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# Application of Molecular Marker Analysis to Vehicular Exhaust for Source Reconciliations

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Molecular marker analysis has been applied to organic matter in vehicular exhaust and various source materials. Vehicular exhaust can be distinguished from the natural background (mainly plant wax and resin residues in ambient aerosols) by the presence of petroleum residues in the form of characteristic homologous compounds and geologically mature molecular markers (steranes, triterpanes, PAH). Incomplete combustion products such as oxy-PAH compounds, ketones, aldehydes and carboxylic acids are also present in vehicular exhausts. These compound suites can be distinguished from emissions of biomass burning, which contain specific thermally-altered biomarker compounds. The characteristic molecular marker signatures of vehicular emissions and smoke can thus be quantified and distinguished from the natural background of vegetative emissions to ambient aerosols.

**KEY WORDS:** Petroleum residues, steranes, triterpanes, PAH, oxy-PAH, vehicular exhaust, smoke.

## INTRODUCTION

The organic species present in the reservoir of the lower troposphere are comprised of gases (volatiles), lipids (bitumen, solvent soluble organic matter) and macromolecular organic matter, derived from

natural biogenic, geologic and synthetic sources.<sup>12, 27, 28, 41, 51, 53, 54, 58, 59, 63-65</sup> The higher molecular-weight, solvent-soluble compounds ( $>C_{12}$ , lipids) have been characterized for urban, rural and oceanic aerosols, in some cases with assignment of sources.<sup>4, 5, 13, 14, 16, 17, 31, 40, 41, 45, 50, 51, 53, 54, 58, 59, 61, 62, 64, 65, 72, 73</sup> Petroleum residues are a major and usually predominant component of the lipids extractable from aerosols in urban and in some suburban air basins.<sup>62, 65, 41, 58, 59</sup>

Here I will describe the application of molecular marker analysis to vehicular exhausts for source reconciliation of petroleum residues. This will be compared with the same approach for smoke and aerosol analyses, to illustrate how these molecular signatures can be traced from sources to the ambient aerosol reservoir. Such data will hopefully serve to stimulate further research on defining and elucidating the spatial variations and geographic sources of organic aerosol burdens in urban versus rural areas.

## EXPERIMENTAL METHODS

### Sampling

Samples of vehicular exhaust and smoke from brush fires and forest slash burns were acquired by filtration using a standard high volume air sampler, fitted with quartz fiber filters (two, back-to-back,  $20 \times 25 \text{ cm}^2$  surface).<sup>65</sup> The quartz filters were annealed for 3 hours at  $560^\circ\text{C}$  prior to sampling in order to pyrolyze and thus remove any adsorbed organic material. The pump was placed about 1.5 m away from the particular engine exhaust pipe and turned on for brief intervals (5 to 30 minutes) during idling and racing periods. An extract of diesel exhaust particulates from an Opel 2.3D engine (1974) was obtained from Dr. R. Gorse of the Ford Motor Company and subjected to the same analytical procedures. The hydrocarbon emission level for the Opel 2.3D was 1.8 g/mile (normal emissions range from 0.5–0.6 g/mile) (F. Ferris, private communication). Smoke aerosol was pumped through the high-volume filter system for 1 hour intervals downwind from the Los Padres National Forest, California fire of August 1, 1977. Two such samples from the Carmel

Valley area were combined for analysis. Additional smoke samples from controlled slash burns in the coastal range of Oregon were acquired in the same manner, but for longer sampling durations (Standley, unpublished data).

After a sampling was completed, the collection filter was stored in a pre-cleaned 1-liter jar to which approximately 5 ml of methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) was added. Samples were stored in this manner until laboratory workup was initiated. Less than about 3% of the material collected on the first filters appeared on the back-up filters and they were therefore not analyzed.

### Lipid isolation and analysis

Filters were extracted using ultrasonic agitation with 400 ml aliquots of distilled-in-glass  $\text{CH}_2\text{Cl}_2$  directly in the storage jars for two 15-minute periods. The chemical procedures are summarized in the flow diagram (Figure 1). Solvent extracts were concentrated to volumes of approximately 5 ml and then filtered using a Gelman Swinney filtration unit fitted with pre-cleaned glass filters for the removal of insoluble particulates and quartz fibers. The resultant filtrates were transferred to 5 ml heavy-walled, conical vials, evaporated to near dryness using a stream of  $\text{N}_2$ , reconstituted with known volumes of  $\text{CH}_2\text{Cl}_2$ , and finally, quantified using a Mettler microanalytical

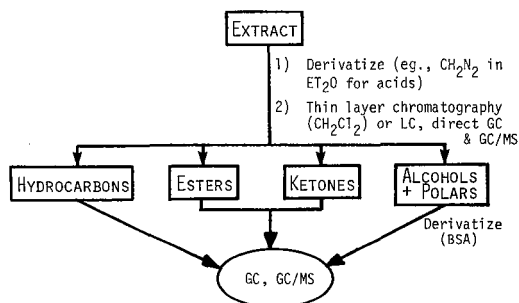


FIGURE 1 Simplified schematic for fractionations and chemical separations of solvent soluble organic matter from samples of aerosols, vehicular emissions, fuels, lubricants and natural vegetation.

balance. The total lipid extracts were treated with 14%  $\text{BF}_3$  in methanol or alternatively with  $\text{CH}_2\text{N}_2$  in diethyl ether to esterify the free acids.<sup>65</sup> The extracts were then concentrated to  $\sim 100 \mu\text{l}$  and subjected to thin layer chromatography (TLC) using silica-gel plates (0.25 mm) and eluting with a mixture of hexane and diethyl ether (9:1). The TLC plates had been cleaned prior to use by repetitive elutions with methanol and methylene chloride. After each solvent washing, the top centimeter of silica-gel was scraped off in order to remove contaminants, then prior to use the TLC plates were activated in an oven at  $120^\circ\text{C}$  for 45 minutes.

The elution regions corresponding to hydrocarbons, esters, ketones, alcohols and origin were visualized by UV and iodine vapor in conjunction with the coelution of a TLC standard mixture (Figure 1). These fractions were scraped off the TLC plate, eluted with  $\text{CH}_2\text{Cl}_2$  (ethyl acetate for alcohols and origin), concentrated, transferred to 2 ml vials and then quantified in some cases using a Mettler microanalytical balance.<sup>65</sup> Internal standards were added to the fractions prior to analysis and recovery studies with model compounds have been carried out,<sup>41,42</sup> Standley, unpublished data. The hydrocarbon, ester and some ketone fractions were subjected to gas chromatographic (GC) and gas chromatography-mass spectrometric (GC-MS) analyses to evaluate the recognizable molecular indicators and the contents of petroleum residues and polynuclear aromatic hydrocarbons (PAH).

The GC analyses were carried out on a Hewlett-Packard Model 5840A gas chromatograph using either a  $25 \text{ m} \times 0.25 \text{ mm}$  i.d. glass capillary column wall-coated with OV-101 or a  $25 \text{ m} \times 0.20 \text{ mm}$  i.d. flexible fused silica capillary column coated with SP-2100 (Hewlett-Packard). The GC-MS analyses were conducted on a Finnigan Model 4021 quadrupole mass spectrometer interfaced directly with a Finnigan Model 9610 gas chromatograph and equipped with a flexible fused silica capillary column wall-coated with SE-54 or DB-5 ( $30 \text{ m} \times 0.25 \text{ mm}$  i.d.). The GC and GC-MS operating conditions are as follows: Temperature program  $35\text{--}280^\circ\text{C}$  at  $4^\circ\text{C}$  per minute, held isothermal at  $280^\circ\text{C}$  for 60-90 minutes and using helium as 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.

Diesel fuel and lubricating oil were analyzed directly as diluted solutions in hexane and also as separated fractions by GC and GC-MS. An 800 ml solvent blank was concentrated to a total volume of 20  $\mu$ l, then analyzed by GC in order to monitor the background and a procedural blank was also carried through the experimental procedure.

