	
Dibenz(a,c,h)anthracene	0.1	0.2			70	
Benzo(g,h,i)perylene	1	3.6		27	500	

1) This work
2) Hites *et al.* (1980), Mono Lake receives fallout from long distance transport of urban plume from west coast; Hitchenbrook Island is a background site.
3) Prahl (1982), receives input from Puget Sound urban region.
4) Wakeham *et al.* (1980), Lake Washington receives atmospheric fallout and street washout from the Metropolitan area of greater Seattle.

Atmospheric Hydrocarbons

Because the hydrocarbon contributions to the lake surface may originate from a variety of natural and anthropogenic sources, air samples were collected on the caldera rim to determine the levels of hydrocarbons in atmospheric particulate matter.

The *n*-alkanes range from C_{16} to C_{33} with a C_{max} at C_{23} or C_{29} and significant odd carbon number predominance. Pristane and phytane are not detectable and the UCM is minor. This indicates a dominant or equal signature from natural sources versus urban aerosol (Simoneit, 1984, 1989; Simoneit and Mazurek, 1982). A bar plot summarizing these distributions and concentrations of petroleum and plant wax *n*-alkanes is shown in Figure VI.8. The plot shows that petroleum and plant wax *n*-alkanes were relatively low (0.03 $\mu g/m^3$) with a higher concentration (0.10 $\mu g/m^3$) in July. During the third air sampling period the concentrations of plant wax *n*-alkanes increase as much as four times compared to the other samples. This increase reflects air sampling variability that occurs at this location caused by changes in wind stress and direction. The general weather conditions during sampling were recorded as follows: May 5-7, low -5°C, high 6°C, SW wind at 3 m/s; July 7-9, low 14°C, high 24°C, SW wind at 2 m/s; and July 9-11, low 12°C, high 20°C, East wind at 2 m/s. The different wind direction from the east on July 9-11, may contribute to the increased hydrocarbon levels observed during that air sampling period.

During the July 9-11 period, when the total *n*-alkanes exceeded 0.17 $\mu g/m^3$, the petroleum *n*-alkane component also increased, confirming that petroleum derived hydrocarbons were adsorbed and transported with atmospheric particulate matter collected during air sampling events. Comparison data for the total extractable organic matter and total hydrocarbons of aerosols from other global areas is given in Table VI.7. The values for the 1996 Crater Lake aerosol samples are significantly higher compared to one sample taken in 1980 during the winter season and those from the other remote areas. The samples reflect higher levels of atmospheric particulate matter from both natural background and vehicular emissions. The high concentration of natural background may be the result of stronger local updraft winds which strip plant wax from vegetation and also resuspend soil detritus, and the components of vehicular emissions may reflect local traffic near the sampling site or longer distance transport of urban aerosol. Long distance transport of aerosols from Asia across the Pacific are too dilute with respect to organic matter to provide a detectable signal at Crater Lake. Their transit across the urbanized areas of California and Oregon result in the overwhelming additive incorporation of the North American emissions. It should be noted that snowmobile traffic in the winter season could also

provide a significant input of petroleum hydrocarbons to the lake surface (this was not tested in this program).

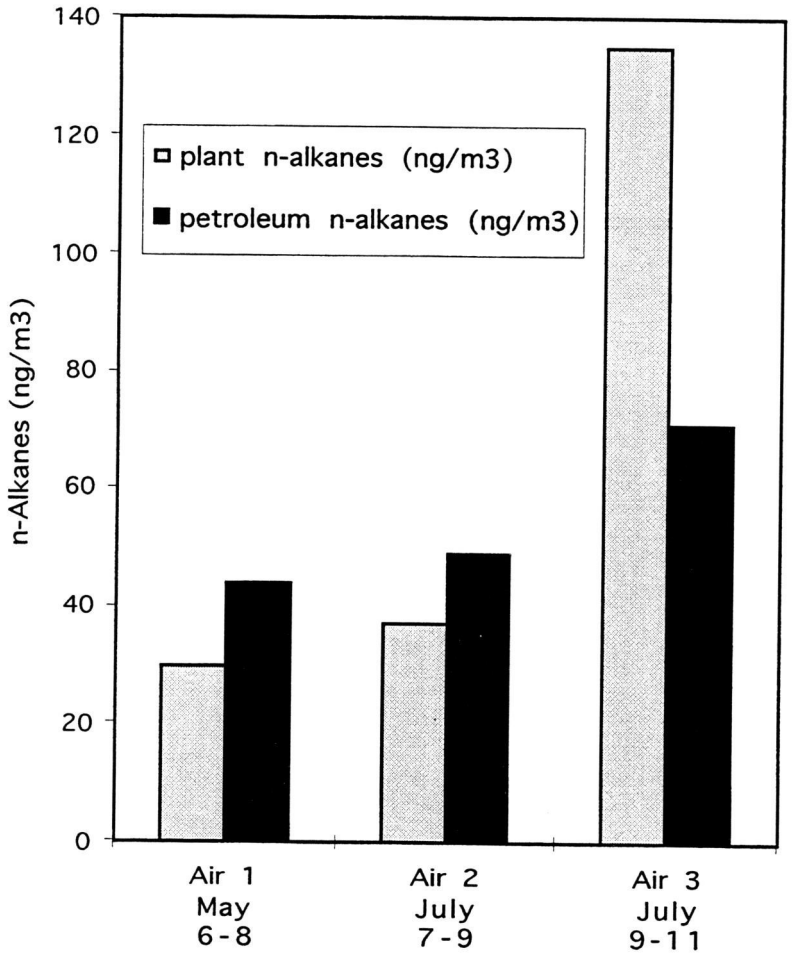

Figure VI.8. Bar plot summarizing the concentrations and distributions of plant and petroleum n-alkane hydrocarbons in Crater Lake air.

Table VI.7. Range of extractable organic matter and hydrocarbons in aerosols at Crater Lake and other global areas for comparison.

Location (year)	Total Extractable OM (ng/m^3)	Hydrocarbons (ng/m^3)	Reference and Comments
Crater Lake (1996)	2200-4700	63-174	This work (summer sample)
Crater Lake (1980)	90	1	Simoneit and Mazurek (1982) (winter sample)
South Atlantic Ocean (1985)	50-120	30-100	Simoneit *et al.* (1991) (also sampled sea spray-slick)
Amazonas (1986)	1300-4000	260-800	Simoneit *et al.* (1990) (primarily natural aerosol)
Lake Tahoe, CA (1978)	500-2300	50-150	Simoneit and Mazurek (1982) (mixture of natural and vehicular traffic)
Los Angeles, suburban (1979)	3000-4000	100-400	Simoneit and Mazurek (1982) (typical residential area)
Los Angeles, urban (1982)	3000-6300	-	Rogge *et al.* (1993b) (heavy traffic in city)

The concentrations of extractable (volatilizable carbon) and elemental carbon (black soot for example from diesel engine exhaust) in Crater Lake air particulate matter are given in Table VI.8. The extractable/volatilizable carbon concentration is high for the second July sample probably due to the different wind direction during the sampling period. The elemental carbon concentrations remained steady. Since petroleum *n*-alkane concentrations increased and elemental carbon concentrations remained steady through the sampling period, these results show that petroleum hydrocarbon components may be transported concurrently with particulate matter from higher plant sources which is consistent with the molecular data discussed above. Furthermore, since petroleum hydrocarbon components present in air particles may derive from both gasoline and diesel engine exhaust, the petroleum hydrocarbon and elemental carbon concentrations and distributions may also reflect the input of petroleum components to air from increased vehicle traffic (tourism) during the time of sampling.

Table VI.8. The concentrations of extractable/volatilizable and elemental carbon in aerosols at Crater Lake.

Sample	Date	Collection Time (hrs)		Extractable/Volatilizable[1] Carbon ($\mu g/m^3$)	Elemental Carbon[2] ($\mu g/m^3$)
1	5/08/96	48	1st filter	2.2	0.31
2	7/09/96	48	1st filter	2.5	0.22
3	7/11/96	48	1st filter	4.7	0.22
Average				3.1	0.25

[1]Carbon analyzed as volatilizable carbon (Birch and Cary, 1996; Johnson *et al.*, 1981).

[2]Carbon remaining analyzed as black soot (elemental C) (Birch and Cary, 1996; Johnson *et al.*, 1981).

Comparison data for other global areas of black carbon and volatile carbon in aerosols is found in Table VI.9. The values for the Crater Lake aerosol samples are relatively elevated compared to other rural or remote areas. This indicates potential localized emissions to the atmosphere from traffic and other detritus; however, more extensive monitoring is needed to fully assess this input.

SUMMARY OF MAJOR FINDINGS

The objective of the present investigation was to conduct the first comprehensive assessment of the levels and distributions of petroleum hydrocarbons in Crater Lake water and sediments. The results of the hydrocarbon analyses show the presence of both anthropogenic and natural hydrocarbons in Crater Lake. Petroleum hydrocarbon abundances greater than background levels have been found in some environmental samples taken. Removal processes such as evaporation or the formation of aerosols cause gasoline (aromatic and naphthenic compounds and *n*-alkanes $<C_{12}$) to disappear quickly from the surface. The presence of higher molecular weight PAH in surface slicks (100 μm film thickness) is essentially uniform in the areas sampled (72-85 ng/m^2) (Appendix VI.3). The distributions and abundances of *n*-alkanes, PAH and UCM from petroleum are similar for all surface slick sampling sites,

Table VI.9. Average concentrations of elemental (black) carbon and volatile carbon in aerosols from Crater Lake and other global areas for comparison.

Location	Elemental Carbon ($\mu g/m^3$)	Volatile Carbon ($\mu g/m^3$)	Reference and Comments
Crater Lake, OR	0.25	3.1	This work
Los Angeles, CA	3.8	6.3	Gray *et al.* (1986), urban
New York, NY	7.7	10.4	Shah *et al.* (1986); Wolff (1985), urban
USA	3.8	6.6	Shah *et al.* (1986), 46 urban areas
Nagoya, Japan	16.7	-	Kadowaki (1994), urban
China	6.6	10.2	Simoneit (unpublished), urban
Australia	0.2	2.5	Simoneit (unpublished), rural
Nigeria	0.5	14.7	Simoneit (unpublished), rural
Carus, OR	1.1	7.2	Watson (1979), rural
Sauvie, OR	1.8	7.3	Watson (1979), rural
Pt. Barrow, AK	0.3	0.9	Rosen *et al.* (1982), remote
Mauna Loa, HI	0.01	-	Weiss and Waggoner (1982), remote
S. Atlantic Ocean	0.005	0.8	Simoneit (unpublished), remote
South Pole	0.0015	-	Hansen *et al.* (1988), remote

however, the slick sample recovered at Wizard Island, has a pronounced UCM (7140 $\mu g/m^2$) and petroleum *n*-alkane component (1610 $\mu g/m^2$) because it was taken in the wake of a tour boat after mooring, idling and launching activities in that more enclosed area.

A comparison of the PAH present in shallow (near shore, 0.04 mg/kg) and deep (North Basin, 0.015 mg/kg) sediments shows that PAH concentrations are lower at depth in Crater Lake. In nearshore sediments collected at Cleetwood Cove and at the Cleetwood Cove boat mooring area, the impact of the increased boating activity is obvious. Concentrations of petroleum *n*-alkanes in sediments collected at 5 m depth at the Cleetwood Cove boat mooring area (1.44 mg/kg) exceed the petroleum and plant *n*-alkane concentrations at the other sites. Another important observation is that petroleum *n*-alkane concentrations are greater than plant *n*-alkane concentrations in all near shore sediments. This observation indicates that boating activities leave a detectable level of petroleum hydrocarbons in the sediments, especially in the Cleetwood Cove boat mooring area. Aliphatic petroleum hydrocarbons are at background in the sediments of North Basin (590 m water depth, 0.016 mg/kg). The

UCM normally associated with major petroleum inputs was not significant in these sediments. However, the presence of biomarkers such as the tricyclic terpanes, hopanes and steranes further confirms petroleum product input to these sediments.

Aerosol fallout is identified as a potentially minor contributor of petroleum hydrocarbons to surface water via atmospheric deposition. Extractable and elemental carbon analyses show that hydrocarbons associated with particles are present at significant concentrations. There is a seasonal input of hydrocarbons from higher plants during spring through summer. Increased tourism to Crater Lake National Park may also contribute to petroleum *n*-alkane concentrations during summer from motor vehicle exhaust sources.

Overall, the total petroleum hydrocarbon concentrations in Crater Lake are low and are found at concentrations similar to background levels in all environmental samples. However, boating activities are introducing petroleum hydrocarbons and their combustion residues to the lake as is evident from chemical analysis of environmental samples. The effect of this contamination on the natural environment of the lake is not known at this time. It is well documented that petroleum products (e.g., UCM, biomarkers) (Bieger *et al.*, 1996) and their combustion residues (e.g., PAH) are persistent (show some resistance to environmental degradation) in the environmental compartments of soil, water and sediment (Howard *et al.*, 1991). Their presence in the lake can ultimately pose problems depending on their concentrations, partitioning behavior between environmental and biological compartments, and lifetimes. Appendix VI.4. provides a best estimate for the levels of petroleum hydrocarbons in surface waters derived from boat activities.

In order to quantitatively estimate the amounts of petroleum hydrocarbons released by combustion emissions from boating it is necessary to understand gasoline engine emission characteristics which include fuel consumption, fine particulate emission rates and bulk content of organic and elemental carbon of the particles. In Crater Lake, all boats are equipped with gasoline engines (described earlier). Since the emission characteristics of the boats were not determined in this study, it is necessary to refer to external studies which model petroleum hydrocarbon emissions from similar internal combustion engines. Hildemann *et al.* (1991) determined the average mass emission rates for a variety of catalyst and non-catalyst equipped gasoline engines of automobiles similar to those of the boats at Crater Lake. Rogge *et al.* (1993b) further applied the same mass emission rates to model the levels of

petroleum derived combustion aerosols released to the atmosphere. By assuming that all tour boat combustion emissions are entering the water surface and are homogeneously distributed, it is possible to apply GC-MS analyses to determine a mass balance for elutable organic matter in exhaust emissions. Since a variety of organic compounds are produced by gasoline engine combustion, conservative marker compounds such as PAH may be used as tracers to determine the levels of petroleum combustion emissions from boat exhaust.

Application of a mass balance calculation (Appendix VI.4) shows that approximately 0.50 $\mu g/m^2$ of the total hydrocarbons found on Crater Lake surface water is attributable to petroleum from daily boating activities. It should be noted that the natural hydrocarbons from plant waxes ranged from 50-5900 $\mu g/m^2$ in the surface slicks (Appendix VI.2). This estimate of petroleum concentration is based on surface slick PAH concentrations. The actual exhaust emission contribution to surface slick is unknown due to primary physical processes (dispersion, dissolution, evaporation) and removal processes (adsorption, biochemical degradation, solubility). Slick formation is also coupled with variations in wind direction and speed which determine the concentrations and distribution of petroleum and natural hydrocarbons on the lake surface, and ultimately their concentrations and distribution in the water column and sediments.

ACKNOWLEDGMENTS

We would like to thank Chris Moser and Dale Hubbard (COAS, Oregon State University) and Mark Buktenica, Scott Girdner, Ashly Gibson and Brad Hecht (National Park Service) for their assistance in the field. Comments and suggestions by Mark Buktenica, Roy Irwin and Mac Brock to clarify and improve this report are greatly appreciated. This project was supported by an USDI-NPS grant (CA-9000-8-0006) to Robert W. Collier and Bernd R.T. Simoneit.

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CHAPTER VII: SUMMARY

The biogeochemistry and cycling of carbon (i.e., organic matter source, composition, transformation and fate) in the environment can be better understood by applying molecular biomarkers as tracers. Organic tracer analysis is primarily used to identify and distinguish between natural (e.g., plant waxes, internal lipid components, etc.) and anthropogenic (e.g., chlorinated synthetics, combustion emission products, etc.) sources of organic matter released to the environment. Natural organic matter is identified by its characteristic biomarkers from plant, animal, microbial and fungal origins (e.g., fatty acids, *n*-alkanes, phytosterols, wax esters, terpenoids, etc.). In the environment these biomarkers can be preserved or are transformed into products which retain the structural characteristics of their parent precursor molecule. This retention of chemical information is useful for determining the transformation mechanisms of the chemical intermediates that are formed along the parent precursor to product reaction pathway. Through biomarker analysis the parent precursors, reaction intermediates and final products can be traced as they are transported and transformed in environmental compartments. Ultimately, they reach their final fate as organic deposits in lacustrine, riverine and marine sediments.

Much of this work has concentrated on the Pacific Northwest region because it is relatively pristine in comparison with most areas of the northern hemisphere and represents natural background conditions with respect to its anthropogenic pollutant levels. The organic compositions of epicuticular waxes from conifers, particle emissions from the burning of both conifers and deciduous trees as well as grasses, natural soils and soils containing wildfire ash residues, and soil and river washout samples from burn areas were determined. The distributions and abundances of the organic components that make up the chemical fingerprints for each sample are strongly dependent on the vegetation type and on the extent of degradation from microbial and thermal alteration processes. The major organic constituents which can be applied as biomarker tracers were identified mainly as natural products and their alteration derivatives.

The lipid biomarker compositions of epicuticular waxes from conifers of western North American were determined. This information provides background data that is useful for chemotaxonomic purposes, identifying natural organic aerosol sources to

the atmosphere, identifying natural organic matter sources to soils, and for applying biomarker tracer analysis to environmental samples. The gross wax composition data is of utility for assessing direct particle emission signatures from biomass and secondary emission compositions from biomass fuels during burning.

The lipid biomarker components and derivatives were identified in smoke samples emitted from the biomass burning of gymnosperms, mainly temperate climate conifers of western North America. The data is of utility for assessing direct organic composition signatures for particle emissions from conifer fuels during biomass burning. The abundance order for the major molecular classes in conifer smoke samples was identified as the following: unresolved complex mixture (UCM)> diterpenoids > carboxylic acids > methoxyphenols > anhydrosaccharides > polycyclic aromatic hydrocarbons (PAH) > alkenes > alkanes > alkanols > steroids > alkanones > wax esters. The major biomarkers (diterpenoids) identified in the smoke samples are source specific thus they are useful as tracers for distinguishing the conifer burning component in atmospheric aerosol source attributions. The relative abundances of key biomarkers in conifer smoke may also be used to distinguish fuel type. The methylphenanthrenes to phenanthrene (MP:P) ratio (0.5-2.6, average = 1.6), average unresolved to resolved components (U:R) ratio (1.0), and the volatile organic carbon to elemental carbon (VOC/EC) ratio (3 to 78, average = 35) are each useful parameters for distinguishing conifer burning emissions from fossil fuel-derived combustion emissions (e.g., coal combustion, gasoline and diesel engine exhaust).

The lipid biomarker components and derivatives were also identified in smoke samples emitted from the biomass burning of angiosperms, mainly deciduous trees. The data is of utility for assessing direct organic composition signatures for particle emissions from deciduous tree fuel types during biomass burning. The abundance order for the major compound classes in deciduous tree smoke samples was identified as the following: UCM > carboxylic acids > *n*-alkanes > methoxyphenols > *n*-alkenes > triterpenoids > n-alkanones > PAH > anhydrosaccharides > steroids > alkylcyclohexanes > *n*-alkanols. The major biomarkers (triterpenoids) identified in the smoke samples are source specific, thus they are useful as tracers for distinguishing the deciduous tree burning component in atmospheric aerosol source attributions. The MP:P ratio (0.5-1.5, average = 1.0), average U:R ratio (0.7), and VOC/EC ratio (9 to 43, average = 23.6) are each useful for distinguishing deciduous

tree burning emissions from fossil fuel-derived emissions and other emissions such as those derived from conifer burning.

Additionally, biomarker tracers were identified in litter and soils, soils containing wildfire ash residues, and soil and river mud washed out after wildfire burning. The distributions and abundances of lipid biomarkers in soils were highly influenced by organic matter origin and on the extent of thermal alteration. The representative chemical fingerprint imparted to these soils showed the following: fatty acids > *n*-alkanes > *n*-alkanols > phytosterols. Under wildfire and prescribed burning conditions, the heat intensity, aeration, and duration of smoldering and flaming conditions determine the distributions and ratios of the homologous compound series that are deposited to soil surfaces. Since the biomarkers are high molecular weight components, they condense on ash particles as the smoke cools and deposit onto soil as internal components of char and heavy particles during wildfire and prescribed burning. The process of rain and river washing releases some of these internal components into the surrounding soil where they are further subjected to biological alteration. The distributions and abundances of homologous compound series coupled with biomarker tracer analysis provides a chemical fingerprint that is useful for identifying the single or multiple plant species contributions to soils. Subsequent alteration of soil organic matter by both thermal and biological processes further refines the chemical fingerprint by including both plant natural products and their alteration derivatives. Such a fingerprint is useful for tracking soils that are transported in the atmosphere by wind as suspended particles in dust storms, on land by erosion and in aquatic systems as suspended particles from field runoff and river washing.

Finally, biomarker tracers were used in a lacustrine setting (Crater Lake, OR) to determine the extent of petroleum hydrocarbon contamination from anthropogenic sources and activities. Overall, the total petroleum hydrocarbon concentrations in Crater Lake are low and are found at concentrations similar to background levels in all environmental samples. However, boating and related activities are introducing trace amounts of petroleum hydrocarbons and their combustion residues to the lake as is evident from biomarker tracer analysis of Crater Lake air, water, soil and sediment samples. The effect of this contamination on the natural environment of the lake is not known. It is well documented that petroleum products (e.g., UCM, biomarkers) and their combustion residues (e.g., PAH) are persistent (show some

resistance to environmental degradation) in the environmental compartments of soil, water and sediment. Their presence in a lake may subsequently pose problems depending on their concentrations, partitioning behavior between environmental and biological compartments, and lifetimes. Hence, the biomarker tracer analysis applied here is useful for developing lake management and mitigation strategies.

