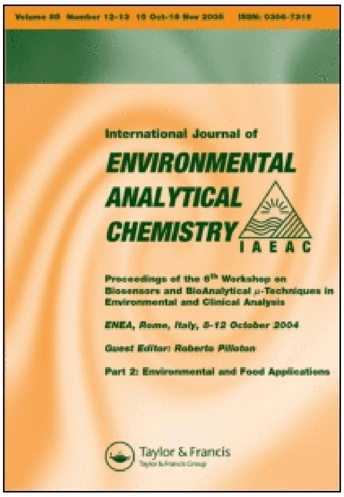

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Simoneit, Bernd R. T.(1986) 'Characterization of Organic Constituents in Aerosols in Relation to Their rigin and Transport: A Review', International Journal of Environmental Analytical Chemistry, 23: 3, 207 — 237
To link to this Article: DOI: 10.1080/03067318608076446
URL: http://dx.doi.org/10.1080/03067318608076446

Intern. J. Environ. Anal. Chem., 1986, Vol. 23, pp. 207–237
0306-7319/86/2303-0207 $18.50/0

Printed in Great Britain

Characterization of Organic Constituents in Aerosols in Relation to Their Origin and Transport: A Review†

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(*Received May 10, 1985; in final form July 6, 1985*)

Organic matter in aerosols is derived from two major sources and is admixed depending on the geographic area. These sources are biogenic detritus (e.g. plant wax, microbes, etc.) and anthropogenic emissions (e.g. oils, soot, etc.). Both biogenic detritus and some of the anthropogenic emissions contain organic materials (C_{14}–C_{40+}) extractable by solvent, which have unique and distinguishable compound distribution patterns. Molecular composition analysis has been applied to such extracts after suitable chemical separation into subfractions (i.e. hydrocarbons, ketones, fatty acids, fatty alcohols, and wax esters). Microbial and vascular plant lipids are the dominant biogenic residues and petroleum hydrocarbons, with lesser amounts of the pyrogenic polynuclear aromatic hydrocarbons (PAH), are the major anthropogenic residues.

These lipid fractions are quantified and characterized in terms of their contents of both homologous compound series and specific molecular markers. Samples from rural sites contain predominantly vascular plant wax (as hydrocarbons, fatty acids and fatty alcohols) and lesser amounts of higher plant resin residues. Urban samples and, to varying degrees, some rural samples contain primarily higher weight residues of petroleum products. Molecular marker compounds from flora (e.g. phytosterols, terpenes, wax esters) are also present. Petroleum residues are comprised of hydrocarbons and are found mainly in urbanized areas, with PAH from combustion at varying

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†Presented at the 2nd Workshop on Chemistry Analysis of Hydrocarbons in the Environment, Barcelona, November 19–20, 1985.

concentrations. Oceanic aerosols contain traces of lipids derived primarily from terrestrial plant waxes and fatty acids (C_{13}–C_{18}) from mainly marine sources.

The sources of the lipid compound classes in aerosols have been reconciled by the application of the same analytical techniques to composited vegetation samples and emissions from vehicles (both gasoline and diesel) and from fires. This detailed approach to the molecular composition of organic aerosols indicates that primary biogenic residues are significant components of the troposphere over continental locations in the Northern Hemisphere and over oceanic areas. These organic materials are important constituents in the global cycling and flux of organic carbon. The comprehensive molecular analysis of all aerosol lipid fractions permits the definition of specific geographic source areas of air parcels and the interaction and admixing of anthropogenic versus natural components.

KEY WORDS: Aerosols, hydrocarbons, ketones, fatty acids, fatty alcohols, wax esters, phytosterols, terpenes, petroleum products, PAH, biogenic and anthropogenic sources.

INTRODUCTION

Organic matter of aerosols in the lower troposphere over urban, rural, remote and oceanic areas is derived from natural biogenic, from geological (fossil fuel) and from synthetic (anthropogenic) sources and is admixed in varying proportions dependent on region.[1–13] The solvent-soluble organic matter is a major fraction of the total aerosol burden in all areas studied. For example, the material balance for the fine aerosol ($d_p < 2.1\,\mu$m) composition in the downtown Los Angeles area shows 26.7% organic matter plus about 15% elemental carbon (Figure 1).[14] It is this organic matter fraction that can be further characterized and thus apportioned to sources. Higher molecular-weight, solvent-soluble compounds ($>C_{12}$, termed lipids) have been analyzed extensively for such geographic areas, in some cases with assignment of general sources.[2,5–10,12,13,15–32]

Rural, remote and oceanic aerosols carry primarily vascular plant waxes and in some cases resin detritus from coniferous vegetation or lipid residues from algae.[2,6,7,17,19,20,22,26,30,33] Petroleum residues are a major and usually predominant component of the lipids extractable from aerosols in urban and in some rural air basins.[5,9,10,13,15,28,34]

Here I will review how molecular signatures can be defined for lipids from specific source emissions or in ambient aerosols and how

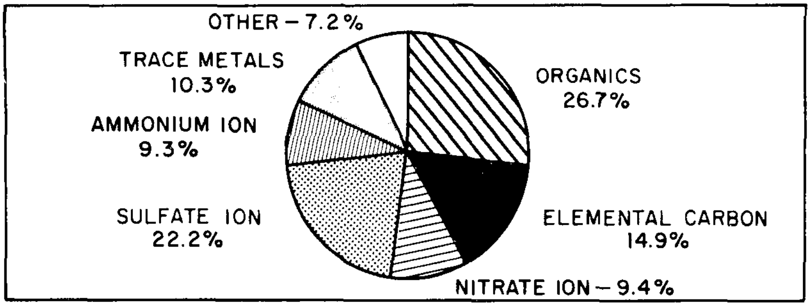

FIGURE 1 Material balance on the fine aerosol ($d_p < 2.1\,\mu m$) composition observed at downtown Los Angeles—1982 annual mean. Total fine aerosol mass averaged $32.7\,\mu g\,m^{-3}$ (from Reference 14, reproduced with permission).

these data can be utilized for potentially tracing air parcels during transit over extended geographic areas. In addition, the utility of characterizing the macromolecular and/or elemental carbon fraction will also be summarized. Data on the organic composition of aerosols will hopefully serve to stimulate further research to define and elucidate the spatial variations and geographic sources of organic aerosol burdens in urban versus remote areas.

EXPERIMENTAL METHODS

Samples

Aerosol samples were acquired from rural and urban sites by filtration of the ambient air using a standard high volume air sampler fitted with quartz fiber filters ($20 \times 25\,cm^2$ surface).[9,13] The quartz filters were annealed for three hours at 560°C prior to sampling in order to pyrolyze and thus remove any adsorbed organic material. After the sampling was completed (usually 12 or 24 hours), the collection filter was stored in a precleaned one-liter jar to which approximately 5 ml of methylene chloride (CH_2Cl_2) was added to inhibit growth of microbes.[9,13] Samples were stored in this manner until laboratory workup was initiated. Similar methodology has been developed for sampling and analysis of oceanic aerosols and in addition cascade impacter samplers have also been utilized there.[2,22]

The sampling times were chosen to be representative of the seasonal meteorologic conditions of the particular region. Sampling in the Lake Tahoe, Mt. Lassen and Oregon areas was carried out on days with good visibility and after prior precipitation had occurred at least three days earlier.[9] The wind conditions for the Corvallis, Oregon samples were from the west off the Pacific Ocean over about 80 km of forest, to represent "cleanest" conditions. All Nigerian samples were acquired during Harmattan episodes.[17] Samples from urban Los Angeles were taken during obviously stagnant smog episodes and during a Santa Ana condition where the dry desert winds blow from the east.[9]

Representative samples of vegetation were taken in various areas to provide a composite for *in situ* wax analysis. This plant material was extracted directly by repeated dipping into CH_2Cl_2 and the lipid concentrate was then treated in the same manner as filter extracts for separation and analysis.[13,29] Various point source emissions (e.g. vehicular exhaust and smoke samples) were also acquired by filtration with standard high-volume air samplers.[9,19,34] These filters were extracted and treated as in the case of aerosol samples.

Lipid isolation and analysis

The detailed procedures for lipid isolation and analysis have been published[9,10,12,13,29,34] and are described briefly here. Filter samples were extracted directly in the glass storage jars with CH_2Cl_2 using ultrasonic agitation. The extracts for each sample were concentrated on a rotary evaporator, treated with BF_3 in methanol to esterify free acids and then subjected to silica gel thin-layer chromatography (TLC) using a hexane:diethyl ether (9:1) eluent mixture. After development with iodine vapor, the bands corresponding to hydrocarbons, esters with ketones and alcohols were scraped from the TLC plate and eluted with CH_2Cl_2 or ethyl acetate. These fractions (alcohols derivatized as trimethyl silyl ethers) were subjected to gas chromatographic (GC) and gas chromatography-mass spectrometric (GC-MS) analyses.