## RESULTS AND DISCUSSIONS

An overview of the analytical results on lipids in vehicular exhausts, smoke aerosols and source materials is given in Table I. The extractable lipid matter of vehicular exhausts is comprised primarily of aliphatic and aromatic hydrocarbons and carboxylic acids, with minor amounts of ketones, aldehydes and various, source specific molecular marker (indicator) compounds. The compositions of the extractable lipids from smoke aerosols reflect their biogenic origin and are composed of aliphatic and aromatic hydrocarbons, carboxylic acids and minor amounts of ketones, aldehydes with some source specific molecular markers. The lipids of the source materials consist of the same compound classes with similar distributions. It should be emphasized that the samples described in Table I are only a limited representation of examples and more extensive sampling should greatly refine the data.

In order to characterize vehicular emissions by molecular marker analysis a detailed interpretation of GC-MS data is necessary. This can be illustrated for example with various figures. The salient features of a GC-MS analysis of the total hydrocarbons from auto exhaust are shown in Figure 2. The total ion current trace (Figure 2a) is approximately equivalent to the gas chromatogram and represents the resolvable and unresolvable (hump) compounds, where in many cases the major peaks are common homologous series. The molecular markers, including biomarkers, usually occur as minor components and are located in the GC-MS data by plotting key fragment ions over their respective GC elution range (i.e. mass chromatograms). A summary of characteristic key ions for various classes and groups of compounds is given in Table II. Thus, the peaks in the mass chromatograms (e.g.  $m/z$  191, 217, 82 in Figure 2c-e) represent the mass spectrum scans where the various

TABLE I  
Lipid extract composition of vehicular engine exhausts, fuels and emissions from fires and natural vegetation.

Sample	Sample amount (m <sup>3</sup> ) or type	Total extract	Total hydrocarbons	n-Alkanes		Branched/cyclic hump		Carboxylic acids				
				Yield	C <sub>max</sub> <sup>b</sup>	U:R <sup>d</sup>	~C <sub>max</sub> <sup>b</sup>	Yield	C <sub>max</sub> <sup>b</sup>	CPI <sup>c</sup>	CPI <sup>c</sup>	
1. Auto exhaust (Mercedes 280SE, 1967, no catalytic converter)	10	1650 µg/m <sup>3</sup>	600 µg/m <sup>3</sup>	20 µg/m <sup>3</sup>	22	0.93	50	26	2.3	50 µg/m <sup>3</sup>	12, 16	3.7
2. Diesel exhaust (International CO 1600, 1968)	15	3550 µg/m <sup>3</sup>	680 µg/m <sup>3</sup>	300 µg/m <sup>3</sup>	21	1.00	2.3	21 (26)	1.05	1070 µg/m <sup>3</sup>	16	2.0
3. Diesel exhaust (Opel 2.3D, 1974, cold run) <sup>a</sup>	42.2 mg particulates	21.8 mg	9430 µg	1560 µg	20	1.04	6.0	30 (21)	0.43	2500 µg	16	1.7
4. Diesel fuel (PEMEX)	25% solution	n.a.	n.a.	n.a.	19	0.96	2.4	19	1.33	n.d.	—	—
5. Lubricating oil (Castrol, SAE 10-50)	LC or TLC 75% = F1	n.a.	n.a.	n.a.	19	1.01	15.0	30	1.05	n.d.	16, 22	25.4
6. Smoke aerosol (brush fire, Los Padres, CA)	88	7600 µg/m <sup>3</sup>	2100 µg/m <sup>3</sup>	1500 µg/m <sup>3</sup>	29	10.0	0	—	n.d.	250 µg/m <sup>3</sup>	16, 24	14.7
7. Smoke aerosol (timber slash fire, OR)	370-1200	6-43 µg/m <sup>3</sup>	0.2-1.1 µg/m <sup>3</sup>	—	23, 25	1.2-5	0.3-3.3	23-27	n.d.	0.05-2.6 µg/m <sup>3</sup>	22, 24	5-8
8. Vegetation (epicuticular wax) (samples representative of temperate and tropical climates)	Composites of representative species	3000-6000 µg/g	150-900 µg/g	100-900 µg/g	29, 31	6.0-30	0-0.2	26	n.d.	200-400 µg/g	16, 24	7-20

n.a.—not applicable.

n.d.—none detectable.

<sup>a</sup>Sample of total particulate extract received from Dr. R. Gorse, Ford Motor Company.

<sup>b</sup>Retention index of maximum homolog or distribution at carbon number indicated.

<sup>c</sup>Carbon preference index, summed over total range (odd-to-even homologs for n-alkanes, even-to-odd homologs for fatty acids, Ref. 52).

<sup>d</sup>Unresolved to resolved components (Ref. 41).

TABLE II

Key fragment ions for mass spectrometric characterization of compound mixtures encountered in aerosols and vehicular emissions.

Compound class	Compound	Key fragment ion (m/z)	
Hydrocarbons	<i>n</i> -alkanes, $C_nH_{2n+2}$	57, 71, 85, 99 etc.	
	alkenes, $C_nH_{2n}$	55	
	alkylcyclohexanes $C_nH_{2n}$	83	
	isoprenoids (pristane, phytane)	183	
	PAH	search for molecular ions, $M^+$ (e.g. pyrene m/z 202, methylpyrene m/z 216, etc.)	
	extended tricyclic terpanes	191	
	cyclic diterpenoid	109, 159	
	triterpanes	191, 177 (for degraded series)	
	triterpenes	189, 191, 367	
	steranes, diasteranes	217, 218, 231, 259	
	aromatic diasteroids	253	
	Ketones	<i>n</i> -alkan-2-ones, $C_nH_{2n}O$	58, 59
		alkenones, $C_nH_{2n-2}O$	96
acyclic isoprenoid		58, 180 ( $C_{13}$ ), 250 ( $C_{18}$ )	
steroid		231, 245	
triterpenoid		175, 191, 205	
aromatic		$M^+$	
Acids (as methyl esters)	<i>n</i> -alkanoic, $C_nH_{2n}O_2$	74, 87	
	alkenoic, $C_nH_{2n-2}O_2$	55, 75, $M^+$	
	$\alpha,\omega$ -alkanedioic, $C_nH_{2n-2}O_4$	98	
	acyclic isoprenoid	74, 88, 101	
	cyclic diterpenoid	239	
	steroid	217	
	triterpenoid	191, 231, 367	
	aromatic—benzoic (alkyl)	105, 119, ...	
	—benzenedicarboxylic	163, 177, ...	
—naphthoic (alkyl)	155, 169, ...		
Alcohols (as trimethylsilyl ethers)	<i>n</i> -alkanols, $C_nH_{2n+2}O$	75, $M^+-15$	
	alkenols, $C_nH_{2n}O$	75, $M^+-15$	
	phytol	143	
	steroid	129, 215, 253, 255	
	triterpenoid	129, 191	
Miscellaneous	wax esters ( $R-CO_2-R'$ )	$M^+$	
	azaarenes	$M^+$	
	aromatic sulfur heterocyclics	$M^+$	
	contaminants—phthalates	149	
	—silicones	73	