In conclusion, this work has demonstrated that biomarker compounds can be applied and are of utility as tracers to determine the sources and fate of natural and anthropogenic organic matter in the environment. The thermal alteration products identified here are especially useful for understanding the contribution of biomass burning to global atmospheric chemistry and carbon cycling.

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APPENDICES
(labeled by their respective chapters)

Appendix II.1. Percent composition of individual lipid components in epicuticular waxes.[1]

Carbon Number	Apache Pine n-Alkanes	Apache Pine n-Alkanoic Acids	Apache Pine n-Alkanols	Big-Cone Douglas Fir n-Alkanes	Big-Cone Douglas Fir n-Alkanoic Acids	Big-Cone Douglas Fir n-Alkanols	Brewer Spruce (CR) n-Alkanes	Brewer Spruce (CR) n-Alkanoic Acids	Brewer Spruce (CR) n-Alkanols	Brewer Spruce (WNF) n-Alkanes	Brewer Spruce (WNF) n-Alkanoic Acids	Brewer Spruce (WNF) n-Alkanols
7		1										
8		1										
9		2										
10												
11												
12		8										
13		5										
14		5	9						1			
15		1										
16	5	29	10		8	12		11	6			5
17	4	1			3	2						1
18	7	13	1		6	10		4	6			15
19	4	1	10		3	2						6
20	7	100	45		19	25		40	10			30
21	12	8	58		8	4	9		1	30		10
22	28	62	10	6	31	50	7	75	32	10	18	87
23	100	21	71	68	12	15	42	9	37	100	6	25
24	16	87	100	12	100	85	12	100	100	12	100	100
25	89	9	5	100	10	35	50	5	30	50	3	38
26	26	26	28	8	90	100	15	43	31	8	25	92
27	76	1	12	38	6	25	80	4	12	70		18
28	25	15	38	6	80	55	12	40	50	6		55
29	76	2		50		1	100	6	11	35		12
30	16	6		3		12	10	97	40	6		48
31	31	2		12			36		20	12		
32	14	7							63			
33	35	3										
34		9										
35												

[1](normalized to Cmax of each component class).

Appendix II.1. (Continued)

Carbon Number	California Redwood n-Alkanoic n-Alkanes	Acids	n-Alkanols	Douglas Fir (CR) n-Alkanoic n-Alkanes	Acids	n-Alkanols	Douglas Fir (UNF) n-Alkanoic n-Alkanes	Acids	n-Alkanols	Montezuma Pine n-Alkanoic n-Alkanes	Acids	n-Alkanols
7												
8											2	
9											3	
10												
11												
12											29	1
13		8										2
14		37	5									4
15											1	2
16		4	3		6	5		9	2		49	3
17						1		5	1		13	2
18		1	3		4	5		4	1	6	16	32
19	32					1		2	1	3	11	1
20		15	6		22	5		18	3	5	100	38
21	36	1	5		3	1	4	3	2	3	5	15
22	14	29	21		28	17	6	75	1	4	79	100
23	36	5	13		7	4	87	9	1	18	12	19
24	50	51	39	10	100	81	20	100	2	32	78	22
25	55	3		50	4	8	100	8	1	28	8	5
26	29	20	100	8	25	100	6	93	100	12	44	38
27	100	2		64		1	30		10	67	13	21
28	29	12		8		30	4		13	15	57	30
29	3	1		100		2	38		6	100	18	
30	10	17		6		63	3		12	6	53	
31	83	1		38		6	10			17	11	
32	7	100				18				2	26	
33	45									6	2	
34											10	
35												

[1](normalized to Cmax of each component class).

Appendix II.1. (Continued)

Carbon Number	Mountain Hemlock n-Alkanoic			Norway Spruce n-Alkanoic			Pacific Silver Fir n-Alkanoic			Ponderosa Pine n-Alkanoic		
	n-Alkanes	Acids	n-Alkanols	n-Alkanes	Acids	n-Alkanols	n-Alkanes	Acids	n-Alkanols	n-Alkanes	Acids	n-Alkanols
7												
8												
9												
10												
11												
12									2			3
13									1			1
14					40				3			6
15					14							2
16		8	1		100	4		18	6			5
17						3		5	3			3
18		10	1		17	2		4	12			5
19						1		3	4			1
20		17	5		19	10		15	12			10
21			2			4	6		3			3
22		18	6		19	5	10	34	23			25
23		8	6			6	55	40	14	14		4
24	1	37	30		15	50	29	100	100	10		100
25	12	28	6	1		25	100	6	37	30		10
26	1	56	50			100	24	59	75	8		54
27	25	20		1		26	95	6	15	48		5
28	2	100	100	1		75	12	54	25	6		43
29	60	82		3		2	38		10	26		6
30	3	75	50	3		25	6		14	4		38
31	100			12			12			12		
32	4			6						22		12
33	25			100						100		
34				12						4		
35				50						12		

[1](normalized to Cmax of each component class).

Appendix II.1. (Continued)

Carbon	Sitka Spruce n-Alkanoic			Western Juniper n-Alkanoic			White Fir n-Alkanoic		
Number	n-Alkanes	Acids	n-Alkanols	n-Alkanes	Acids	n-Alkanols	n-Alkanes	Acids	n-Alkanols
7		8							
8		2							
9		1							
10									
11									
12									
13									
14		1							
15		2							
16		4				1			12
17		2				1			2
18	6	2	4			2			10
19	5	1	12			1			2
20	18	28	100			14			14
21	6	16	30	6		4	30		5
22	6	100	86	12		10	4		100
23	18	34	20	60		9	40		5
24	16	100	17	18		50	12		24
25	20	7	5	100		25	70		6
26	18	32	15	12		100	10		12
27	36	3	12	45		6	62		6
28	15	88	4	6		25	8		38
29	100	3		42		6	25		4
30		36		5		25	5		7
31	26	3		25			28		
32		7					9		
33							100		
34							2		
35							10		

[1](normalized to Cmax of each component class).

Appendix III.1.Concentrations (μg/kg of conifer fuel burned) of the major organic constituents in conifer smoke.

Compound Name	Composition	M.W.	Apache Pine	California Redwood	Douglas Fir	Eastern White Pine	Lodgepole Pine	Montezuma Pine	Mountain Hemlock	Noble Fir	Pacific Silver Fir	Ponderosa Pine	Port Orford Cedar	Sitka Spruce	Western White Pine	ID Basis
I. HOMOLOGOUS SERIES																
n-Alkanes																
Natural Products																
n-tetradecane	$C_{14}H_{30}$	198	0	0	0	0	0	0	0	0	0	0	0	224	0	A
n-pentadecane	$C_{15}H_{32}$	212	0	0	1033	0	699	0	0	0	0	0	0	104	0	A
n-hexadecane	$C_{16}H_{34}$	226	67	586	2305	29	156	0	196	0	120	0	934	778	723	A
n-heptadecane	$C_{17}H_{36}$	240	112	56	4368	13	86	0	113	26	143	0	90	88	192	A
n-octadecane	$C_{18}H_{38}$	254	134	59	7997	71	74	32	156	67	244	0	196	157	472	A
n-nonadecane	$C_{19}H_{40}$	268	251	314	7653	108	383	40	384	94	699	180	509	184	1496	A
n-eicosane	$C_{20}H_{42}$	282	4397	927	18391	134	775	43	446	77	1753	1477	354	497	1408	A
n-heneicosane	$C_{21}H_{44}$	296	688	516	11558	338	720	77	982	315	1422	204	1050	8624	1934	A
n-docosane	$C_{22}H_{46}$	310	861	641	12705	277	660	114	743	185	1045	385	795	798	710	A
n-tricosane	$C_{23}H_{48}$	324	787	680	3853	271	787	403	1306	201	700	577	866	1310	718	A
n-tetracosane	$C_{24}H_{50}$	338	417	1116	1706	432	1140	82	1421	63	335	386	844	529	846	A
n-pentacosane	$C_{25}H_{52}$	352	287	488	408	185	303	277	636	93	238	331	634	476	655	A
n-hexacosane	$C_{26}H_{54}$	366	363	246	650	97	159	77	32	209	64	273	427	155	611	A
n-heptacosane	$C_{27}H_{56}$	380	409	277	1856	212	137	167	412	927	1780	127	945	746	196	A
n-octacosane	$C_{28}H_{58}$	394	144	279	1751	97	707	52	94	307	399	110	393	176	81	A
n-nonacosane	$C_{29}H_{60}$	408	265	477	2713	239	110	138	266	441	833	81	1253	560	116	A
n-triacontane	$C_{30}H_{62}$	422	870	1157	1882	108	669	49	0	586	393	179	377	706	1327	A
n-hentriacontane	$C_{31}H_{64}$	436	3713	3350	0	391	1307	72	37	571	483	0	2866	262	111	A
n-dotriacontane	$C_{32}H_{66}$	450	48	0	0	35	0	44	0	646	739	0	310	0	0	A
n-tritriacontane	$C_{33}H_{68}$	464	49	0	0	118	1629	13	0	0	0	0	9157	0	0	A
n-tetratriacontane	$C_{34}H_{70}$	478	45	0	0	0	0	0	0	0	0	0	465	0	0	A
Total Alkanes			13906	11168	80830	3156	10502	1679	7224	4808	11390	4310	22467	16371	11595	
CPI			0.9	1.2	0.7	1.5	1.4	2.4	1.3	1.2	1.2	0.5	3.4	3.1	0.9	
Cmax			20	31	20	24	33	23	24	27	27	20	33	21	21	
n-Alkenes																
Alteration Products																
n-tridec-1-ene	$C_{13}H_{26}$	182	0	0	445	0	0	0	0	0	0	0	0	0	0	S
n-tetradec-1-ene	$C_{14}H_{28}$	196	0	0	1473	0	0	0	0	0	0	0	638	556	0	S
n-pentadec-1-ene	$C_{15}H_{30}$	210	0	0	1880	0	0	0	0	0	0	0	0	0	0	S
n-hexadec-1-ene	$C_{16}H_{32}$	224	782	508	4951	0	148	0	100	0	713	0	0	129	413	S
n-heptadec-1-ene	$C_{17}H_{34}$	238	893	61	8648	0	121	38	122	90	392	0	359	0	0	S
n-octadec-1-ene	$C_{18}H_{36}$	252	482	385	17981	0	338	33	476	135	1053	0	1454	510	555	A
n-nonadec-1-ene	$C_{19}H_{38}$	266	671	417	24158	0	607	35	840	206	1337	83	1066	190	796	S
n-eicos-1-ene	$C_{20}H_{40}$	280	923	142	25723	36	1139	39	1111	255	1753	208	0	453	0	A
n-heneicos-1-ene	$C_{21}H_{42}$	294	692	870	73067	0	675	38	1169	192	1474	438	1047	443	32945	S

n-docos-1-ene	$C_{22}H_{44}$	308	1583	1459	8450	0	1972	114	1667	709	5534	1010	1617	1342	2431	S
n-tricos-1-ene	$C_{23}H_{46}$	322	614	426	24109	0	263	31	44	134	517	258	727	668	494	S
n-tetracos-1-ene	$C_{24}H_{48}$	336	1566	484	3166	192	746	332	1244	262	1313	605	599	516	958	S
n-pentacos-1-ene	$C_{25}H_{50}$	350	112	469	408	0	163	35	201	197	357	0	902	499	2216	S
n-hexacos-1-ene	$C_{26}H_{52}$	364	363	0	1547	0	89	0	79	0	97	0	513	134	611	S
n-heptacos-1-ene	$C_{27}H_{54}$	378	409	0	703	0	128	0	203	0	0	0	479	0	196	S
n-octacos-1-ene	$C_{28}H_{56}$	392	144	0	0	0	210	0	0	0	0	0	455	0	81	S
n-nonacos-1-ene	$C_{29}H_{58}$	406	134	0	0	0	0	0	0	0	0	0	0	0	0	S
Total Alkenes			9234	5220	196709	229	6599	696	7256	2179	14541	2602	9857	5440	41697	
CPI			0.6	0.8	2.1	nd	0.4	0.3	0.6	0.6	0.4	0.4	0.9	0.5	7.3	
Cmax			22	22	21	24	22	24	22	22	22	22	22	22	21	
Isoprenoids																
Alteration Product																
neophytadiene	$C_{20}H_{38}$	278	452	0	0	0	0	0	0	0	0	0	704	0	0	I
Carboxylic Acids																
Natural Products																
n-heptanoic acid	$C_7H_{14}O_2$	130	0	0	293	0	0	0	0	0	0	0	0	0	0	S
n-octanoic acid	$C_8H_{16}O_2$	144	2904	717	2264	1690	0	2167	0	0	3313	0	538	0	473	S
n-nonanoic acid	$C_9H_{18}O_2$	158	2931	1248	1092	3278	0	1620	0	0	2754	0	4115	0	511	S
n-decanoic acid	$C_{10}H_{20}O_2$	172	3028	947	209	2725	232	1775	0	0	1505	0	3205	0	586	S
n-undecanoic acid	$C_{11}H_{22}O_2$	186	1579	1060	763	1317	395	889	0	0	1251	74	1778	0	1445	S
n-dodecanoic acid	$C_{12}H_{24}O_2$	200	25856	14213	1337	19445	12521	16194	0	0	4985	345	5897	1578	4186	S
n-tridecanoic acid	$C_{13}H_{26}O_2$	214	1986	1980	1846	1296	418	778	0	0	1379	157	0	715	614	S
n-tetradecanoic acid	$C_{14}H_{28}O_2$	228	31530	26817	3283	29728	10462	11498	602	71	8346	748	16240	8859	5252	S
n-pentadecanoic acid	$C_{15}H_{30}O_2$	242	9331	868	10110	6362	1757	3945	1384	66	7480	1095	52940	2890	1785	S
n-hexadecanoic acid	$C_{16}H_{32}O_2$	256	102702	41515	12040	51891	27103	19701	1773	699	39672	4503	57036	39278	32165	A
n-heptadecanoic acid	$C_{17}H_{34}O_2$	270	7222	3033	5605	9465	1219	2631	4297	115	3007	800	5411	2491	1821	S
n-octadecanoic acid	$C_{18}H_{36}O_2$	284	26167	6940	5098	48436	7284	7659	4991	316	17814	2728	8303	12766	18372	A
n-nonadecanoic acid	$C_{19}H_{38}O_2$	298	21778	7750	727	20680	0	6623	827	137	6086	0	3005	0	0	S
n-eicosanoic acid	$C_{20}H_{40}O_2$	312	83678	16842	13656	170310	14261	26293	8479	387	23511	10161	18324	17892	29838	S
n-heneicosanoic acid	$C_{21}H_{42}O_2$	326	3831	1688	2579	22901	846	4693	285	81	12799	1390	3209	30749	841	S
n-docosanoic acid	$C_{22}H_{44}O_2$	340	30243	28652	37705	65029	13468	17720	34397	895	41689	13004	43635	45229	12015	S
n-tricosanoic acid	$C_{23}H_{46}O_2$	354	8257	3664	2640	14190	1339	4302	290	110	5884	3465	5921	4484	1968	S
n-tetracosanoic acid	$C_{24}H_{48}O_2$	368	20002	12056	22822	31058	7294	18283	28638	401	25663	10639	33639	26668	1822	S
n-pentacosanoic acid	$C_{25}H_{50}O_2$	382	0	1053	782	3405	372	1367	523	227	1533	0	2511	1403	407	S
n-hexacosanoic acid	$C_{26}H_{52}O_2$	396	1863	1801	1845	2772	696	4226	4362	307	5135	1856	4572	2066	1089	S
n-heptacosanoic acid	$C_{27}H_{54}O_2$	410	0	441	0	331	0	218	0	161	430	0	516	341	0	S
n-octacosanoic acid	$C_{28}H_{56}O_2$	424	0	1846	430	664	0	1286	82	172	2596	35	4371	760	0	S
n-nonacosanoic acid	$C_{29}H_{58}O_2$	438	0	0	0	834	0	121	0	170	1126	0	3254	0	0	S
n-triacontanoic acid	$C_{30}H_{60}O_2$	452	0	1851	1404	3109	0	0	0	793	4725	0	0	0	527	S
n-hentriacontanoic acid	$C_{31}H_{62}O_2$	466	0	0	0	726	0	0	0	331	3472	0	0	0	0	S
n-dotriacontanoic acid	$C_{32}H_{64}O_2$	480	0	5818	488	9410	0	0	0	729	1608	0	0	0	552	S
n-tritriacontanoic acid	$C_{33}H_{66}O_2$	494	0	0	0	0	0	0	0	0	1012	0	0	0	0	S
n-tetratriacontanoic acid	$C_{34}H_{68}O_2$	508	0	2830	0	0	0	0	0	0	0	0	0	0	0	S

n-octadecadienoic acid	$C_{18}H_{32}O_2$	280	0	0	3517	0	17116	0	186	0	0	0	399	0	0	S
n-octadecenoic acid	$C_{18}H_{34}O_2$	282	45835	385	17981	111978	35673	0	476	0	1053	0	1454	510	555	S
α,ω-nonanedioc acid	$C_9H_{16}O_4$	188	0	0	2677	0	0	0	421	0	0	0	0	0	0	S
α,ω-undecanedioc acid	$C_{11}H_{20}O_4$	216	0	331	0	0	4073	0	0	0	0	0	0	0	0	S
α,ω-tridecanedioc acid	$C_{13}H_{24}O_4$	244	6526	464	0	0	0	0	149	0	0	0	0	0	0	S
α,ω-tetradecanedioic acid	$C_{14}H_{26}O_4$	258	0	0	0	0	0	0	197	0	0	0	0	0	0	S
α,ω-pentadecenedioic acid	$C_{15}H_{26}O_4$	270	0	727	0	0	0	0	0	0	9775	0	0	0	0	S
α,ω-pentadecanedioic acid	$C_{15}H_{28}O_4$	272	0	1287	0	0	0	0	209	0	0	0	0	0	0	S
α,ω-hexadecenedioic acid	$C_{16}H_{28}O_4$	284	0	683	0	0	0	0	0	0	0	0	0	0	0	S
α,ω-hexadecanedioic acid	$C_{16}H_{30}O_4$	286	0	276	7970	0	0	0	0	0	5665	0	1141	0	0	A
α,ω-heptadecanedioic acid	$C_{17}H_{32}O_4$	300	0	0	2865	0	0	0	278	0	0	0	0	0	0	S
α,ω-octadecenedioc acid	$C_{18}H_{32}O_4$	312	0	0	2469	0	0	0	0	0	3231	0	0	0	0	S
α,ω-octadecanedioc acid	$C_{18}H_{34}O_4$	314	0	0	4902	0	0	0	1273	0	1565	0	0	0	0	S
α,ω-nonadecanedioc acid	$C_{19}H_{36}O_4$	328	0	0	3732	0	0	0	352	0	1790	0	0	0	0	S
α,ω-eicosanedioic acid	$C_{20}H_{38}O_4$	342	0	0	2460	0	152	0	573	0	1172	211	0	0	0	S
α,ω-heneicosanedioic acid	$C_{21}H_{40}O_4$	356	0	0	1388	0	0	0	176	0	0	0	0	0	0	S
α,ω-docosanedioic acid	$C_{22}H_{42}O_4$	370	0	0	321	0	0	0	378	0	0	67	0	0	0	S
α,ω-tricosenedioic acid	$C_{23}H_{42}O_4$	382	0	0	0	0	1366	0	0	0	0	0	0	0	0	S
α,ω-tricosanedioic acid	$C_{23}H_{44}O_4$	384	0	0	0	0	0	11897	0	0	0	0	0	0	0	S
α,ω-pentacosenedioic acid	$C_{25}H_{46}O_4$	410	0	0	0	0	628	0	0	0	0	0	0	0	0	S
α,ω-pentacosanedioic acid	$C_{25}H_{48}O_4$	412	0	0	0	0	985	419	0	0	0	0	0	0	0	S
α,ω-heptacosenedioic acid	$C_{27}H_{50}O_4$	438	0	0	0	0	136	0	0	0	0	0	0	0	0	S
α,ω-heptacosanedioic acid	$C_{27}H_{52}O_4$	440	0	0	0	0	4627	9305	0	0	0	0	0	0	0	S
α,ω-nonacosanedioic acid	$C_{29}H_{56}O_4$	468	0	0	0	0	1200	9305	0	0	0	0	0	0	0	S
7-phenylheptanoic acid	$C_{13}H_{18}O_2$	206	0	0	0	0	1589	9305	0	0	0	0	0	0	0	I
8-phenyloctanoic acid	$C_{14}H_{20}O_2$	220	0	0	0	0	1287	9305	0	0	0	0	0	0	0	I
ω-methoxystearic acid	$C_{19}H_{38}O_3$	312	0	0	0	0	0	0	0	0	0	0	6994	0	0	I
ω-methoxy-10-hydroxystearic acid	$C_{19}H_{38}O_4$	330	0	0	0	0	0	0	0	0	1279	0	12129	0	0	I
11,18-dimethoxy-10-hydroxystearic acid	$C_{20}H_{40}O_5$	360	0	0	0	0	0	0	0	0	0	0	5858	0	0	I
Total Carboxylic Acids			437248	189783	179300	633032	156680	153988	95598	6169	253023	51279	281412	198678	116825	
CPI			6.1	7.9	4.1	5.4	15.6	5.0	11.0	3.4	4.0	6.4	2.5	3.6	14.2	
Cmax			16	16	22	20	16	20	22	22	22	22	16	22	16	
n-Alkanones																
Natural Products																
n-hexadecan-2-one	$C_{16}H_{32}O$	240	0	0	0	0	0	0	59	0	0	0	2530	0	0	S
n-heptadecan-2-one	$C_{17}H_{34}O$	254	0	0	0	0	0	0	24	0	0	0	2187	0	0	S
n-octadecan-2-one	$C_{18}H_{36}O$	268	1920	0	0	0	194	0	202	0	0	0	1474	0	0	S
n-nonadecan-2-one	$C_{19}H_{38}O$	282	0	0	0	0	371	0	818	225	0	0	1031	0	0	S
n-eicosan-2-one	$C_{20}H_{40}O$	296	0	0	0	0	88	0	630	113	0	0	1326	0	0	S
n-heneicosan-2-one	$C_{21}H_{42}O$	310	0	961	0	0	386	0	1396	183	0	0	3212	0	0	S
n-docosan-2-one	$C_{22}H_{44}O$	324	0	0	0	0	1000	0	628	113	0	0	1396	0	0	S
n-tricosan-2-one	$C_{23}H_{46}O$	338	5660	298	0	0	484	160	210	232	0	0	1675	2950	0	S
n-tetracosan-2-one	$C_{24}H_{48}O$	352	14793	297	0	0	94	177	105	117	715	0	1605	0	0	S
n-pentacosan-2-one	$C_{25}H_{50}O$	366	1090	193	0	0	74	160	358	444	842	0	606	805	0	S
n-hexacosan-2-one	$C_{26}H_{52}O$	380	0	149	0	0	28	0	710	105	0	0	1735	0	0	S