Diesel fuel and lubricating oil were analyzed directly as diluted solutions in hexane or also as separated fractions by GC and GC-

MS. Solvent blanks were concentrated to total volumes of 20 μl, then analyzed by GC in order to monitor the background and periodically procedural blanks were carried through the experimental procedure.

The GC analyses were conducted with either a 25 m × 0.25 mm i.d. glass capillary column wall-coated with OV-101 or a 25 m × 0.20 mm i.d. flexible fused silica capillary column coated with SP-2100 (Hewlett-Packard GC). The GC-MS analyses were conducted on a Finnigan Model 4000 quadrupole mass spectrometer interfaced directly with a Finnigan Model 9610 gas chromatograph and equipped with the same capillary columns. The typical GC and GC-MS operating conditions were as follows: Temperature program 35–280°C at 4°C per minute, held isothermal at 280°C for 60–120 minutes and using He as a carrier gas. Mass spectrometric data were acquired and processed using a Finnigan-Incos Model 2300 data system. Molecular markers were identified by GC and GC-MS comparison with authentic standards and characterized mixtures.

Humic substances and residual carbon

Humic substances and residual carbon were isolated by NaOH treatment, followed by HF demineralization and filter dissolution according to the methods described.[8,35] Carbon, hydrogen and ash contents were determined by microanalysis. Stable carbon isotope analyses were carried out by the method of Kaplan *et al.*[36] and the results are given in the "δ" notation versus Chicago PDB standard.

RESULTS AND DISCUSSION

Analytical results are summarized in Table I for the lipid fractions and detrital carbon in aerosols from urban versus rural/remote areas and in various contributing sources of organic emissions. The locations of the major sampling areas discussed here for Central Africa are shown in Figure 2 and those for the Western United States appear in Figure 3.

The extractable lipid material consists primarily of hydrocarbons, fatty acids and fatty alcohols, minor amounts of ketones, and other molecular markers. The highest yields are observed for urban

TABLE I

Summary of analytical results for aerosol and source organic matter

General Location	Hydrocarbons				Fatty Acids			Fatty Alcohols			Detrital Carbon		Data References
	Yield (ng m^{-3})	CPI (for *n*)^a	C_{max} (for *n*)^b	U:R^c	Yield (ng m^{-3})	CPI^a	C_{max}^{b}	Yield (ng m^{-3})	CPI^a	C_{max}^{b}	Yield (ng m^{-3})	Atomic H/C	
Western United States													
Rural	1–390	1.6–8.4	27, 29	0.2–4	90–300	5.0–12	*16*, 22, 24	200–1390	5.0–9.4	16, 28, 22, 24, *26*, 28	1000–2200	0.8–1.03	12, 13
Urban	180–360	1.8–2.8	29	0.9–25	220–310	8.0–23	16, 22, 24, 28	1360–2020	6.0–12.1	12, 16, 18 *26*, 28	1400–3300 (1000–20,000)	0.6–0.8	12, 13 (14, 47)
Central Africa (Nigeria)													
Rural	110–1700	3.0–7.8	*29*, 31	1.4–4	80–960	4.4–10	*16*, 24, 30	230–2200	4.2–10.8	16, 18, 26, 28, *30*	(400–1000 μg m^{-3} total particulates)	—	17
Urban	820–2600	1.7–3.3	*29*, 31	3.9–7.7	630–960	7.4–10.2	*16*, 24, 30	460–3000	6.2–9	16, 18, 26, 28, *30*		—	17
Oceanic Aerosols													
Atlantic	10^{-3}–13	1.2–10	27, *29* 31	<0.1	10^{-3}–230	4–26	*16*, 24, 26	10^{-2}–10	4.0	16, 18, *28*	70–920	0.8–1.2	6, 7, 22, 33
Pacific	0.02–0.5	2–4	27, *29* 31, 33	<0.1	0.1–0.4	3–6	*16*, 24, 26	0.05–0.5	5–10	26, 28, *30*	n.c.	—	2, 20, 25

Vascular Plants													
Wax	100–1000 $\mu g\,g^{-1}$	6–30	27, *29* 31, 33	<0.1	200–400 $\mu g\,g^{-1}$	7–20	*16*, 24, 28, 30	300–2000 $\mu g\,g^{-1}$	15–20	16, 18, 24, *28*, 30	n.d.	—	12, 13
Smoke													
Natural fires	1,500,000	10	*29*, 31	<0.1	250,000	15	*16*, 24	n.d.	—	—	n.c.	—	34
Slash burns	200–1100	1.2–5	23, 25	0.3–3	50–2600	5–8	*22*, 24	n.d.	—	—	n.c.	—	34
Vehicular Exhaust													
Auto (no catalytic converter)	20,000	0.93	22	50	50,000	3.7	*12*, 16	tr.	n.c.	n.c.	n.c.	—	9, 10, 34
Diesel	300,000	1.02	21	4	1,070,000	1.8	16	tr.	n.c.	n.c.	n.c.	0.3–0.5	9, 10, 34
Petroleum Products													
Total crude	n.a.	1.01	10	2–→100	tr.	1.0	—	n.d.	—	—	n.d. (varying amounts of asphalt)		9, 10, 34
Diesel fuel	n.a.	0.96	19	2.4	n.d.	—	—	n.d.	—	—	n.d.	—	9, 10, 34
Lubricating oil	n.a.	1.01	19	15	tr.	25	*16*, 22	n.d.	—	—	n.d.	—	9, 10, 34

n.a.—not applicable; n.d.—not detectable; n.c.—not characterized; tr.—trace.

[a] Carbon Preference Index, summed from C_{10} to C_{35}, odd-to-even for *n*-alkanes, even-to-odd for *n*-fatty acids and *n*-fatty alcohols.[5]

[b] The predominant homolog is italicized.

[c] Ratio of unresolved to resolved hydrocarbons, a measure of the contribution from petroleum residues.[5]

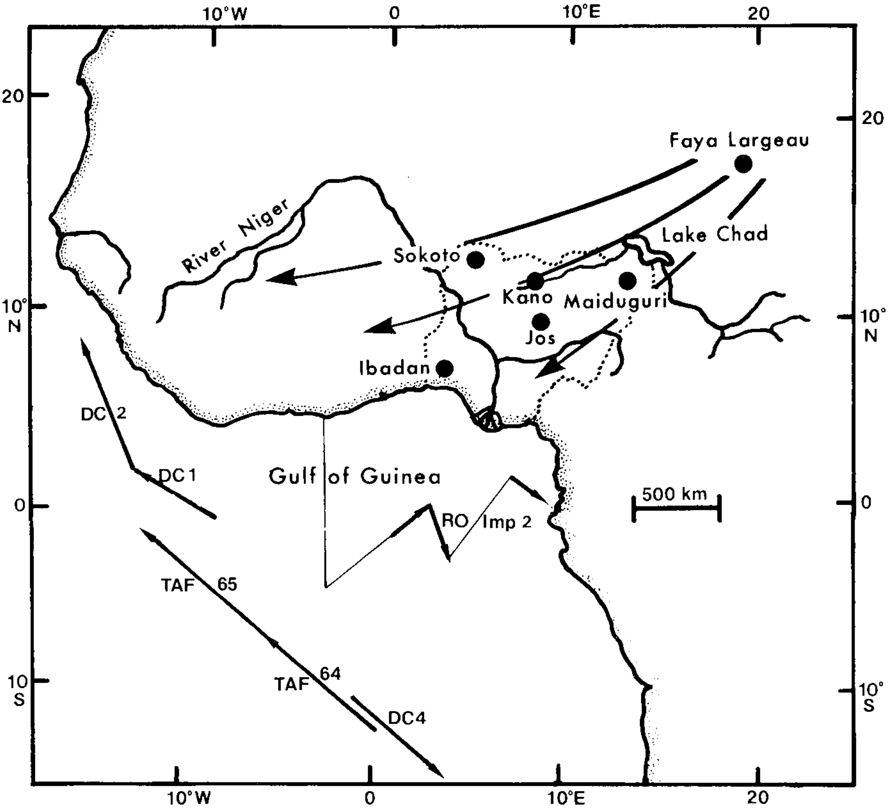

FIGURE 2 Location map of the sampling sites, Harmattan wind (arrows) and cruise tracks[6, 33] in West Africa.

samples and range to extremely low levels over oceanic areas. Hydrocarbons are comprised of *n*-alkanes and a complex mixture of branched and cyclic hydrocarbons (hump or unresolved complex mixture) in urban areas and in remote regions the lipids are dominated by natural products (e.g. wax alkanes, fatty acids, fatty alcohols, etc. all with high carbon preference index [CPI†]

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†Carbon Preference Index: For hydrocarbons it is expressed as a summation of the odd carbon number homologs over a range divided by a summation of the even carbon number homologs over the same range (splitting the alkane CPI range can distinguish bacterial, algal matter—C_{10}–C_{25} and higher plant wax—C_{26}–C_{35}[5]); for fatty acids and alcohols it is the same ratio only inverted to have even-to-odd homologs.