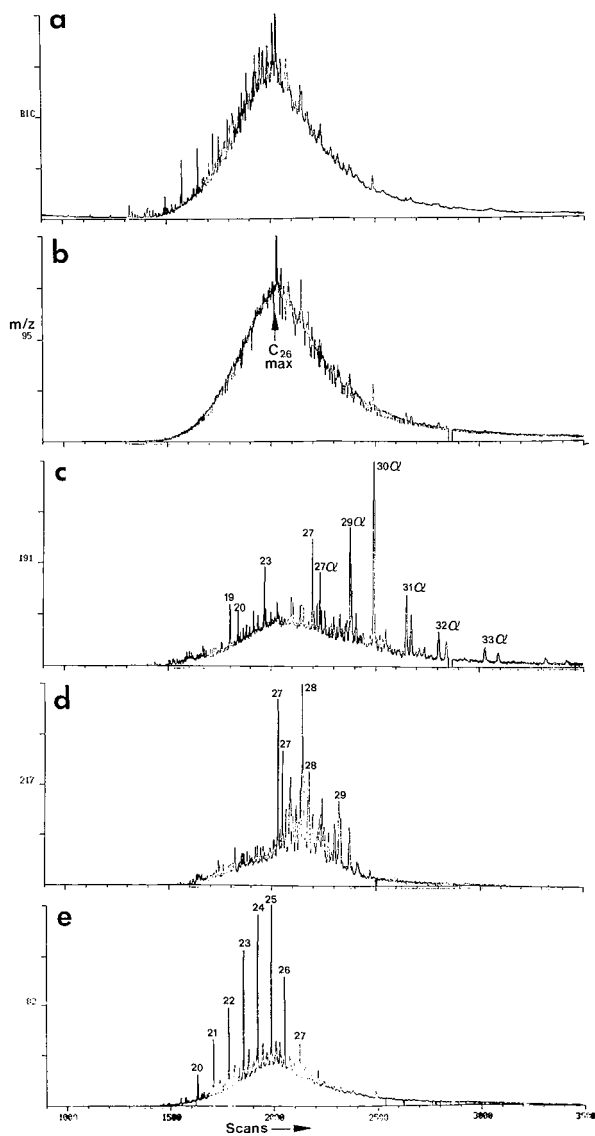


FIGURE 2 Salient features of the GC-MS data for a sample of automobile exhaust (total hydrocarbons):

- Total ion current trace (equivalent to capillary GC trace);
- $m/z$  95 mass chromatogram, indicator for naphthenes (i.e. hump);
- $m/z$  191 mass chromatogram, indicator for triterpanes and extended tricyclic terpanes (cf. Table III);
- $m/z$  217 mass chromatogram, indicator for steranes (cf. Table III);
- $m/z$  82 mass chromatogram, indicator for alkylcyclohexanes.

(The carbon numbers of the various compounds are indicated by the numerical labels.)

compounds elute. A comparison, where possible, of these mass spectra with those of authentic standards permits the assignment of specific structures, and in the case of unknowns, the interpretation of the mass spectrometric fragmentation pattern permits the assignment of at least the molecular weight (with empirical formula) or partial to full suggested structures. The relative GC retention time is also utilized for molecular assignment, especially for defining structural or stereoisomers. For example, the peak at scan number 2491 in the  $m/z$  191 mass chromatogram (Figure 2c) fits both the fragmentation pattern and GC retention time of  $17\alpha(\text{H})$ -hopane ( $\text{C}_{30}\text{H}_{52}$ ). The doublet at scan numbers 2651 and 2673 (Figure 2c) fits the fragmentation pattern of  $17\alpha(\text{H})$ -homohopane ( $\text{C}_{31}\text{H}_{54}$ ) and the GC retention time indicates the elution order of the 22S before the 22R stereoisomer. A detailed listing of the characteristic triterpenoids from petroleum is given in Table III and further data is published elsewhere.<sup>60</sup>

### Hydrocarbons

Auto exhaust (Figure 2a) 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. Homologous compounds can be plotted as histograms or distribution diagrams versus concentration (cf. Figures 3 and 4). (Here the distributions are plotted by point-to-point connection in order to clearly emphasize the carbon number predominances, also termed carbon preference index, CPI.<sup>8,32,52</sup> For normal hydrocarbons and ketones or aldehydes 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; for normal fatty acids and fatty alcohols it is the same ratio, only inverted to have even-to-odd homologs). Thus the *n*-alkanes of auto exhaust are plotted in Figure 3h, with a range from  $\text{C}_{15}$ – $\text{C}_{27}$  and maximum at  $\text{C}_{21}$  (CPI=0.93). This can be compared with the distributions of *n*-alkanes in petroleum (Figure 3d), diesel fuel (Figure 3e) and lubricating oil used in the test vehicle (Figure 3i). The lubricating oil is the most likely source of the hydrocarbons in auto exhaust.<sup>58,59</sup> On the other hand, diesel exhaust does contain some uncombusted fuel components. Essenti-

TABLE III

Triterpenoidal and steroidal hydrocarbons commonly found in petroleum and some of its products.