n-heptacosan-2-one	$C_{27}H_{54}O$	394	0	387	0	0	54	164	174	825	416	0	5334	0	0	S
n-octacosan-2-one	$C_{28}H_{56}O$	408	0	267	0	0	0	0	0	108	0	0	928	0	0	S
n-nonacosan-2-one	$C_{29}H_{58}O$	422	0	319	0	0	0	134	0	238	383	0	3457	0	0	S
n-triacontan-2-one	$C_{30}H_{60}O$	436	0	0	0	0	0	0	0	0	0	0	847	0	0	S
n-hentriacontan-2-one	$C_{31}H_{62}O$	450	0	97	0	0	0	0	0	206	328	0	2991	0	0	S
n-dotriacontan-2-one	$C_{32}H_{64}O$	464	0	0	0	0	0	0	0	0	0	0	401	0	0	S
n-tritriacontan-2-one	$C_{33}H_{66}O$	478	0	0	0	0	0	0	0	0	0	0	234	0	0	S
6,10,14-trimethyl-2-pentadecan-2-one	$C_{18}H_{36}O$	268	473	0	0	2837	0	0	0	0	0	0	0	0	0	S
n-nonacosan-10-one	$C_{29}H_{58}O$	422	777	73	0	868	0	625	0	0	0	0	0	0	0	S
Total Alkanones			24712	3040	0	3705	2774	1419	5314	2908	2685	0	32969	3755	0	
CPI			0.4	3.2	nd	nd	1.0	3.5	1.3	4.2	2.8	nd	1.7	nd	nd	
Cmax			24	21	nd	nd	22	24	21	27	25	nd	27	23	nd	
n-Alkanols																
Natural Products																
n-octadecanol	$C_{18}H_{38}O$	270	0	0	333	0	0	0	0	0	0	0	0	0	0	A
n-nonadecanol	$C_{19}H_{40}O$	284	0	0	415	0	0	0	0	0	0	0	0	0	0	A
n-eicosanol	$C_{20}H_{42}O$	298	0	0	634	0	0	0	0	0	0	0	0	0	0	A
n-heneicosanol	$C_{21}H_{44}O$	312	0	0	316	0	0	0	0	0	0	0	0	0	0	A
n-docosanol	$C_{22}H_{46}O$	326	2610	136	3291	10065	131	2007	292	2653	4588	325	1096	1018	954	A
n-tricosanol	$C_{23}H_{48}O$	340	0	0	510	0	0	0	0	1184	0	0	0	0	0	A
n-tetracosanol	$C_{24}H_{50}O$	354	3701	153	878	3768	86	2883	314	1230	1418	244	962	745	355	S
n-pentacosanol	$C_{25}H_{52}O$	368	0	0	429	0	0	0	0	0	0	0	0	0	0	A
n-hexacosanol	$C_{26}H_{54}O$	382	0	0	1753	0	134	0	0	650	0	0	0	0	0	S
n-heptacosanol	$C_{27}H_{56}O$	396	0	0	0	0	0	0	0	0	0	0	0	0	0	A
n-octacosanol	$C_{28}H_{58}O$	410	0	0	0	0	97	0	0	1005	0	0	0	0	0	S
n-nonacosanol	$C_{29}H_{60}O$	424	0	0	0	0	0	0	0	0	0	0	0	0	0	S
n-triacontanol	$C_{30}H_{62}O$	438	0	0	0	0	0	0	0	1207	0	0	0	0	0	S
n-nonacosan-10-ol	$C_{29}H_{60}O$	424	14494	2088	1710	13938	929	15547	378	4590	6073	119	4729	3872	360	S
Total Alkanols			20805	2377	10269	27771	1377	20437	984	12518	12079	688	6787	5635	1669	
CPI			nd	nd	4.1	nd	nd	nd	nd	5.7	nd	nd	nd	nd	nd	
Cmax			24	24	22	22	22	24	24	22	22	22	22	22	22	
Wax Esters																
Natural Products																
nonyl dodecanoate	$C_{21}H_{42}O_2$	326	357	0	0	0	0	0	0	0	0	0	0	0	0	S
decyl dodecanoate	$C_{22}H_{44}O_2$	340	1232	0	0	0	0	0	0	0	0	0	0	0	0	S
undecyl dodecanoate	$C_{23}H_{46}O_2$	354	937	0	0	0	0	0	0	0	0	0	0	0	0	S
dodecadienyl dodecanoate	$C_{24}H_{44}O_2$	364	2074	0	0	0	0	0	0	0	0	0	0	0	0	S
dodecyl dodecanoate	$C_{24}H_{48}O_2$	368	0	851	0	0	415	0	0	0	0	0	0	0	0	S
tridecyl dodecanoate	$C_{25}H_{50}O_2$	382	1012	1509	0	0	0	0	0	0	0	365	0	0	0	S
tetradecadienyl dodecanoate	$C_{26}H_{48}O_2$	392	0	0	0	0	0	1749	0	0	0	0	0	0	0	S
tetradecenyl dodecanoate	$C_{26}H_{50}O_2$	394	5314	0	0	0	0	0	0	0	0	0	0	0	0	S
tetradecyl dodecanoate	$C_{26}H_{52}O_2$	396	0	0	0	4607	0	0	0	0	0	0	0	0	0	S
pentadecyl dodecanoate	$C_{27}H_{54}O_2$	410	0	1412	0	0	0	0	0	0	0	0	0	0	0	S

hexadecenyl dodecanoate	$C_{28}H_{54}O_2$	422	0	3250	0	0	0	0	0	0	0	0	0	0	0	S
hexadecyl dodecanoate	$C_{28}H_{56}O_2$	424	0	0	0	0	0	1333	0	0	0	0	0	0	0	S
heneicosanyl dodecanoate	$C_{33}H_{66}O_2$	494	0	0	0	3164	0	0	0	0	0	0	0	0	0	S
dodecenyl tetradecanoate	$C_{26}H_{50}O_2$	394	0	3350	0	0	0	0	0	0	0	0	0	0	0	S
dodecyl tetradecanoate	$C_{26}H_{52}O_2$	396	0	0	0	615	3435	0	0	0	0	0	0	924	0	S
tridecyl tetradecanoate	$C_{27}H_{54}O_2$	410	0	0	0	0	0	0	0	0	0	0	0	488	0	S
tetradecyl tetradecanoate	$C_{28}H_{56}O_2$	424	1513	0	0	5243	1026	0	0	0	0	0	0	724	0	S
octadecyl tetradecanoate	$C_{32}H_{64}O_2$	480	0	0	0	604	0	0	0	0	0	0	0	0	0	S
hexadecyl hexadecanoate	$C_{32}H_{64}O_2$	480	0	0	0	0	0	0	0	0	0	0	0	0	645	S
Total Wax Esters			12439	10373	0	14234	4876	3083	0	0	0	365	0	2136	645	
II. BIOMARKERS																
Sesquiterpenoids (C_{15})																
Natural Products																
5-hydroxycalamanene	$C_{15}H_{22}O$	218	0	0	0	0	0	0	0	0	0	0	14606	0	0	I
α-calacorene	$C_{15}H_{20}O$	200	0	0	0	0	0	0	0	0	0	0	1446	0	0	I
aromadendrol	$C_{15}H_{24}O$	220	0	0	0	0	0	0	0	0	0	0	694	0	0	I
β-oplopenone	$C_{15}H_{24}O$	220	0	0	0	0	0	0	0	0	0	0	16900	0	0	I
6-deoxygeigerin	$C_{15}H_{20}O_3$	248	0	0	0	0	0	0	0	0	0	0	16836	0	0	I
Alteration Products																
cadalene	$C_{15}H_{18}$	198	0	0	0	0	0	0	0	0	0	0	921	0	1263	I
calamenene	$C_{15}H_{22}$	202	0	0	0	0	0	1317	0	0	0	0	3460	0	0	I
Diterpenoids (C_{20})																
Natural Products																
dehydroabietane	$C_{20}H_{30}$	270	0	0	7971	2714	607	2872	228	160	0	0	2899	1023	0	A
hibaene	$C_{20}H_{32}$	272	0	0	0	0	0	183	0	0	0	0	28482	0	0	I
isophyllocladene	$C_{20}H_{32}$	272	0	0	0	0	0	0	0	0	0	0	0	645	0	I
Isopimaradiene	$C_{20}H_{32}$	272	0	0	0	0	0	0	0	0	0	0	0	0	3309	I
laurene	$C_{20}H_{32}$	272	0	0	0	0	0	372	0	0	0	0	0	468	0	I
5β-podocarpa-8,11,13-trien-16-oic acid	$C_{16}H_{24}O_2$	272	0	0	0	0	0	9362	0	0	0	2805	0	0	0	I
rimuene	$C_{20}H_{32}$	272	947	0	0	0	0	4798	0	0	0	0	0	789	0	I
manoyl oxide	$C_{20}H_{34}O$	290	488	0	0	0	0	0	0	0	0	0	3467	0	14048	I
totarol	$C_{20}H_{30}O$	286	0	0	0	0	0	0	0	0	0	0	57197	0	0	I
abietol	$C_{20}H_{32}O$	288	0	0	4390	0	3773	0	0	0	0	0	0	0	0	I
abietic acid	$C_{20}H_{30}O_2$	302	0	0	17488	24338	8524	13178	0	2885	26141	13127	0	6456	3651	A
iso-pimaric acid	$C_{20}H_{30}O_2$	302	124568	3387	1649	59988	7983	6143	1388	0	0	7627	3916	12399	19284	A
palustric acid	$C_{20}H_{30}O_2$	302	18956	0	6044	0	7407	8018	0	2400	16365	872	0	0	4673	A
pimaric acid	$C_{20}H_{30}O_2$	302	17284	0	0	22722	0	7637	0	0	0	6116	0	2990	0	A
sandaracopimaric acid	$C_{20}H_{30}O_2$	302	0	0	2550	0	4266	4807	695	0	0	3955	0	0	5712	A
daniellic acid	$C_{20}H_{28}O_3$	316	0	26314	0	0	113	0	0	0	0	3313	0	0	0	I
polyaltic acid	$C_{20}H_{28}O_3$	316	0	10773	0	0	0	0	0	0	0	0	0	0	0	I
copalic acid	$C_{20}H_{34}O_2$	318	0	0	0	0	0	0	0	0	0	0	0	0	274	I
agatholic acid	$C_{20}H_{34}O_3$	322	596	0	0	0	3331	9790	0	0	0	0	0	0	0	I

pinifolic acid	$C_{22}H_{36}O_4$	364	267	0	0	0	0	402	0	0	0	1561	0	0	0	I
Alteration Products																
bisnorsimonellite	$C_{17}H_{20}$	224	0	0	0	0	0	0	0	0	0	0	0	0	2637	I
retene	$C_{18}H_{18}$	234	25003	274	6510	25339	4165	25043	573	963	3842	7797	0	2634	34717	A
dihydroretene	$C_{18}H_{20}$	236	2105	0	0	2554	0	6024	0	90	0	931	0	1376	5050	I
tetrahydroretene	$C_{18}H_{22}$	238	5044	0	0	5808	1500	9891	0	0	0	1674	0	2493	16133	I
methylretene	$C_{19}H_{20}$	248	0	0	0	0	194	0	0	0	0	801	0	0	0	I
7-isopropyl-1,2,3,4-tetrahydrophenanthrene-1-aldehyde	$C_{18}H_{20}O$	252	1209	0	0	0	0	0	0	0	0	0	0	0	0	I
18-norabieta-4,6,8,11,13-pentaene	$C_{19}H_{24}$	252	0	0	0	0	0	2077	0	0	0	0	0	0	1768	I
simonellite	$C_{19}H_{24}$	252	0	0	2333	2268	446	0	0	4737	802	392	584	865	2411	I
dihydrosimonellite	$C_{19}H_{26}$	254	0	0	0	0	548	6620	0	0	0	0	0	0	0	I
18-norabieta-2,8,11,13-tetraene	$C_{19}H_{26}$	254	0	0	14379	0	1358	7731	0	0	0	0	0	0	0	I
18-norabieta-3,8,11,13-tetraene	$C_{19}H_{26}$	254	1761	0	0	0	0	0	0	194	0	0	0	231	0	I
18-norabieta-4,8,11,13-tetraene	$C_{19}H_{26}$	254	4397	0	0	0	0	4485	0	0	0	1477	0	0	14267	I
18-norabieta-4(19),8,11,13-tetraene	$C_{19}H_{26}$	254	0	0	0	0	0	4000	0	0	0	0	0	0	0	I
19-norabieta-4(18),8,11,13-tetraene	$C_{19}H_{26}$	254	1403	0	0	0	0	0	0	0	1276	1280	0	291	12614	I
19- or 18-norabieta-6,8,11,13-tetraene	$C_{19}H_{26}$	254	554	0	0	0	0	0	0	0	0	0	0	0	0	I
dehydroabietin	$C_{19}H_{28}$	256	0	0	11338	3307	804	3540	0	0	1264	684	0	1053	27770	A
18-norabieta-8,11,13-triene	$C_{19}H_{28}$	256	1329	0	6551	1823	574	5644	263	0	0	2857	0	317	9986	I
deisopropyldehydroabietic acid	$C_{17}H_{22}O_2$	258	0	0	1807	0	7516	0	0	1179	0	1076	0	5073	0	I
7-oxo-19-norabieta-8,11,13-triene	$C_{19}H_{24}O$	270	0	0	0	0	0	0	0	0	0	0	0	0	385	I
16,17-bisnordehydroabietic acid	$C_{18}H_{24}O_2$	272	0	0	0	0	902	0	0	0	0	1543	0	0	460	I
pimara-8(9),15-diene	$C_{20}H_{32}$	272	0	0	0	0	0	0	0	0	0	0	0	125	4474	I
abieta-8,11,13,15-tetraen-18-al	$C_{20}H_{26}O$	282	0	0	0	0	0	0	0	0	0	0	0	645	0	I
3-oxo-12-hydroxysimonellite	$C_{19}H_{22}O_2$	282	0	0	0	0	0	0	0	0	0	0	7011	0	0	I
abieta-8,11,13-triene-7-one	$C_{20}H_{28}O$	284	0	0	0	0	0	0	563	0	0	0	0	0	0	I
dehydroabietal	$C_{20}H_{28}O$	284	0	0	6908	0	5813	0	984	1741	13596	0	0	8956	0	A
6,7-dehydroferruginol	$C_{20}H_{28}O$	284	0	1564	0	0	0	0	0	0	0	0	19396	0	0	I
dehydroabietol	$C_{20}H_{30}O$	286	0	0	0	0	0	0	0	0	0	0	0	1097	0	I
3-oxo-16,17-bisnordehydroabietic acid	$C_{18}H_{22}O_3$	286	0	0	0	0	0	0	0	0	0	121	0	0	0	I
7-oxo-16,17-bisnordehydroabietic acid	$C_{18}H_{22}O_3$	286	0	0	0	0	0	0	0	0	0	0	0	6761	0	I
13-oxopodocarp-8(14)-en-18-oic acid	$C_{18}H_{26}O_3$	290	0	0	674	0	1419	0	0	0	0	3850	0	0	0	I
1-methyl-7-isopropyl-1,2,3,4-tetrahydrophenanthrene-1-carboxylic acid	$C_{19}H_{24}O_2$	296	79153	0	1371	0	2510	15162	786	186	12799	7873	0	30749	155	I
abieta-6,8,11,13,15-pentaen-18-oic acid	$C_{20}H_{24}O_2$	296	9521	0	0	0	0	0	0	0	0	1764	0	457	4012	I
13-isopropenyl-5α-podocarpa-6,8,11,13-tetraen-16-oic acid	$C_{20}H_{24}O_2$	296	1497	0	0	0	0	0	0	0	0	0	0	0	0	I
13-isopropyl-5α-podocarpa-6,8,11,13-tetraen-16-oic acid	$C_{20}H_{26}O_2$	298	1474	0	0	911	2360	587	5386	0	731	774	0	8002	435	I
abieta-6,8,11,13-tetraen-18-oic acid	$C_{20}H_{26}O_2$	298	0	0	6298	39070	0	4802	0	0	0	5398	0	9527	8777	A
abieta-8,11,13,15-tetraen-18-oic acid	$C_{20}H_{26}O_2$	298	18874	0	6937	39844	3173	9465	0	0	3121	3275	0	609	2892	A
abieta-7,13,15-trien-18-oic acid	$C_{20}H_{28}O_2$	300	0	0	0	0	0	0	0	0	0	974	0	0	0	I
abieta-8,11,13-trien-18-oic acid	$C_{20}H_{28}O_2$	300	0	0	0	0	0	6552	0	0	0	1544	0	17892	0	I
dehydroabietic acid	$C_{20}H_{28}O_2$	300	137919	4054	14891	57798	12764	28689	5476	6732	24103	19508	972	26019	24384	A
8,11,15-isopimaratrien-18-oic acid	$C_{20}H_{28}O_2$	300	0	0	0	23723	0	0	0	0	0	0	0	188	0	I
13-isopropyl-5α-podocarpa-8,11,13-trien-16-oic acid	$C_{20}H_{28}O_2$	300	1474	0	0	5235	195	617	0	0	0	523	0	7265	102	I
6,8,15-pimaratrien-18-oic acid	$C_{20}H_{28}O_2$	300	0	0	0	41741	0	0	0	0	0	0	0	0	0	I
13α-abieta-7,9(11)-dien-18-oic acid	$C_{20}H_{30}O_2$	302	12820	0	0	0	0	0	0	0	0	0	0	0	0	I
abieta-8,13(15)-dien-18-oic acid	$C_{20}H_{30}O_2$	302	23335	0	6937	29000	4304	10808	0	2270	5301	0	0	0	1014	I

