

## Review Articles: Air Pollution

# A Review of Biomarker Compounds as Source Indicators and Tracers for Air Pollution\*

Bernd R.T. Simoneit

Environmental and Petroleum Geochemistry Group, College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331, U.S.A.

### Abstract

An overview of the application of organic geochemistry to the analysis of organic matter on aerosol particles is presented here. This organic matter is analyzed as solvent extractable bitumen/lipids by gas chromatography-mass spectrometry. The organic geochemical approach assesses the origin, the environmental history and the nature of secondary products of organic matter by using the data derived from specific molecular analyses. Evaluations of production and fluxes, with cross-correlations can thus be made by the application of the same separation and analytical procedures to samples from point source emissions and the ambient atmosphere. This will be illustrated here with typical examples from the ambient atmosphere (aerosol particles) and from emissions of biomass burning (smoke).

Organic matter in aerosols is derived from two major sources and is admixed depending on the geographic relief of the air shed. These sources are biogenic detritus (e.g., plant wax, microbes, etc.) and anthropogenic particle emissions (e.g., oils, soot, synthetics, etc.). Both biogenic detritus and some of the anthropogenic particle emissions contain organic materials which have unique and distinguishable compound distribution patterns ( $C_{14}$ - $C_{40}$ ). Microbial and vascular plant lipids are the dominant biogenic residues and petroleum hydrocarbons, with lesser amounts of the pyrogenic polynuclear aromatic hydrocarbons (PAH) and synthetics (e.g., chlorinated compounds), are the major anthropogenic residues.

Biomass combustion is another important primary source of particles injected into the global atmosphere. It contributes many trace substances which are reactants in atmospheric chemistry and soot particulate matter with adsorbed biomarker compounds, most of which are unknown chemical structures. The injection of natural product organic compounds into smoke occurs primarily by direct volatilization/steam stripping and by thermal alteration based on combustion temperature. Although the molecular composition of organic matter in smoke particles is highly variable, the molecular tracers are generally still source specific. Retene has been utilized as a tracer for conifer smoke in urban aerosols, but is not always detectable. Dehydroabietic acid is generally more concentrated in the atmosphere from the same emission sources.

Degradation products from biopolymers (e.g., levoglucosan from cellulose) are also excellent tracers. An overview of the biomarker compositions of biomass smoke types is presented here. Defining additional tracers of thermally-altered and directly-emitted natural products in smoke aids the assessment of the organic matter type and input from biomass combustion to aerosols. The precursor to product approach of compound characterization by organic geochemistry can be applied successfully to provide tracers for studying the chemistry and dispersion of ambient aerosols and smoke plumes.

**Keywords:** Air pollution; biomarkers; biomass burning; dehydroabietic acid; homologous compounds; levoglucosan; organics ( $C_{10}$ - $C_{40}$ ); PAH; particulate matter; petroleum; triterpenyl fatty acid esters; wax esters

### 1 Introduction

Aerosols influence the radiative balance of the Earth through absorption and scattering of solar radiation back to space, known as the direct effect, and by increasing the amount of solar radiation that clouds reflect, the indirect effect (CHARLSON et al., 1992). The direct radiative effect of aerosols is strongly influenced by particle size and composition. The radiative effects of anthropogenic aerosols are relatively large compared to their mass contribution because they are in the size range which is radiatively most active (SEINFELD, 1986).

Biogenic organic matter, consisting predominantly of lipids, soot and humic and fulvic acids, is now firmly established as a major carbonaceous fraction in atmospheric particles (i.e. ARPINO et al., 1972; BARBIER et al., 1981; BRODDIN et al., 1980; COX et al., 1982; DUCE et al., 1983; EICHMANN et al., 1979, 1980; FRASER et al., 1997, 1998; GAGOSIAN et al., 1981, 1982, 1987; MARTY and SALIOT, 1982; MATSUMOTO and HANYA, 1980; MAZUREK and SIMONEIT, 1984, 1997; ROGGE et al., 1991, 1993a-e, 1994, 1997a,b, 1998; SCHAUER et al., 1996; SIMONEIT, 1977, 1979, 1980, 1984a,b, 1985, 1986a, 1989; SIMONEIT et al., 1977, 1980, 1988, 1990, 1991a,b,c; SIMONEIT and MAZUREK, 1982, 1989; ZHENG et al., 1997). However, in comparison to the relatively extensive studies that have been carried out on hydrocarbons of both bio-

\*Presented at the 6th FECS Conference on Chemistry and the Environment, Atmospheric Chemistry and Air Pollution, August 26-28, 1998, Copenhagen.

genic and anthropogenic origins in aerosols from urban and rural/remote regions, only limited molecular information is available on polar compounds (e.g., GAGOSIAN et al., 1987; GAGOSIAN and PELTZER, 1986; MAZUREK et al., 1989; ROGGE et al., 1993a, SCHNEIDER et al., 1983; SICRE et al., 1987; SIMONEIT, 1985, 1989; SIMONEIT and MAZUREK, 1982, 1989; SIMONEIT et al., 1983, 1988, 1993, 1999a). Chemical fingerprints of emission sources have commonly been utilized to distinguish specific inputs from point sources rather than correlation of an air parcel to its regional source. Most urban/industrial regions produce a similar suite of organic compounds associated with atmospheric particulate matter (i.e., combustion products, vehicular exhaust plus a variety of industrial emissions: e.g., HILDEMANN et al., 1991; ROGGE et al., 1993c; SIMONEIT, 1984a). Regional vegetation cover has been shown to also produce distinct signatures and molecular markers (CHEN, 1992; ROGGE et al., 1993d; SIMONEIT et al., 1983, 1988; SIMONEIT and MAZUREK, 1982; STANDLEY, 1987). It is therefore useful to apply the biogenic constituents from both natural and combustion emissions and the anthropogenic emissions as tracers in tropospheric chemistry.

Biomass burning is another important primary source of many trace substances which are reactants in atmospheric chemistry and of soot particulate matter that decreases visibility and absorbs incident radiation (e.g., CRUTZEN and ANDREAE, 1990; LEVINE, 1991, 1996). Thus, there is a need to demonstrate additional specific tracers for this input process.

The application of biomass burning as a method for clearing vegetated (forest and grassland) areas significantly increases the input of organic aerosol components to the atmosphere. The composition data of smoke particulate matter is important for understanding the organic component contribution of biomass burning emissions to atmospheric chemistry and complements existing work on the characterization of direct organic emissions from biomass sources (ABAS et al., 1995; HAWTHORNE et al., 1988, 1989; RAMDAHL, 1983; SIMONEIT et al., 1993, 1999a,b; STANDLEY and SIMONEIT, 1987, 1994). The varying temperature conditions during burning determine the molecular alteration and transformation of the organic compounds emitted from biomass (SIMONEIT et al., 1993). The heat intensity, aeration, and duration of smoldering and flaming conditions determine the distributions and ratios of the natural versus altered compounds present in smoke (SIMONEIT et al., 1999a,b). The primary chemical reactions which occur under flaming conditions (temperature >300°C) include pyrolysis, bond cleavage, fission, and formation of tarry and volatile products. It is generally accepted that free radical reactions control the pyrolysis chemistry of most organic substances. Under smoldering conditions (temperature <300°C) organic compounds and their altered products are released by a steam stripping/volatilization effect. The extent of these processes is dependent on the moisture content of the biomass fuel. The primary chemical reactions which occur under smoldering conditions include depolymerization, water elimination, fragmentation, oxidation, char formation and steam stripping/volatilization of molecular tracers (MAZUREK and SIMONEIT,

1997; SIMONEIT et al., 1996). Thus, the directly emitted and thermally altered molecular tracers in these combustion products provide a chemical fingerprint which is source specific and useful for identifying single or multiple species contributions in samples of atmospheric particulate matter. An insight is presented here into the chemical composition of typical ambient aerosol particulate matter and of burning of arctic, temperate and tropical climate biomass fuels.

## 2 Experimental Methods

### 2.1 Sampling

Aerosol samples are typically acquired by high volume filtration with or without a particle size preseparator on quartz fiber filters. Sampling is carried out from a few hours to up to 24 hour periods and the extraction, separation and analyses procedures are the same as described below. Samples for biomass burning (twigs, branches, needles/leaves) were collected from single vegetation species in various climate zone areas of western North America, Brazil, Malaysia, and Yukon, Canada, all away from urban areas and major roads. Samples were taken from throughout the canopy of each tree species and grasses were composited from fields. After drying over a two week period the samples were burned using a controlled fire to embers under both flaming and smoldering conditions. The emitted smoke was collected on quartz fiber filters (annealed at 550°C for 3 hrs to reduce background) by high volume filtration for approximately 5 min at 1.5 m diagonally above and to the side of the flames in the smoke plume. Emissions from burning biomass are primarily fine particles (ROGGE et al., 1993a, 1998; SCHAUER et al., 1996), thus no provisions were made to remove coarse particles during sampling of these burn tests.