Compound <sup>a</sup>	Composition	Molecular weight	Figure citation or chemical structure
Extended tricyclic terpanes	C <sub>19</sub> H <sub>34</sub> to C <sub>30</sub> H <sub>56</sub>	262 to 416	2c-19,20,23(III)
<b>Triterpanes</b> (cf. Figure 2c)			
22,29,30-trisnorneohopane	C <sub>27</sub> H <sub>46</sub>	370	27neo(IV)
17 $\alpha$ (H)-22,29,30-trisnorhopane	C <sub>27</sub> H <sub>46</sub>	370	27 $\alpha$ (II,R=H)
17 $\alpha$ (H),18 $\alpha$ (H),21 $\beta$ (H)-28,30-bisnorhopane	C <sub>28</sub> H <sub>48</sub>	384	(VI)
17 $\alpha$ (H)-29-norhopane	C <sub>29</sub> H <sub>50</sub>	398	29 $\alpha$ (II,R=C <sub>2</sub> H <sub>5</sub> )
17 $\alpha$ (H),21 $\beta$ (H)-hopane	C <sub>30</sub> H <sub>52</sub>	412	30 $\alpha$ (II,R=C <sub>3</sub> H <sub>7</sub> )
22S-17 $\alpha$ (H),21 $\beta$ (H)-homohopane	C <sub>31</sub> H <sub>54</sub>	426	31 $\alpha$ (V,R=H)
22R-17 $\alpha$ (H),21 $\beta$ (H)-homohopane	C <sub>31</sub> H <sub>54</sub>	426	31 $\alpha$ (V,R=H)
22S-17 $\alpha$ (H),21 $\beta$ (H)-bishomohopane	C <sub>32</sub> H <sub>56</sub>	440	32 $\alpha$ (V,R=CH <sub>3</sub> )
22R-17 $\alpha$ (H),21 $\beta$ (H)-bishomohopane	C <sub>32</sub> H <sub>56</sub>	440	32 $\alpha$ (V,R=CH <sub>3</sub> )
22S-17 $\alpha$ (H),21 $\beta$ (H)-trishomohopane	C <sub>33</sub> H <sub>58</sub>	454	33 $\alpha$ (V,R=C <sub>2</sub> H <sub>5</sub> )
22R-17 $\alpha$ (H),21 $\beta$ (H)-trishomohopane	C <sub>33</sub> H <sub>58</sub>	454	33 $\alpha$ (V,R=C <sub>2</sub> H <sub>5</sub> )
22S-17 $\alpha$ (H),21 $\beta$ (H)-tetrakishomohopane	C <sub>34</sub> H <sub>60</sub>	468	34 $\alpha$ (V,R=C <sub>3</sub> H <sub>7</sub> )
22R-17 $\alpha$ (H),21 $\beta$ (H)-tetrakishomohopane	C <sub>34</sub> H <sub>60</sub>	468	34 $\alpha$ (V,R=C <sub>3</sub> H <sub>7</sub> )
22S-17 $\alpha$ (H),21 $\beta$ (H)-pentakishomohopane	C <sub>35</sub> H <sub>62</sub>	482	(V,R=C <sub>4</sub> H <sub>9</sub> )
22R-17 $\alpha$ (H),21 $\beta$ (H)-pentakishomohopane	C <sub>35</sub> H <sub>62</sub>	482	(V,R=C <sub>4</sub> H <sub>9</sub> )
<b>Steranes and diasteranes</b> (cf. Figure 6)			
20S-13 $\beta$ (H),17 $\alpha$ (H)-diacholestane	C <sub>27</sub> H <sub>48</sub>	372	1 (IX,R=H)
20R-13 $\beta$ (H),17 $\alpha$ (H)-diacholestane	C <sub>27</sub> H <sub>48</sub>	372	2 (IX,R=H)
20S-13 $\alpha$ (H),17 $\beta$ (H)-diacholestane	C <sub>27</sub> H <sub>48</sub>	372	3 (IX,R=H)
20S-13 $\beta$ (H),17 $\alpha$ (H)-diaergostane	C <sub>28</sub> H <sub>50</sub>	386	4 (IX,R=CH <sub>3</sub> )
20R-13 $\alpha$ (H),17 $\beta$ (H)-diacholestane	C <sub>27</sub> H <sub>48</sub>	372	5 (IX,R=H)
20R-13 $\beta$ (H),17 $\alpha$ (H)-diaergostane	C <sub>28</sub> H <sub>50</sub>	386	6 (IX,R=CH <sub>3</sub> )
20S-13 $\beta$ (H),17 $\alpha$ (H)-diasitostane	C <sub>29</sub> H <sub>52</sub>	400	7 (IX,R=C <sub>2</sub> H <sub>5</sub> )
20S-13 $\alpha$ (H),17 $\beta$ (H)-diaergostane	C <sub>28</sub> H <sub>50</sub>	386	8 (IX,R=CH <sub>3</sub> )
20S-5 $\alpha$ (H),14 $\alpha$ (H)-cholestane	C <sub>27</sub> H <sub>48</sub>	372	9 (VII,R=H)
20R-5 $\alpha$ (H),14 $\alpha$ (H),17 $\alpha$ (H)-cholestane	C <sub>27</sub> H <sub>48</sub>	372	10 (VII,R=H)
20S-5 $\alpha$ (H),14 $\beta$ (H),17 $\beta$ (H)-cholestane	C <sub>27</sub> H <sub>48</sub>	372	11 (VIII,R=H)
20R-5 $\alpha$ (H),14 $\beta$ (H),17 $\beta$ (H)-cholestane	C <sub>27</sub> H <sub>48</sub>	372	12 (VIII,R=H)
20S-13 $\alpha$ (H),17 $\beta$ (H)-diasitostane	C <sub>29</sub> H <sub>52</sub>	400	13 (IX,R=C <sub>2</sub> H <sub>5</sub> )
20S-5 $\alpha$ (H),14 $\alpha$ (H),17 $\alpha$ (H)-ergostane	C <sub>28</sub> H <sub>50</sub>	386	14 (VII,R=CH <sub>3</sub> )
20R-13 $\alpha$ (H),17 $\beta$ (H)-diasitostane	C <sub>29</sub> H <sub>52</sub>	400	15 (IX,R=C <sub>2</sub> H <sub>5</sub> )
C <sub>28</sub> sterane	C <sub>28</sub> H <sub>50</sub>	386	16 —
C <sub>27</sub> sterane	C <sub>27</sub> H <sub>48</sub>	372	17 —
20S-5 $\alpha$ (H),14 $\beta$ (H),17 $\beta$ (H)-ergostane	C <sub>28</sub> H <sub>50</sub>	386	18 (VIII,R=CH <sub>3</sub> )
20R-5 $\alpha$ (H),14 $\beta$ (H),17 $\beta$ (H)-ergostane	C <sub>28</sub> H <sub>50</sub>	386	19 (VIII,R=CH <sub>3</sub> )
20R-5 $\alpha$ (H),14 $\alpha$ (H),17 $\alpha$ (H)-ergostane	C <sub>28</sub> H <sub>50</sub>	386	20 (VII,R=CH <sub>3</sub> )
20S-5 $\alpha$ (H),14 $\alpha$ (H),17 $\alpha$ (H)-sitostane	C <sub>29</sub> H <sub>52</sub>	400	21 (VII,R=C <sub>2</sub> H <sub>5</sub> )
20S-5 $\alpha$ (H),14 $\beta$ (H),17 $\beta$ (H)-sitostane	C <sub>29</sub> H <sub>52</sub>	400	22 (VIII,R=C <sub>2</sub> H <sub>5</sub> )
20R-5 $\alpha$ (H),14 $\beta$ (H),17 $\beta$ (H)-sitostane	C <sub>29</sub> H <sub>52</sub>	400	23 (VIII,R=C <sub>2</sub> H <sub>5</sub> )
20R-5 $\alpha$ (H),14 $\alpha$ (H),17 $\alpha$ (H)-sitostane	C <sub>29</sub> H <sub>52</sub>	400	24 (VII,R=C <sub>2</sub> H <sub>5</sub> )

<sup>a</sup>Listed in order of GC elution.

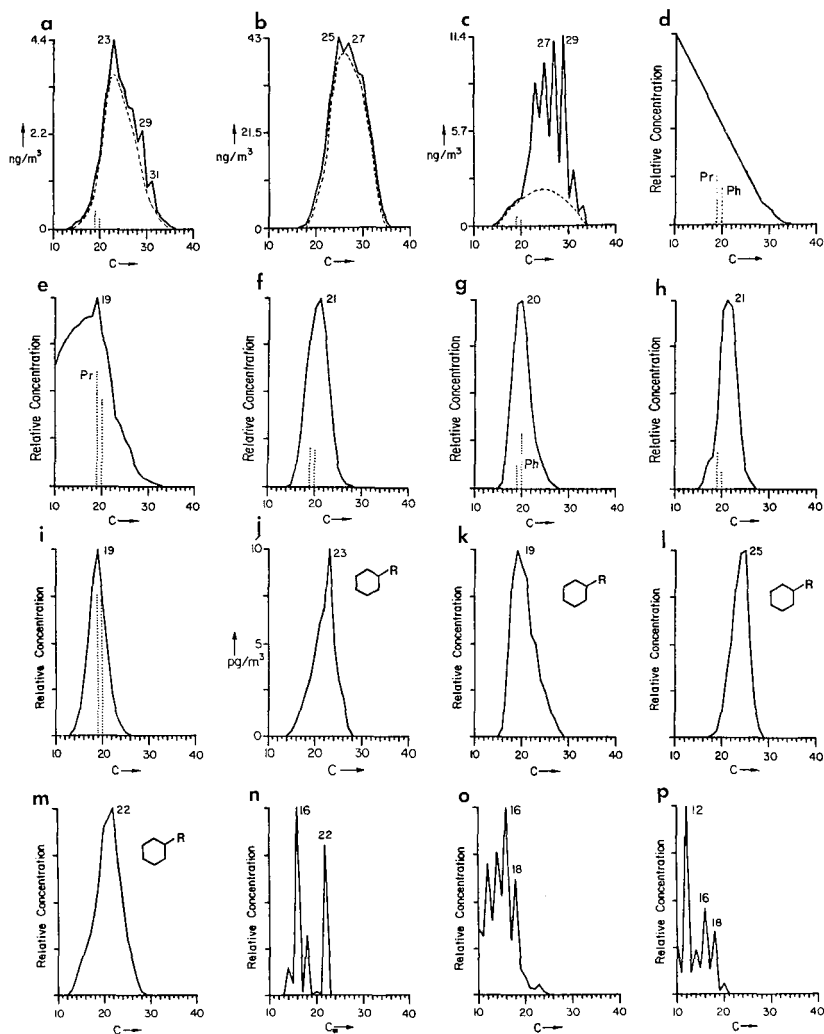


FIGURE 3 Distribution diagrams (concentration versus carbon number) for *n*-alkanes (a-i) (height of dotted lines indicates isoprenoid hydrocarbon concentration, envelope under dashed line indicates contribution from petroleum residues), for alkylcyclohexanes (j-m), and for *n*-carboxylic acids (n-p):

- a) Aerosol, Sugarpine Point State Park, Lake Tahoe, CA, winter;
- b) Los Angeles (date plotted from reference 23), dashed line—inferred petroleum components;
- c) Aerosol, Sugarpine Point State Park, Lake Tahoe, CA, summer, daytime;
- d) Typical crude petroleum;
- e) Diesel fuel (PEMEX);
- f) Diesel engine exhaust (International CO 1600 truck);
- g, k, o) Diesel engine exhaust (Opel 2.3D auto);
- h, l, p) Automobile engine exhaust (Mercedes 280SE);
- i, m, n) Lubricating oil (Castrol);
- j) Aerosol, Sierra Ski Ranch, Lake Tahoe area.

ally all the *n*-alkanes present (Figures 3*f* and *g*)<sup>58,59</sup> are derived from the fuel and the second higher weight naphthenic hump, with the associated triterpenoidal molecular markers, originates from engine lubricants.