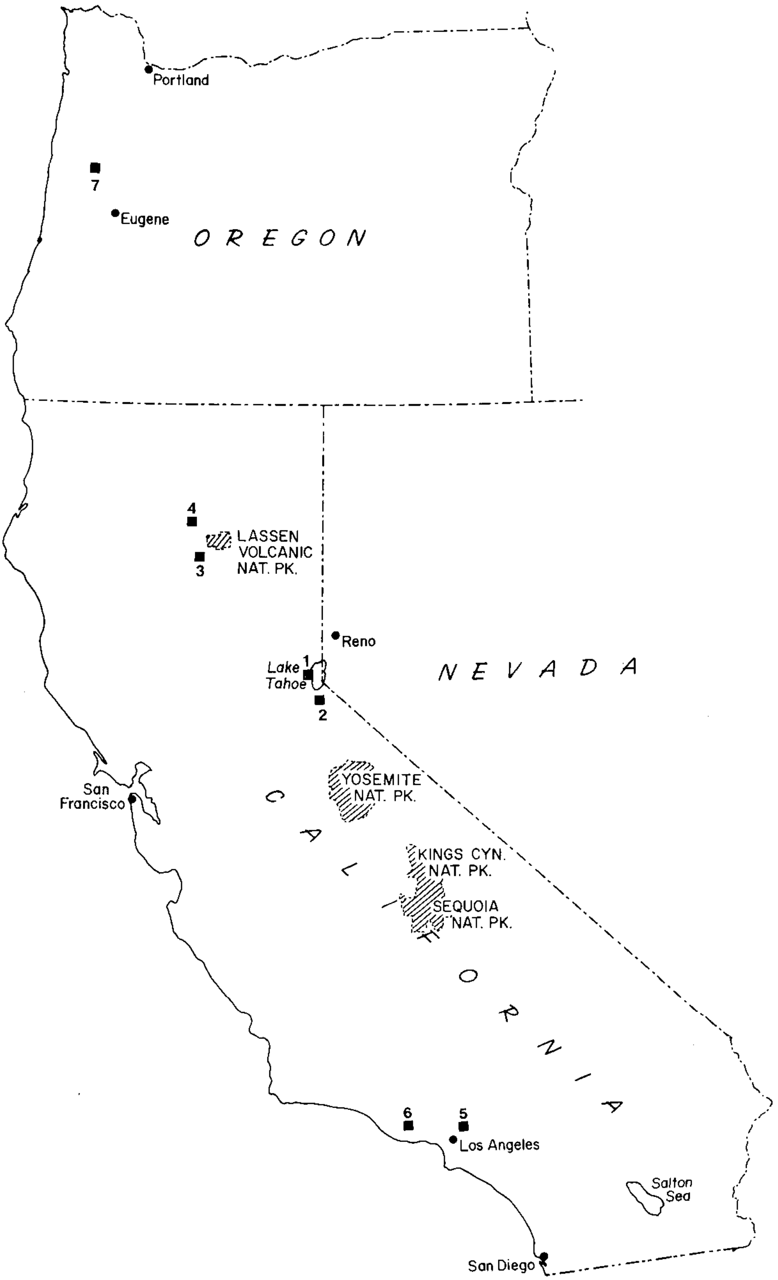


FIGURE 3 Location map of the Western United States showing the sampling sites.

values).[37–39] Vehicular emissions (Table I) contain large amounts of petroleum derived organic matter, confirmed primarily as hydrocarbons.[9,34] Typical concentration ranges for total lipids in continental areas are 100–10,000 ng/m^3, considerably higher than the typical values of 0.1–100 ng/m^3 observed for oceanic regions.[2,6,7,12,13,17,20,22,25]

The yields of lipid materials from aerosol samples represent up to ~30 percent of the total organic carbon,[8,14] and up to ~10 percent in the case of oceanic aerosol samples.[1,6,8,20] This lipid material has been classified earlier as part of the total particulate organic carbon[1] and is now being considered as a separate fraction.

Lipid compositions

Some typical examples of total ion current traces of GC-MS analyses are shown in Figure 4. The hydrocarbon fraction of an aerosol sample from the Corvallis, OR vicinity[9,10] consists of pure vascular plant wax, whereas the hydrocarbon fraction of a sample from the Lake Tahoe air basin[28] consists of a mixture of petroleum residues with only traces of plant wax (Figure 4a *vs* 4b). The envelope indicated by the dashed line (Figure 4b) represents an estimate of the relative magnitude of the hydrocarbons (both resolved and hump) that are derived from petroleum residues and the remainder of the *n*-alkanes above that envelope represents the plant wax component.[28] The total hydrocarbons from the exhaust of a diesel truck are shown in Figure 4c, where the major components are *n*-alkanes with no carbon number preference and a maximum at C_{21} (the dashed line represents the distribution envelope similar to that in Figure 4b[9,10]). The source of these hydrocarbons from petroleum is confirmed by the suite of biomarkers found in such materials as for example the tricyclic terpanes and triterpanes discussed below and indicated in Figure 4d.[9,10]

The total *n*-fatty acid (as methyl esters) and ketone fraction from a Corvallis aerosol sample[12,13] consists of homologs derived from vascular plant wax and from microbial residues (Figure 4e). The major ketone is 6,10,14–trimethylpentadecan-2-one labeled (a) in Figure 4e, with minor amounts of 6,10–dimethylundecan-2-one.

The total *n*-fatty alcohol (as trimethylsilyl ethers) fraction of an aerosol sample from Battle Creek Meadow Ranch, Mt. Lassen area,

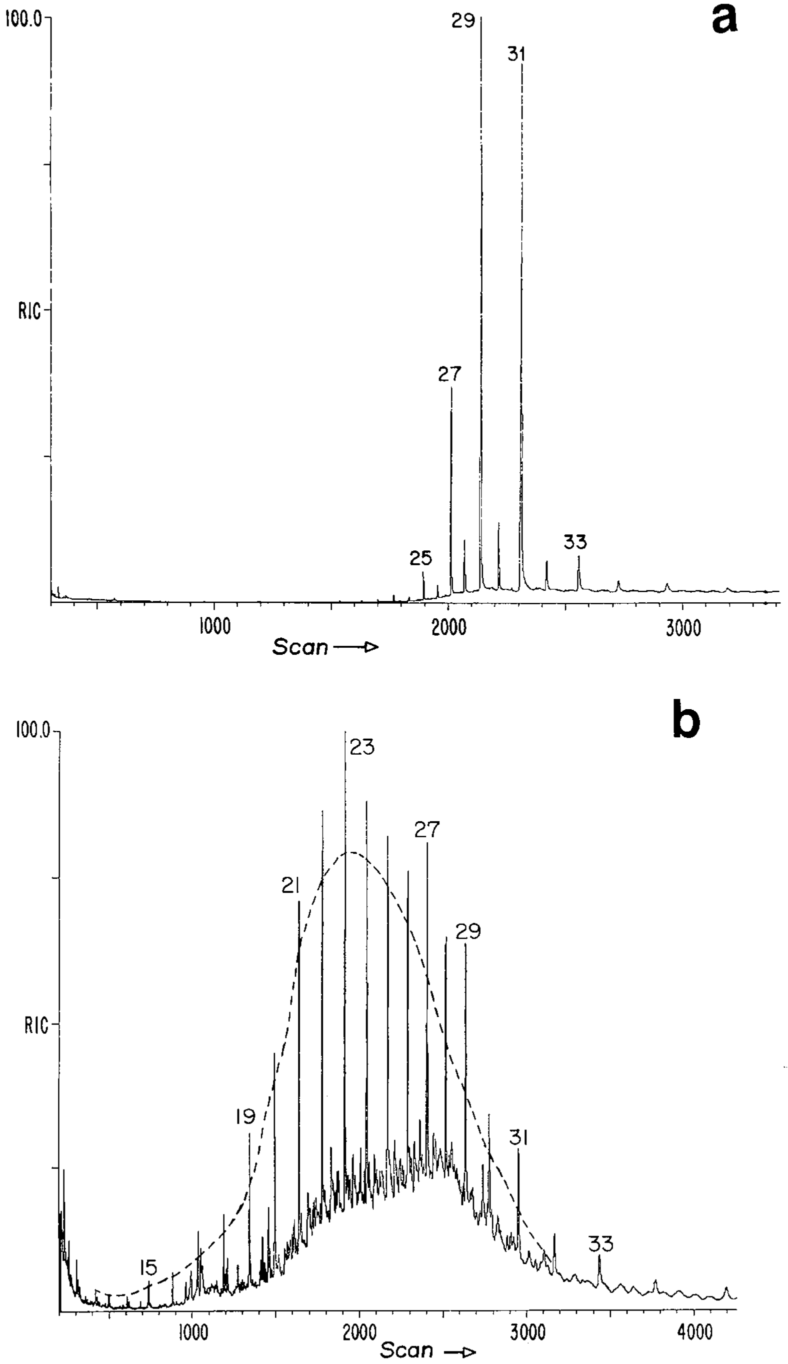
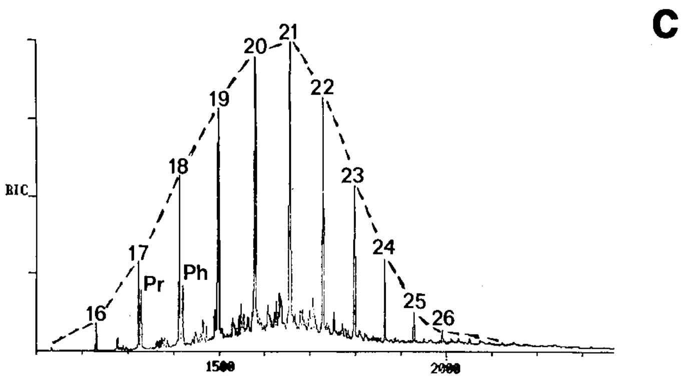