### 2.2 Extraction and fractionation

A schematic of the sample treatment, extraction, and separation procedure is given in Figure 1. The separation procedure follows the method first used by Simoneit and Mazurek (1982) for data comparison purposes and includes some modifications. Each filter was extracted using ultrasonic agitation for three 20-min periods using 200 ml of dichloromethane ( $\text{CH}_2\text{Cl}_2$ ). 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 by a stream of filtered nitrogen gas. The final volume was adjusted to exactly 4.0 ml by addition of  $\text{CH}_2\text{Cl}_2$ . 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.).

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

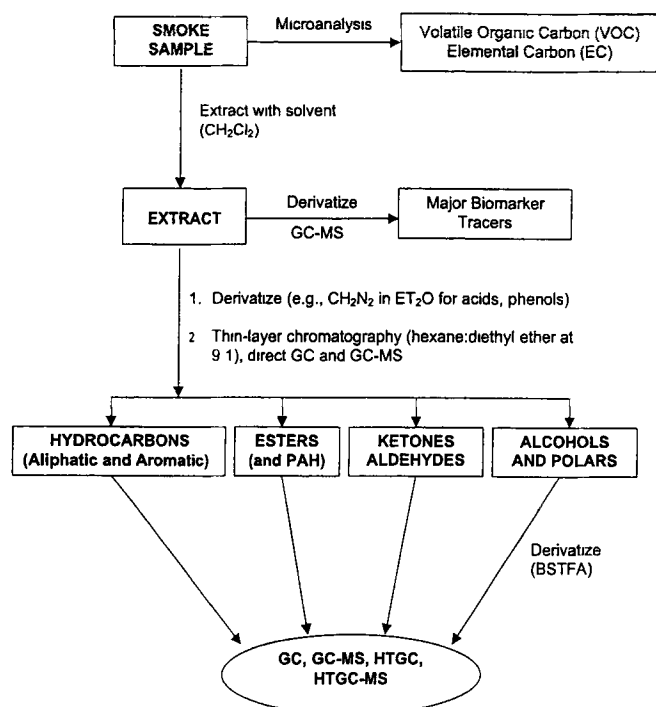


Fig. 1: Schematic of the extraction, separation and analysis procedures

ether (9:1). This procedure allows for the determination of chemical information on single molecular groups or homologous series, which may not be detected due to coelution in the total extract mixture. It also provides chemical information on molecular polarity or functional group constituents which aids in structure elucidation and identification. The four fractions removed from the TLC plates contained the following classes of compounds ( $\rightarrow$  Fig. 1): (1) *n*-alkanes, *n*-alkenes and saturated and unsaturated cyclic di- and triterpenoid hydrocarbons, (2) *n*-alkanones and polycyclic aromatic hydrocarbons, (3) *n*-alkanoic acids (as methyl esters) and saturated and unsaturated di- and triterpenoid ketones, and (4) *n*-alkanols, sterols, terpenols and polar organics. The fourth fraction was converted to trimethylsilyl derivatives prior to analysis by reaction with *N,O*-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) plus 1% trimethylchlorosilane for approximately 3 hours at 70 °C.

### 2.3 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, film thickness 0.25 mm) 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. capillary column coated with DB-5 (J&W Scientific, film thickness 0.25 mm) and operated using the same temperature program described above with helium as carrier gas.

Some samples were also analyzed by high temperature (HT) GC and high temperature GC-MS using custom-made capillary columns coated with OV-1701-OH and GC oven temperatures to 400 °C (ELIAS et al., 1998). All compound identifications are based on comparisons with authentic standards, GC retention time, literature mass spectra and interpretation of mass spectrometric fragmentation patterns.

## 3 Results and Discussion

### A. Ambient Aerosol Particles

Numerous reports have appeared where the organic composition of ambient aerosols has been described (cf. citations in the introduction). The compound composition of an urban aerosol sample will be described here as an illustrative example. Representative GC traces for the separated fractions of the total extract (lipids) for a sample from Kuala Lumpur, Malaysia (KL9/91) are shown in Figure 2.

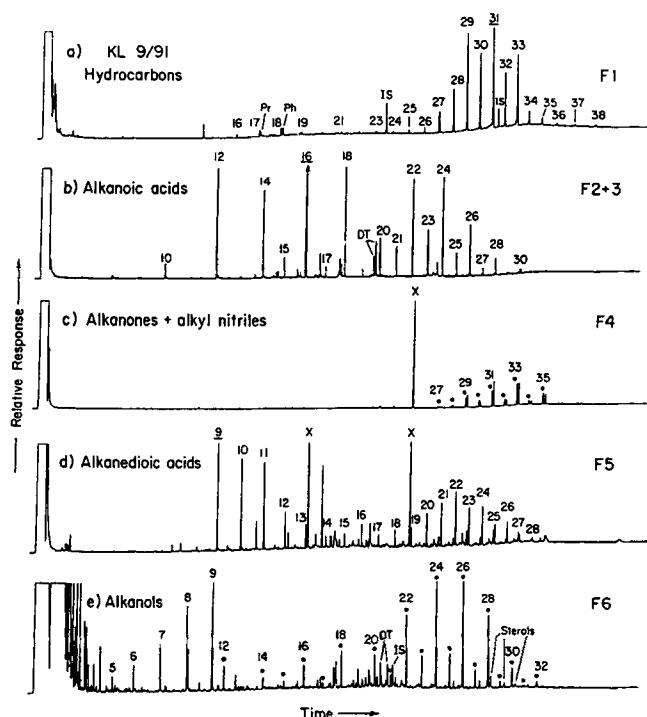


Fig. 2: Gas chromatograms of the separated fractions (F1 to F6) of the extractable organic matter from the aerosol sample KL9/91: a) hydrocarbons, b) alkanolic acids, c) alkanones and alkyl nitriles, d) alkanedioic acids, and e) alkanols (acids are analyzed as methyl esters, F6 as trimethylsilyl derivatives, numbers over peaks refer to carbon chain length, IS = internal standard *n*-C<sub>24</sub>D<sub>50</sub> and *n*-C<sub>32</sub>D<sub>66</sub>, Pr = pristane, Ph = phytane, DT = diterpenoid, n:i = monounsaturated homolog, x = phthalate ester, 5-9 in F6 are alkanedioic acids) (ABAS and SIMONEIT, 1996)

The dominant components consist of homologous series of *n*-alkanes, *n*-alkanoic acids and *n*-alkanols, and minor amounts of *n*-alkanedioic acids, *n*-alkanones, terpenoids and phthalate contaminants (ABAS and SIMONEIT, 1996).

### A.1. Homologous Compound Series

The distribution of the *n*-alkanes ranges from  $C_{16}$  to  $C_{40}$  with a  $C_{max}$  at 31 and CPI = 1.75 (MAZUREK and SIMONEIT, 1984). The unresolved complex mixture (UCM), although minor with U:R = 1.9, and the *n*-alkanes from  $C_{16}$  to  $C_{22}$  with pristane (Pr) and phytane (Ph) indicate a direct input of petroleum fuel use (SIMONEIT, 1984a). The higher molecular weight components ( $>C_{23}$ ) represent the typical petroleum components on urban atmospheric particles with a minor amount of natural plant wax alkanes superimposed (ROGGE et al., 1993a; SIMONEIT, 1984a, 1985, 1989).

The *n*-alkanoic acids are the dominant components in the extractable lipids ( $\rightarrow$  Fig. 2b) and range from  $C_{10}$  to  $C_{32}$  with a strong even carbon number predominance (CPI = 8.6) and bimodal distribution with  $C_{max}$  at 16 and minor 24. They are interpreted to be of a biogenic origin. The homologs  $< n-C_{20}$  may be derived in part from microbial sources, although these acids are ubiquitous in biota (SIMONEIT and MAZUREK, 1982). Another source is from cooking, grilling and food preparation, where these compounds are directly volatilized into the fumes (ROGGE et al., 1991). The homologs  $> n-C_{22}$  are derived primarily from vascular plant wax (SIMONEIT, 1977, 1978).

A minor series of *n*-alkan-2-ones is present in fraction 4 ( $\rightarrow$  Fig. 2c) and ranges from  $C_{25}$  to  $C_{37}$  with an odd carbon number predominance (CPI = 3.7). These compounds have been described for aerosols enriched in anthropogenic components (SIMONEIT, 1985, 1986a) and since they have essentially the same distribution and range as the wax alkanes shown in Figure 2a, indicate an origin from oxidation of vegetation wax alkanes, probably by burning (LEIF et al., 1992). A homologous series of alkyl nitriles (cyanides), ranging from  $C_{25}$  to  $C_{34}$  and  $C_{max} = 30$ , is also present in fraction 4 ( $\rightarrow$  Fig. 2c) (ABAS and SIMONEIT, 1996). This series occurs at an approximately equal concentration as the alkan-2-ones. The nitriles may form during thermal alteration (pyrolysis) by burning from alkanolic acids and ammonia via the amide intermediate (EVANS et al., 1985).