3- or 7-hydroxyabietal	$C_{20}H_{30}O_2$	302	0	0	0	49582	0	0	0	0	0	0	0	0	0	I
8,15-isopimaradien-18-oic acid	$C_{20}H_{30}O_2$	302	69603	0	0	87918	0	0	0	0	4646	32772	0	0	16903	I
8,15-pimaradien-18-oic acid	$C_{20}H_{30}O_2$	302	84439	0	15110	29055	10158	27103	496	0	4646	54743	0	11821	162206	A
10α(H)-9,10-secodehydroabietic acid	$C_{20}H_{30}O_2$	302	0	0	0	0	0	0	682	0	5637	0	0	6767	0	I
10β(H)-9,10-secodehydroabietic acid	$C_{20}H_{30}O_2$	302	0	0	690	8755	17972	7518	1003	0	5639	7382	0	5572	0	I
16-norisocopalan-15-oic acid	$C_{20}H_{34}O_2$	306	0	0	0	0	0	0	0	0	0	0	3620	0	0	I
7-oxoabieta-5,8,11,13-tetraen-18-oic acid	$C_{20}H_{24}O_3$	312	27716	0	0	13080	1473	339	0	0	85	6176	0	1705	0	I
3- or 7-oxoabieta-8,11,13,15-tetraen-18-oic acid	$C_{20}H_{24}O_3$	312	0	0	0	11966	0	2037	0	0	0	384	0	0	0	I
3- or 7-oxoabieta-8,11,13-trien-18-oic acid	$C_{20}H_{26}O_3$	314	0	0	3322	0	0	0	0	0	2456	2142	0	4312	0	I
3- or 7-hydroxyabieta-8,11,13,15-tetraen-18-oic acid	$C_{20}H_{26}O_3$	314	0	0	0	18318	0	0	0	0	0	0	0	0	0	I
methyl dehydroabietate	$C_{21}H_{30}O_2$	314	36110	0	1287	0	0	6623	0	0	0	12667	0	0	25716	I
3-oxodehydroabietic acid	$C_{20}H_{26}O_3$	314	0	0	0	2161	0	0	0	0	0	0	0	2750	0	I
7-oxodehydroabietic acid	$C_{20}H_{26}O_3$	314	24301	0	980	10335	1223	6639	457	0	696	11824	0	3180	1114	A
12- or 14-hydroxydehydroabietic acid	$C_{20}H_{28}O_3$	316	0	0	0	0	2905	0	0	0	0	0	0	0	696	I
15-hydroxydehydroabietic acid	$C_{20}H_{28}O_3$	316	0	0	0	0	0	0	0	0	0	1145	0	0	1489	A
methyl-13-(2'-oxopropyl)-podocarpa-8,11,13-trien-15-oic acid	$C_{20}H_{28}O_3$	316	0	0	0	0	0	0	0	0	0	3478	0	0	0	I
3-oxoabietic acid	$C_{20}H_{28}O_3$	316	0	0	0	0	0	0	0	0	0	0	0	0	2695	I
3- or 7-oxopimaric acid	$C_{20}H_{28}O_3$	316	0	0	0	0	0	0	0	0	0	0	0	0	0	I
acetyldihydroabietol	$C_{22}H_{36}O_2$	332	0	0	0	1928	0	0	0	0	0	0	0	0	0	I
propyl-abieta-8,11,13,15-tetraenoate	$C_{23}H_{32}O_2$	340	0	0	0	0	0	0	0	0	0	0	0	382	0	I
3-oxopinifolic acid	$C_{20}H_{30}O_5$	350	2060	0	0	0	0	298	0	0	0	0	0	0	0	I
3- or 7-acetoxyabietic acid	$C_{22}H_{32}O_4$	360	0	0	0	7730	0	0	0	0	0	409	0	0	0	I
dimethyl dihydroagathate	$C_{22}H_{36}O_4$	364	596	0	0	0	88	0	0	0	0	0	0	0	0	I
succinyl-7-oxodehydroabietol	$C_{24}H_{32}O_5$	400	0	923	144	0	0	0	0	0	0	0	0	1004	0	I
Total Diterpenoids			733880	46367	148413	619352	116951	259767	18981	23538	133145	238205	127543	193502	433517	
Abietane skeletons/Pimarane skeletons (A/P)			1.3	1.6	4.6	1.4	2.4	3.3	6.4	8.3	4.2	1.1	2.9	4.3	0.9	
Triterpenoids																
Natural Products																
24,25-dinorlupa-1,3,5(10)-triene	$C_{28}H_{42}$	378	0	0	0	3491	0	0	1060	1718	0	0	0	2659	0	I
3α-methoxyfriedelene	$C_{31}H_{52}O$	440	0	0	0	0	0	0	1060	0	0	0	0	0	0	I
3β-methoxyfriedelene	$C_{31}H_{52}O$	440	0	0	0	0	0	0	1676	0	0	0	0	0	0	I
3α-ethoxyfriedelene	$C_{32}H_{54}O$	456	0	0	0	0	0	0	2506	0	0	0	0	0	0	I
3β-ethoxyfriedelene	$C_{32}H_{54}O$	456	0	0	0	0	0	0	743	0	0	0	0	0	0	I
Steroids																
Natural Products																
campesterol	$C_{28}H_{48}O$	400	180	3	84	148	98	95	0	0	0	8	173	184	0	I
stigmasterol	$C_{29}H_{48}O$	412	85	0	0	0	0	0	0	0	0	0	0	0	0	I
β-sitosterol	$C_{29}H_{50}O$	414	2253	421	568	2310	849	1284	282	1876	1282	141	1407	1300	66	I
Alteration Products																
5-pregnene	$C_{21}H_{34}$	286	0	0	0	0	3163	0	0	0	0	3633	0	0	0	I
7-pregnene	$C_{21}H_{34}$	286	0	0	0	0	4907	0	0	0	0	4251	0	0	0	I
24-ethyl-19-norcholesta-1,3,5(10),6,8,14-hexaene	$C_{28}H_{38}$	374	651	0	0	433	205	0	0	0	465	0	0	518	359	I
24-ethyl-19-norcholesta-1,3,5(10),6,8-pentaene	$C_{28}H_{40}$	376	367	0	1693	311	295	0	377	561	0	119	0	488	657	I

24-ethyl-19-norcholesta-1,3,5(10),8-tetraene	$C_{28}H_{42}$	378	3713	0	0	0	0	0	0	0	891	0	2870	0	0	I
24-methyl-19-norcholesta-1,3,5(10)-triene	$C_{28}H_{44}$	380	56	0	0	0	0	0	0	0	0	0	0	0	0	I
24-ethyl-14α(H)-1(10->6)-abeo-19-norcholesta-5,7,9-triene	$C_{28}H_{44}$	380	1228	0	0	0	0	0	0	0	0	0	0	0	0	I
24-ethyl-14β(H)-1(10->6)-abeo-19-norcholesta-5,7,9-triene	$C_{28}H_{44}$	380	0	0	0	0	0	0	0	1566	0	0	0	1157	0	I
24-ethyl-1-methyl-19-norcholesta-5,7,9,14-tetraene	$C_{29}H_{44}$	392	511	0	0	0	0	0	0	0	0	0	0	0	0	I
24-ethyl-1-methyl-19-norcholesta-5,7,9-triene	$C_{29}H_{46}$	394	1908	0	0	0	0	0	0	431	0	0	0	0	0	I
24-ethyl-4-methyl-19-norcholesta-1,3,5(10)-triene	$C_{29}H_{46}$	394	145	0	0	0	327	0	425	537	500	140	0	0	1126	I
24-ethyl-4-methyl-19-norcholesta-1,3,5(10)-triene (isomer)	$C_{29}H_{46}$	394	547	550	0	306	0	0	0	0	0	0	0	486	0	I
24-ethyl-4-methyl-19-norcholesta-1,3,5(10)-triene (isomer)	$C_{29}H_{46}$	394	1908	0	2152	0	0	0	0	0	0	0	1006	0	0	I
24-ethyl-14β(H)-1(10-6)-abeo-cholesta-5,7,9-triene	$C_{29}H_{46}$	394	0	0	0	1590	0	0	0	0	1276	0	0	0	0	I
24-ethylcholesta-2,4-diene	$C_{29}H_{46}$	396	870	0	0	0	0	0	0	0	0	0	0	0	0	I
24-ethylcholesta-4,22-diene	$C_{29}H_{46}$	396	0	0	0	0	0	0	0	0	0	0	0	0	3721	I
stigmasta-3,5-diene	$C_{29}H_{48}$	396	2114	298	785	1562	1757	0	0	1879	0	122	782	0	0	I
5α(H)-24-ethylcholest-2-ene	$C_{29}H_{48}$	398	221	0	0	0	0	0	0	0	0	0	0	0	0	I
stigmast-4-ene	$C_{29}H_{50}$	398	371	0	1413	0	0	0	379	722	0	0	0	0	864	I
stigmast-5-ene	$C_{29}H_{50}$	398	187	0	1319	0	0	0	578	670	0	0	0	0	0	I
stigmasta-3,5-dien-7-one	$C_{29}H_{46}$	410	0	0	0	0	0	0	576	268	0	258	0	0	0	I
stigmasta-4,6-dien-3-one	$C_{29}H_{46}O$	410	0	0	0	0	0	0	0	1283	0	0	0	0	0	I
stigmast-4-en-3-one	$C_{29}H_{48}O$	412	0	0	0	0	496	0	0	268	0	0	0	0	0	I
Total Steroids			17315	1271	8014	6660	12097	1379	2617	10061	4414	8671	6237	4133	6792	
III. POLYCYCLIC AROMATIC HYDROCARBONS (PAH)																
Alteration Products																
phenanthrene	$C_{14}H_{10}$	178	2073	639	1479	4197	1477	7687	7861	396	7475	743	3284	715	2001	A
anthracene	$C_{14}H_{10}$	178	207	64	315	606	714	2917	56	90	1330	140	647	0	183	A
4(H)-cyclopenta[def]phenanthrene	$C_{15}H_{10}$	190	0	0	0	512	0	0	0	88	2430	336	0	0	428	A
9-methylanthracene	$C_{15}H_{12}$	192	83	47	96	167	57	557	326	76	1095	35	122	19	67	A
1-methylphenanthrene	$C_{15}H_{12}$	192	1714	113	672	3490	739	7920	1895	232	2458	951	421	346	2864	A
2-methylphenanthrene	$C_{15}H_{12}$	192	968	488	480	1503	568	3506	3440	165	2929	352	547	124	1362	A
3-methylphenanthrene	$C_{15}H_{12}$	192	308	314	259	761	205	1897	1027	71	6697	381	261	41	339	A
9-methylphenanthrene	$C_{15}H_{12}$	192	103	744	396	297	164	1450	3930	83	3285	124	498	41	270	A
C_1-anthracenes/phenanthrenes	$C_{15}H_{12}$	192	3176	1705	1903	6219	1733	15331	10619	627	16463	1843	1848	570	4902	A
fluoranthene	$C_{16}H_{10}$	202	0	1728	0	0	1535	6467	6633	669	6742	1194	1750	3240	4493	A
pyrene	$C_{16}H_{10}$	202	1071	865	1009	0	1480	1861	3191	521	4318	6370	0	426	3394	A
2-phenylnaphthalene	$C_{16}H_{12}$	204	0	0	0	0	0	0	0	0	1148	0	0	0	932	A
C_2-anthracenes/phenanthrenes	$C_{16}H_{14}$	206	5507	1568	2247	6168	1084	7608	0	194	365	2318	0	2176	16710	A
11(H)-benzo[a]fluorene	$C_{17}H_{12}$	216	0	355	0	0	26104	0	922	0	0	0	0	0	1188	A
C_1-pyrenes	$C_{17}H_{12}$	216	0	493	1300	0	0	0	2524	381	0	0	0	0	7963	A
C_3-anthracenes/phenanthrenes	$C_{17}H_{16}$	220	9829	0	1946	8486	1681	5252	215	0	744	3033	0	1301	11397	S
benzo[ghi]fluoranthene	$C_{18}H_{10}$	226	0	305	0	0	0	639	0	0	0	0	0	0	1919	A
cyclopenta[cd]pyrene	$C_{18}H_{10}$	226	0	0	0	0	1979	0	0	429	1059	0	0	0	1919	S
benz[a]anthracene	$C_{18}H_{12}$	228	0	0	0	0	0	0	0	0	127	0	0	0	0	A
chrysene	$C_{18}H_{12}$	228	0	179	531	0	581	0	204	251	1724	566	0	0	1210	A
triphenylene	$C_{18}H_{12}$	228	0	794	979	0	960	0	697	489	1497	487	0	0	2313	A
C_1-chrysenes	$C_{19}H_{14}$	242	0	263	0	0	0	0	0	48	0	0	0	0	0	A

benzo[b/k]fluoranthene	$C_{20}H_{12}$	252	0	0	582	0	0	0	0	0	0	0	0	0	364	A
benzo[a]pyrene	$C_{20}H_{12}$	252	0	0	0	0	376	0	38	253	578	1045	0	0	2321	A
benzo[e]pyrene	$C_{20}H_{12}$	252	0	0	0	0	803	0	402	0	0	0	0	0	0	A
perylene	$C_{20}H_{12}$	252	0	0	0	0	0	0	0	0	0	0	0	0	426	A
anthanthrene	$C_{22}H_{12}$	276	0	0	0	0	0	0	0	0	0	0	0	0	290	A
benzo[ghi]perylene	$C_{22}H_{12}$	276	0	0	0	0	0	0	81	0	0	0	0	0	190	A
indeno[1,2,3-cd]pyrene	$C_{22}H_{12}$	276	0	0	0	0	0	0	499	0	0	0	0	0	515	A
Total PAH			25039	10663	14193	32406	42239	63094	44561	5063	62461	19918	9378	8998	69961	
Methylphenanthrenes/Phenanthrene (MP:P)			1.5	2.6	1.2	1.4	1.1	1.9	1.3	1.4	2.1	2.4	0.5	0.8	2.4	
IV. PHENOLS (Lignin Pyrolysis)																
Natural Products																
catechol	$C_6H_6O_2$	110	38264	5182	9586	20885	6372	10898	4101	5252	32152	1381	27840	13169	2047	A
resorcinol	$C_6H_6O_2$	110	0	0	0	0	4317	0	0	8291	0	0	0	0	0	A
cinnamic acid	$C_9H_8O_2$	148	0	0	0	0	560	0	354	0	0	0	0	0	0	A
p-coumaric acid	$C_9H_8O_3$	164	7218	0	430	0	0	0	0	5585	0	0	0	0	0	A
eugenol	$C_{10}H_{12}O_2$	164	17034	0	0	30522	973	17285	0	2294	0	0	13252	0	0	A
Alteration Products																
hydroquinone	$C_6H_6O_2$	110	0	4769	5163	25729	0	0	0	7540	15711	0	0	0	0	I
benzoic acid	$C_7H_6O_2$	122	4206	0	0	0	698	0	354	0	0	0	0	0	0	I
dihydroxytoluene	$C_7H_8O_2$	124	17570	0	0	0	0	0	0	0	0	0	0	0	0	S
guaiacol	$C_7H_8O_2$	124	0	324	0	0	0	4674	0	0	0	0	0	0	0	I
4-hydroxyphenylethanol	$C_8H_{10}O_2$	138	0	0	0	0	0	0	0	2043	0	0	0	0	0	I
dihydrocinnamol	$C_9H_{12}O_2$	152	0	0	0	0	7615	0	0	0	0	0	0	0	0	I
3-hydroxybenzoic acid	$C_7H_6O_3$	152	0	0	0	0	0	0	1614	2405	0	0	0	0	0	I
4-hydroxybenzoic acid	$C_7H_6O_3$	152	0	2618	4345	0	5807	0	4425	3559	23206	40	0	2968	0	I
vanillin	$C_8H_8O_3$	152	9897	1559	3239	11498	2546	9641	405	0	7015	424	7196	2802	279	I
vanillyl alcohol	$C_8H_{10}O_3$	154	0	0	0	0	0	0	0	224	0	0	0	0	0	I
acetovanillone	$C_9H_{10}O_3$	166	0	1220	3441	0	2251	6718	0	0	5411	511	5587	0	292	I
vanillic acid	$C_8H_8O_4$	168	6707	1126	4307	8351	3609	5706	1783	0	7833	790	5125	2194	477	I
pyrogallol	$C_9H_{14}O_3$	170	19044	1246	2455	17808	4192	4296	0	3872	12883	0	5861	2472	48	I
guaiacylpropenal	$C_{10}H_{10}O_3$	178	12253	3207	1098	0	0	0	1174	0	7106	1063	8550	7413	0	I
coniferyl alcohol	$C_{10}H_{12}O_3$	180	0	0	0	0	0	0	0	330	8797	0	0	0	0	I
guaiacylacetone	$C_{10}H_{12}O_3$	180	10064	2007	3860	10881	0	10885	888	0	10137	521	8108	0	262	I
4-methoxy-3-hydroxybenzoic acid	$C_9H_{10}O_4$	182	0	0	0	0	0	0	0	275	0	0	0	0	0	I
homovanillyl alcohol	$C_{10}H_{14}O_3$	182	0	1266	6644	34634	9791	12886	861	0	14053	370	10376	9700	177	A
3-vanillylpropanol	$C_{10}H_{14}O_3$	182	12139	0	0	15990	0	13364	0	2840	0	0	0	0	0	I
3-methylcatechol	$C_{10}H_{14}O_2$	196	0	2839	7236	0	4151	14674	0	2624	13810	0	17024	0	0	I
4-methylcatechol	$C_{10}H_{14}O_2$	196	0	0	0	22952	0	2961	2621	1359	0	1250	0	0	0	I
homovanillic acid	$C_{10}H_{12}O_4$	196	7083	999	4053	8087	3514	4641	1139	0	6400	1067	3870	2621	951	A
3,3'-dimethoxy-4,4'-dihydroxystilbene	$C_{16}H_{16}O_4$	272	11728	1854	3644	17183	4664	11996	559	2636	6331	532	6899	7394	0	I
divanillyl	$C_{16}H_{18}O_4$	274	18874	601	0	0	0	0	0	1331	4679	0	0	465	0	I
1,2-divanillylethane	$C_{18}H_{22}O_4$	302	0	0	0	0	0	0	0	133	0	0	0	0	0	I
tetrahydro-3,4-divanillylfuran	$C_{20}H_{24}O_5$	344	7597	1191	2546	7400	5227	3474	575	1376	3951	308	4384	3378	419	I

pinoresinol	$C_{20}H_{22}O_6$	358	0	0	0	0	0	0	0	740	0	0	0	0	0	I
Total Phenolics			199678	32006	62049	231919	66285	134097	20852	54710	179475	8258	124070	54577	4952	
V. MONOSACCHARIDES (Cellulose Pyrolysis)																
Alteration Products																
galactosan	$C_6H_{10}O_5$	162	14537	5384	3707	21005	3058	12148	107	4958	13385	214	8850	1804	229	A
mannosan	$C_6H_{10}O_5$	162	11773	818	3787	21019	3212	14619	341	5100	12217	584	6964	3645	744	A
levoglucosan	$C_6H_{10}O_5$	162	40878	11256	16189	57468	14791	27977	2750	19452	40707	3381	43522	10448	422	A
Total Monosaccharides			67188	17457	23683	99492	21061	54745	3198	29510	66309	4179	59335	15897	1396	
VI. UNKNOWNS																
Total Unknowns			117441	56639	429	321648	1916	13219	0	68163	48043	0	212328	2559	35223	
VII. MISCELLANEOUS																
Unresolved Complex Mixture (µg/kg)			581006	110939	307576	1129924	270713	710099	85892	305	685106	68573	688853	344263	113813	
Unresolved Components:Resolved Components (U:R)			0.6	0.8	1.2	1.0	1.1	1.2	0.8	1.4	1.1	0.7	0.9	0.9	0.8	
Volatile Organic Carbon (mg/kg)			46908	3040	3030	35104	5194	16069	2599	2663	21393	1495	31957	11466	2395	
Elemental Carbon (mg/kg)			1663	159	178	451	188	284	59	163	640	158	468	224	915	
Volatile Organic Carbon/Elemental Carbon (VOC/EC)			28	19	17	78	28	57	44	16	33	9	68	51	3	
Methylphenanthrenes/Phenanthrene (MP:P)			1.5	2.6	1.2	1.4	1.1	1.9	1.3	1.4	2.1	2.4	0.5	0.8	2.4	

Identification Criteria

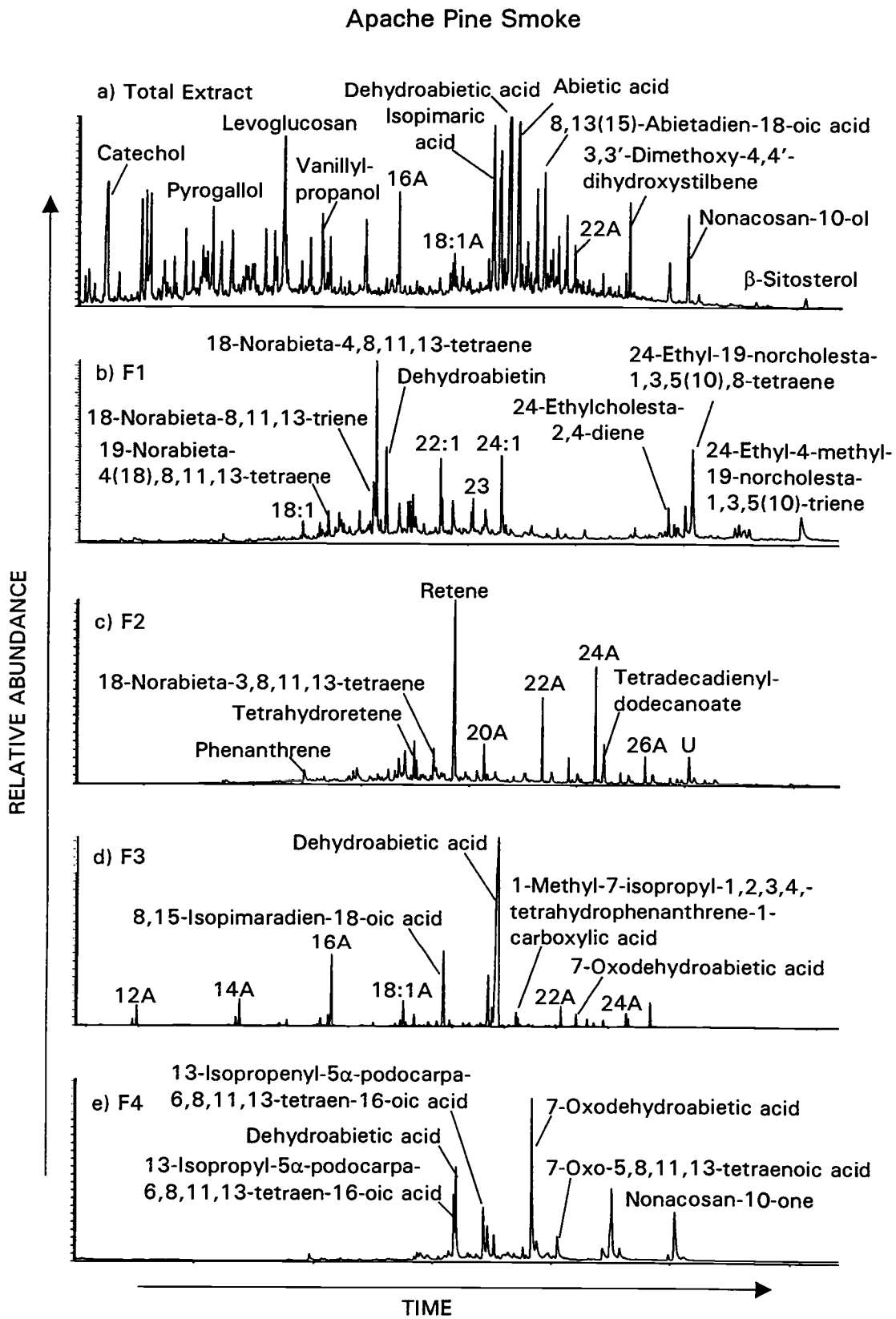
nd=not determined; A=matches with authentic standard; S=interpolated from homologous series fragmentation pattern; I=interpreted from mass spectrum fragmentation pattern.