FIGURE 4 Total ion current traces from GC/MS analyses of some examples: (*a*) Corvallis, Oregon, total hydrocarbons; (*b*) Sugarpine Point State Park (winter), Lake Tahoe, California, total hydrocarbons; (*c*) Diesel truck exhaust, total hydrocarbons; (*d*) Diesel truck exhaust, m/z 191 mass chromatogram, indicator for triterpanes (27α–32α) and extended tricyclic terpanes (19–29); (*e*) Corvallis, Oregon, total fatty acid (as methyl esters) and ketone fraction; (*f*) Battle Creek Meadow Ranch, Mt. Lassen, total fatty alcohol fraction (as trimethylsilyl ethers). (The carbon numbers of the normal homologs are indicated by the arabic numerals).[9,13]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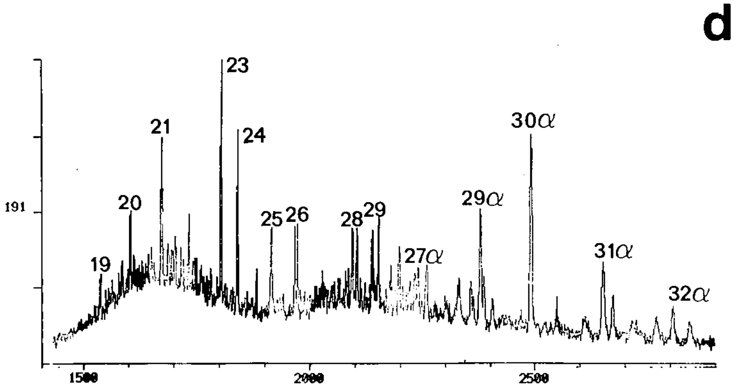
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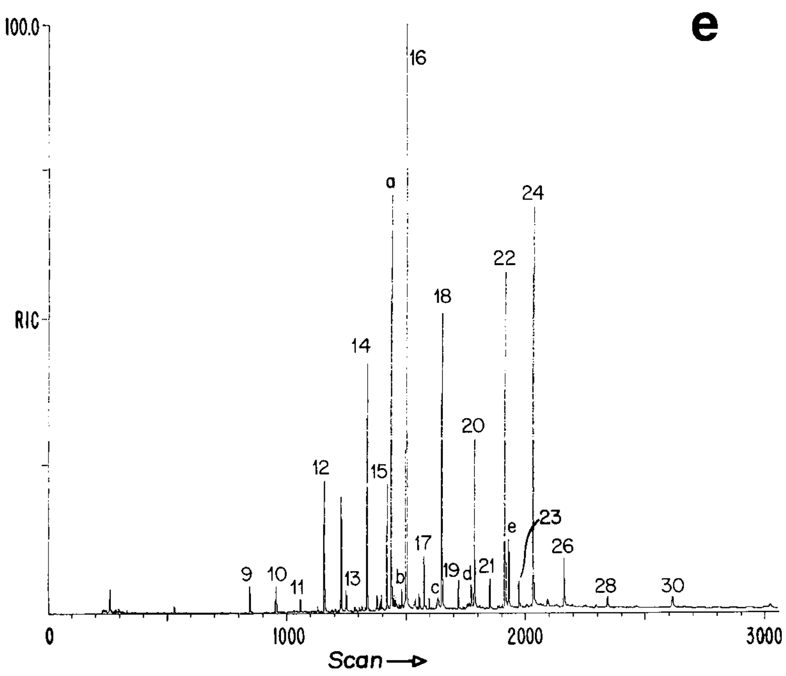
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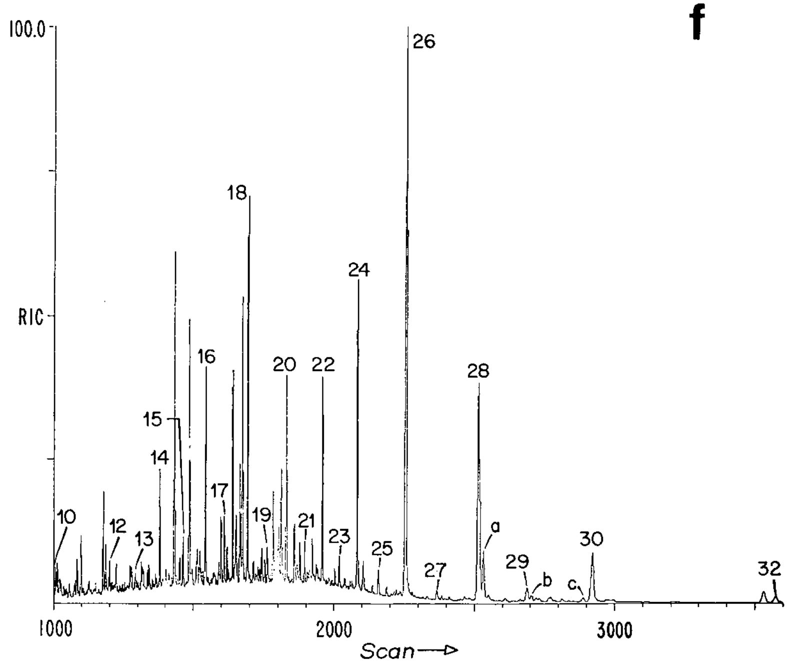
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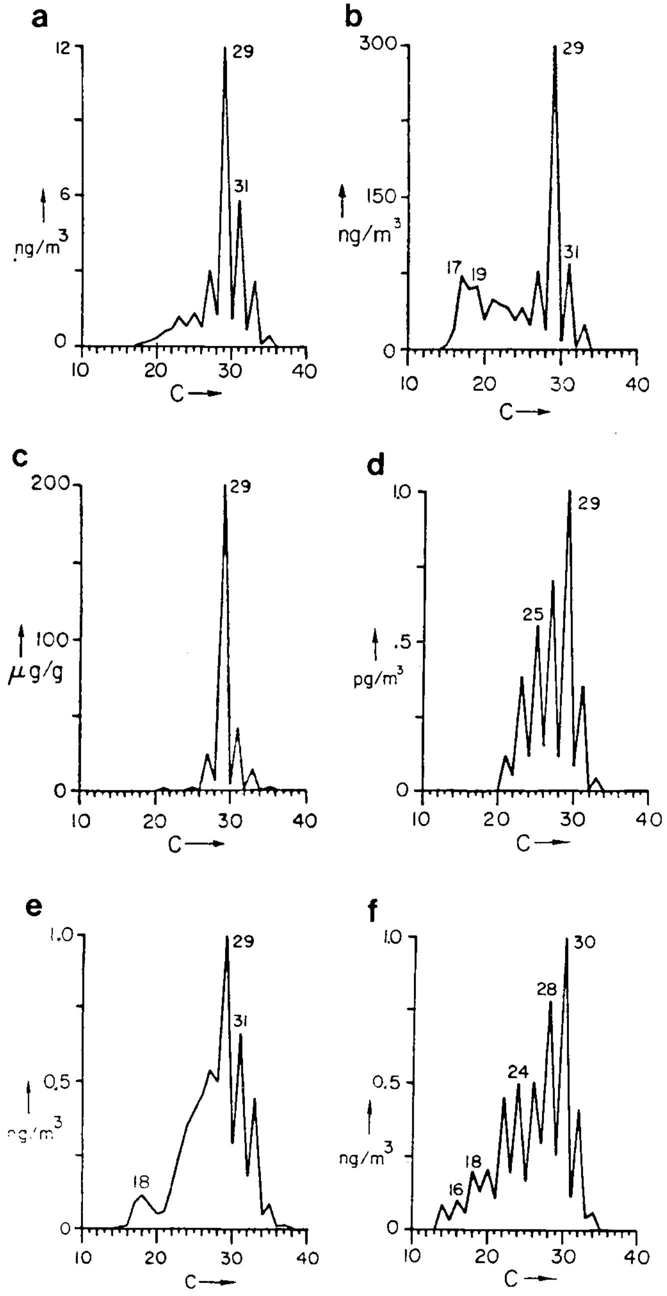
CA[12,13] is given in Figure 4f. The *n*-fatty alcohols are indicated by the numerals and are derived primarily from vascular plant wax. Minor phytosterol molecular markers are also present and they are indicated by the letters a–c (a = cholesterol).[29]

Homologous compounds: The identification of the homologous compound series present in aerosol lipid extracts is further defined by the CPI[5,39] and the Carbon Number Maximum (C_{max}[5]), which lend supportive evidence for the relative incorporation of recent biogenic organic matter to that of anthropogenic materials.