For comparison purposes the data for some examples of aerosols contaminated by petroleum residues are also shown (Figure 3*a-c*). Both the *n*-alkane distributions and the hump observed for the aerosols correlate with vehicular emissions.<sup>54,58,59</sup> Thus, the Lake Tahoe air basin is contaminated to varying degrees by petroleum components (greatest in winter and least during summer nights, Figure 3*a,c*) and this contamination is even greater in the Los Angeles air basin (Figure 3*b*).<sup>23</sup> The natural plant wax component is superimposed on and greatly diluted by the petroleum-derived *n*-alkanes (cf. Figure 3*c*).<sup>54,58,59,65</sup>

Some examples of normal alkane, alkanolic acid and alkanol distributions from typical uncontaminated rural aerosols and from plant waxes are shown in Figure 4*a-h*.<sup>6,64,65</sup> All these distributions exhibit very strong carbon number predominances, i.e. the CPI values are high (cf. Table I). Thermal stress on these compound classes results in: (1) loss or reduction of carbon number predominance (CPI decrease); (2) decarboxylation or partial oxidation; (3) dehydration or partial oxidation of especially alcohols; and (4) in the presence of excess oxygen and high temperature (>450°C) complete combustion to CO<sub>2</sub> and H<sub>2</sub>O. Thermal stress due to incomplete combustion is observable in smoke aerosols as described for the following examples. The first is from a brush fire (chaparral, Los Padres National Forest, CA), which is a relatively low temperature process as indicated by the unaltered *n*-alkane signature (Figure 4*i*) in the smoke, comparable to typical plant wax (e.g. Figure 4*d*). This is a case of essentially direct volatilization into the smoke aerosol of the wax alkanes at the advancing fire front.<sup>59</sup> The second case is from hotter fires, as for example conifer slash burning (Figure 4*m-p*), where the products from incomplete combustion are altered and do not necessarily reflect the original plant wax distribution (cf. Figure 4*d, f*). This thermal alteration also appears to be time and temperature dependent. Freshly emitted smoke still has some carbon number predominance (CPI=2), but overnight equilibration results in essentially complete loss of this predominance (CPI=1) (cf. Figure 4*m* versus *n*). Thus smoke aerosols are a

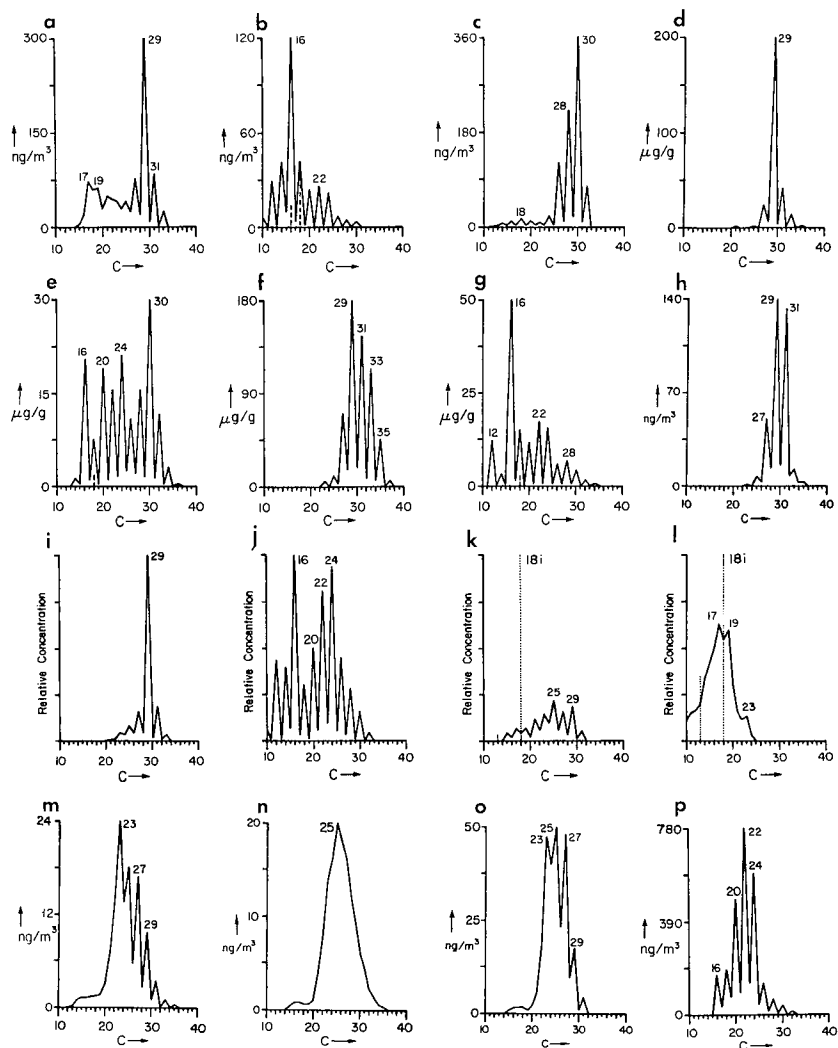


FIGURE 4 Distribution diagrams (concentration versus carbon number) for *n*-alkanes (*a*, *d*, *f*, *h*, *i*, *m*-*o*), for *n*-carboxylic acids (*b*, *e*, *g*, *j*, *p*) (height of dashed lines indicates unsaturated acids), for *n*-alkan-2-ones (height of dotted lines indicates isoprenoidal ketones) (*k* and *l*), and for *n*-alkanols (*c*):

- a*, *b*, *c*) Harmattan aerosol, Jos, Nigeria, upwind (sample 17, Ref. 9);
- d*, *e*) Compositated vegetation wax, Nigeria (Ref. 41);
- f*, *g*) Compositated vegetation wax, Carlsbad, NM (Ref. 41);
- h*) Aerosol, Corvallis, OR (Ref. 65);
- i*, *j*, *k*) Brush fire, Los Padres National Forest, CA;
- l*) Diesel engine exhaust (Opel 2.3D auto);
- m*) Conifer slash burn, OR (fresh smoke);
- n*) Conifer slash burn, OR (overnight smoke);
- o*, *p*) Conifer slash burn, OR (fresh smoke).

significant injection mechanism for organic compounds to the troposphere and varying levels of the biogenic homolog distributions may be preserved depending on the combustion temperature and residence time. Further analyses of ambient smoke aerosols are necessary to provide more detailed characterizations of compound signatures.

### Unresolvable complex mixture (hump)

The major hydrocarbon components of both auto and diesel exhausts are an unresolvable mixture by gas chromatography. This envelope of unresolved complex hydrocarbons (branched and cyclic—the hump) (e.g.  $m/z$  95, an ion typical in mass spectra of naphthenic hydrocarbon mixtures, in Figure 2b) when present in the GC traces can be expressed as a ratio of unresolved branched and cyclic hydrocarbons (hump) to the resolved *n*-alkanes (i.e. U:R).<sup>41</sup> This can then be used as an approximate measure of the level of contamination by petroleum residues.<sup>58,59,62</sup> Values of 1–30 have been observed for aerosols contaminated with petroleum residues, whereas natural hydrocarbons derived from higher vascular plants exhibit no hump,<sup>64,65</sup> and this ratio is  $<1.0$  for aerosols over remote or oceanic areas.<sup>51</sup> The hump: *n*-alkane ratios (U:R)<sup>41</sup> are determined from GC by the area of unresolved material above background (measured by planimetry or integration) divided by the sum of the GC area of resolved *n*-alkanes and other major components.