All compositions and molecular weights are as the compounds occur in smoke (i.e., underivatized).

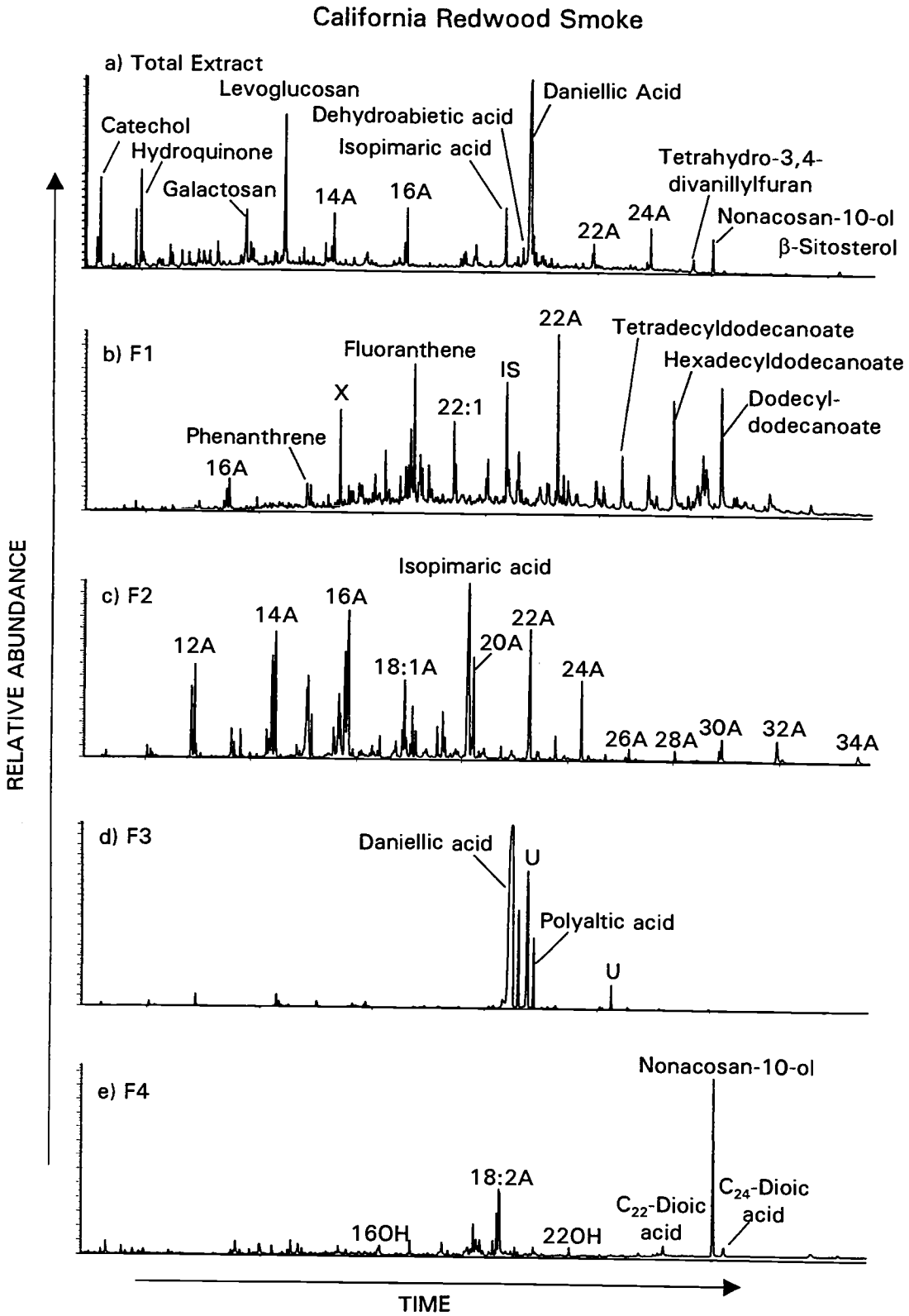
CPI for n-alkanes, n-alkenes and n-alkanones: [CPI = ΣC_{13}-$C_{33}/\Sigma C_{12}$-C_{34}] from Mazurek and Simoneit (1984)

CPI for n-alkanoic acids and n-alkanols: [CPI = ΣC_{12}-$C_{34}/\Sigma C_{13}$-C_{35}] from Mazurek and Simoneit (1984)

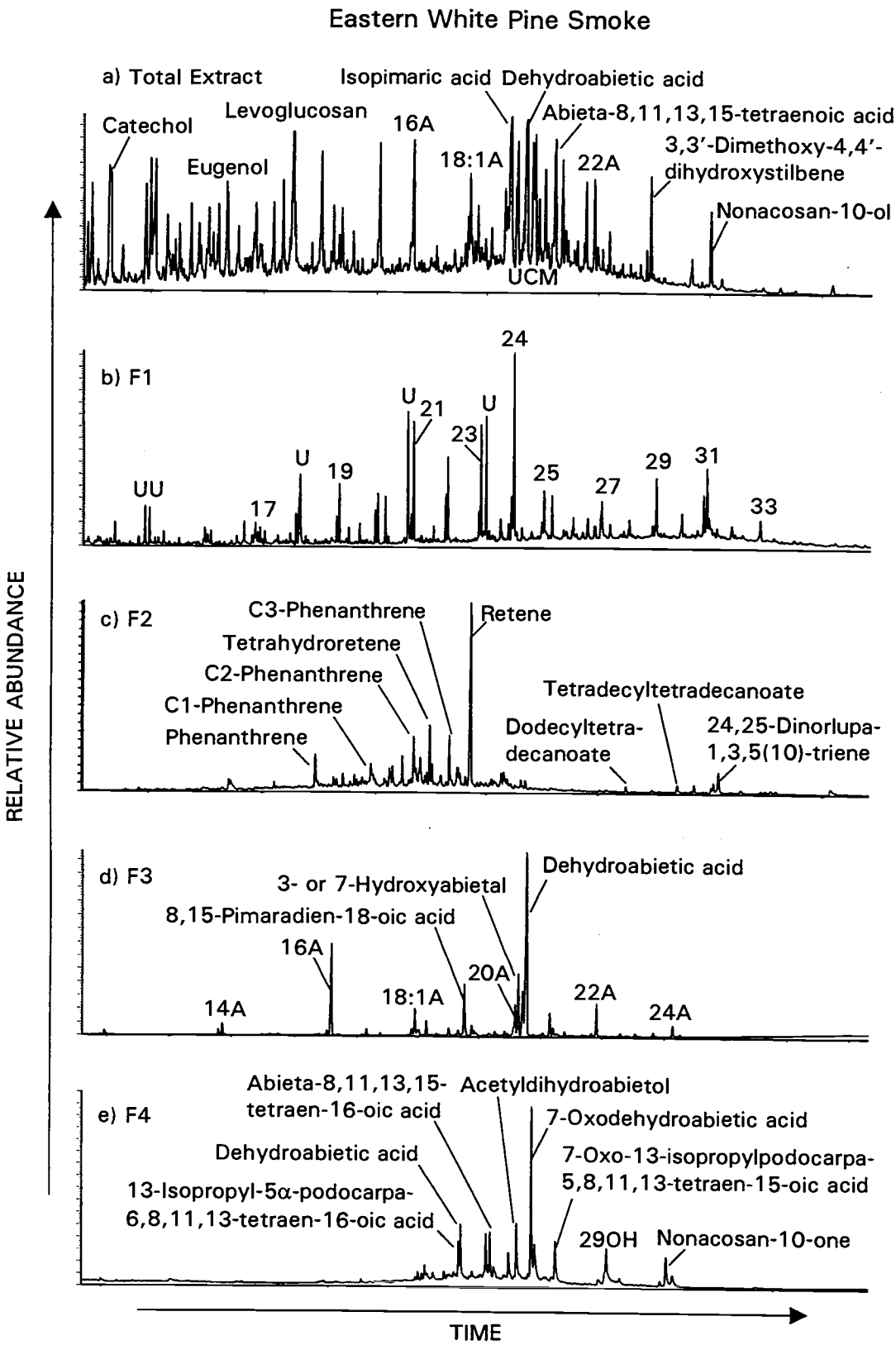
Volatile organic carbon in this case represents the solvent extractable matter.



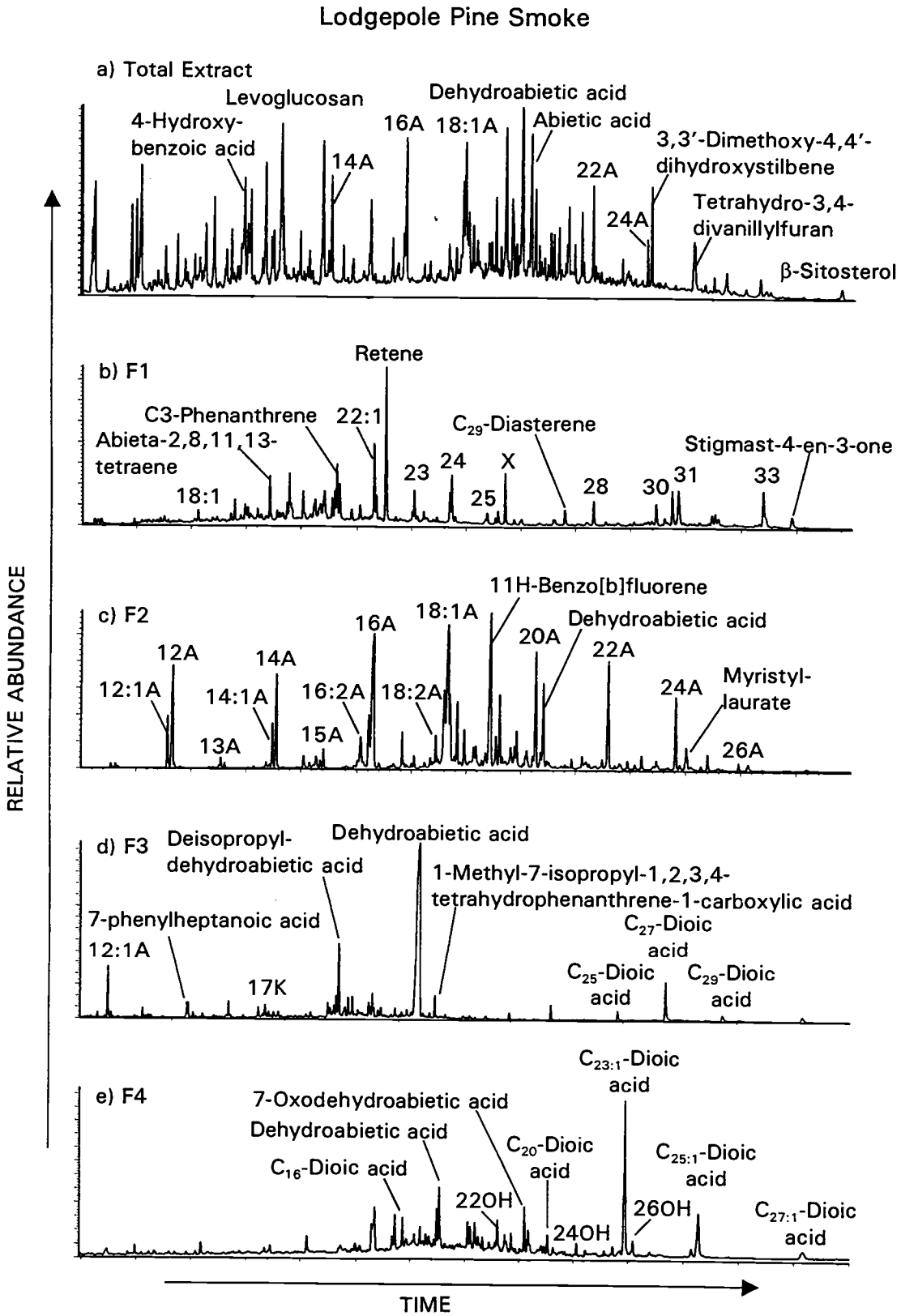
Appendix III.2. GC-MS TIC traces of Apache Pine smoke particulate matter.



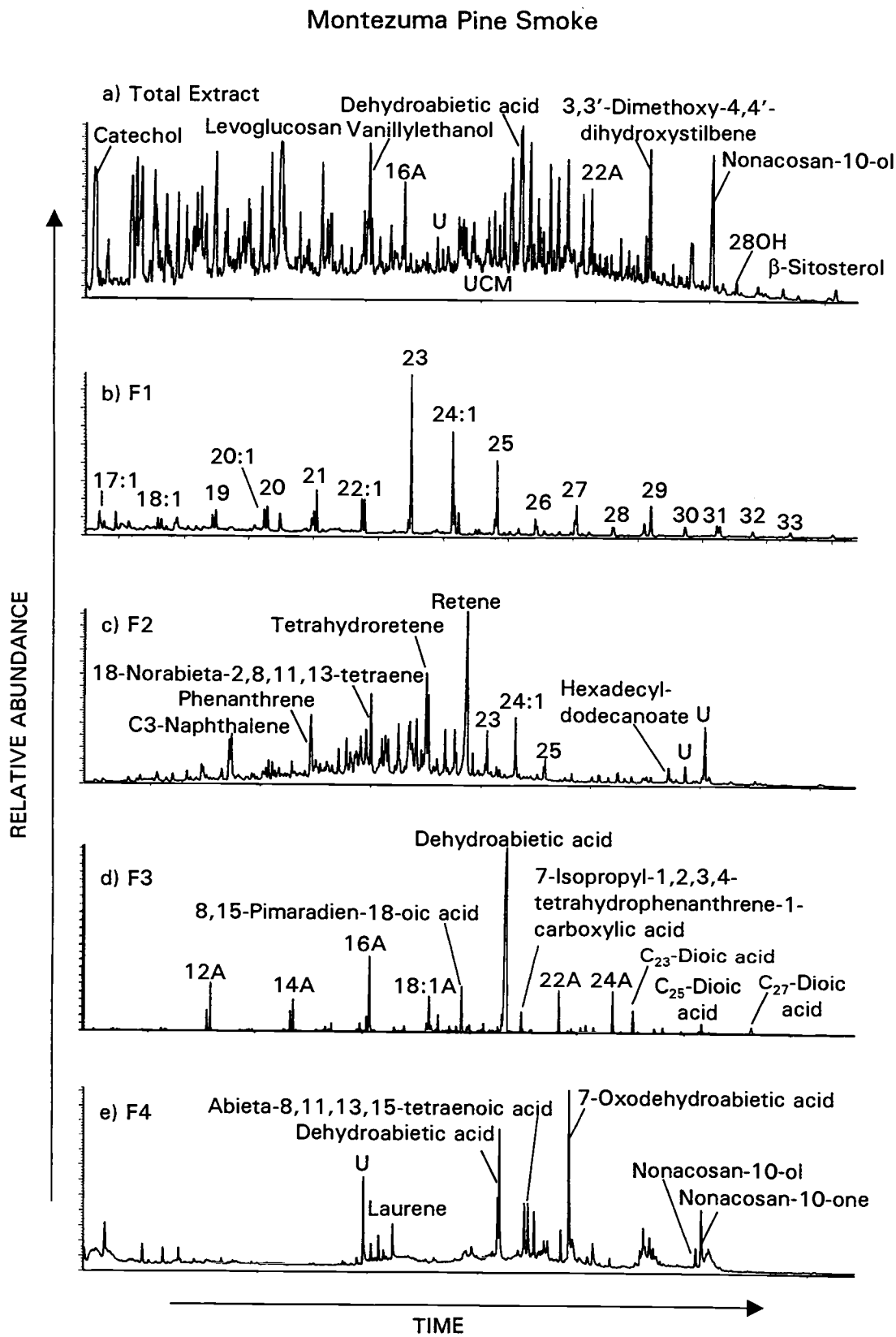
Appendix III.3. GC-MS TIC traces of California Redwood smoke particulate matter.



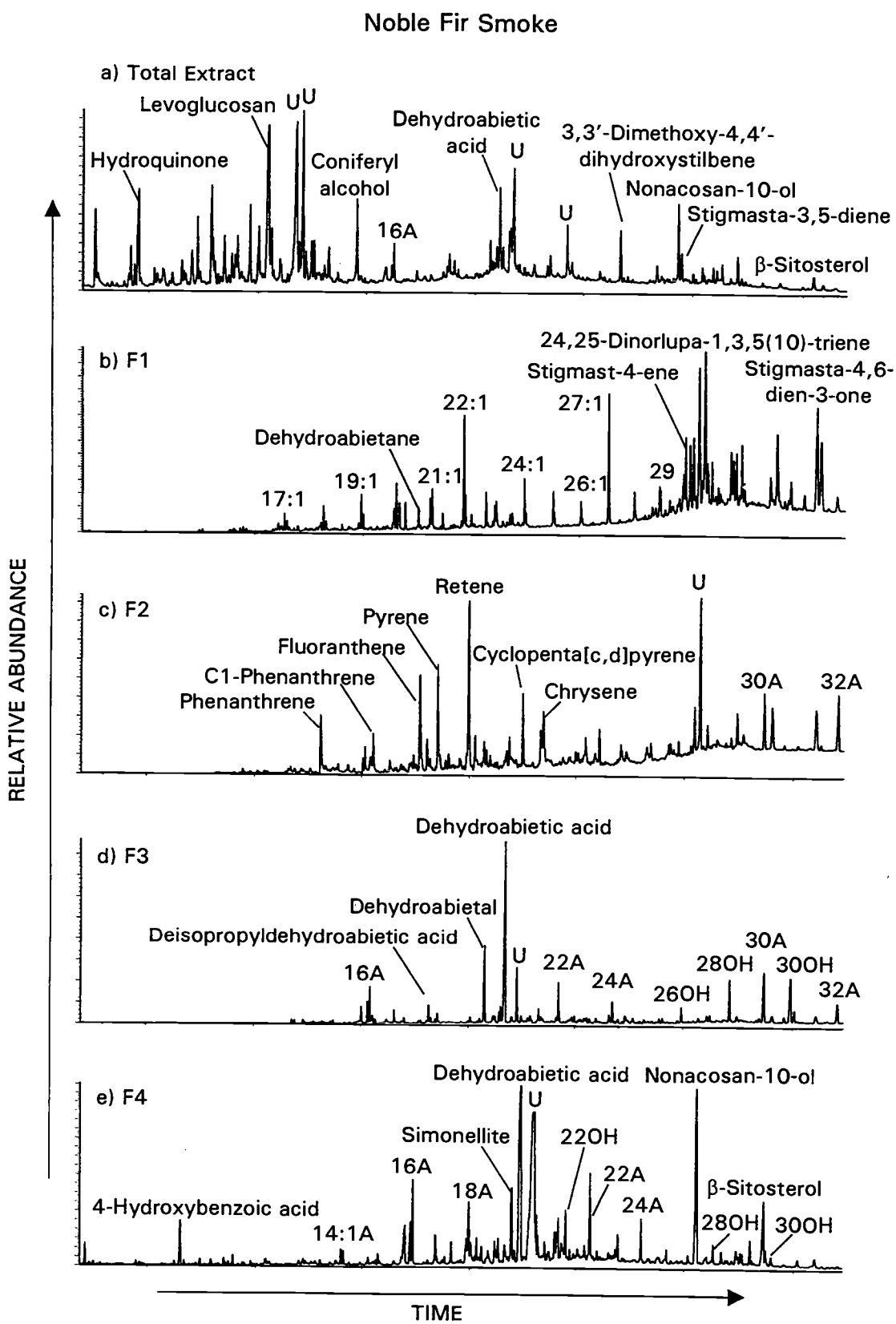
Appendix III.4. GC-MS TIC traces of Eastern White Pine smoke particulate matter.