Typical distribution diagrams for *n*-alkanes, *n*-fatty acids and *n*-fatty alcohols in aerosols are shown in Figure 5. The *n*-alkanes of the Central African samples (Figure 2) range from about C_{15} to C_{35} with a strong odd carbon number predominance above C_{25} ($CPI > 1.4$, cf. Table I). The homologs $> n\text{-}C_{23}$ of the aerosol samples (e.g., Figure 5a and b) are derived chiefly from epicuticular waxes of vascular plants.[6–8,27] These saw-tooth distributions (odd > even) compare directly with the *n*-alkane distributions in wax from specific plant communities, e.g., composited sample of the local African vegetation (Figure 5c). The same higher plant wax signature is still recognizable in aerosols over the equatorial Atlantic Ocean (e.g. Figure 5d)[6] or over the Gulf of Guinea (e.g. Figure 5e,[33] for sample location cf. Figure 2). Although, the aerosol samples from Nigeria were taken during Harmattan episodes[17] and those over the equatorial Atlantic during the off-season, the close correspondence of the plant wax signatures indicates some terrestrially-derived aerosol transport out to sea. The dominance (C_{max}) of $n\text{-}C_{29}$ in these samples appears to indicate a mixed origin from forest and grassland.[13] However, this interpretation does not fit with the vegetation cover at all the sampling sites[17] and thus further data are necessary.

The *n*-fatty acids of the Nigerian aerosol samples (Figures 5f and g) compare well with such samples taken over the Atlantic Ocean (Figure 5i and others)[6] and in part with the wax of the composited vegetation (Figure 5h). They range from less than $n\text{-}C_{10}$ to about $n\text{-}C_{34}$ with a strong even carbon number predominance ($CPI > 3.0$, cf. Table I). These distribution patterns are characteristic of a biogenic origin, where the homologs $< n\text{-}C_{20}$ and probably in part $< n\text{-}C_{24}$ are derived from microbial sources and the homologs $> n\text{-}C_{22}$ are derived from vascular plant wax.[6,13,39]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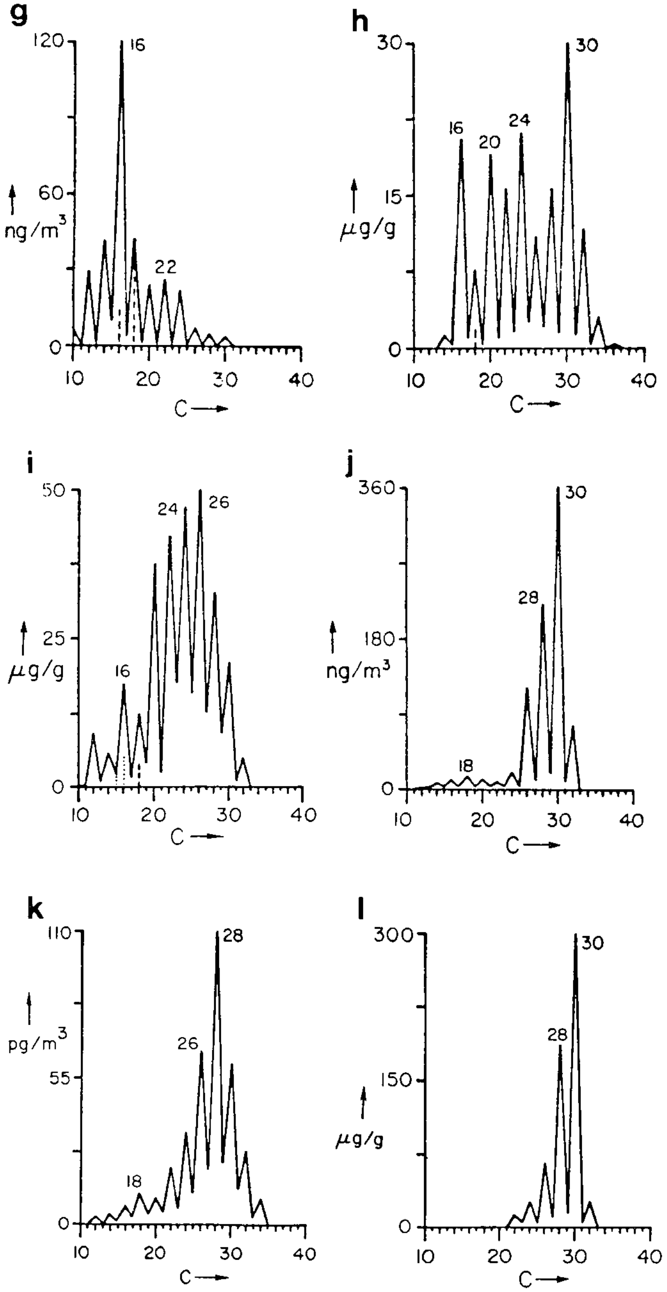


FIGURE 5 Distribution diagrams (concentration versus carbon number) for *n*-alkanes (*a–e*); *n*-fatty acids (*f–i*) (height of dashed lines indicate mono-unsaturated fatty acid concentrations); and *n*-fatty alcohols (*j–l*): (*a, f*) Aerosol, Jos 2, upwind of town, Harmattan episode, Nigeria; (*b, g, j*) Aerosol, Jos 3, upwind of town, Harmattan episode, Nigeria;[17] (*c, h, l*) Composited vegetation wax, Jos vicinity, Nigeria; (*d*) Atlantic Ocean, equatorial (sample TAF64);[6] (*e*) Gulf of Guinea, sample RO Imp 2;[33] (*i*) Atlantic Ocean, south (sample DC4);[6] (*k*) Atlantic Ocean, equatorial (sample TAF65).[6]

Examples of distribution diagrams of *n*-fatty alcohols are given in Figures 5j and k (cf. example of GC/MS trace in Figure 4f). They also range from n-C_{10} to about n-C_{34} with a strong even carbon number predominance (CPI 4–20, cf., Table I). The homologs $>n$-C_{20} are characteristic of vascular plant wax (cf. Figure 5l)[29,40] and the homologs $<n$-C_{20} may be derived from microbial sources, since they are not prevalent in fresh vascular plant waxes.[6,7,13,39,41] The *n*-fatty alcohols of the Nigerian aerosols and wax of ambient vegetation exhibit a C_{max} at n-C_{30}, which does not reflect the signature over the Atlantic Ocean, where the C_{max} observed is at n-C_{28}.[6,17] This may be due to the different seasons during sample acquisition.

Anthropogenic activity: The overprint of petroleum hydrocarbons from anthropogenic emissions (mainly vehicular) over the natural components in aerosols can be illustrated with the samples from the Lake Tahoe air basin (Figures 6a and b, Table I).[9,10,28] Crude petroleum contains *n*-alkanes ranging from $>C_{10}$ to about C_{35} with essentially no carbon number predominance (CPI ~1.0) (e.g. Figure 4b and Figure 6c), and it is the C_{15}–C_{35} homologs that can in part become superimposed on the natural biogenic background of vascular plant wax. Such contamination is significantly less or essentially nondetectable in rural or remote areas (e.g. Corvallis, Figure 4a; Jos, Nigeria, Figure 5a).

A diagnostic parameter that can be utilized to assess the magnitude of petroleum contributions to aerosols is the ratio of Unresolved to Resolved hydrocarbon components (U:R).[5,9,10] This ratio is determined from GC data by the area of unresolved material above background to the sum of the GC area of the resolved *n*-alkanes and other major resolved components. Example ranges are found in Table I, where values >2 reflect significant contamination by petroleum products.