A series of  $\alpha,\omega$ -alkanedioic acids is present in fraction 5 ( $\rightarrow$  Fig. 2d), ranging from  $C_5$  to  $C_{29}$  with  $C_{max}$  at 9 and 22 and CPI = 1.2. These compounds could be oxidation products from biopolymers or other lipid components (e.g.,  $\omega$ -hydroxyalkanoic acids), or incomplete combustion products (e.g., ABAS et al., 1995). Alkanols are significant components of the extractable lipids ( $\rightarrow$  Fig. 2e) and range from  $n-C_{12}$  to  $n-C_{34}$ , with a strong even carbon number predominance (CPI = 4.9) and  $C_{max}$  at 26. The homologs  $> n-C_{20}$  are characteristic of vascular plant wax and those  $< n-C_{20}$  may be derived

from microbial sources, because they are not major constituents of plant waxes (SIMONEIT, 1977, 1986b; SIMONEIT and MAZUREK, 1982; TULLOCH, 1976).

### A.2. Biomarkers

Petroleum biomarkers are specific indicator compounds contained mainly in hydrocarbon fractions which can be utilized to define both the fossil origin and geological source of petroleum residues (SIMONEIT, 1984a, 1985). These compounds are relatively stable in ambient environments. An example of a biomarker distribution pattern is shown in Figure 3. The  $17\alpha(H),21\beta(H)$ -hopane series (I, cf. Appendix I) is present as the predominant biomarker group (steranes are present at trace levels). The hopanes range from  $C_{29}$  to  $C_{35}$  and gammacerane (II) is also detectable. The presence of hopane biomarkers in aerosols confirms an input source from fossil fuel utilization (i.e., vehicular traffic). However, it should be noted that the unusual hopane distribution pattern observed for this sample is attributable to some blow-off from the filters, i.e. compounds  $< C_{30}$  have been retained less effectively by the filter due to their volatility.

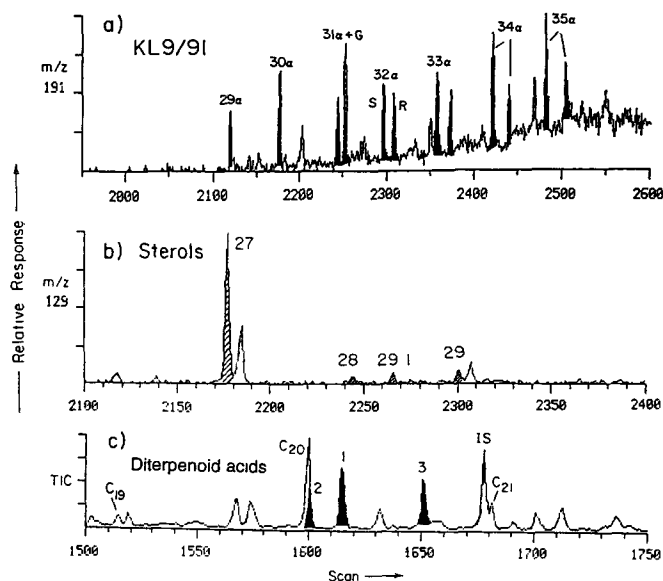


Fig. 3: Key ion fragmentograms for: (a) hopanes (petroleum biomarkers,  $m/z$  191), (b) sterols ( $m/z$  129) and (c) total ion current trace for the diterpenoid acids in fraction 6 of sample KL9/91 (in a: ia = carbon skeleton size of 17  $\alpha(H)$ -hopanes, G = gammacerane, in b: 27 = cholesterol, 28 = campesterol, 29 =  $\beta$ -sitosterol, 29:1 = stigmasterol, in c: 1 = dehydroabietic acid, 2 = 3-oxodehydroabietic acid, 3 = 7-oxodehydroabietic acid) (ABAS and SIMONEIT, 1996)

The natural product biomarkers detected are sterols, triterpenones and diterpenoid acids ( $\rightarrow$  Fig. 3). The sterols (III) consist primarily of cholesterol (R = H) and minor amounts of campesterol (R =  $CH_3$ ) and  $\beta$ -sitosterol (R =  $C_2H_5$ ). The origin of the significant amount of cholesterol is from food preparation (ROGGE et al., 1991) or also from rendering and other operations. The triterpenones consist of  $\alpha$ - and  $\beta$ -

amyrone (IV, V, respectively) which are oxidative derivatives from amyriins (e.g., VI), the natural product precursors. The precursors are dominant constituents of higher plant epicuticular wax and gums and are converted to the ketones after direct emission and/or by combustive processes (e.g., ABAS et al., 1995). The diterpenoid acids present are all based on the abietane skeleton and consist of dehydroabietic acid (X) and 3-oxo-(XI) and 7-oxodehydroabietic (XII) acids. The resin acid precursors or retene were not detectable in this sample. The presence of the diterpenoid compounds indicates an input from conifer wood combustion (SIMONEIT et al., 1993). Conifers are not common in tropical regions (ABAS et al., 1995) and thus additional imported wood may be used as fuel.

## B. Biomass Burning Smoke

The major compound groups identified in smoke particles from biomass burning are given in Table 1 and consist of natural and combustion alteration products (e.g., oxygenated, aromatized, dehydrated, decarboxylated, etc., compounds). The compound classes include the following: homologous series of *n*-alkanes, *n*-alkenes, *n*-alkanoic acids and *n*-alkanols; polycyclic aromatic hydrocarbons (PAH); methoxyphenolics from lignin; monosaccharide derivatives from cellulose; and steroid and terpenoid biomarkers. The distributions and abundances of the biomass smoke constituents are strongly dependent on combustion temperature (smoldering versus flaming conditions), aeration, and duration. Thus, the information summarized here should not be used as absolute but as relative chemical fingerprints for these sources. The molecular biomarkers are source specific and may be used as confirming tracers for transport and fate studies of smoke emissions from these biomass fuel sources.

The total extracts were analyzed to show the distributions and relative abundances of all the major organic constitu-

**Table 1: Major compound groups identified in smoke particles from biomass burning**

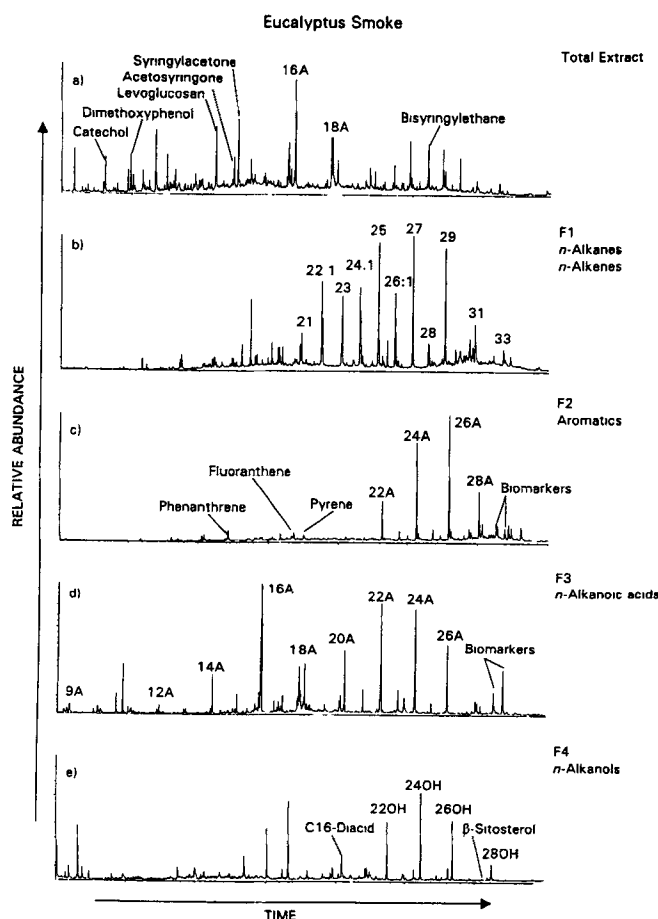
Compound Group <sup>a</sup>	Plant Source	Product
<i>n</i> -Alkanes	Epicuticular waxes	Natural
<i>n</i> -Alkenes	Epicuticular waxes/lipids	Altered
<i>n</i> -Alkanoic Acids	Internal lipid substances	Natural
<i>n</i> -Alkanols	Epicuticular waxes	Natural
Diterpenoids	Gymnosperm resin, wax	Natural/ Altered
Triterpenoids	Angiosperm wax, gum	Natural/ Altered
Monosaccharides	Cellulose biopolymer	Altered
Methoxyphenols	Lignin biopolymer	Altered
Polycyclic Aromatic Hydrocarbons	Multiple sources	Altered
Steroids	Internal lipid substances	Natural/ Altered
Wax Esters	Lipid membrane, wax	Natural
Triterpenoid Esters	Internal lipid substances	Natural

<sup>a</sup>Includes natural product precursors and/or thermally altered derivatives

ents present in each smoke sample. TLC fractions (F1 to F4) were analyzed to determine the distributions of homologous aliphatic series, PAH and biomarkers separated according to functional group and polarity properties. In order to identify a source specific chemical fingerprint for smoke emissions, the following discussion will focus on the identity and distributions of aliphatic homologous series and biomarkers from the three major vegetation types (i.e., angiosperm, gymnosperm and gramineae).

### B.1. Angiosperm

The GC-MS data of the total extract and TLC fractions from Eucalyptus (*Eucalyptus dalrympleana*) smoke are summarized in Figure 4. The primary components in the total extract are the C<sub>16</sub> and C<sub>18</sub> fatty acids, which are basic units of plant fats, oils and phospholipids. A series of methoxyphenols derived from the thermal breakdown of wood lignin are also present.