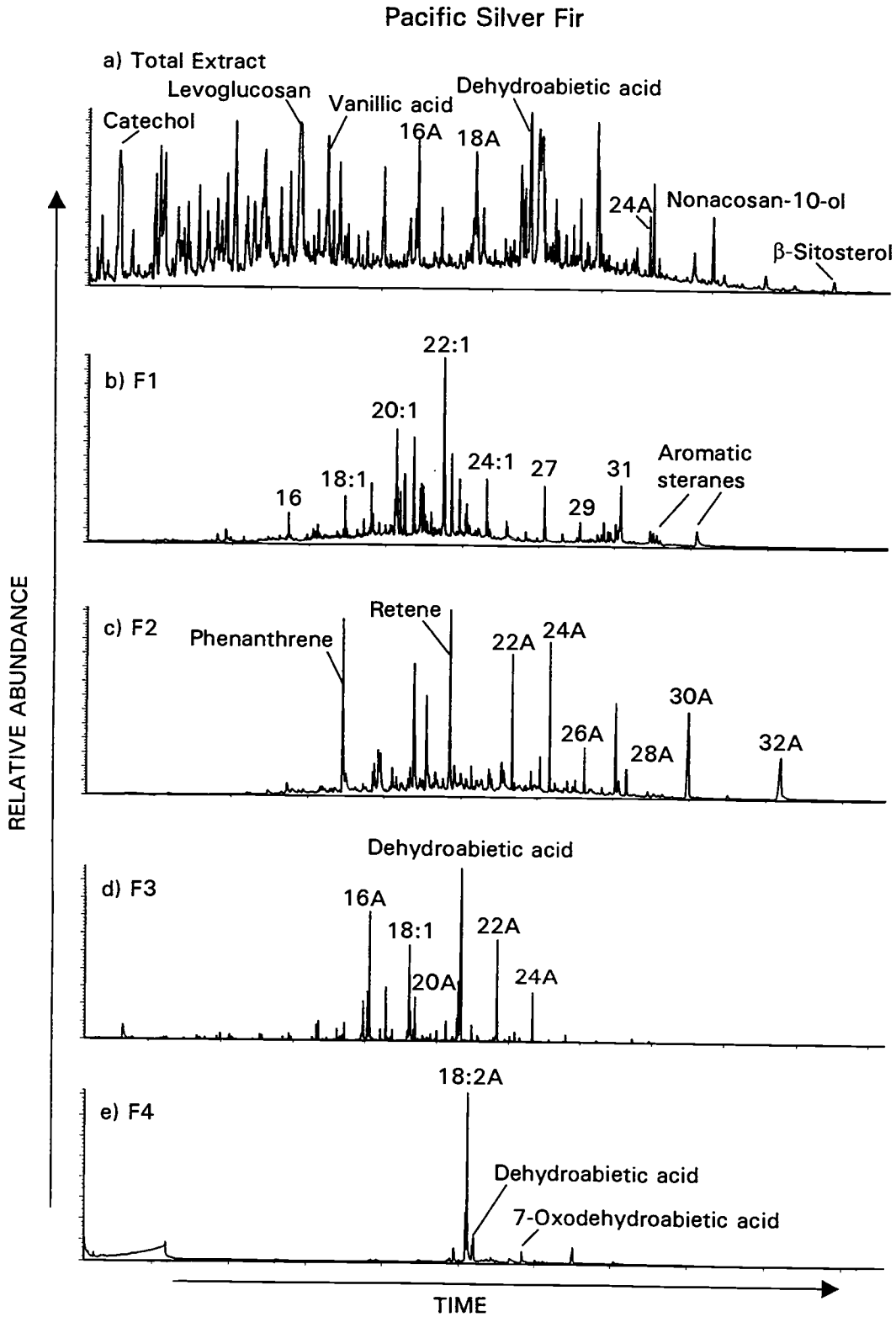
Appendix III.5. GC-MS TIC traces of Lodgepole Pine smoke particulate matter.



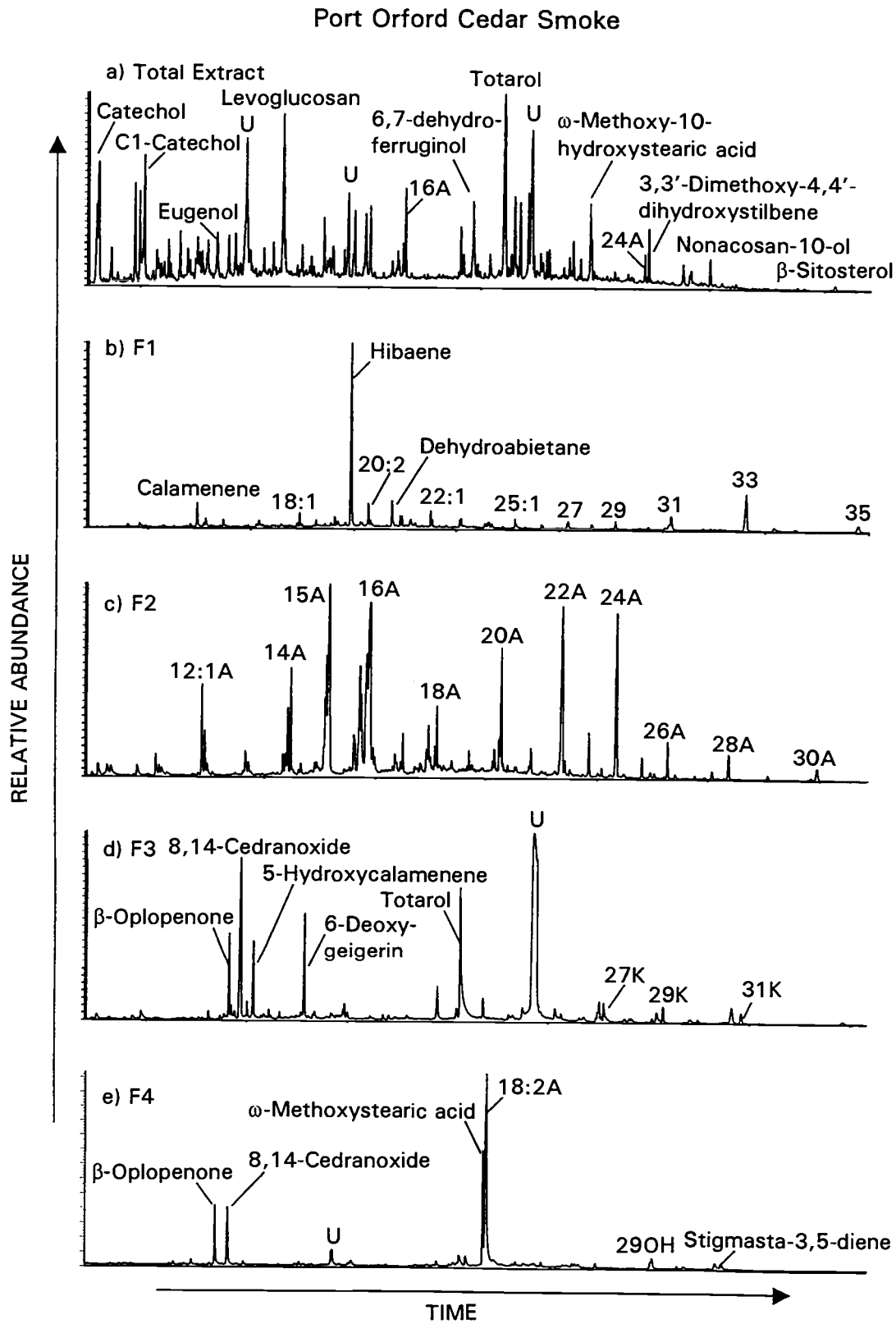
Appendix III.6. GC-MS TIC traces of Montezuma Pine smoke particulate matter.



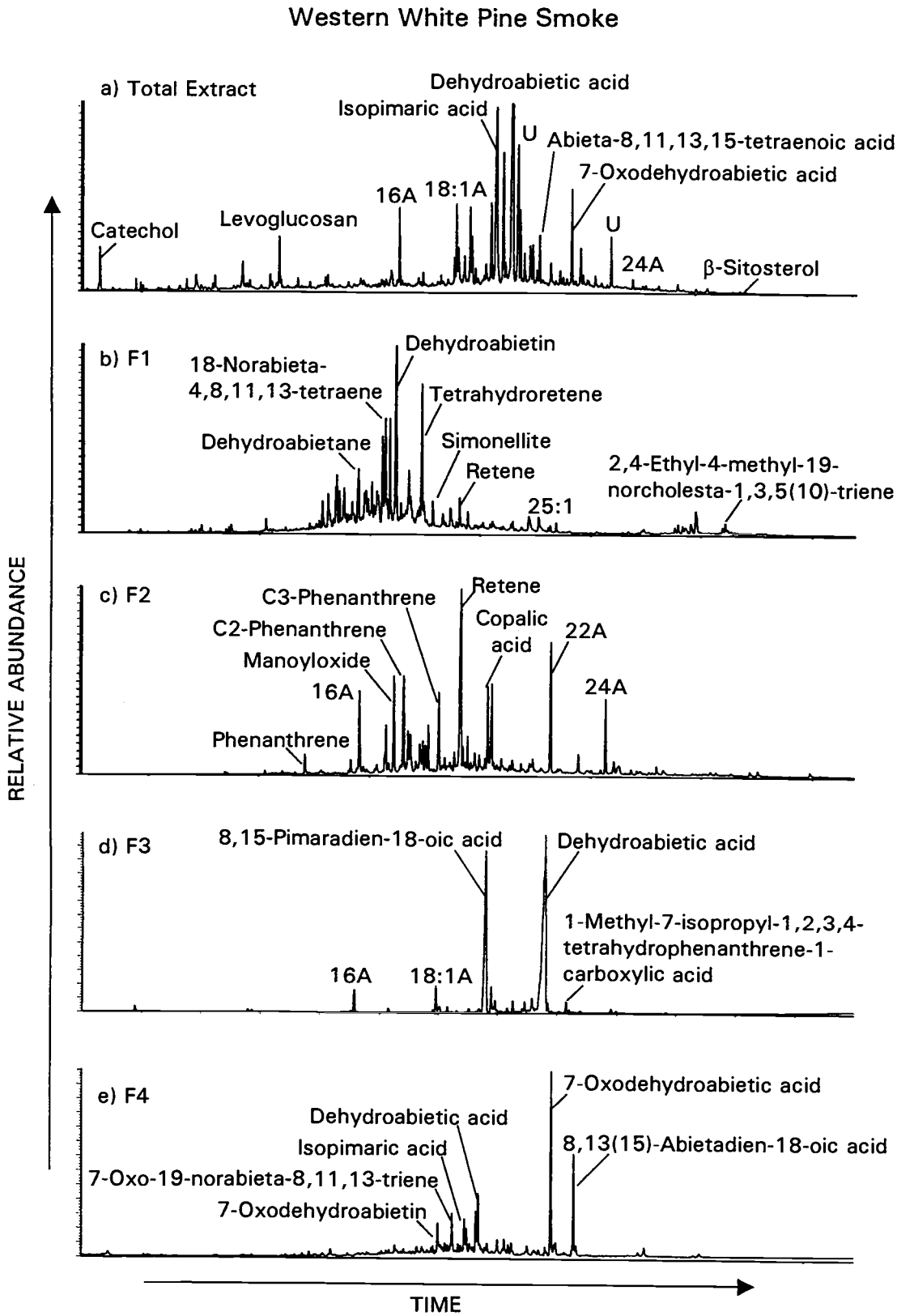
Appendix III.7. GC-MS TIC traces of Noble Fir smoke particulate matter.



Appendix III.8. GC-MS TIC traces of Pacific Silver Fir smoke particulate matter.



Appendix III.9. GC-MS TIC traces of Port Orford Cedar smoke particulate matter.



Appendix III.10. GC-MS TIC traces of Western White Pine smoke particulate matter.

Appendix IV.1. Concentrations (μg/kg of deciduous tree fuel burned) of the major organic constituents in smoke.

Compound Name	Composition	M.W.	Eucalyptus	Oregon Maple	Red Alder	Silver Birch	Dwarf Birch	ID Basis
I. HOMOLOGOUS SERIES								
n-Alkanes								
Natural Products								
n-tetradecane	$C_{14}H_30$	198	0	79	0	782	0	A
n-pentadecane	$C_{15}H_{32}$	212	0	195	0	1568	0	A
n-hexadecane	$C_{16}H_{34}$	226	0	121	0	1428	0	A
n-heptadecane	$C_{17}H_{36}$	240	0	253	0	2201	0	A
n-octadecane	$C_{18}H_{38}$	254	169	396	138	1909	65	A
n-nonadecane	$C_{19}H_{40}$	268	291	537	342	2562	331	A
n-eicosane	$C_{20}H_{42}$	282	383	833	526	3164	614	A
n-heneicosane	$C_{21}H_{44}$	296	722	1031	926	3706	1235	A
n-docosane	$C_{22}H_{46}$	310	898	1249	1792	184	2362	A
n-tricosane	$C_{23}H_{48}$	324	1437	1174	2024	996	2591	A
n-tetracosane	$C_{24}H_{50}$	338	1186	1313	1412	14377	3569	A
n-pentacosane	$C_{25}H_{52}$	352	3088	2313	11753	66272	8025	A
n-hexacosane	$C_{26}H_{54}$	366	632	505	1149	721	4420	A
n-heptacosane	$C_{27}H_{56}$	380	3056	13179	19293	64090	25977	A
n-octacosane	$C_{28}H_{58}$	394	496	3075	692	1084	2268	A
n-nonacosane	$C_{29}H_{60}$	408	3064	21521	3523	15076	15879	A
n-triacontane	$C_{30}H_{62}$	422	1149	1289	139	2429	1262	A
n-hentriacontane	$C_{31}H_{64}$	436	1725	8381	1678	20986	23860	A
n-dotriacontane	$C_{32}H_{66}$	450	163	738	0	1005	710	A
n-tritriacontane	$C_{33}H_{68}$	464	495	1548	0	1166	1931	A
n-tetratriacontane	$C_{34}H_{70}$	478	266	0	0	0	0	A
n-pentatriacontane	$C_{35}H_{72}$	492	193	0	0	0	0	A

Total n-Alkanes			19414	59731	45388	205704	95098	
CPI			2.6	5.2	6.8	6.6	5.2	
Cmax			25	29	27	25	27	
n-Alkenes								
Alteration Products								
n-tetradec-1-ene	$C_{14}H_{28}$	196	0	0	0	556	414	A
n-pentadec-1-ene	$C_{15}H_{30}$	210	0	0	0	1722	0	A
n-hexadec-1-ene	$C_{16}H_{32}$	224	233	78	0	3234	0	A
n-heptadec-1-ene	$C_{17}H_{34}$	238	98	69	0	2786	0	A
n-octadec-1-ene	$C_{18}H_{36}$	252	206	259	0	3550	3604	A
n-nonadec-1-ene	$C_{19}H_{38}$	266	311	380	0	5261	303	S
n-eicos-1-ene	$C_{20}H_{40}$	280	361	794	250	3907	622	A
n-heneicos-1-ene	$C_{21}H_{42}$	294	437	476	265	6472	866	S
n-docos-1-ene	$C_{22}H_{44}$	308	1762	468	1164	19081	3291	S
n-tricos-1-ene	$C_{23}H_{46}$	322	426	536	289	625	1232	S
n-tetracos-1-ene	$C_{24}H_{48}$	336	1665	698	770	537	4092	S
n-pentacos-1-ene	$C_{25}H_{50}$	350	130	131	0	19879	2079	S
n-hexacos-1-ene	$C_{26}H_{52}$	364	1639	4291	363	11434	7120	S
n-heptacos-1-ene	$C_{27}H_{54}$	378	0	0	0	2481	0	S
n-octacos-1-ene	$C_{28}H_{56}$	392	496	0	0	3939	0	A
n-nonacos-1-ene	$C_{29}H_{58}$	406	0	0	0	634	0	S
Total n-Alkenes			7763	8180	3100	86099	23622	
CPI			0.2	0.2	0.2	0.9	0.2	
Cmax			22	26	22	25	26	
Carboxylic Acids								
Natural Products								
n-octanoic acid	$C_8H_{16}O_2$	144	953	4255	0	7264	0	S

n-nonanoic acid	$C_9H_{18}O_2$	158	1250	4853	1699	4367	0	S
n-decanoic acid	$C_{10}H_{20}O_2$	172	295	3015	0	2225	0	S
n-undecanoic acid	$C_{11}H_{22}O_2$	186	508	999	0	1610	0	S
n-dodecanoic acid	$C_{12}H_{24}O_2$	200	553	7104	1634	3662	1283	S
n-tridecanoic acid	$C_{13}H_{26}O_2$	214	361	1107	725	2584	1193	S
n-tetradecanoic acid	$C_{14}H_{28}O_2$	228	2967	30258	6475	18815	20667	S
n-pentadecanoic acid	$C_{15}H_{30}O_2$	242	1532	4073	4102	7064	5742	S
n-hexadecanoic acid	$C_{16}H_{32}O_2$	256	18058	97969	62887	90225	172686	A
n-heptadecanoic acid	$C_{17}H_{34}O_2$	270	1297	6733	3914	7127	7821	S
n-octadecanoic acid	$C_{18}H_{36}O_2$	284	4340	21460	8326	14242	48503	S
n-nonadecanoic acid	$C_{19}H_{38}O_2$	298	513	3898	2664	3414	5452	S
n-eicosanoic acid	$C_{20}H_{40}O_2$	312	5248	3898	7352	9894	55822	S
n-heneicosanoic acid	$C_{21}H_{42}O_2$	326	1864	3860	4527	2830	12404	S
n-docosanoic acid	$C_{22}H_{44}O_2$	340	13124	18687	18250	7541	85295	S
n-tricosanoic acid	$C_{23}H_{46}O_2$	354	2606	8069	5256	2342	12482	S
n-tetracosanoic acid	$C_{24}H_{48}O_2$	368	14531	16789	14605	2072	47050	S
n-pentacosanoic acid	$C_{25}H_{50}O_2$	382	1321	4541	323	2843	8160	S
n-hexacosanoic acid	$C_{26}H_{52}O_2$	396	10061	5749	10840	1935	55648	S
n-heptacosanoic acid	$C_{27}H_{54}O_2$	410	191	2543	1041	1722	12314	S
n-octacosanoic acid	$C_{28}H_{56}O_2$	424	1535	16206	11671	3275	146571	S
n-nonacosanoic acid	$C_{29}H_{58}O_2$	438	0	2683	1086	0	9592	S
n-triacontanoic acid	$C_{30}H_{60}O_2$	452	574	15797	3522	0	21681	S
n-hentriacontanoic acid	$C_{31}H_{62}O_2$	466	0	1158	0	0	0	S
n-dotriacontanoic acid	$C_{32}H_{64}O_2$	480	0	2359	0	0	2217	S
n-hexadecenoic acid	$C_{16}H_{32}O_2$	268	2351	0	0	44921	4023	S
n-octadecadienoic acid	$C_{18}H_{32}O_2$	280	1664	0	0	0	0	S
n-octadecenoic acid	$C_{18}H_{34}O_2$	282	5164	0	0	9769	7894	S
α,ω-nonanedioic acid	$C_9H_{16}O_4$	188	0	427	0	0	641	S
α,ω-hexadecanedioic acid	$C_{16}H_{30}O_4$	286	98	293	232	1292	629	A
α,ω-octadecanedioc acid	$C_{18}H_{34}O_4$	314	0	0	82	977	505	S