Various engine emissions, lubricants and fuels have been analyzed for comparison purposes to assess their contributions to ambient aerosols (Table I, Figures 4c and d and Figures 6d–g).[9,10,34] Diesel exhaust contains some uncombusted fuel components, where all the *n*-alkanes present (Figures 4c and d and Figure 6d)[9,10,34] are derived from the fuel (Figure 6g) and a minor secondary hump of higher molecular weight naphthenic hydrocarbons, with associated

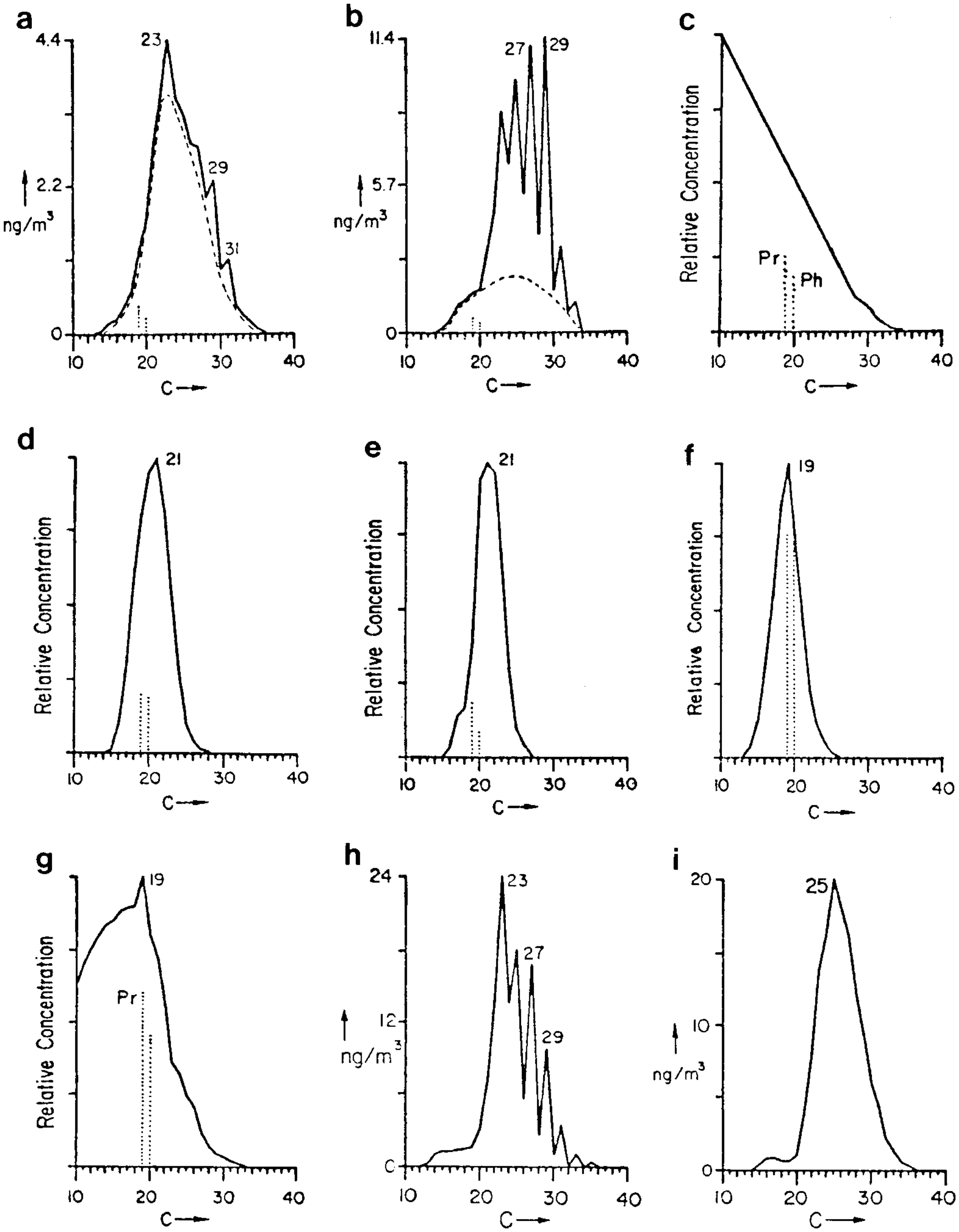


FIGURE 6 Distribution diagrams (concentration versus carbon number) for *n*-alkanes (height of dotted lines indicates isoprenoid hydrocarbon concentration, envelope under dashed line indicates contribution from petroleum residues): (*a*) Aerosol, Sugarpine Point State Park, Lake Tahoe, CA, winter; (*b*) Aerosol, Sugarpine Point State Park, Lake Tahoe, CA, summer, daytime; (*c*) Typical crude petroleum; (*d*) Diesel engine exhaust (International CO 1600 truck); (*e*) Automobile engine exhaust (Mercedes 280SE); (*f*) Lubricating oil (Castrol); (*g*) Diesel fuel (PEMEX); (*h*) Smoke from slash burn, downwind (Standley, unpublished results); (*i*) Overnight smoke haze from slash burn (Standley, unpublished results).

molecular markers, originates from engine lubricants (Figure 6f). Whereas, auto exhaust (Figure 6e) exhibits only low concentrations of *n*-alkanes (any uncombusted gasoline residues would not be sampled by this filtration technique), which in part reflect the distribution of these compounds in lubricating oil (Figure 6f).

Alteration of the lipid signature by thermal stress under incomplete combustion conditions is observed in smoke aerosols from fires. Injection of organic matter to the atmosphere can be significant and the products generated are combustion temperature dependent. Thus, low temperature fires (e.g. brush fire of chaparral)[34] essentially steam-distill the vascular plant waxes unaltered into the smoke. Whereas, higher temperature fires (e.g. slash burns, Standley, unpublished data) result in some thermal alteration of the plant wax signature (cf. Figures 6h and i). This alteration also appears to be time dependent, where freshly emitted smoke still has some carbon number predominance (CPI = 2), but overnight equilibration results in essentially complete loss of this predominance (CPI = 1). Thus smoke aerosols are a significant injection mechanism for organic compounds to the troposphere, with varying degrees of preservation of the biogenic homolog distributions.

Molecular markers: Molecular markers are indicator compounds that can be utilized in correlations of genetic sources.[39,41,42] Such molecules have definitive chemical structures that are correlatable either directly or indirectly via a set of diagenetic changes to their source. Such sources can be biogenic, geologic or synthetic.[9,10,34,39,41–44] All three source categories are represented in emissions from anthropogenic activity. The major molecular markers encountered in the various source categories are summarized in Table II and some examples of typical chemical structures are given in Figure 7.

Molecular markers have been utilized as precise indicators for petroleum residues and for the higher plant wax and resin components which are part of aerosol lipids.[7–10,12,13,17,28,29,34,45] Hydrocarbon fractions of aerosol lipids may contain the molecular markers that are characteristic of petroleum.[9,10,34] These compounds are geologically mature (formed over millions of years) and are relatively stable in ambient environments. Examples are the extended tricyclic terpanes (Structure I in Figure 7), the 17α(H)-

TABLE II

Examples of molecular markers of utility for fingerprinting of vascular plant (biogenic) components, petroleum residues and pyrogenic compounds in aerosols.

Molecular marker compound class	Usual compositional range	Usual major analog or homolog	Occurrence
Vascular Plant (also microbiota) *Sources*—			
n-Alkanes	n-C_{23} to n-C_{35}	n-C_{29} (n-C_{27})	ubiquitous (biogenic)
n-Fatty acids	n-C_{24} to n-C_{32}	n-C_{26}	ubiquitous (biogenic)
n-Fatty alcohols	n-C_{24} to n-C_{32}	n-C_{28}	ubiquitous (biogenic)
Alkanes (*n*, *iso*, *anteiso*)	n-C_{17}–C_{20}	n-C_{17}	microbial
n-Fatty acids	n-C_{10} to n-C_{20}	n-C_{16}	microbial (ubiquitous)
Alkenoic acids	n-$C_{14:1}$ to n-$C_{18:1}$	n-$C_{18:1}$	microbial (short half life)
iso- and *anteiso*- Fatty acids	C_{15}–C_{19}	C_{15}	bacterial
Phytosterols (and triterpenols)	C_{27}–C_{30}	C_{29}	higher plants
Diterpenoid hydrocarbons and acids	C_{19}–C_{20}	C_{20}	resinous plants
ω-Hydroxy fatty acids	C_{10}–C_{24}	C_{24}	higher plants
α,ω-Dicarboxylic acids	C_{10}–C_{24}	C_{16}	various
Wax esters	C_{32}–C_{40}	C_{40}	higher plants (also microbial)
Petroleum Residue (primary) *Sources*—			
Isoprenoid hydrocarbons (pristane, phytane, etc.)	C_{10}–C_{20}	Pr (C_{19})	ubiquitous (fossil fuel, not in gasoline)
Alkylcyclohexanes	C_{16}–C_{29}	C_{23}	ubiquitous (fossil fuel)
Triterpenoid hydrocarbons	C_{27}–C_{35}	C_{30}	ubiquitous (not in gasoline & diesel fuel)
Tricyclic terpane hydrocarbons	C_{19}–C_{29} (low C_{22}, C_{27})	C_{23}	ubiquitous (not in gasoline)
Steranes and diasteranes	C_{27}–C_{29}	C_{27}	ubiquitous (not in gasoline & diesel fuel)
Unresolved naphthenic compounds (hump)	C_{14}–C_{31}	various	ubiquitous