Most petroleums contain branched and cyclic (naphthenic) hydrocarbons ranging from  $C_{12}$  to about  $C_{35}$ , with various retention time maxima (usually at  $C_{22}$  and  $C_{26}$ ).<sup>26,70</sup> The refining process to fuels and lubricants consists of distillation, cracking and reforming of the feed stock, yielding the products as compound mixtures with discrete boiling ranges. Thus gasoline does not contain the heavy ends of petroleum and diesel fuel has a cut-off at about  $C_{25}$ , which also excludes the steroidal and triterpenoidal markers. Lubricating oil derived from petroleum consists primarily of naphthenes (hump), with a minor *n*-alkane content ( $<C_{25}$ , cf. Figure 3i) and traces of the heavy molecular markers (steranes and triterpanes). Typical boiling ranges have maxima at about carbon number 30, but this varies over a range according to the viscosity of the oil. Various synthetic and

natural additives are present in lubricating fluids to enhance physical properties (e.g. trace amounts of *n*-fatty acids, cf. Figure 3*n*, to increase detergent action). Naphthenic hydrocarbons (hump) are, however, not present in vascular plant waxes.

### Molecular markers

Molecular markers are indicator compounds that can be utilized in reconciliations of genetic sources of organic matter.<sup>52, 55-59</sup> Such molecules have specific chemical structures which can be related either directly or indirectly via a set of diagenetic changes to their unique source. These sources may be biogenic, geogenic or anthropogenic (i.e. synthetic).<sup>52</sup> The molecular markers of utility for fingerprinting petroleum residues are detailed below and summarized in Tables II and III. These hydrocarbon marker compounds are not present in most biogenic detritus (e.g. plant wax), but these skeletal structures do occur there as functionalized molecules (e.g. phytosterols).<sup>67</sup>

Pristane (2,6,10,14-tetramethylpentadecane, Pr) and phytane (2,6,10,14-tetramethylhexadecane, Ph) are diagenetic products of phytol and are not primary constituents of most terrestrial biota.<sup>11, 37</sup> The presence of these isoprenoidal markers in hydrocarbon fractions (cf. Figure 3), coupled with the naphthene hydrocarbons (hump), confirms an origin from petroleum, since they are not separated by refining processes. Pristane and phytane are present in ambient aerosols, exhaust from auto and diesel engines, in diesel fuel and in lubricating oil.

A homologous series of alkylcyclohexanes (Structure I, all chemical structures cited are given in the Appendix),  $C_nH_{2n}$ , ranging from  $n=16-29$ , with no carbon number preference and usually a maximum at  $C_{23}$  has been found in aerosols from contaminated areas (e.g. Lake Tahoe basin, Figure 3*j*).<sup>58, 59</sup> These compounds are not present in lipids of recent biogenic origin but are common in petroleum and its distillation products (e.g. diesel fuel and lubricating oil, cf. Figure 3*m*). Alkylcyclohexanes are major resolved components of auto exhaust (e.g. Figure 3*l*), however, they are only trace constituents in diesel exhausts (e.g. Figure 3*k*).

The triterpenoid hydrocarbons characteristic of petroleum are the geologically mature (usually millions of years) and stable isomers of



the  $17\alpha(\text{H})$ -hopane series (Structure II), originally derived from biogenic precursors with the  $17\beta(\text{H})$  configuration via various diagenetic and catagenetic pathways.<sup>10,15,38,47-49,55-58,60,62</sup> The identifications of these compounds are based primarily on their mass spectra and gas chromatographic retention times.<sup>60</sup> Their occurrence is usually at low concentrations, but their overall distribution signatures within samples can be easily determined by GC-MS and utilized for comparison purposes. This is based on the  $m/z$  191 ion intensity in the GC-MS data, which is the base peak of most of the triterpanes and also the extended tricyclic terpanes (Structure III).

An example of the  $m/z$  191 data is found in Figure 2c for auto exhaust. The predominant analog is  $17\alpha(\text{H})$ -hopane (Structure II,  $\text{R} = i\text{-C}_3\text{H}_7$ ), with subordinate amounts of  $17\alpha(\text{H})$ -22,29,30-trisnorhopane (Structure II,  $\text{R} = \text{H}$ ), trisnorneohopane (Structure IV),  $17\alpha(\text{H})$ -29-norhopane (Structure II,  $\text{R} = \text{C}_2\text{H}_5$ ), and extended homologs of the  $17\alpha(\text{H})$ -hopane series (Structure II,  $\text{R} = \text{C}_4\text{H}_9\text{-C}_8\text{H}_{17}$ ). The extended  $17\alpha(\text{H})$ -hopane homologs from  $\text{C}_{31}$  to  $\text{C}_{35}$  (homolog series) are found as the C-22 diastereomers (Structure V) with a 22S to 22R ratio of 1.0 to 1.3, which also indicates geological maturity.<sup>10,15,52,54-57,60</sup> The distribution patterns of the  $m/z$  191 GC-MS data can be represented as bar graphs to facilitate pattern comparisons (Figure 5). The distributions of the  $17\alpha(\text{H})$ -hopanes are essentially identical for auto exhaust (Figure 5a) and for diesel exhausts (Figure 5b and c), confirming these emissions as the major source of petroleum residues in aerosols. Gasoline and diesel fuel do not contain these triterpanes, but the same distribution is found in lubricating oil (cf. Figure 5d). This indicates that primarily lubricants adsorbed on particulates or as vapor microdroplets impart the molecular indicator signature of petroleum residues to vehicular emissions.<sup>58,59</sup>

These triterpane patterns can be compared with those of various examples of aerosols from the Lake Tahoe and Los Angeles air basins (Figure 5e-g), which contain an additional compound not found in the other areas studied, namely  $17\alpha(\text{H}),18\alpha(\text{H}),21\beta(\text{H})$ -28,30-bisnorhopane (Structure VI).<sup>66</sup> This compound is found in many California crude oils and has been characterized in shales and natural seeps from the same area.<sup>47,62</sup> Such additional markers within a compound class may prove useful as tags for specific