α,ω-eicosanedioic acid	$C_{20}H_{38}O_4$	342	0	0	0	473	308	S
α,ω-docosanedioic acid	$C_{22}H_{42}O_4$	370	0	0	0	429	239	S
6-(2'-hexylphenyl)heptanoic acid	$C_{18}H_{28}O_2$	276	0	0	0	0	1605	S
7-(2'-pentylphenyl)heptanoic acid	$C_{18}H_{28}O_2$	276	0	0	0	0	1790	S
9-(2'-propylphenyl)nonanoic acid	$C_{18}H_{28}O_2$	276	0	9531	0	0	1481	S
10-(2'-ethylphenyl)decanoic acid	$C_{18}H_{28}O_2$	276	0	0	0	0	1554	S
11-(2'-methylphenyl)undecanoic acid	$C_{18}H_{28}O_2$	276	1762	0	0	0	1466	S
9-oxo-octadecanoic acid	$C_{18}H_{34}O_3$	298	0	13905	0	0	0	S
7-phenylheptanoic acid	$C_{13}H_{18}O_2$	206	0	0	537	0	0	I
8-phenyloctanoic acid	$C_{14}H_{20}O_2$	220	0	0	564	0	0	I
Total Carboxylic acids			94718	312219	172314	254914	754719	
CPI			7.3	6.1	6.2	5.1	8.7	
Cmax			16	16	16	16	16	
n-Alkanones								
Natural Products								
n-hexadecan-2-one	$C_{16}H_{32}O$	240	0	0	0	0	3567	S
n-heptadecan-2-one	$C_{17}H_{34}O$	254	0	2481	209	0	2164	S
n-octadecan-2-one	$C_{18}H_{36}O$	268	0	3115	0	0	796	S
n-nonadecan-2-one	$C_{19}H_{38}O$	282	0	6784	210	0	2303	S
n-eicosan-2-one	$C_{20}H_{40}O$	296	0	931	0	0	551	S
n-heneicosan-2-one	$C_{21}H_{42}O$	310	0	1861	274	0	4578	S
n-docosan-2-one	$C_{22}H_{44}O$	324	0	1024	44	0	778	S
n-tricosan-2-one	$C_{23}H_{46}O$	338	0	2140	296	2638	2205	S
n-tetracosan-2-one	$C_{24}H_{48}O$	352	0	1117	93	1593	1122	S
n-pentacosan-2-one	$C_{25}H_{50}O$	366	72	1163	194	1063	371	S
n-hexacosan-2-one	$C_{26}H_{52}O$	380	0	1070	170	384	1367	S
n-heptacosan-2-one	$C_{27}H_{54}O$	394	233	2053	308	486	5417	S
n-octacosan-2-one	$C_{28}H_{56}O$	408	0	1048	32	618	1584	S

n-nonacosan-2-one	$C_{29}H_{58}O$	422	0	2056	303	11782	21543	S
n-triacontan-2-one	$C_{30}H_{60}O$	436	0	388	0	210	964	S
n-hentriacontan-2-one	$C_{31}H_{62}O$	450	0	2915	0	657	2398	S
n-dotriacontan-2-one	$C_{32}H_{64}O$	464	0	76	0	0	0	S
n-tritriacontan-2-one	$C_{33}H_{66}O$	478	0	756	0	0	166	S
6,10,14-trimethyl-pentadecan-2-one	$C_{18}H_{36}O$	268	0	5903	435	3041	1527	S
Total Alkanones			305	36880	2568	22473	53399	
CPI			nd	2.5	5.3	5.9	3.8	
Cmax			27	19	27	29	29	
n-Akanols								
Natural Products								
n-heneicosanol	$C_{21}H_{44}O$	312	57	0	0	0	0	S
n-docosanol	$C_{22}H_{46}O$	326	363	0	0	0	0	A
n-tricosanol	$C_{23}H_{48}O$	340	41	0	0	0	0	S
n-tetracosanol	$C_{24}H_{50}O$	354	520	424	0	708	0	S
n-pentacosanol	$C_{25}H_{52}O$	368	35	0	0	47	0	S
n-hexacosanol	$C_{26}H_{54}O$	382	399	1115	0	95	0	S
n-heptacosanol	$C_{27}H_{56}O$	396	0	15	0	95	0	S
n-octacosanol	$C_{28}H_{58}O$	410	163	3845	0	0	0	S
n-triacontanol	$C_{30}H_{62}O$	438	0	3574	0	0	0	S
Total n-Alkanols			1579	5399	0	946	0	
CPI			18	nd	nd	nd	nd	
Cmax			24	28	nd	24	nd	
n-Alkylcyclohexanes								
Alteration Products								
n-octylcyclohexane	$C_{14}H_{28}$	196	0	0	380	0	0	I

n-decylcyclohexane	$C_{16}H_{32}$	224	0	0	268	0	0	I
n-dodecylcyclohexane	$C_{18}H_{36}$	252	0	116	255	0	0	I
n-octadecylcyclohexane	$C_{24}H_{48}$	336	0	0	3841	0	0	I
n-eicosanylcyclohexane	$C_{26}H_{52}$	364	0	488	4683	0	0	I
n-docosanylcyclohexane	$C_{28}H_{56}$	392	0	987	0	0	0	I
n-tetracosanylcyclohexane	$C_{30}H_{60}$	420	0	906	0	0	0	I
n-hexacosanylcyclohexane	$C_{32}H_{64}$	448	0	844	0	0	0	I
Total Alkylcyclohexanes			0	3340	9426	0	0	
n-Alkylbenzenes								
Alteration Products								
docosanylbenzene	$C_{28}H_{50}$	386	0	0	0	0	245	I
Wax Esters								
Natural Products								
heptadecyl hexadecanoate	$C_{33}H_{66}O_2$	494	0	0	0	4450	0	I
n-Alkylnitriles								
Alteration Products								
hexadecanenitrile	$C_{16}H_{31}N$	237	0	0	0	0	1811	S
octadecanenitrile	$C_{18}H_{35}N$	265	0	0	0	0	241	S
eicosanenitrile	$C_{20}H_{39}N$	293	0	0	0	0	161	S
docosanenitrile	$C_{22}H_{43}N$	321	0	0	0	0	174	S
tricosanenitrile	$C_{23}H_{45}N$	335	0	0	0	0	77	S
tetracosanenitrile	$C_{24}H_{47}N$	349	0	0	0	0	112	S
hexacosanenitrile	$C_{26}H_{51}N$	377	0	0	0	0	168	S
octacosanenitrile	$C_{28}H_{55}N$	405	0	0	0	0	335	S

II. BIOMARKERS

Sesquiterpenoids (C_{15})								
Alteration Products								
cis-thuja-10-oic acid	$C_{10}H_{16}O_2$	168	981	0	0	0	0	I
caryophylla-2(12),5-dien-13-aldehyde	$C_{15}H_{22}O$	218	0	0	0	3815	0	I
sesquiterpanol	$C_{15}H_{26}O_2$	238	0	0	0	40439	0	I
geigerone	$C_{15}H_{18}O_4$	262	0	0	0	4968	0	I
Diterpenoids (C_{20})								
Alteration Products								
dihydroretene	$C_{18}H_{20}$	236	0	0	1616	0	0	I
19-norabieta-4(18),8,11,13-tetraene	$C_{19}H_{26}$	254	653	0	0	0	0	I
Triterpenoids (C_{30})								
Natural Products								
allobetul-2-ene	$C_{30}H_{48}O$	424	0	0	0	952	0	I
α-amyrin	$C_{30}H_{50}O$	426	0	412	0	0	0	I
β-amyrin	$C_{30}H_{50}O$	426	0	1235	743	0	0	I
3-α-lupeol	$C_{30}H_{50}O$	426	0	851	4829	0	0	I
3-β-lupeol	$C_{30}H_{50}O$	426	0	0	1497	0	0	I
Alteration Products								
des-A-allobetulin	$C_{24}H_{38}O$	342	0	0	0	0	6046	I
nortriterpene	$C_{29}H_{48}$	396	0	0	0	0	1536	I
triterpadiene	$C_{30}H_{46}$	406	0	0	238	0	813	I
lupa-2,22-diene	$C_{30}H_{48}$	408	787	904	0	4379	0	I
oleana-2,12-diene	$C_{30}H_{48}$	408	552	760	705	0	0	I
ursa-2,20-diene	$C_{30}H_{48}$	408	0	2451	0	0	0	I
nortriterpenone	$C_{29}H_{46}O$	410	0	0	0	0	4173	I
lupa-1,22(29)-dien-3-one	$C_{30}H_{46}O$	422	0	619	0	0	0	I

lupa-2,22(29)-dien-28-al	$C_{30}H_{46}O$	422	175	0	0	0	0	I
α-amyrone	$C_{30}H_{48}O$	424	0	35	0	0	0	I
β-amyrone	$C_{30}H_{48}O$	424	0	285	349	0	0	I
glutin-5-en-3-one	$C_{30}H_{48}O$	424	0	0	9269	0	0	I
lupa-2,22(29)-dien-3-ol	$C_{30}H_{48}O$	424	0	634	0	1132	0	I
lupenone	$C_{30}H_{48}O$	424	534	271	1487	0	0	I
olean-13(18)-en-3-one	$C_{30}H_{48}O$	424	0	0	3726	0	0	I
taraxerone	$C_{30}H_{48}O$	424	0	0	1260	0	0	I
isomultifluorenone	$C_{30}H_{48}O$	424	0	0	1748	0	0	I
24-norolean-2,12-en-28-oic acid	$C_{29}H_{46}O_2$	426	325	0	0	0	0	I
24-norursana-2,12-dien-28-oic acid	$C_{29}H_{46}O_2$	426	0	0	0	0	3157	I
lupa-2,22(29)-dien-28-oic acid	$C_{30}H_{46}O_2$	438	849	0	0	34289	0	I
3-methoxylupa-2,22(29)-diene	$C_{31}H_{50}O$	438	0	0	2764	0	0	I
olean-2,12-dien-18-oic acid	$C_{30}H_{46}O_2$	438	5948	0	0	455	3012	I
olean-2,12-dien-28-oic acid	$C_{30}H_{46}O_2$	438	3052	0	0	0	0	I
ursa-2,12-dien-28-oic acid	$C_{30}H_{46}O_2$	438	5240	0	0	0	0	I
dihydrohyctanthanoic acid	$C_{30}H_{50}O_2$	442	0	0	1777	0	0	I
olean-13(18)-en-3-one-28-oic acid	$C_{31}H_{48}O_3$	454	0	0	604	0	0	I
29-chlorolup-1-en-3-one	$C_{30}H_{47}ClO$	458	0	0	1428	0	0	I
Total Triterpenoids			17462	8456	32425	41208	18737	
Steroids								
Natural Products								
campesterol	$C_{28}H_{48}O$	400	0	271	0	0	0	I
stigmasterol	$C_{29}H_{48}O$	412	0	674	1260	0	0	I
β-sitosterol	$C_{29}H_{50}O$	414	254	3339	1821	2528	2187	I
Alteration Products								
24-ethyl-19-norcholesta-1,3,5(10),6,8,14-hexaene	$C_{28}H_{38}$	374	0	0	0	1212	384	I

24-ethyl-19-norcholesta-1,3,5(10),6,8-pentaene	$C_{28}H_{40}$	376	0	0	0	846	430	I
24-ethyl-19-norcholesta-1,3,5(10),8-tetraene	$C_{28}H_{42}$	378	0	0	0	254	0	I
24-ethyl-14β(H)-1(10-6)-abeo-cholesta-5,7,9-triene	$C_{29}H_{46}$	394	0	0	228	0	398	I
24-ethyl-4-methyl-19-norcholesta-1,3,5(10)-triene	$C_{29}H_{46}$	394	336	0	202	3159	1035	I
stigmasta-3,5-diene	$C_{29}H_{48}$	396	0	0	0	1662	0	I
stigmasta-4,6-diene	$C_{29}H_{48}$	396	0	0	0	104	0	I
24-ethylcholesta-4,22-diene	$C_{29}H_{46}$	396	0	0	0	254	0	I
stigmast-5-ene	$C_{29}H_{50}$	398	0	0	0	6338	145	I
stigmasta-3,5-dien-7-one	$C_{29}H_{46}$	410	0	0	0	0	1665	I
Total Steroids			590	4284	3512	16357	6243	
III. POLYCYCLIC AROMATIC HYDROCARBONS (PAH)								
Alteration Products								
fluorene	$C_{13}H_{10}$	166	0	1100	0	0	0	A
C_1-fluorenes	$C_{14}H_{12}$	180	0	0	0	0	0	I
anthracene	$C_{14}H_{10}$	178	0	0	0	1302	0	A
phenanthrene	$C_{14}H_{10}$	178	364	7741	2012	1606	1496	A
4(H)-cyclopenta[def]phenanthrene	$C_{15}H_{10}$	190	0	1093	0	0	0	A
C_1-anthracenes/phenanthrenes	$C_{15}H_{12}$	192	345	3956	1972	1857	2233	I
fluoranthene	$C_{16}H_{10}$	202	153	4203	2351	2669	822	A
pyrene	$C_{16}H_{10}$	202	259	947	2352	984	3067	A
C_2-anthracenes/phenanthrenes	$C_{16}H_{14}$	206	121	1953	3914	1108	806	A
11(H)-benzo[a]fluorene	$C_{17}H_{12}$	216	0	362	1083	293	0	A
11(H)-benzo[b]fluorene	$C_{17}H_{12}$	216	0	291	2664	192	0	A
C_1-pyrenes	$C_{17}H_{12}$	216	0	1242	0	675	0	I
C_3-anthracenes/phenanthrenes	$C_{17}H_{16}$	220	103	118	0	0	1873	A
benzo[ghi]fluoranthene	$C_{18}H_{10}$	226	0	979	4527	823	0	A
benz[a]anthracene	$C_{18}H_{12}$	228	0	793	965	211	0	A
chrysene	$C_{18}H_{12}$	228	0	0	1116	147	0	A

C_4-anthracenes/phenanthrenes	$C_{18}H_{18}$	234	0	0	0	0	1641	A
C_1-chrysenes	$C_{19}H_{14}$	242	0	209	0	0	0	A
benzo[a]pyrene	$C_{20}H_{12}$	252	0	467	3225	147	0	A
3,3,7-trimethyl-1,2,3,4-tetrahydrochrysene	$C_{21}H_{22}$	274	36	0	0	0	0	I
Total PAH			1726	31952	3225	14548	14172	
Methylphenanthrenes/Phenanthrene (MP:P)			0.9	0.5	1.0	1.1	1.5	
IV. PHENOLS (Lignin Pyrolysis)								
Natural Products								
cinnamic acid	$C_9H_8O_2$	148	0	0	372	0	0	A
coumaric acid	$C_9H_8O_3$	164	1713	0	0	0	0	A
eugenol	$C_{10}H_{12}O_2$	164	0	0	0	10991	0	A
α-tocopherol	$C_{29}H_{50}O_2$	430	0	1903	0	0	0	I
Alteration Products								
catechol	$C_6H_6O_2$	110	0	0	0	27440	9493	I
benzoic acid	$C_7H_6O_2$	122	0	0	1341	0	0	I
guaiacol	$C_7H_8O_2$	124	0	1398	0	0	0	I
3-oxy-benzoic acid	$C_7H_6O_3$	138	0	0	423	0	0	I
3,4-diol-benzoic acid	$C_7H_6O_4$	154	101	0	0	0	0	I
3,5-dimethylphenol	$C_8H_{10}O$	122	0	770	0	0	0	I
3,5-dimethoxy-4-hydroxytoluene	$C_9H_{12}O_3$	168	0	17884	0	0	0	I
3,4-(methylenedioxy)-5-methoxybenzaldehyde	$C_9H_8O_4$	180	0	0	0	0	0	I
1,1'-biphenyl-4,4'-dimethyl	$C_{14}H_{14}$	182	0	682	0	0	0	I
vanillin	$C_8H_8O_3$	152	0	9055	0	0	0	A
2,6-dimethoxyphenol	$C_8H_{10}O_3$	154	377	36097	0	23817	0	I
acetovanillone	$C_9H_{10}O_3$	166	62	5762	743	0	0	I
vanillic acid	$C_8H_8O_4$	168	57	4547	1225	1775	3393	A

pyrogallol	$C_9H_{14}O_3$	170	0	0	0	1022	5006	I
guaiacylacetone	$C_{10}H_{12}O_3$	180	88	0	0	0	0	I
homovanillyl alcohol	$C_{10}H_{14}O_3$	182	48	16123	1602	2903	2951	I
acetosyringone	$C_{10}H_{12}O_4$	196	278	5692	1530	0	0	I
homovanillic acid	$C_{10}H_{12}O_4$	196	79	0	0	0	3921	A
syringic acid	$C_9H_{10}O_5$	198	86	2089	732	0	0	I
valeric acid	$C_{12}H_{14}O_3$	206	0	1974	0	0	0	I
3,5-dimethoxy-4-coumaraldehyde	$C_{11}H_{12}O_4$	208	1125	0	655	0	0	I
syringylacetone	$C_{11}H_{14}O_4$	210	589	3616	869	0	0	I
syringylpropanal	$C_{11}H_{14}O_4$	210	61	0	0	0	0	I
2,3,5-trimethoxybenzoic acid	$C_{10}H_{12}O_5$	212	0	655	0	0	0	I
8-phenyloctanoic acid	$C_{14}H_{20}O_2$	220	0	3638	0	0	0	I
3,5-dimethoxy-4-coumaric acid	$C_{11}H_{12}O_5$	224	0	5148	0	0	0	I
3,3'-dimethoxy-4,4'-dihydroxystilbene	$C_{16}H_{16}O_4$	272	0	5649	0	0	0	I
divanillyl	$C_{16}H_{16}O_4$	274	43	0	1006	0	0	I
syringylvanillylmethane	$C_{17}H_{20}O_5$	304	28	0	0	0	0	I
disyringyl	$C_{18}H_{22}O_6$	334	364	0	788	0	0	I
tetrahydro-3,4-divanillylfuran	$C_{20}H_{24}O_5$	344	0	2071	781	1236	1249	I
Total Phenols			5099	124754	12068	69184	26012	
Syringyl skeletons/vanillyl skeletons (S/V)			6.1	1.6	0.8	1.5	0.4	
V. MONOSACCHARIDE DERIVATIVES								
Alteration Products								
galactosan	$C_6H_{10}O_5$	162	231	7040	4041	7359	8101	A
mannosan	$C_6H_{10}O_5$	162	154	5527	1172	3793	3429	A
levoglucosan	$C_6H_{10}O_5$	162	30	18281	9785	23299	23213	A
Total Monosaccharides			386	12567	5213	11153	11529	

VI. UNKNOWNS					
	0	0	0	43134	0
VI. MISCELLANEOUS					
Unresolved Complex Mixture (μg/kg)	388	687129	211938	548937	462
Unresolved:Resolved (U:R)	0.01	0.8	0.9	0.8	0.8
Volatile Organic Carbon (mg/kg)	2051	25476	9926	19436	4260
Elemental Carbon (mg/kg)	219	595	368	1855	145
Volatile Organic Carbon/Elemental Carbon	9	43	27	10	29
Methylphenanthrenes/Phenanthrene (MP:P)	0.9	0.5	1.0	1.1	1.5

Identification Criteria

A = matches with authentic standard; S = interpolated from homologous series fragmentation pattern; I = interpreted from mass spectrum fragmentation pattern

All compositions and molecular weights are as the compounds occur in smoke (i.e., underivatized).

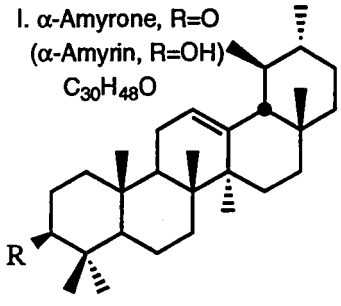
CPI for n-alkanes, n-alkenes and n-alkanones: [CPI = ΣC_{13}-$C_{35}/\Sigma C_{12}$-C_{34}] from Mazurek and Simoneit (1984)

CPI for n-alkanoic acids and n-alkanols: [CPI = ΣC_{12}-$C_{34}/\Sigma C_{13}$-C_{35}] from Mazurek and Simoneit (1984)

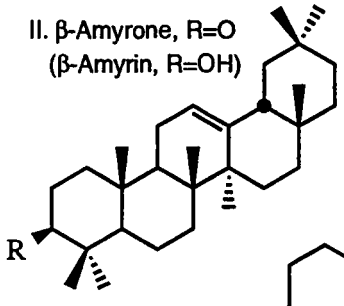
Volatile organic carbon in this case represents the solvent extractable matter.

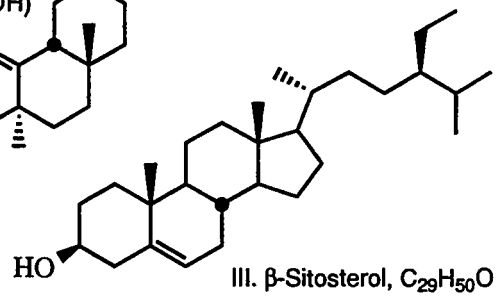
Appendix V.1. Structures of compounds cited in text.

I. α-Amyrone, R=O
(α-Amyrin, R=OH)
$C_{30}H_{48}O$



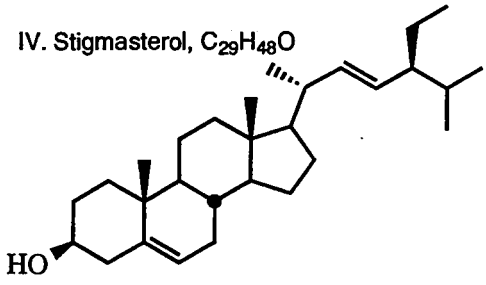
II. β-Amyrone, R=O
(β-Amyrin, R=OH)

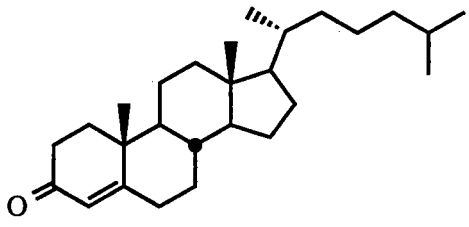




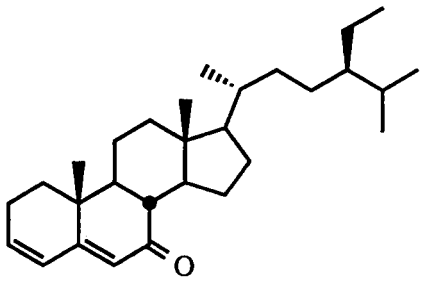
III. β-Sitosterol, $C_{29}H_{50}O$

IV. Stigmasterol, $C_{29}H_{48}O$

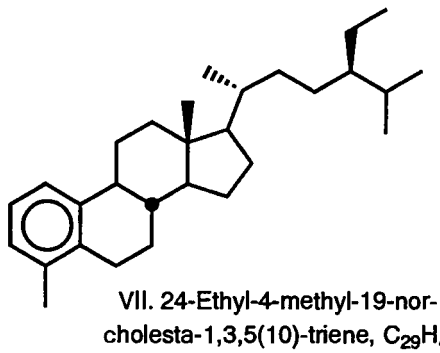




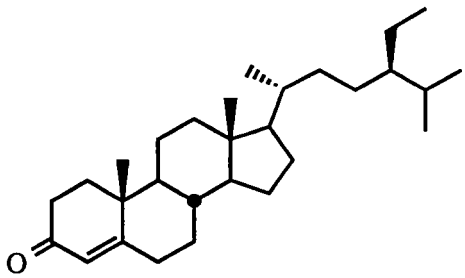
V. Cholest-4-en-3-one, $C_{27}H_{44}O$



VI. Stigmasta-3,5-dien-7-one, $C_{29}H_{46}O$

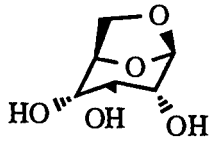


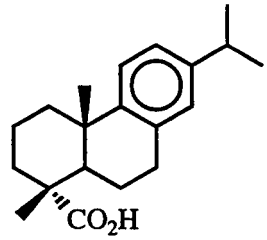
VII. 24-Ethyl-4-methyl-19-nor-cholesta-1,3,5(10)-triene, $C_{29}H_{46}$



VIII. Stigmast-4-en-3-one, $C_{29}H_{48}O$

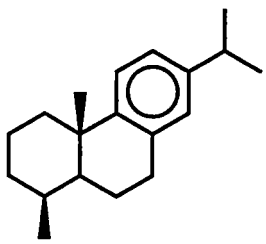
IX. Levoglucosan (1,6-anhydro-β-D-gluco-pyranose, $C_6H_{10}O_5$)