TABLE II (continued)

Molecular marker compound class	Usual compositional range	Usual major analog or homolog	Occurrence
Pyrogenic Emissions—			
Polynuclear aromatic hydrocarbons (PAH)	C_{10}–C_{24+}	C_{16}	ubiquitous (high temperature)
Ketones and aldehydes ($C_nH_{2n}O$)	C_{10}–C_{32}	C_{18}	ubiquitous (low temperature)
n-Fatty acids	C_{10}–C_{20}	C_{16}	vehicular emissions
Alkylbenzoic acids	C_7–C_9	C_7	vehicular emissions
Alkylnaphthoic acids	C_{11}–C_{13}	C_{11}	vehicular emissions
Alkylbenzenedioic acids	C_8–C_{10}	C_8	vehicular emissions
Alkylphenanthroic acids	C_{15}–C_{17}	C_{15}	vehicular emissions
Oxy-PAH (e.g. quinones, ketones, etc.)	C_{10}–C_{16}	—	vehicular emissions
Retene and other diterpenoid derivatives	C_{16}–C_{19}	$C_{18}H_{18}$	smoke (conifers)

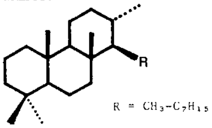
hopanes (II, Figure 7), 17α(H),18α(H),21β(H)-28,30–bisnorhopane (III, Figure 7), alkylcyclohexanes, steranes and the isoprenoids, pristane (IV, Figure 7) and phytane (V, Figure 7). Pyrogenic molecular markers that can be present in hydrocarbon fractions are polynuclear aromatic hydrocarbons (PAH, e.g. VI–XI, Figure 7), where the unsubstituted analogs are usually the characteristic species.[11] PAH and oxy-PAH are also emitted by vehicular exhausts, but with different and recognizable distribution patterns.[10,34]

The *n*-fatty acid and *n*-fatty alcohol fractions contain relatively labile compounds, which are diagnostic of biogenic material of recent origin. For example, dehydroabietic acid (XII, Figure 7) in the fatty acid fraction is used as a biogenic source indicator for conifer resin.[46] Normal fatty acids (e.g. XIII, Figure 7) of higher molecular weight (C_{24}–C_{30}) are characteristic molecular markers for vascular plant wax components. Minor amounts of C_{12}–C_{25} *n*-alkan-2-ones with an odd carbon number predominance in ketone fractions may indicate microbial degradation products of plant wax components.[13]

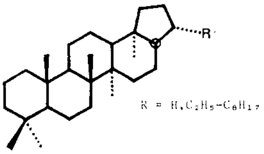
MOLECULAR MARKERS

HYDROCARBONS

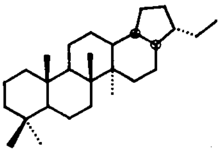
Geogenic



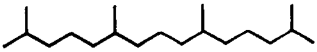
I. Extended tricyclic terpanes



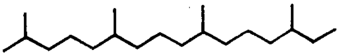
II. 17α(H)-hopanes



III. 17α(H),18α(H),21β(H)-28,30-Bisnorhopane

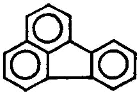


IV. Pristane

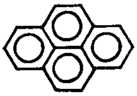


V. Phytane

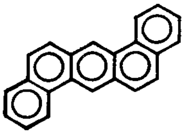
Pyrogenic



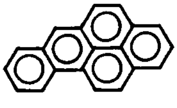
VI. Fluoranthene



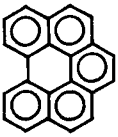
VII. Pyrene



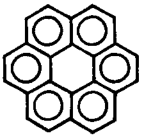
VIII. Dibenzanthracenes



IX. Benzo(a)pyrene



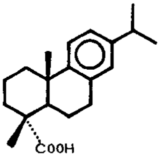
X. Benzo(g,h,i)perylene



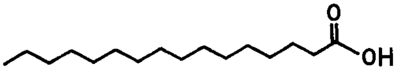
XI. Coronene

FATTY ACIDS & KETONES

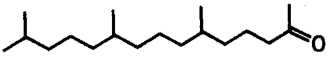
Biogenic



XII. Dehydroabietic acid

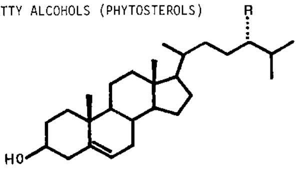


XIII. Saturated n-fatty acids (eg. palmitic acid, $C_{16}H_{32}O_2$)



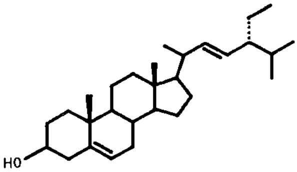
XIV. 6,10,14-Trimethylpentadecan-2-one

FATTY ALCOHOLS (PHYTOSTEROLS)



XV.

Cholesterol R=H (C_{27})
Campesterol R=αCH_3 (C_{28})
β-Sitosterol R=αC_2H_5 (C_{29})



XVI. Stigmasterol (C_{29})

FIGURE 7 Examples of typical molecular markers in various aerosol lipid fractions.

Isoprenoidal ketones, especially 6,10,14-trimethylpentadecan-2-one (XIV, Figure 7) have been identified in aerosols and in vehicular exhaust.[13,34] Their origin appears to be from partial oxidation products of isoprenoid hydrocarbons in vehicular exhaust, rather than photo-oxidation of phytol from vascular plants. These molecular indicators need further source specific definition.

More polar compounds in the alcohol fractions, such as phytosterols and various triterpenols, have also been observed for aerosol samples.[29] Phytosterols are specific tracers of higher plant waxes and have been confirmed in various composited plant wax mixtures. The major phytosterols are cholesterol (XV, $R=H$, Figure 7) and β-sitosterol (XV, $R=C_2H_5$, Figure 7), with stigmasterol (XVI, Figure 7) and other analogs.

Various other minor molecular marker series or compounds have been described for aerosols and some can be reconciled to specific sources, while others are ubiquitous.[9,10,13,34] These are also summarized in Table II. For example, unsaturated fatty acids are exclusively of a recent biogenic origin (viable microbes or vascular plants), wax esters have analogous sources and ω-hydroxy fatty acids and α,ω-dicarboxylic acids appear to be derived from degradation/hydrolysis products of biogenic lipids.

Blanks: It should be stressed that the reduction of background contaminant levels is paramount to these types of trace analyses and that system and experimental blanks should be carried out and reported with the general analytical data.

The major contaminants commonly observed are mainly residual phthalate esters (diethyl, dibutyl and diethylhexyl), minor amounts of *n*-fatty acids (as methyl esters) ranging from C_{10} to C_{22}, and traces of *n*-alkanes ranging from C_{19} to C_{30}, with no carbon number predominance and maximum at C_{25}.[13] PAH are generally not detectable.

The major proportion of the contaminants can be distinguished by their distribution and concentration fingerprints and they can be subtracted from the corresponding sample signal.

Detrital organic matter

Limited analytical data for humic substances and for residual organic carbon have been reported.[8,14,47] Fulvic substances have been assessed only qualitatively regarding their presence. The yields of humic acids are in some cases significant and constitute a major organic carbon fraction for some rural and oceanic aerosols. The H/C values generally are in the range typical of terrestrial humates (1.0–1.2).[8,35] The H/C value of 1.4 for an oceanic sample is intermediate between the ranges for terrestrial and algal (1.5–1.7)[8,35] humates, possibly indicating a mixed origin from soils and lacustrine muds at the source. The $\delta^{13}C$ values of humic acids range from -21 to $-24‰$ and these data are consistent with the source inference drawn from the H/C values.[8]

Residual carbon represents the dominant fraction of the organic carbon in aerosols, comprising about 2–5% of the particulates of oceanic aerosols to about 10–20% of urban aerosol particulates.[8,14,47] The appearance of the major fraction of this material is black and fine-grained. H/C data range from 0.8 to 1.2,[8] which is rather aliphatic compared to diesel exhaust soot (H/C$=$0.4). Algal protokerogen has an H/C range of 1.3–1.6 and terrestrial portokerogen 0.9–1.1.[35] The $\delta^{13}C$ values of such residual organic carbon ranges from -22 to $-25‰$ and this can be compared with the value of $-25.3‰$ for diesel soot.[8] Petroleum has a $\delta^{13}C$ range from about -24 to $-29‰$ with a mean of approximately $-27‰$.[39,48,49] The thermal stress of incomplete combustion results in isotopically heavier residual carbon due to the preferential loss of the lighter isotope ^{12}C.[50] Thus, the residual carbon of aerosols may have a multiple origin, but is derived primarily from incomplete combustion residues of petroleum products.