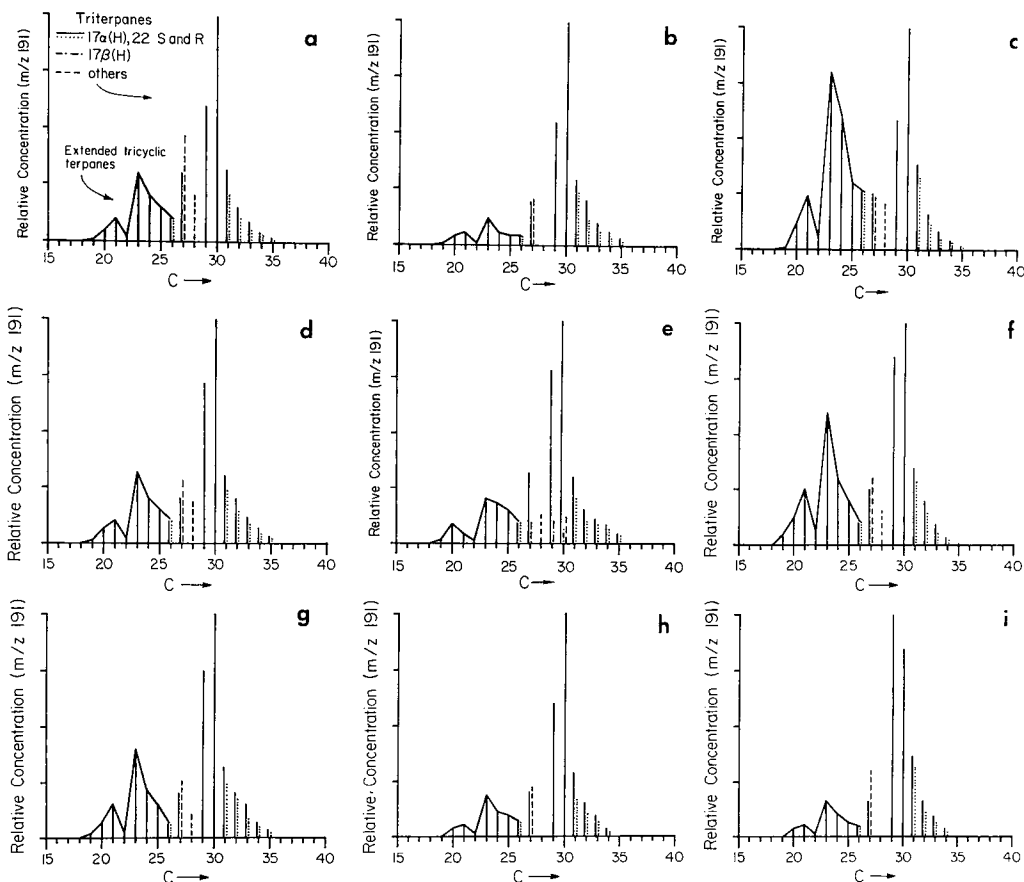


FIGURE 5 Relative distribution histograms for triterpanes and extended tricyclic terpanes (based on the  $m/z$  191 mass chromatograms or gas chromatographic response) of some aerosol and source examples (— extended tricyclic terpanes, III and  $17\alpha(H)$ -hopane series, II; ..... pairs of C-22 S and R diastereomers; ---- trisnorhopane, IV— $C_{27}H_{46}$  and  $17\alpha(H), 18\alpha(H), 21\beta(H)$ -28,30-bisnorhopane, VI— $C_{28}H_{48}$ );

- Automobile engine exhaust (Mercedes 280SE);
- Diesel engine exhaust (Opel 2.3D auto);
- Diesel engine exhaust (International CO 1600 truck);
- Lubricating oil (Castrol);
- Aerosol, Sugarpine Point State Park, Lake Tahoe area, winter;
- Aerosol, Canoga Park, Los Angeles area;
- Aerosol, Pasadena, Los Angeles area;
- Aerosol, D and D Ranch, Mt. Lassen area, winter;
- Aerosol, urban Ibadan, Nigeria.

aerosol parcels in tracing their transit. The triterpanes and extended tricyclic terpanes in aerosols from the Los Angeles area match each other closely (cf. Figure 5*f* versus *g*), but differ from those in samples of the Mt. Lassen area (Figure 5*h*) primarily by the absence of the 28,30-bisnorhopane. The varying differences of the total amounts of extended tricyclic terpanes to triterpanes may be due to the effect of ambient temperature on the collection efficiency of the more volatile compounds. Contaminated aerosols of Nigeria have a different triterpenoid distribution (Figure 5*i*), where 17 $\alpha$ (H)-29-norhopane (Structure II, R=C<sub>2</sub>H<sub>5</sub>) predominates over 17 $\alpha$ (H)-hopane and the C<sub>28</sub> analog is not detectable. It should be pointed out that triterpenoidal hydrocarbons (e.g., diploptene, 17 $\beta$ (H)-hopanes) from primary biogenic sources (e.g. microbes) have not been detected in vehicular exhaust and aerosol samples.

The extended tricyclic terpanes (Structure III) are found in vehicular emissions, diesel fuel, and lubricating oil and can be present in aerosols (Figure 5). They are associated with the 17 $\alpha$ (H)-hopanes and are also derived from petroleum. They have a slightly lower boiling range and are therefore prevalent in samples that retain significant amounts of material <C<sub>25</sub>.

Steranes (Structures VII and VIII) and diasteranes (Structure IX) are additional molecular markers commonly found in petroleum that can be used for source correlations and apportionment. These hydrocarbons are not present in contemporary biogenic materials. The diagenesis of steroids occurs via many routes and results in numerous products and isomers.<sup>39</sup> However, the distribution signature in GC-MS data of for example the *m/z* 217 (Figures 2*d* and 6*a*) and *m/z* 218 (Figure 6*b*) ion peaks for steranes or *m/z* 259 for diasteranes and *m/z* 253 for monoaromatic diasteroid hydrocarbons are useful supporting evidence for a petroleum component.<sup>47,48</sup> The chemical structures of the steranes and diasteranes present in petroleum are listed in Table III according to their elution order in a typical GC-MS analysis (Figure 6). These compounds are found in lubricants of vehicular engines but not in gasoline or diesel fuel. They are therefore introduced into the atmosphere from vehicular emissions.

### Polynuclear aromatic hydrocarbons (PAH)

Polynuclear or polycyclic aromatic hydrocarbons (PAH) are ubiquitous in the environment and in vehicular emissions. They have

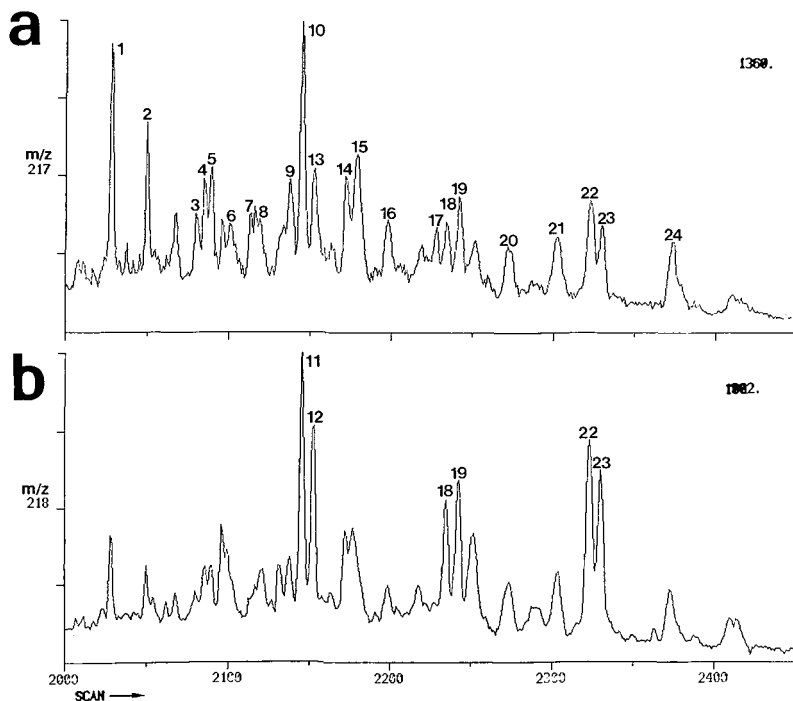


FIGURE 6 Mass chromatograms for steranes and diasteranes typical of petroleum (numbers refer to compounds in Table III):

- a)  $m/z$  217;
- b)  $m/z$  218.

been extensively analyzed in environmental sinks and their sources were found to be primarily from combustion processes.<sup>18, 19, 24, 25, 33, 68, 74-76</sup> The presence of PAH mixtures in combustion emissions and smokes from vegetative and fossil fuel materials has been amply demonstrated.<sup>6, 20, 22, 29, 30, 34-36, 43, 69, 71</sup>

PAH are present in aerosol samples and concentration ranges observed for the major compounds have been summarized.<sup>43, 58</sup> The PAH distributions in aerosol samples from the Lake Tahoe air basin and the Mt. Lassen area, both during the winter, are very similar, and their concentrations are higher in these areas than in the samples from the Los Angeles air basin. The highest levels of PAH were observed from aerosols from urban areas of Nigeria (e.g.