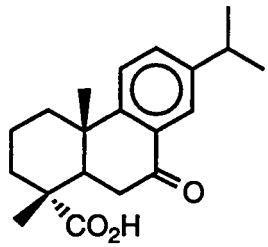


X. Dehydroabietic acid, $C_{20}H_{28}O_2$

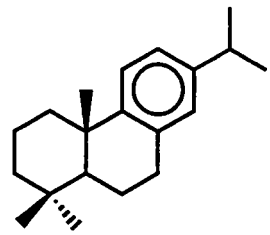
Appendix V.1. (Continued)



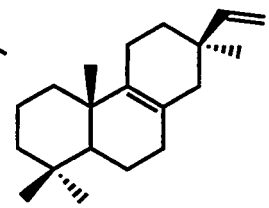
XI. 18-Norabieta-8,11,13-triene, $C_{19}H_{28}$



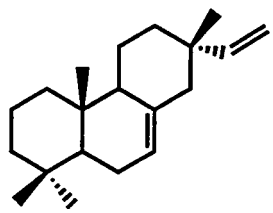
XII. 7-Oxodehydro-abietic acid, $C_{20}H_{26}O_3$



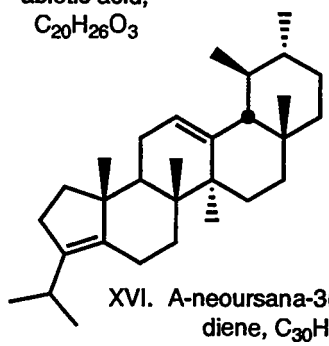
XIII. Dehydroabietane, $C_{20}H_{30}$



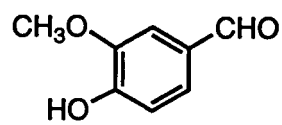
XIV. Pimara-8,15-diene, $C_{20}H_{32}$



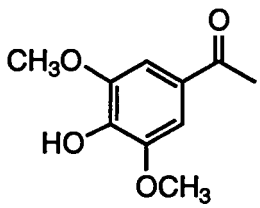
XV. Isopimara-7,15-diene, $C_{20}H_{32}$



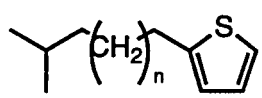
XVI. A-neoursana-3(5),12-diene, $C_{30}H_{48}$



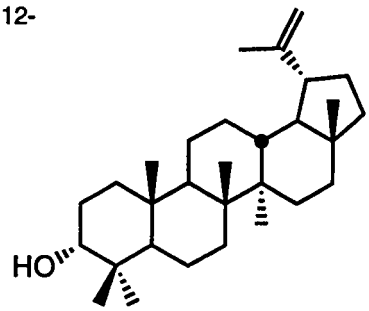
XVII. Vanillin, $C_8H_8O_3$



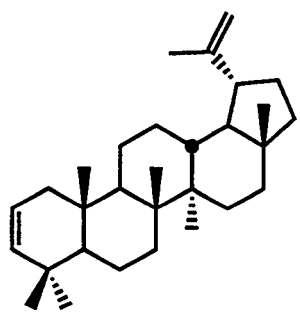
XVIII. Acetosyringone, $C_{10}H_{12}O_4$



XIX. Methylalkylthiophenes

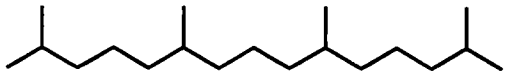


XX. 3α-Lupeol, $C_{30}H_{50}O$

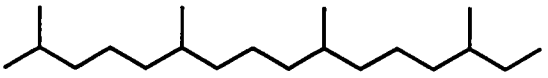


XXI. Lupa-2,22-diene, $C_{30}H_{48}$

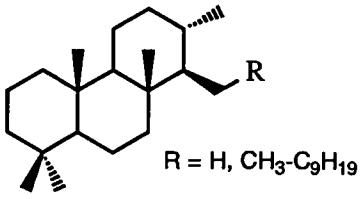
Appendix VI.1. Petroleum biomarker hydrocarbons.



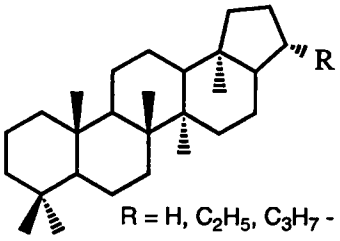
1. Pristane, $C_{19}H_{40}$



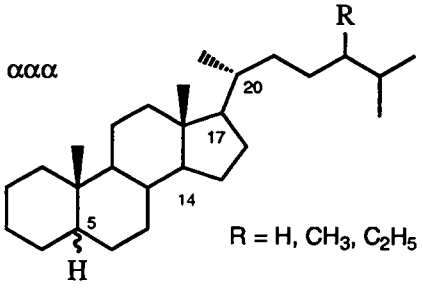
2. Phytane, $C_{20}H_{42}$



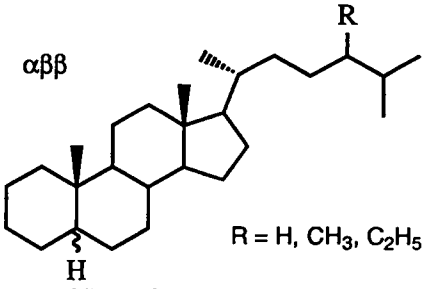
3. Extended Tricyclic Terpanes



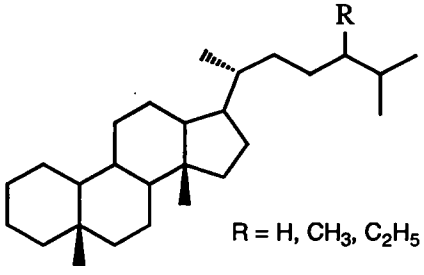
4. 17α(H),21β(H)-Hopanes



5. 5α/β(H),14α(H),17α(H)-Steranes, C_{26} - C_{30}



6. 5α/β(H),14β(H),17β(H)-Steranes, C_{26} - C_{30}



7. Diasteranes, C_{27} - C_{29}

Appendix VI.2. Data of the *n*-alkane, UCM and isoprenoid hydrocarbon constituents in Crater Lake samples.

Sample Date-ID	Sampling Site	Description	C_{range}	C_{max}	CPI[1]	Plant Wax[2] *n*-Alkanes	Petroleum *n*-Alkanes	Total *n*-Alkanes	UCM	Pr/Ph
AIR						(ng/m^3)	(ng/m^3)	(ng/m^3)	(ng/m^3)	
6/05/96-1	Crater Lake Rim	48 hrs/1 filter	12-29	25	3.3	94	139	233	-	-
9/07/96-1	Crater Lake Rim	48 hrs/2 filters	15-29	23	1.8	118	155	274	-	-
9/07/96-2	Crater Lake Rim	48 hrs/2 filters	14-31	16	1.4	430	227	657		1.7
SURFACE SLICKS						($\mu g/m^2$)	($\mu g/m^2$)	($\mu g/m^2$)	($\mu g/m^2$)	
7/27/95-1	Cleetwood Cove	Interior of boat dock	16-34	22	1.2	50	630	680	3440	1.4
7/27/95-3	Cleetwood Cove	Outboard motor exhaust	14-35	21	1.8	400	790	1190	2190	2
7/27/95-5	Cleetwood Cove	Slick with foam	14-36	28	0.5	280	220	500	1680	1.2
7/27/95-13	Wizard Island	Tour boat wake at dock	16-26	18	1	300	1610	1910	7140	1.9
7/27/95-16	Spring 42	2 filters	16-25	22	1.4	340	1060	1410	-	2.8
8/11/96-1	Wizard Island	4 filters/GERG	NA	NA	NA	NA	NA	NA	NA	NA
8/11/96-3	Phanthom Ship	4 filters/GERG	NA	NA	NA	NA	NA	NA	NA	NA
8/11/96-5	Midlake Mooring	4 filters/GERG	NA	NA	NA	NA	NA	NA	NA	NA
8/11/96-7	Cleetwood Mooring	4 filters/GERG	NA	NA	NA	NA	NA	NA	NA	NA
9/26/95-1	Helicopter Crash Site	2 filters	15-28	28	0.3	1200	840	2030	3920	0.7
9/26/95-2	Phanthom Ship	2 filters	14-29	28	0.1	5050	710	5760	4330	1.8
9/26/95-5	Midlake Mooring	2 filters	14-30	28	0.1	5120	830	5950	4870	2
9/26/95-6	The Palisade	2 filters/3m to shore	16-28	28	0.1	5860	3700	6230		1.1
WATER										
8/11/96-2	Wizard Island	500 ml/GERG	NA	NA	NA	NA	NA	NA	NA	NA
8/11/96-4	Phanthom Ship	500 ml/GERG	NA	NA	NA	NA	NA	NA	NA	NA
8/11/96-6	Midlake Mooring	500 ml/GERG	NA	NA	NA	NA	NA	NA	NA	NA
8/11/96-8	Cleetwood Mooring	500 ml/GERG	NA	NA	NA	NA	NA	NA	NA	NA
SEDIMENTS						($\mu g/kg$)	($\mu g/kg$)	($\mu g/kg$)	($\mu g/kg$)	
8/11/96-8	SE Deep	416 m Depth/GERG	NA	NA	NA	NA	NA	NA	NA	NA
8/11/96-9	Near Shore	5 m Depth/GERG	NA	NA	NA	NA	NA	NA	NA	NA
9/08/95-27	Cleetwood Cove	5 m Depth/Diver collected	15-33	29	0.7	243	505	748	-	2.2
9/08/95-28	Cleetwood Cove	10 m Depth/Diver collected	15-33	29	2.1	210	290	500	-	1.4
9/08/95-29	Cleetwood Mooring	5 m Depth/Diver collected	15-33	29	1.1	236	1439	1675	-	1.2
9/08/95-30	Cleetwood Mooring	10 m Depth/Diver collected	15-33	29	1	115	503	618	-	1.5
9/08/95-31	North Basin	590 m Depth/Box core	16-33	21	2.6	13	16	29	0	0

Appendix VI.2. (Continued)

Sample Date-ID	Sampling Site	Description	C_{range}	C_{max}	CPI[1]	Plant Wax[2] *n*-Alkanes	Petroleum *n*-Alkanes	Total *n*-Alkanes	UCM	Pr/Ph
SOILS						(µg/kg)	(µg/kg)	(µg/kg)	(µg/kg)	
7/27/95-6	Cleetwood Cove	Next to gas pump	12-26	13	1	6.1E06	3.9E07	4.5E07	-	2.8
7/27/95-15	Spring 42	Mud composite	18-30	25	4.7	9.8E04	4.5E04	1.4E05	-	-
7/27/95-17	Sinot Memorial	Mud composite	17-36	27	2.4	2.1E04	2.3E04	4.3E04	4.4E05	-
7/27/95-25	Watchman Overlook	Lake side of road	17-36	29	3.6	2.9E04	2.2E04	5.1E04	-	-
PETROLEUM						(mg/L)	(mg/L)	(mg/L)	(mg/L)	
7/27/95-2	Cleetwood Cove	Gasoline	to C_{10}	-	-	-	-	-	-	-
7/27/95-4	Cleetwood Cove	Gasoline/Lube oil mixture	to C_{10}	-	-	-	-	-	-	-
7/27/95-9	Cleetwood Cove	Gasoline/GERG	NA	NA	NA	NA	NA	NA	NA	NA
7/27/95-22	Cleetwood Cove	Purple lube oil/Whaler	12-22	12	0.5	2.0E06	5.2E09	5.4E06	1.1E07	1.1
8/11/96-10	Cleetwood Cove	Lube oil/SAE 30/GERG	NA	NA	NA	NA	NA	NA	NA	NA
8/11/96-11	Cleetwood Trail	Diesel	10-25	16	1	-	-	-	-	-
SURFACE DEBRIS						($\mu g/m^2$)	($\mu g/m^2$)	($\mu g/m^2$)	($\mu g/m^2$)	
9/26/95-3	Phanthom Ship	White foam	14-36	18	1.2	90	480	570	1870	1
9/26/95-4	Phanthom Ship	White foam	17-28	21	1.6	2940	2700	5640	-	-
9/26/95-7	Helicopter Crash Site	Pilot book/Page with fuel	12-19	13	0.4	1.3E08	1.6E09	1.7E09	1.7E09	3.6
9/26/95-8	Helicopter Crash Site	Pilot book/Cover with fuel	12-18	13	0.2	1.3E11	8.0E10	2.1E11	2.1E11	1.2
SNOW										
7/27/95-18	Sinot Memorial	Surface scraping	15-30	20	0.5	-	-	-	-	3
7/27/95-20	Southeast Shore	Surface scraping	17-35	20	0.9	-	-	-	-	-
7/27/95-26	Watchman Overlook	Surface scraping	16-31	20	0.7	-	-	-	-	2.4
BIOLOGY						(µg/kg)	(µg/kg)	(µg/kg)	(µg/kg)	
7/27/95-8	Cleetwood Cove	Aquatic moss beneath dock	17-33	17	2.1	1.3E07	8.1E06	2.1E07	-	-
7/27/95-11	Cleetwood Beach	Pollen pudding at water line	15-29	21	4.2	1.0E05	8.4E04	2.0E05	-	0.4
7/27/95-24	Traffic Stop/Rim Village	Mountain Hemlock (waxes)	24-36	34	0.9	3.9E07	7.2E07	1.1E08	-	-

[1]CPI determined from C_{16} through C_{33} *n*-alkanes.

[2]Remaining concentration after subtraction of the petroleum *n*-alkane concentration (Simoneit *et al.*, 1991).
NA: Not applicable

Appendix VI.3. PAH compounds analyzed and their concentrations.

PAH	Surface Slicks				Sediments	
	Phanthom Ship (ng/m^2)	Wizard Island (tourboat wake) (ng/m^2)	East of Midlake Mooring (ng/m^2)	Cleetwood Cove Mooring (ng/m^2)	Cleetwood Cove (µg/kg dry wt)	SE Deep (0-2 cm) (µg/kg dry wt)
Naphthalene	2.29 J	2.76 J	2.20 J	2.21 J	2.8 J	6.7
C_1-Naphthalenes	2.04 J	1.19 J	1.19 J	1.59 J	1.4 J	2.6 J
C_2-Naphthalenes	ND	ND	ND	ND	ND	ND
C_3-Naphthalenes	ND	ND	ND	ND	ND	ND
C_4-Naphthalenes	ND	ND	ND	ND	ND	ND
Biphenyl	0.18 J	0.56	0.71	1.03	0.3 J	1
Acenaphthylene	0.30 J	0.35 J	0.21 J	0.33 J	0.3 J	0.05 J
Acenaphthene	0.31 J	0.38 J	0.50 J	0.71	0.7 J	0.5 J
Fluorene	0.41 J	0.31 J	0.58 J	0.26 J	0.2 J	0.5 J
C_1-Fluorenes	ND	ND	ND	ND	ND	ND
C_2-Fluorenes	ND	ND	ND	ND	ND	ND
C_3-Fluorenes	ND	ND	ND	ND	ND	ND
Phenanthrene	0.34 J	0.42 J	0.45 J	0.61 J	0.4 J	2.3 J
Anthracene	0.38 J	0.16 J	0.34 J	0.15 J	0.4 J	0.4 J
C_1-Phenanthrenes/ Anthracenes	ND	ND	ND	ND	ND	ND
C_2-Phenanthrenes/ Anthracenes	ND	ND	ND	ND	ND	ND
C_3-Phenanthrenes/ Anthracenes	ND	ND	ND	ND	ND	ND
C_4-Phenanthrenes/ Anthracenes	ND	ND	ND	ND	ND	ND
Dibenzothiophene	0.34 J	0.12 J	0.18 J	0.26 J	0.3 J	0.9
C_1-Dibenzothiophenes	ND	ND	ND	ND	ND	ND
C_2-Dibenzothiophenes	ND	ND	ND	ND	ND	ND
C_3-Dibenzothiophenes	ND	ND	ND	ND	ND	ND
Fluoranthene	0.27 J	0.28 J	0.45 J	0.34 J	0.3 J	3.2
Pyrene	0.30 J	0.20 J	0.36 J	0.34 J	0.5 J	3.1 J

Appendix VI.3. (Continued)

PAH	Surface Slicks: Phanthom Ship (ng/m²)	Surface Slicks: Wizard Island (tourboat wake) (ng/m²)	Surface Slicks: East of Midlake Mooring (ng/m²)	Surface Slicks: Cleetwood Cove Mooring (ng/m²)	Sediments: Cleetwood Cove (µg/kg dry wt)	Sediments: SE Deep (0-2 cm) (µg/kg dry wt)
C_1-Fluoranthenes/ Pyrenes	ND	ND	ND	ND	ND	ND
Benzo[a]anthracene	0.07 J	0.06 J	0.06 J	0.07 J	0.2 J	0.8
Chrysene	0.08 J	0.09 J	0.02 J	0.12 J	0.2 J	1.8 J
C_1-Chrysene	ND	ND	ND	ND	0.5 J	ND
C_2-Chrysenes	ND	ND	ND	ND	2.9	ND
C_3-Chrysenes	ND	ND	ND	ND	1.0 J	ND
C_4-Chrysenes	ND	ND	ND	ND	ND	ND
Benzo[b]fluoranthene	0.02 J	0.06 J	0.06 J	0.10 J	0.2 J	3 J
Benzo[k]fluoranthene	0.06 J	0.02 J	0.02 J	0.03 J	0.1 J	0.9 J
Benzo[a]pyrene	0.06 J	0.03 J	0.06 J	0.07 J	0.5 J	1.5 J
Benzo[e]pyrene	0.06 J	0.04 J	0.06 J	0.05 J	0.6 J	1.7 J
Perylene	0.04 J	0.05 J	0.05 J	0.12 J	0.3 J	0.6 J
Indeno[1,2,3-c,d]pyrene	0.03 J	0.02 J	0.03 J	0.06 J	0.3 J	4.2
Dibenzo[a,h]anthracene	0.04 J	0.06 J	0.02 J	0.03 J	0.1 J	0.2 J
Benzo[g,h,i]perylene	0.02 J	0.02 J	0.02 J	0.05 J	1 J	3.6 J
Total PAH	7.65	7.18	7.56	8.52	15.5	39.6

J = <Minimum Detection Limit
ND = Not Detected

Appendix VI.4. Estimation of petroleum input from boating activity.

Estimation of the levels of PAH and petroleum hydrocarbon contributions to surface waters from tour boats.

A full description of the methods used to determine the emission levels of petroleum hydrocarbons by noncatalyst combustion engines is given in Rogge *et al.*, (1993a). In exhaust emissions, PAH compounds make up approximately 48% of the identifiable components. Their presence in Crater Lake surface slicks is due to input from petroleum combustion emissions from boating activities (that is the strongest point source). Given that PAH concentrations in surface slicks were measured in this work, a rough estimate of the PAH and total petroleum contribution from tour boating activities can be made.

Tour Boating Data

Noncatalyst Engine:	1 per tour boat
Boat Travel Distance:	25 km/tour loop
Total of Tour Boats:	4
PAH Emission Rate:	2800 mg/km (assumes twice engine size of cars) (Rogge *et al.*, 1993a)

Crater Lake Physical Data

Surface Area: 53.2 km^2

Volume: 17.3 km^3

CALCULATIONS

1) Estimate the daily PAH emission for each tour boat:

(2800 mg/km)(75 km/day) = 210,000 mg/day of PAH

2) Estimate the daily PAH emission for all tour boat activity:

(210,000 µg/day)(4 boats) = 840,000 µg/day (0.84 g/day) of PAH

3) Assume that all PAH products produced by tour boat engines accumulate in surface slicks and divide by the lake surface area:

840,000 µg/53.2 km^2 = 15.8 mg/km^2 of PAH

4) Convert units to those measured in Crater Lake (this work)

(15.8 mg/km^2)(1 km^2/1E6 m^2)(1000 µg/1 mg)

Product of above equals: 0.016 µg/m^2

Appendix VI.4. (Continued)

This value is the estimated total tour boat contribution of petroleum PAH to surface slick per day in Crater Lake, assuming uniform distribution over the total lake surface.

Estimation of the total petroleum products emitted

An estimation of the total petroleum products emitted to surface waters daily from tour boating activities can be derived following the methods for achieving a total mass balance described by Rogge *et al.* (1993a). They found the following to be true for determining the levels of petroleum hydrocarbons using GC and GC-MS analyses:

1) Of the total petroleum products emitted by noncatalyst combustion engines, the resolved organic compounds make up 10%.
2) Of the resolved organic compounds, 68% are identifiable.
3) Of the identifiable compounds, PAH make up 48%.

CALCULATIONS

Given: 0.016 $\mu g/m^2$ (determined above in #4)

1) Solve for the concentration of total identifiable organic components:

[PAH] = 48% of [Identifiable Components]

0.016/0.48 = 0.033

The identifiable component concentration = 0.033 $\mu g/m^2$

2) Solve for the concentration of total resolved organic components:

[Identifiable Components] = 68% of [Resolved Organics]

0.033/0.68 = 0.049

The resolved organic component concentration = 0.05 $\mu g/m^2$

3) Solve for the **TOTAL PETROLEUM PRODUCTS** emitted daily to surface slicks (100 μm film thickness assumed) by all boating activities:

[Resolved Organics] = 10% of [Total Petroleum Products]

0.049/0.10 = 0.5 $\mu g/m^2$

RELATED WORK BY AUTHOR

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