**Fig. 4:** Salient features of GC-MS total ion current traces of Eucalyptus smoke particulate matter: a) total extract showing major compounds, b) F1 fraction showing *n*-alkanes and *n*-alkenes, c) F2 fraction showing PAH and aromatic biomarkers, d) F3 fraction showing *n*-alkanoic acids, and biomarkers, and e) F4 fraction showing polar *n*-alkanols, *n*-alkanoic acids and phytosterol biomarkers (numbers refer to carbon chain length of *n*-alkanes, A = alkanolic acid, OH = alkanols, K = alkan-2-one, IS = internal standard, DHA = dehydroabietic acid, UCM = unresolved complex mixture)

These compounds are derivatives of syringyl alcohol bound in lignin and include mainly syringic acid (XIX), syringyl acetone (XX), acetosyringone and the dimer species bisyringyl. 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. Levoglucosan (XXV), the major tracer from thermal decomposition of cellulose (SIMONEIT et al., 1999a) is also a significant component.

The *n*-alkanes (F1) have an odd to even carbon number predominance (CPI = 2.6) and range from C<sub>18</sub> to C<sub>33</sub> with C<sub>max</sub> at 27 (MAZUREK and SIMONEIT, 1984). The presence of odd carbon number homologs > *n*-C<sub>24</sub> reflects a major contribution of epicuticular wax alkanes from leaf surfaces (KOLATTUKUDY, 1976; SIMONEIT, 1989). The major *n*-alkenes (F1) range from C<sub>16</sub> to C<sub>26</sub> (CPI = 0.2) with C<sub>max</sub> at 22 and are probably derived mainly from the dehydration of *n*-alkanols. A similar distribution is observed for the *n*-alkanols and an origin from reduction of *n*-alkanoic acids is less likely.

The major PAH (F2) include phenanthrene, fluoranthene and pyrene with minor contributions of C<sub>1</sub> to C<sub>3</sub> phenanthrenes/anthracenes. These compounds are common constituents of combustion emissions and are not source specific tracers (SIMONEIT, 1998). Only low concentrations of high molecular weight PAH (> m/z 228) are present.

The molecular markers included oleana-2,12-dien-18-oic and ursana-2,12-dien-18-oic acids which are the thermal degradation products of oleanolic and ursolic acids, respectively, major triterpenoids found in angiosperm gums and mucilages. β-Sitosterol (III, R = C<sub>2</sub>H<sub>5</sub>) was also identified but as the only phytosterol emitted in the smoke. Its dehydration product, stigmasta-3,5-diene (IX) is a minor biomarker component.

The *n*-alkanoic acids (F3) have a bimodal distribution with an even to odd carbon number predominance, range from C<sub>8</sub> to C<sub>26</sub>, a C<sub>max</sub> at 16 and CPI = 7.3. The *n*-alkanols (F4) show an even to odd carbon number predominance (CPI = 9.6) and range from C<sub>22</sub> to C<sub>28</sub> with C<sub>max</sub> at 24. A C<sub>16</sub> α,ω-alkanedioic acid is also present, but *n*-alkan-2-ones were not detectable. These homologous series indicate a general origin from lipid sources and are not specific for angiosperms.

## B.2. Gymnosperm

The GC-MS data of the total extract and TLC fractions from Mountain Hemlock (*Tsuga mertensiana*) smoke are given in Figure 5. The total extract contains predominant *n*-alkanoic acids ranging from C<sub>8</sub> to C<sub>28</sub> with an even to odd carbon number predominance (CPI = 4.0) and C<sub>max</sub> at 22. Phenolics from breakdown of lignin are major components and include catechol, 4-hydroxybenzoic acid and vanillic acid

(XXII). Vanillic acid, is derived from coniferyl alcohol, the primary aromatic alcohol monomer of gymnosperm lignin, and is a source specific tracer for gymnosperms (SIMONEIT et al., 1993). Levoglucosan (XXV) is the predominant component, confirming the biomass burning source (SIMONEIT et al., 1999a). The diterpenoid dehydroabietic acid (X) is present in the total extract and is the major partially altered product from resin acids, which are biosynthesized mainly by gymnosperms in temperate regions and are source specific (SIMONEIT et al., 1993).

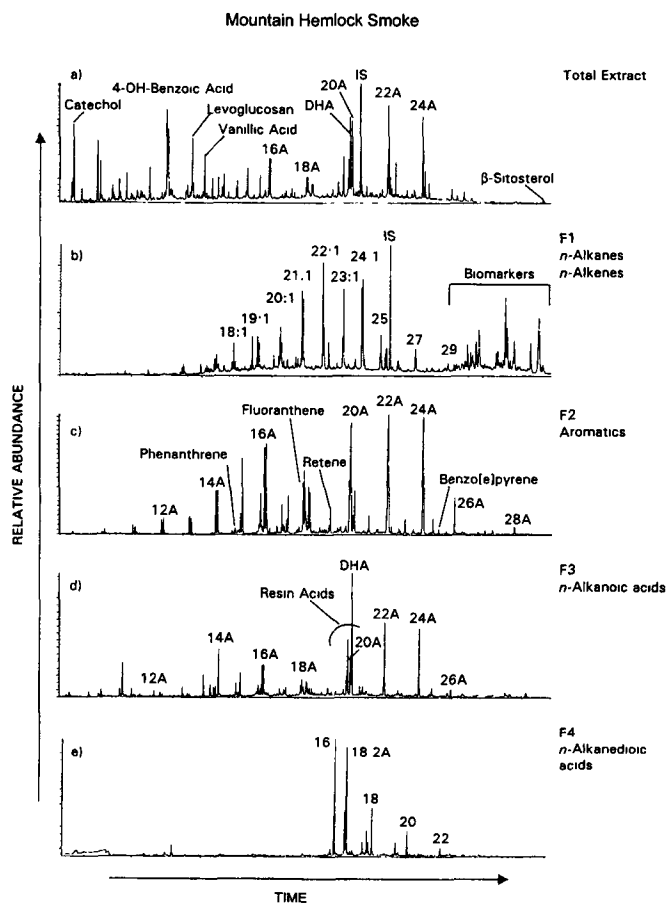


Fig. 5: Salient features of GC-MS total ion current traces of Mountain Hemlock smoke particulate matter: a) total extract showing major compounds, b) F1 fraction showing *n*-alkanes and *n*-alkenes, c) F2 fraction showing PAH and *n*-alkanoic acids, d) F3 fraction showing *n*-alkanoic acids and resin acid biomarkers, and e) F4 fraction showing *n*-alkanedioic acids (abbreviations as in Fig. 4)

The *n*-alkanes (F1) range from C<sub>16</sub> to C<sub>31</sub> with C<sub>max</sub> at 27 and CPI = 1.2, and the *n*-alkenes range from C<sub>16</sub> to C<sub>26</sub> with C<sub>max</sub> at 22 and CPI = 0.4. The *n*-alkenes are probably derived from the dehydration of *n*-alkanols. A similar *n*-alkane/*n*-alkene emission was observed for Eucalyptus and other angiosperm smoke samples, thus making these compounds non-source specific. The minor *n*-alkane components indicate that epicuticular wax *n*-alkanes are not a major component of this smoke sample.

The molecular markers (F2 and F3) identified included aromatic sterane hydrocarbons, dehydroabietal and dehydroabietic acid (X), which are all thermal degradation derivatives of the natural product precursors, the phytosterols and diterpenoid acids (i.e., abietic, pimaric, iso-pimaric, etc.). The precursor diterpenoid markers were also present as abietic (XV), pimaric (XVI), iso-pimaric (XVII), and sandaracopimaric (XVIII) acids.

The major PAH (F2) include phenanthrene, fluoranthene and pyrene with minor contributions of anthracene, C<sub>1</sub> and C<sub>2</sub> phenanthrenes/anthracenes, benzo[a]pyrene, benz[a]anthracene, chrysene, cyclopenta[c,d]pyrene and benzo[ghi]perylene. Retene (XIV) and lesser amounts of pimanthrene (XIII) and simonellite, thermal degradation products from diterpenoids, are also present. Retene has been previously proposed as a tracer for conifer combustion sources (RAMDAHL, 1983). The *n*-alkanoic acids (F3) show an even to odd carbon number predominance and range from C<sub>8</sub> to C<sub>32</sub> with C<sub>max</sub> at 22 and CPI = 4.0. Alkanoic acids are emitted in all burn experiments with biomass fuels and thus are not source specific. A series of *n*-alkan-2-ones is present and ranges from C<sub>19</sub> to C<sub>27</sub> with C<sub>max</sub> at 22. These compounds are derived from combustive oxidation of aliphatic moieties and/or alkanes (LEIF et al., 1992) and are not source specific.