Injection, transport and apportionment

The biogenic lipid components of aerosols are derived mainly from epicuticular waxes of vegetation as demonstrated by the ubiquitous compounds with strong carbon number predominances and by markers such as phytosterols and triterpenols.[12,13,29] A minor component from plant resins is also found in some instances (e.g. diterpenoids).[13] These biogenic lipids can be introduced into the atmosphere by mechanical action (sloughing and wind abrasion) and also by distillation/volatilization at advancing combustive fronts of fires (grass, brush or forest). Such vegetative emissions are more concentrated in the larger particle size fraction ($d_p > 1\,\mu m$) of aerosols.[30,33,51,52] The major molecular markers typical of vegetation are summarized in Table II.

The injection of petroleum residues to ambient aerosols in the study areas is mainly from vehicular emissions.[9,10,34] The fuel, lubricants and engine emissions analyzed here compare well with the same suites of homologous and molecular marker compounds found in the ambient aerosols. Thus it was concluded that the petroleum residues of aerosols are derived from motor lubricating oils, possibly with some incompletely combusted diesel fuel, all adsorbed on the particulate emissions from engines (e.g. soot).[9,10] These emissions are concentrated in the fine particle size fractions ($d_p < 2\,\mu$m) of aerosols. The major molecular markers (hydrocarbons) characteristic of petroleum residues are summarized in Table II.

Pyrogenic lipid components of aerosols may be confirmed by analysis of the polycyclic aromatic hydrocarbons (PAH) and the oxygenated PAH derived from incomplete combustive processes.[34] Thermally altered molecular markers, as for example retene and other diterpenoid derivatives which are characteristic of conifer smoke[53,54] are found in aerosols and represent lower temperature products from the combustive processes. Whereas, the PAH, especially the unsubstituted analogs reflect resynthesis products from the higher temperatures of combustion.[55] Thus, a whole range of pyrogenic products can be injected to ambient aerosols depending on the temperature regimes of the respective fires. The common organic compound suites attributable to combustion processes are summarized in Table II.

The transport of organic components in aerosols can be over short distances or over global distances. Transport in the case of a restricted air basin (e.g. Los Angeles) is relatively short, covering the basin until ventilation occurs. Whereas, the global trade wind patterns or other major wind systems (e.g. Harmattan, Figure 2) can transport terrestrially derived organic matter over vast areas and across the oceans.[2,6,20,26,33] Thus, the knowledge of the specific sources of organic matter in aerosols is important for tracing both types of air parcels.

For modeling purposes it is also desirable to provide an apportionment of the organic materials in aerosols to sources. A summary of such an attempt for aerosol lipids is given in Table III. The apportionment of soot carbon and other macromolecular organic detritus has been carried out primarily for urban areas[14,47]

TABLE III

Apportionment of lipid components in aerosols to contributions from plant wax, petroleum residues and pyrogenic compounds

Geographic Area	Plant Wax (%)[a]	Petroleum Residues (%)[a]	Pyrogenic (PAH, %)[a]
Western United States			
Rural, summer	46–100 (81)	0–54 (19)	0.01–0.05 (0.03)
winter	20–40 (30)	60–80 (70)	0.03–2.0 (0.64)
Urban, summer	6–37 (17)	63–94 (83)	0.04–0.06 (0.05)
winter	21	77	1.8
Europe (Delft)[32]			
Urban, summer	37–46 (42)	n.r.[b]	n.r.
winter	1–18 (7)	n.r.	n.r.
Central Africa (Nigeria)			
Rural	100	0	n.d.[c]
Urban	15	85	n.r.
Oceanic Aerosols			
Atlantic	100	0	n.d.
Pacific, Samoa[51]	94	6	n.r.

[a] Range, mean is given in parentheses.
[b] Not reported.
[c] Not detectable.

The lipids were apportioned into plant wax contributions, petroleum residues and pyrogenic PAH as follows:

a) Plant wax—summation of the concentrations of *n*-alkanes, C_{23}–C_{35} with CPI > 2; *n*-fatty acids, C_{22}–C_{34}; *n*-fatty alcohols, C_{22}–C_{34}; *n*-methyl ketones, C_{22}–C_{35}; wax esters; ω-hydroxy fatty acids; and phytosterols.

b) Petroleum residues—summation of the concentrations of *n*-alkanes, C_{10}–C_{35} with CPI < 2; *n*-fatty acids, C_{10}–C_{18} with CPI < 1.5; all of the unresolved branched and cyclic hydrocarbon mixture; isoprenoid and triterpenoid hydrocarbons; alkylcyclohexanes; ketones and aldehydes with CPI < 1.5; dicarboxylic and aromatic acids.

c) Pyrogenic compounds—summation of the concentrations of PAH (naphthalene, anthracene, phenanthrene and all the PAH with molecular ions at m/z 202, 228, 252, 278 and 300) and of dominant oxy-PAH (e.g. quinones).

The major conclusion that can be drawn from the limited data in Table III is the concentrations of vascular plant wax in aerosols are highest in the summer in temperate regions and more uniform throughout the year in more tropical regions. Urban areas have a significant plant wax component in ambient aerosols, whereas rural and remote areas have from 50 to 100% wax. The balance of the organic lipid loading of aerosols is primarily from the various petroleum residues and the pyrogenic PAH only represent trace components. This approach to lipid apportionment can be further refined by more detailed characterizations of other anthropogenic point emission sources.

CONCLUSIONS

Summary

Aerosols from rural and remote areas contain lipids which are comprised primarily of vascular plant wax residues and minor amounts of plant resin detritus. These materials are concentrated in the larger sized particles and can be transported over great distances.

Plant waxes in aerosols correlate with their sources from vegetation and are characterized by the homolog distributions of mainly the *n*-alkanes (odd carbon numbers, C_{23}–C_{33}) and *n*-fatty alcohols (even, C_{24}–C_{32}), with the lesser *n*-fatty acids (even, C_{20}–C_{32}) ω-hydroxy fatty acids, wax esters, α,ω-dicarboxylic acids and molecular markers (e.g., phytosterols). Resin residues are identified mainly from the diterpenoidal compounds. The aerosol loadings of plant wax components in temperate regions are greater during summer than during winter, whereas in tropical areas they are essentially constant throughout the year.

The major proportion of petroleum residues and pyrogenic PAH components are found in hydrocarbon fractions of extracts from aerosol filtrates. Petroleum residues present in aerosols are comprised of resolved normal alkanes, with no carbon number preference and usual range from C_{15}–C_{26}, an unresolved mixture of naphthenic hydrocarbons (the hump) and minor molecular markers specific for petroleum. Highest concentrations are observed in urban areas and traces can be detected in rural and remote regions. The predominant source of the atmospheric petroleum residues is from mobile sources in the form of lubricating oils, which was confirmed by the molecular analyses of vehicular exhausts, fuels and lubricants.

A minor pyrogenic component is present in aerosols derived from various combustive processes injecting smoke, as for example from wood fires. This consists of a series of PAH ranging from naphthalene to dibenzanthracene, with pyrene as the usual dominant analog.

Rural and remote aerosols contain traces of fulvic and humic substances (approximately 50 ng/m^3). The humic substances are derived principally from soils. All aerosols also contain residual organic carbon which resembles amorphous carbon (soot). This material exhibits a relatively low H/C ratio and $\delta^{13}C$ values typical of thermally stressed petroleum. It is derived primarily from incomplete combustion residues of petroleum products and is concentrated in the fine particulate fractions.

Thus, the anthropogenic components of aerosols, i.e. petroleum residues and pyrogenic PAH can be quantitated and distinguished from the natural background signatures of higher plant waxes and resins. Diagnostic data (e.g. CPI, C_{max}, U:R and molecular markers) permit the formulation of definitive statements regarding the mass balance and likely source materials of ambient higher molecular weight organic matter present in localized air parcels. Such organic species can then also be applied as tracers for air parcels.

Recommendations

The application of these analytical methods by other researchers should be encouraged and the characterization of the higher molecular weight ($>C_{15}$) organic matter should be coupled with similar data for the volatile organic components ($<C_{15}$).

Cognizance of filter and sampler contamination and the value of procedural blanks should always be demonstrated and reported with new data.

Regional versus local (e.g. urban) air parcels need to be considered. In addition, what are the various air parcel cleansing mechanisms of importance—is it wash-out, fall-out or ventilation?

The apportionment of the types of organic matter to the major particle size fractions needs further definition. What are the effects of photochemistry on organic components, especially lipids on particles?

The molecular definition of organic matter in aerosols can ultimately be utilized as a tracer for air parcels, to apportion sources and to model global budgets, possibly even aided by remote sensing.

Acknowledgements

I thank Dr. Monica A. Mazurek and Ms. Laurel J. Standley for technical assistance. Financial support from the Atmosphere Research Section, National Science Foundation (Grants ATM 81-16622, ATM 81-18101 and ATM 85-09184) is gratefully acknowledged.

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