### B.3. Gramineae

The GC traces of the total extract and TLC fractions from smoke of a mixed Rye grasses (*Lolium sp.*) burn are given in Figure 6. The total extract consists mainly of levoglucosan, *n*-alkanoic acids, and phenolic compounds which include catechol, dimethoxyphenol, syringyl acetone, syringic acid, guaiacylacetone, vanillic acid, vanillyl acetic acid and the dimer bisyringylethane. The grasses contain all phenolic moieties from the lignin precursor alcohols, thus the thermal breakdown products are not indicative tracers for this source, although they can be used as ratios with other compounds. The major compound in the total extract is levoglucosan (XXV) derived from cellulose (SIMONEIT et al., 1999a), a confirming tracer for biomass burning. There are lesser contributions of the C<sub>16</sub> and C<sub>18</sub> *n*-alkanoic acids, C<sub>27</sub> to C<sub>33</sub> *n*-alkanes and the C<sub>26</sub> *n*-alkanol. The biomarkers identified in total extract include the triterpenoids oleana-2,12-diene (VII), ursana-2,12-diene, and lupua-2,22-diene (VIII) and the sterols  $\beta$ -sitosterol, campesterol and stigmasterol (III). The relatively high concentration of *n*-alkanes (F1) is derived from the grass wax. They show an odd to even carbon number predominance (CPI = 11.8) and range from C<sub>23</sub> to C<sub>33</sub> with C<sub>max</sub> at 31. Alkenes are not significant components. The major PAH (F2) are phenanthrene, fluoranthene and pyrene with minor contributions of anthracene, C<sub>1</sub> and C<sub>2</sub> phenanthrenes, 11H-benzo[b]fluorene, C<sub>1</sub> pyrenes, cyclopenta[cd]pyrene, benz[a]anthracene and chrysene. The *n*-alkanoic acids (F3) have an even to odd carbon number predominance (CPI = 4.1) and range from C<sub>9</sub> to C<sub>30</sub> with C<sub>max</sub> at 16. The *n*-alkanols (F4) are even carbon numbered (CPI = 23.4) and range from C<sub>22</sub> to C<sub>30</sub> with C<sub>max</sub> at 26. A single

alkanone homolog, *n*-nonadecan-2-one, was identified as a minor component in this smoke sample. All three of these homologous series are ubiquitous in biomass burning smoke and are thus not source specific.

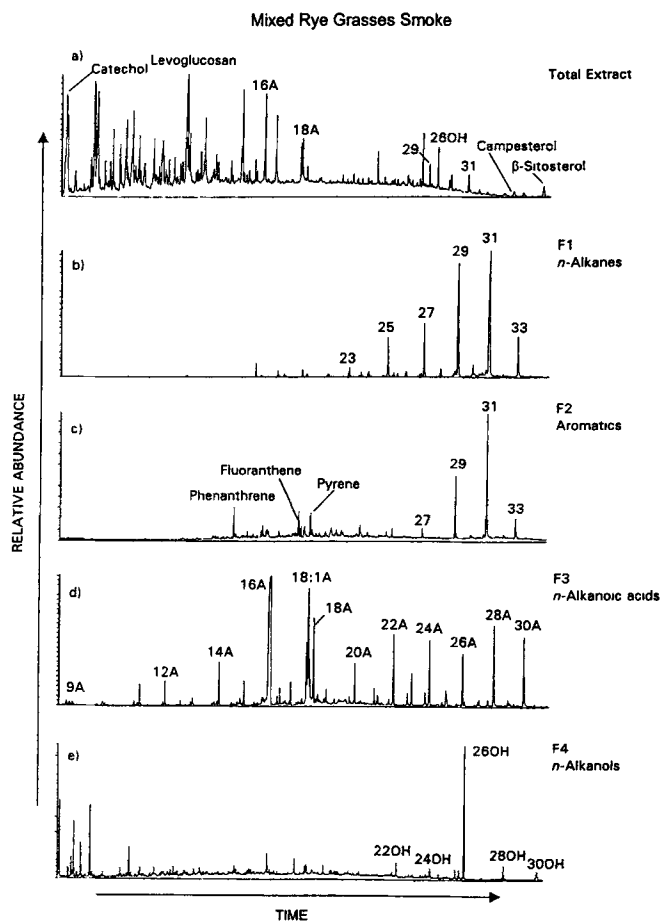


Fig. 6: Salient features of GC-MS total ion current traces of mixed Rye Grasses smoke particulate matter: a) total extract showing major compounds, b) F1 fraction showing *n*-alkanes, c) F2 fraction showing PAH, d) F3 fraction showing *n*-alkanoic acids, and e) F4 fraction showing *n*-alkanols and phytosterols (abbreviations as in Fig. 4)

### C. High Temperature GC-MS

Various total extracts and separate fractions of smoke samples were analyzed by high temperature (HT) GC and HTGC-MS (ELIAS et al., 1998). Many samples have high molecular weight components in the range of 350 to 900 dalton. A couple of examples are shown in Figure 7 to illustrate these results.

Long chain wax esters (LCWE) are present in smoke from burning of many plant species. For example, smoke aerosol from burning of Cupuaçu presented LCWE from 38 up to 58 total carbon numbers with a strong even carbon number predominance typical as reported for plant wax ( $\rightarrow$  Fig. 7a). The LCWE series is comprised of mainly palmitic acid esterified with the fatty alcohols ranging from C<sub>22</sub> to C<sub>34</sub> and minor amounts of stearic and eicosanoic acids esterified with the C<sub>32</sub>

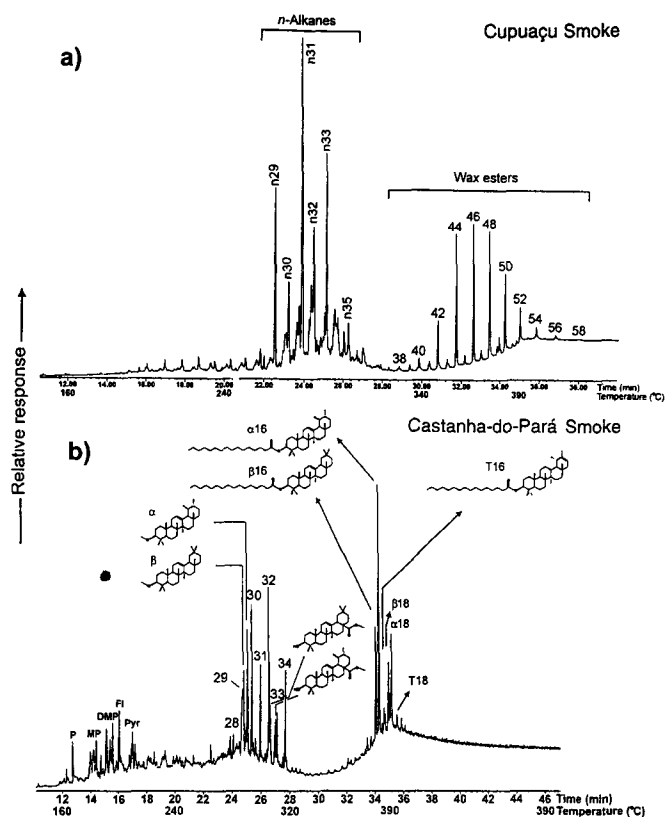


Fig. 7: Representative total ion current traces (HTGC-MS) of: (a) the fraction containing wax esters in smoke extract from burning of Cupuaçu (numbers refer to the total carbon chain length of the wax esters,  $n_i$ -normal alkane carbon chain length), and (b) the ester fraction in smoke extract from burning of Castanha-do-Pará. (Numbers refer to the carbon chain length of free fatty acids, analyzed as the methyl esters. P = phenanthrene; MP = methylphenanthrenes; DMP = dimethylphenanthrenes; F1 = fluoranthene and Pyr = pyrene. a, b and T are the esterified triterpenols:  $\alpha$ -amyrin,  $\beta$ -amyrin and taraxasterol, respectively) (ELIAS et al., 1998)

and  $C_{34}$  alcohols. Although wax esters have been described extensively in the literature, LCWE are reported as such for a few cases of higher plant waxes despite their likely widespread occurrence (KOLATTUKUDY, 1976). The reason for this is that they were simply not detected when analyzed on conventional GC columns used to analyze lipid mixtures. LCWE are reported for the first time to occur in smoke aerosols (ELIAS et al., 1998) and are found in abundances comparable to the  $n$ -alkanes in some smoke samples, indicating their magnitude in biomass burning emissions. This compound signature is further evidence for direct volatilization of very high molecular weight (HMW) compounds into smoke.

Some ester fractions separated from extracts of smoke particulate matter from burning of different species of plants contained compounds, in relatively high abundance, eluting late in the total ion current traces (TIC) of HTGC-MS analyses (e.g.,  $\rightarrow$  Fig. 7b) (ELIAS et al., 1997, 1998). The most intense peaks of these HMW components have mass spectra resembling the characteristic fragmentation pattern of pentacyclic triterpenoids with a double bond in the struc-

ture that are esterified with  $n$ -alkanoic acids, analogous as the normal wax esters described above. Essentially, the fragmentation patterns of the triterpenyl fatty acid esters (TFAE) consist of molecular ion ( $M^+$ ),  $M-CH_3$ ,  $M$ -fatty acid, and then fragments characteristic of the esterified triterpenol (ELIAS et al., 1997). The TFAE have acyl carbon chain lengths extending from 5 up to 20 carbon numbers ( $\rightarrow$  Fig. 7b) (ELIAS et al., 1997). The dominant esters are with  $\alpha$ - and  $\beta$ -amyrin and a minor amount with taraxasterol. These compounds were reported for the first time in smoke aerosol (ELIAS et al., 1997, 1998). They are novel natural products believed to be constituents of the plants which are volatilized directly into smoke during burning.

## 4 Conclusions

Organic matter of aerosol particles is derived from two major sources and is admixed depending on environmental conditions. These sources are natural biogenic detritus (e.g., plant wax, pollen, etc.) and anthropogenic emissions (e.g., soot, oils, etc.), which also includes biomass burning smoke. This was illustrated with an example of airborne particles collected on a hazy day of September, 1991 in the outskirts of Kuala Lumpur, Malaysia (ABAS and SIMONEIT, 1996). This material contained 30% organic carbon. Normal alkanolic acids were the major constituents of the identified organic compounds. Almost all the compounds quantified in sample KL9/91 are of greater magnitude than in another sample from less hazy conditions, which was interpreted to be due to local particle build-up, an increase in the production of secondary organics as a result of photochemical reactions, as well as input from air masses transported from outside the region (ABAS and SIMONEIT, 1996). A high ratio of unresolved to resolved components (U:R) of this sample (i.e., 35.6) indicated a predominant contribution from fossil fuel utilization as a source of organic matter. This was further confirmed by the low concentration of  $n$ -alkanes from plant wax.

Biomass burning introduces similar yet distinguishable compound suites into the atmosphere as from the natural background emissions. The lipid and molecular marker components of smoke from burning of representative biomass fuels (mainly the major vegetation classes, i.e., angiosperm, gymnosperm and gramineae) from arctic, temperate and tropical climate areas was presented. The major molecular groups identified in the smoke particle extract fractions include alkanes, alkenes, aldehydes, ketones, fatty acids, fatty alcohols, methoxyphenols, monosaccharide derivatives, phytosterols, diterpenoids, triterpenoids and wax esters ( $\rightarrow$  Table 1). The dominant organic components of smoke particles from burning of biomass fuel sources are monosaccharide derivatives from the breakdown of cellulose, phenolics from the breakdown of lignin, accompanied by generally lesser amounts of straight-chain, aliphatic and oxygenated compounds and terpenoids from vegetation waxes, resins/gums, and other biopolymers. The major molecular tracers identified to be specific for angiosperms, gymnosperms and gramineae are given in Table 2.



**Table 2: Major molecular tracers identified in smoke particles from biomass burning**

Compound Group	Molecular Tracers	Source
Monosaccharides	Levoglucosan	All
Methoxyphenols	Vanillin, vanillic acid	Gymnosperm
	Syringaldehyde, syringic acid	Angiosperm
	p-Hydroxybenzaldehyde, p-hydroxybenzoic acid	Gramineae
Diterpenoids	Abietic, pimaric, iso-pimaric, sandaracopimaric acids	Gymnosperm
	Dehydroabietic acid	Gymnosperm
	Pimanthrene, retene	Gymnosperm
Triterpenoids	$\alpha$ -Amyrin, $\beta$ -amyrin, lupeol	Angiosperm
	Phytosterols	$\beta$ -Sitosterol, stigmasterol
Campesterol		Gramineae

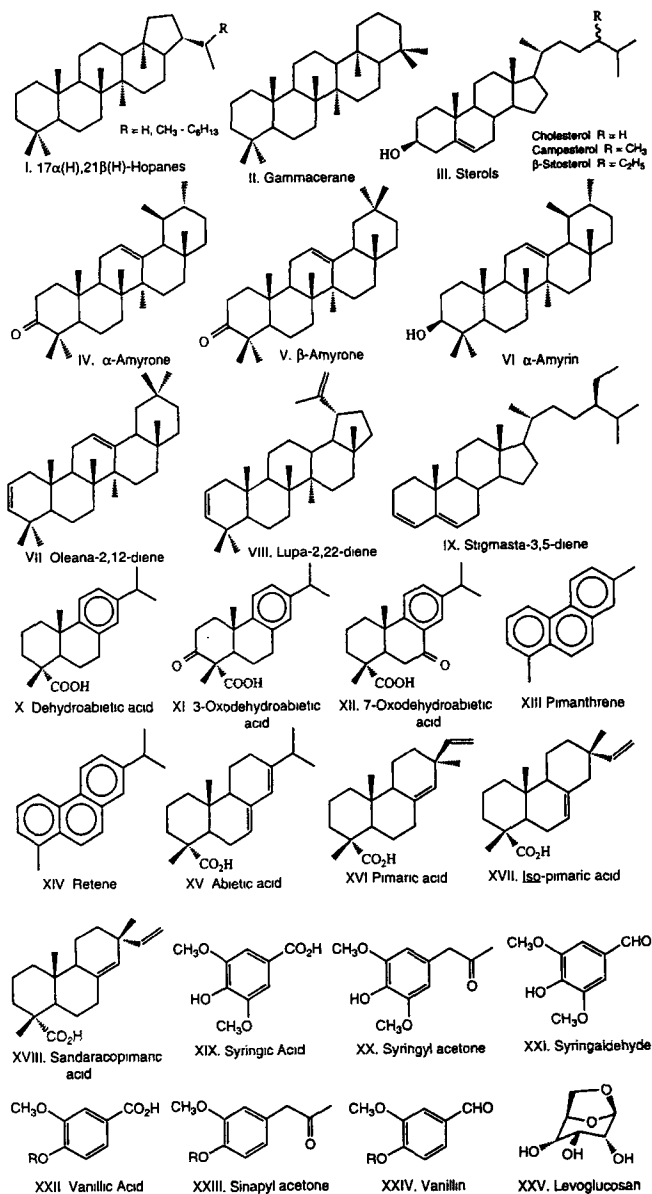
Thus, various ratios of the major molecular groups in smoke (e.g., vanillyl-, syringyl- and coumaryl-type compounds from lignin) and other biomarker tracers are useful for identifying the vegetation source that was burned. The *n*-alkanes, *n*-alk-1-enes, *n*-alkanoic acids, *n*-alkan-2-ones, *n*-alkanols, PAH, levoglucosan and phytosterols are not source specific, because they are generally found in all biomass combustion emissions (ABAS et al., 1995; SIMONEIT, 1984a, 1989). However, most of these compound series are indicative of biomass burning, which when coupled with the directly emitted and thermally altered molecular markers may be used as key tracers for assessing and tracking emissions from burning of specific biomass fuels.

### Acknowledgments

Partial funding of this work by the U.S. Environmental Protection Agency (Grant CR 823990-01-0) is gratefully acknowledged. I thank M. RADZI BIN ABAS, D.R. OROS and V.O. ELIAS for data and assistance.

### 5 References

- ABAS, M.E.; SIMONEIT, B.R.T. (1996): Composition of extractable organic matter of air particles from Malaysia: Initial study. *Atmos. Environ.* 30:2779-2793
- ABAS, M.R.; SIMONEIT, B.R.T.; ELIAS, V.; CABRAL, J.A.; CARDOSO, J.N. (1995): Composition of higher molecular weight organic matter in smoke aerosol from biomass combustion in Amazonia. *Chemosphere* 30:995-1015
- ARPINO, P.; VAN DORSELAER, A.; SEVIER, K.D.; OURISSON, G. (1972): Cires aériennes dans une forêt de pins. *C.R. Acad. Sci. (Paris)* 275D, 2837-2840
- BARBIER, M.; TUSSEAU, D.; MARTY, J.C.; SALIOT, A. (1981): Sterols in aerosols, surface microlayer and subsurface water in the North-Eastern tropical Atlantic. *Oceanol. Acta* 4, 77-84
- BRODDIN, G.; CAUTREELS, W.; VAN CAUWENBERGHE, D. (1980): On the aliphatic and polyaromatic hydrocarbon levels in urban and background aerosols from Belgium and the Netherlands. *Atmos. Environ.* 14, 895-910
- CHARLSON, R.J.; SCHWARTZ, S.E.; HALES, J.M.; CESS, R.D.; COAKLEY, Jr., J.A.; HANSEN, J.E.; HOFMANN, D.J. (1992): Climate forcing by anthropogenic aerosols. *Science* 255, 423-430
- CHEN, X.-J. (1992): Oxygenated natural products in tropospheric aerosols—sources and transport. M.S. Thesis, Oregon State University, Corvallis, 133 p
- COX, R.E.; MAZUREK, M.A.; SIMONEIT, B.R.T. (1982): Lipids in Harmattan aerosols of Nigeria. *Nature* 296, 848-849
- CRUTZEN, P.J.; ANDREA, M.O. (1990): Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles. *Science* 250, 1669-1378
- DUCE, R.A.; MOHNEN, V.A.; ZIMMERMAN, P.R.; GROSJEAN, D.; CAUTREELS, W.; CHATFIELD, R.; JAENICKE, R.; OGREN, J.A.; PELLIZZARI, E.D.; WALLACE, G.T. (1983): Organic material in the global troposphere. *Rev. Geophys. Space Phys.* 21, 921-952
- EICHMANN, R.; NEULING, P.; KETSERIDIS, G.; HAHN, J.; JAENICKE, R.; JUNGE, C. (1979): *n*-Alkane studies in the troposphere—I: Gas and

**Appendix I: Molecular structures of major biomarkers identified in aerosols and smoke**

- particulate concentrations in North Atlantic air. *Atmos. Environ.* 13, 587-599
- EICHMANN, R.; KETSERIDIS, G.; SCHEBESKE, G.; JAENICKE, R.; HAHN, J.; WARNECK, P.; JUNGE, C. (1980): n-Alkane studies in the troposphere-II: Gas and particulate concentrations in Indian Ocean air. *Atmos. Environ.* 14, 695-703
- ELIAS, V.O.; SIMONEIT, B.R.T.; PEREIRA, A.S.; CARDOSO, J.N. (1997): Mass spectra of triterpenyl alkanooates, novel natural products. *J. Mass Spectrometry* 32:1356-1361
- ELIAS, V.O.; SIMONEIT, B.R.T.; PEREIRA, A.S.; CABRAL, J.A.; CARDOSO, J.N. (1998): The detection of heavy molecular weight organic tracers in vegetation smoke samples by high temperature gas chromatography - mass spectrometry, *Environ. Sci. Technol.*, in press
- EVANS, E.J.; BATTS, B.D.; CANT, N.W.; SMITH, J.W. (1985): The origin of nitriles in shale oil. *Org. Geochem.* 8:367-374
- FRASER, M.P.; CASS, G.R.; SIMONEIT, B.R.T.; RASMUSSEN, R.A. (1997): Air quality model evaluation data for organics: 4. C<sub>2</sub> to C<sub>36</sub> non-aromatic hydrocarbons. *Environ. Sci. Technol.* 31:2356-2367
- FRASER, M.P.; CASS, G.R.; SIMONEIT, B.R.T. (1998): Measurement of gas-phase and particle-phase compounds in a roadway tunnel. *Environ. Sci. Technol.* 32:2051-2060
- GAGOSIAN, R.B.; PELTZER, E.T. (1986): The importance of atmospheric input of terrestrial organic material to deep sea sediments. In: *Advances in Organic Geochemistry 1985*, *Org. Geochem.* 10, 661-669
- GAGOSIAN, R.B.; PELTZER, E.T.; MERRILL, J.T. (1987): Long-range transport of terrestrially derived lipids in aerosols from the South Pacific. *Nature* 325, 800-803
- GAGOSIAN, R.B.; PELTZER, E.T.; ZAFIRIOU, O.C. (1981): Atmospheric transport of continentally derived lipids to the tropical North Pacific. *Nature* 291, 321-324
- GAGOSIAN, R.B.; PELTZER, E.T.; ZAFIRIOU, O.C.; ALFORD, J.B. (1982): Lipids in aerosols from the tropical North Pacific: Temporal variability. *J. Geophys. Res.* 87, 11133-11144
- HAWTHORNE, S.B.; MILLER, D.J.; BARKLEY, R.M.; KRIEGER, M.S. (1988): Identification of methoxylated phenols as candidate tracers for atmospheric wood smoke pollution. *Environ. Sci. Technol.* 22:1191-1196
- HAWTHORNE, S.B.; KRIEGER, M.S.; MILLER, D.J.; MARIASON, M.B. (1989): Collection and quantification of methoxylated phenol tracers for atmospheric pollution from residential wood stoves. *Environ. Sci. Technol.* 23:470-475
- HAWTHORNE, S.B.; MILLER, D.J.; LANGENFELD, J.J.; KRIEGER, M.S. (1992): PM-10 high volume collection and quantitation of semi- and nonvolatile phenols, methoxylated phenols, alkanes and polycyclic aromatic hydrocarbons for winter urban air and their relationship to wood smoke emissions. *Environ. Sci. Technol.* 26:2251-2262
- HEDGES, J.I.; ERTEL, J.R. (1982): Characterization of lignin by gas capillary chromatography of cupric oxide oxidation products. *Anal. Chem.* 54:174-178
- HILDEMANN, L.M.; MAZUREK, M.A.; CASS, G.R.; SIMONEIT, B.R.T. (1991): Quantitative characterization of urban sources of organic aerosol by high-resolution gas chromatography. *Environ. Sci. Technol.* 25, 1311-1325
- KOLATTUKUDY, P.E., ed. (1976). *Chemistry and Biochemistry of Natural Waxes*, Elsevier, Amsterdam, 459 pp.
- LEIF, R.N.; SIMONEIT, B.R.T.; KVENVOLDEN, K.A. (1992): Hydrous pyrolysis of n-C<sub>32</sub>H<sub>66</sub> in the presence and absence of inorganic components. *Amer. Chem. Soc., Div. Fuel Chem., 204th Nat. Meet., Preprints*, 37:1748-1753
- LEVINE, J.S. (1991): Introduction: Global biomass burning: Atmospheric, climatic, and biospheric implications. In: *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications*, J.S. LEVINE (ed.), MIT Press, Cambridge, MA, pp. xxv-xxx
- LEVINE, J.S. (1996): Introduction. In: *Biomass Burning and Global Change*, J.S. LEVINE (ed.), Vols. 1 and 2, MIT Press, Cambridge, MA, pp. xxxv-xliii
- MARTY, J.-C.; SALIOT, A. (1982): Aerosols in equatorial Atlantic air: n-alkanes as a function of particle size. *Nature* 298, 144-147
- MATSUMOTO, G.; HANYA, T. (1980): Organic constituents in atmospheric fallout in the Tokyo area. *Atmos. Environ.* 14, 1409-1419
- MAZUREK, M.A.; SIMONEIT, B.R.T. (1984): Characterization of biogenic and petroleum-derived organic matter in aerosols over remote, rural and urban areas. In: *Identification and Analysis of Organic Pollutants in Air*, ACS Symp., L.H. KEITH (ed.), Ann Arbor Science/Butterworth Publishers, Woburn, MA, pp. 353-370
- MAZUREK, M.A.; SIMONEIT, B.R.T. (1997): Higher molecular weight terpenoids as indicators of organic emissions from terrestrial vegetation. In: *Molecular Markers in Environmental Geochemistry*, R. EGANHOUSE (ed.), Amer. Chem. Soc. Symp. Ser. 671, Amer. Chem. Soc., Washington, DC, pp. 92-108
- MAZUREK, M.A.; SIMONEIT, B.R.T.; CASS, G.R. (1989): Interpretation of high-resolution gas chromatography and high resolution gas chromatography/mass spectrometry data acquired from atmospheric organic aerosol samples. In: *Proc. 3rd Int. Conf. Carbonaceous Particles in the Atmosphere*, *Aerosol Sci. Tech.* 10, 408-420
- RAMDAHL, T. (1983): Retene - A molecular marker of wood combustion in ambient air. *Nature* 306:580-582
- ROGGE, W.F.; HILDEMANN, L.M.; MAZUREK, M.A.; CASS, G.R.; SIMONEIT, B.R.T. (1991): Sources of fine organic aerosol: 1 - Charbroilers and meat cooking operations. *Environ. Sci. Technol.* 25, 1112-1125
- ROGGE, W.F.; MAZUREK, M.A.; HILDEMANN, L.M.; CASS, G.R.; SIMONEIT, B.R.T. (1993a): Quantification of organic aerosols on a molecular level: Identification, abundance and seasonal variation. *Proc. Fourth Int. Conf. on Carbonaceous Particles in the Atmosphere*. *Atmos. Environ.* 27A, 1309-1330
- ROGGE, W.F.; HILDEMANN, L.M.; MAZUREK, M.A.; CASS, G.R.; SIMONEIT, B.R.T. (1993b): Sources of fine organic aerosol: 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. *Environ. Sci. Technol.* 27, 636-651
- ROGGE, W.F.; HILDEMANN, L.M.; MAZUREK, M.A.; CASS, G.R.; SIMONEIT, B.R.T. (1993c): Sources of fine organic aerosol: 3. Road dust, tire debris, and organometallic brake lining dust: roads as sources and sinks. *Environ. Sci. Technol.* 27, 1892-1904
- ROGGE, W.F.; HILDEMANN, L.M.; MAZUREK, M.A.; CASS, G.R.; SIMONEIT, B.R.T. (1993d): Sources of fine organic aerosol: 4. Particulate abrasion products from leaf surfaces of urban plants. *Environ. Sci. Technol.* 27, 2700-2711
- ROGGE, W.F.; HILDEMANN, L.M.; MAZUREK, M.A.; CASS, G.R.; SIMONEIT, B.R.T. (1993e): Sources of fine organic aerosol: 5. Natural gas home appliances. *Environ. Sci. Technol.* 27, 2736-2744
- ROGGE, W.F.; HILDEMANN, L.M.; MAZUREK, M.A.; CASS, G.R.; SIMONEIT, B.R.T. (1994): Sources of fine organic aerosol: 6. Cigarette smoke in the urban atmosphere. *Environ. Sci. Technol.* 28, 1375-1388
- ROGGE, W.F.; HILDEMANN, L.M.; MAZUREK, M.A.; CASS, G.R.; SIMONEIT, B.R.T. (1997a): Sources of fine organic aerosol: 7. Hot asphalt roofing tar pot fumes. *Environ. Sci. Technol.* 31:2726-2730
- ROGGE, W.F.; HILDEMANN, L.M.; MAZUREK, M.A.; CASS, G.R.; SIMONEIT, B.R.T. (1997b): Source of fine organic aerosol: 8. Boilers burning No. 2 distillate fuel oil. *Environ. Sci. Technol.* 31:2731-2737
- ROGGE, W.F.; HILDEMANN, L.M.; MAZUREK, M.A.; CASS, G.R.; SIMONEIT, B.R.T. (1998): Sources of fine organic aerosol: 9. Pine, oak, and synthetic log combustion in residential fireplaces. *Environ. Sci. Technol.* 32:13-22

- SCHAUER, J.J.; ROGGE, W.F.; HILDEMAN, L.M.; MAZUREK, M.A.; CASS, G.R.; SIMONEIT, B.R.T. (1996): Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmos. Environ.* 30:3837-3855
- SCHNEIDER, J.K.; GAGOSIAN, R.B.; COCHRAN, J.K.; TRULL, T.W. (1983): Particle size distributions of n-alkanes and  $^{210}\text{Pb}$  in aerosols off the coast of Peru. *Nature* 304, 429-432
- SEINFELD, J.H. (1986): *Atmospheric Chemistry and Physics of Air Pollution*, J. Wiley & Sons, New York, pp. 286-302
- SICRE, M.A.; MARTY, J.C.; SALIOT, A.; APARICIO, X.; GRIMALT, J.; ALBAIGES, J. (1987): Aliphatic and aromatic hydrocarbons in different sized aerosols over the Mediterranean Sea: Occurrence and origin. *Atmos. Environ.* 21, 2247-2259
- SIMONEIT, B.R.T. (1977): Organic matter in eolian dusts over the Atlantic Ocean, Proceedings of Symposium on Concepts in Marine Organic Chemistry. *Mar. Chem.* 5, 443-464
- SIMONEIT, B.R.T. (1978): The organic chemistry of marine sediments. In: *Chemical Oceanography*, 2nd Edition, J.P. RILEY and R. CHESTER (eds.), Academic Press, New York, Vol. 7, Chap. 39, pp. 233-311
- SIMONEIT, B.R.T. (1979): Biogenic lipids in eolian particulates collected over the ocean. In: *Proceedings Carbonaceous Particles in the Atmosphere*, T. NOVAKOV (ed.), NSF-LBL, pp. 233-244
- SIMONEIT, B.R.T. (1980): Eolian particulates from oceanic and rural areas – Their lipids, fulvic and humic acids and residual carbon. In: *Advances in Organic Geochemistry 1979*, A.G. DOUGLAS and J.R. MAXWELL (eds.), Pergamon Press, Oxford, pp. 343-352
- SIMONEIT, B.R.T. (1984a): Organic matter of the troposphere: III – Characterization and sources of petroleum and pyrogenic residues in aerosols over the Western United States. *Atmos. Environ.* 18, 51-67
- SIMONEIT, B.R.T. (1984b): Application of molecular marker analysis to reconcile sources of carbonaceous particulates in tropospheric aerosols. *Sci. Total Environ.* 36, 61-72
- SIMONEIT, B.R.T. (1985): Application of molecular marker analysis to vehicular exhaust for source reconciliations. *Int. J. Environ. Anal. Chem.* 22, 203-233
- SIMONEIT, B.R.T. (1986a): Characterization of organic constituents in aerosols in relation to their origin and transport: A review. *Int. J. Environ. Anal. Chem.* 23, 207-237
- SIMONEIT, B.R.T. (1986b): Cyclic terpenoids of the geosphere. In: *Biological Markers in the Sedimentary Record, Methods in Geochemistry and Geophysics*, Vol. 24, R.B. Johns, ed., Elsevier Science Publishers, Amsterdam, pp. 43-99
- SIMONEIT, B.R.T. (1989): Organic matter of the troposphere-V: Application of molecular marker analysis to biogenic emissions into the troposphere for source reconciliations. *J. Atmos. Chem.* 8, 251-275
- SIMONEIT, B.R.T. (1998): Biomarker PAHs in the environment. In: *The Handbook of Environmental Chemistry A.H. NIELSON (ed.)*, Vol. 3. Part 1, PAHs and Related Compounds, Springer-Verlag, Berlin, pp. 176-221
- SIMONEIT, B.R.T.; MAZUREK, M.A. (1982): Organic matter of the troposphere – II. Natural background of biogenic lipid matter in aerosols over the rural western United States. *Atmos. Environ.* 16, 2139-2159
- SIMONEIT, B.R.T.; MAZUREK, M.A. (1989): Organic tracers in ambient aerosols and rain. In: *Proc. 3rd Int. Conf. Carbonaceous Particles in the Atmosphere*. *Aerosol Sci. Technol.* 10, 267-291
- SIMONEIT, B.R.T.; CHESTER, R.; EGLINTON, G. (1977): Biogenic lipids in particulates from the lower atmosphere over the eastern Atlantic. *Nature* 267, 682-685
- SIMONEIT, B.R.T.; MAZUREK, M.A.; CAHILL, T.A. (1980): Contamination of the Lake Tahoe air basin by high molecular weight petroleum residues. *J. Air Poll. Contr. Assoc.* 30, 387-390
- SIMONEIT, B.R.T.; MAZUREK, M.A.; REED, W.E. (1983): Characterization of organic matter in aerosols over rural sites: Phytosterols. In: *Advances in Organic Geochemistry 1981*, M. BJOROY et al. (eds.), J. Wiley and Sons Ltd., Chichester, pp. 355-361
- SIMONEIT, B.R.T.; COX, R.E.; STANDLEY, L.J. (1988): Organic matter of the troposphere-IV: Lipids in Harmattan aerosol particles of Nigeria. *Atmos. Environ.* 22, 983-1004
- SIMONEIT, B.R.T.; CARDOSO, J.N.; ROBINSON, N. (1990): An assessment of the origin and composition of higher molecular weight organic matter in aerosols over Amazonia. *Chemosphere* 21, 1285-1301
- SIMONEIT, B.R.T.; CARDOSO, J.N.; ROBINSON, N. (1991a): An assessment of terrestrial higher molecular weight lipid compounds in air particulate matter over the South Atlantic from about 30-70°S. *Chemosphere* 23, 447-465
- SIMONEIT, B.R.T.; SHENG, G.; CHEN, X.; FU, J.; ZHANG, J.; XU, Y. (1991b): Molecular marker study of extractable organic matter in aerosols from urban areas of China. *Atmos. Environ.* 25A, 2111-2129
- SIMONEIT, B.R.T.; CRISP, P.T.; MAZUREK, M.A.; STANDLEY, L.J. (1991c): Composition of extractable organic matter of aerosols from the Blue Mountains and southeast coast of Australia. *Environ. Internat.* 17, 405-419
- SIMONEIT, B.R.T.; ROGGE, W.F.; MAZUREK, M.A.; STANDLEY, L.J.; HILDEMAN, L.M.; CASS, G.R. (1993): Lignin pyrolysis products, lignans and resin acids as specific tracers of plant classes in emissions from biomass combustion. *Environ. Sci. Technol.* 27, 2533-2541
- SIMONEIT, B.R.T.; RADZI BIN ABAS, M.; CASS, G.R.; ROGGE, W.F.; MAZUREK, M.A.; STANDLEY, L.J.; HILDEMAN, L.M. (1996): Natural compounds as tracers for biomass combustion in aerosols. In: *Biomass Burning and Global Change*, J.S. LEVINE (ed.), Vol. 1, MIT Press, Cambridge, MA, pp. 504-518
- SIMONEIT, B.R.T.; SCHAUER, J.J.; NOLTE, C.G.; OROS, D.R.; ELIAS, V.O.; FRASER, M.P.; ROGGE, W.F.; CASS, G.R. (1999a): Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. *Atmos. Environ.*, 33, 173-182
- SIMONEIT, B.R.T.; ROGGE, W.F.; LANG, Q.; JAFFÉ, R. (1999b): Molecular characterization of smoke from campfire burning of pine wood (*Pinus elliottii*). *Chemosphere*, submitted
- STANDLEY, L.J. (1987): Determination of molecular signatures of natural and thermogenic products in tropospheric aerosols – input and transport. Ph.D. thesis, Oregon State University, Corvallis, 200 pp
- STANDLEY, L.J.; SIMONEIT, B.R.T. (1987): Composition of extractable organic matter in smoke particles from prescribed burns. *Environ. Sci. Technol.* 21, pp. 163-169
- STANDLEY, L.J.; SIMONEIT, B.R.T. (1994): Resin diterpenoids as tracers for biomass combustion aerosols. *J. Atmos. Chem.* 18, 1-15
- TULLOCH, A.P. (1976): Chemistry of waxes of higher plants. In: *Chemistry and Biochemistry of Natural Waxes*, P.E. KOLATTUKUDY (ed.), Elsevier, Amsterdam, pp. 235-287
- Zheng, M.; Wan, T.S.M.; Fang, M.; Wang, F. (1997): Characterization of the non-volatile organic compounds in the aerosols of Hong Kong – Identification, abundance and origin. *Atmos. Environ.* 31, 227-237

Received: October 10th, 1998  
Accepted: November 30th, 1998