Ibadan and Jos). Combustion of wood and fossil fuel was evident in all the areas with elevated PAH concentrations. The PAH mixtures are composed of primarily the unsubstituted ring systems, ranging from phenanthrene to dibenzanthracene, and the dominant analogs are fluoranthene, pyrene, benzanthracene and benzofluoranthene.<sup>58</sup> The presence of five-membered alicyclic ring compounds (e.g. fluorene, fluoranthene) with the pericondensed PAH is a characteristic for a high temperature origin of these hydrocarbons.<sup>2, 3, 46</sup> The distributions are comparable with similar data for ambient forest and brush fire smoke aerosols, indicating a possible origin from wood smoke, which is further supported by the presence of retene in the aerosols from the western United States.<sup>65</sup> Retene has been shown to be an enhanced product from wood combustion (especially coniferous vegetation).<sup>44</sup>

The PAH content of vehicular emissions is significant, especially for diesel engines.<sup>1, 43, 71, 77</sup> However, the distributions of the PAH and their alkyl-substituted homologs reflect an origin from petroleum. Pericondensed PAH by far exceed the concentrations of the five-membered alicyclic ring compounds and the alkyl-substituted PAH homologs are present in highest amounts. This is illustrated with the GC-MS data of auto exhaust for the phenanthrene series (Figure 7), where only phenanthrene is present (no anthracene) in the  $m/z$  178 plot and the various homolog isomers with additional one-to-three carbon substituents occur at greater relative concentrations in the other mass chromatograms. The presence of anthracene has been demonstrated as about 20–25% of phenanthrene in auto exhaust.<sup>21</sup> It should be pointed out that hi-vol filtration of uncooled vehicular exhausts collects only the phenanthrene series adsorbed on particulates with potentially a considerable blow-off effect. Thus the filtrate may represent a somewhat biased PAH-distribution, with less phenanthrene/anthracene than present in the exhausts. Nevertheless, the general trend of homologous substitution can be represented versus concentration as in Figure 8. Both auto and diesel exhaust exhibit a similar pattern of low amounts of phenanthrene and maximum  $C_1$ - or  $C_2$ -phenanthrenes, whereas petroleum has an essentially linear concentration increase to higher homologs (Figure 8). Therefore, the distributions of phenanthrenes in vehicular exhausts reflect partial reforming of petroleum compounds at relatively lower temperatures. On the other hand, this distribution for smoke

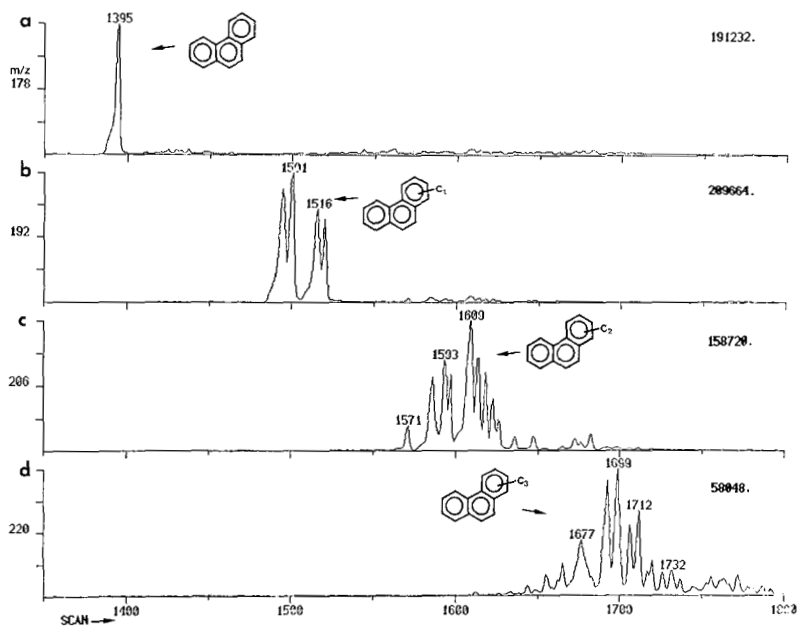


FIGURE 7 Salient features of the GC-MS data for alkylphenanthrenes in diesel engine exhaust:

- $m/z$  178, unsubstituted;
- $m/z$  192,  $C_1$ -substitution;
- $m/z$  206,  $C_2$ -substitution;
- $m/z$  220,  $C_3$ -substitution.

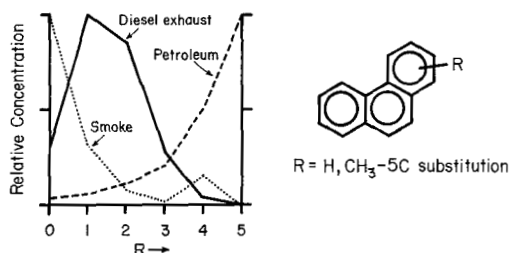


FIGURE 8 Alkyl homolog distribution plot for the phenanthrene-type series ( $C_nH_{2n-18}$ ) in typical crude petroleum (---), diesel engine exhaust (—), and wood smoke (····). The relative abundance of the major homolog in each sample was normalized to 100.

aerosols (e.g. Figure 8) drops exponentially from phenanthrene to the C<sub>3</sub> homolog and in some cases there is a slight maximum at the C<sub>4</sub> homolog due to the presence of retene.<sup>37</sup> PAH are not detectable in primary detritus from vegetation (e.g. plant wax).

### Oxygenated compounds

Both auto and diesel exhaust contain *n*-carboxylic acids, ranging from less than C<sub>10</sub> to C<sub>24</sub>, with maxima at C<sub>16</sub> and C<sub>12</sub> and CPI values of 1.4 to 4 (Table I). Examples of carboxylic acid distributions are shown in Figure 3*o* and *p* and also in the GC-MS data of Figure 9*b*. The acid distribution for auto exhaust does not match the carboxylic acid additive distribution of the lubricating oil (Figure 3*n* versus *p*), indicating further formation during combustion. This is also the case for the acids in diesel exhaust. The relatively strong carbon number predominance in the case of these combustive emissions should be noted and it may reflect preferential carbon-carbon bond cleavage biased to <sup>13</sup>C-<sup>12</sup>C > <sup>12</sup>C-<sup>12</sup>C from the original biosynthetic imprint. Further samples need to be analyzed to evaluate the CPI ranges and distribution patterns, so that a correction can be applied to the naturally-derived *n*-carboxylic acids (e.g. from plant wax, Figure 4*b*, *e* and *g*).<sup>64,65</sup>  $\alpha,\omega$ -Dicarboxylic acids are not detectable as significant components in auto exhaust and they occur as trace components in diesel exhaust. Unsaturated fatty acids (e.g. 18:1) are not detectable in vehicular exhaust.

Ketones and to a lesser extent aldehydes are the other oxygenated homologous series present as major components in vehicular exhaust. Diesel emissions contain higher concentrations than automobile and these compounds reflect partial combustion residues from the fuel hydrocarbons, since they are not detectable in lubricants. Both *n*-alkan-2-ones (e.g. Figure 4*l* and GC-MS data in Figure 9*c*) and *n*-alkan-1-ones (aldehydes) range from <C<sub>10</sub> to C<sub>24</sub>, with maxima at C<sub>17</sub> or C<sub>19</sub> and essentially no carbon number predominance. The presence of isoprenoidal ketones, namely 6,10,14-trimethylpentadecan-2-one (X) and lesser amounts of 6,10-dimethylundecan-2-one, further supports the partial combustion of hydrocarbon biomarkers, in this case pristane and phytane.

Normal carboxylic acids, ketones and aldehydes are also major components of various smoke aerosols (e.g. Figure 4*j*, *k* and *p*) and

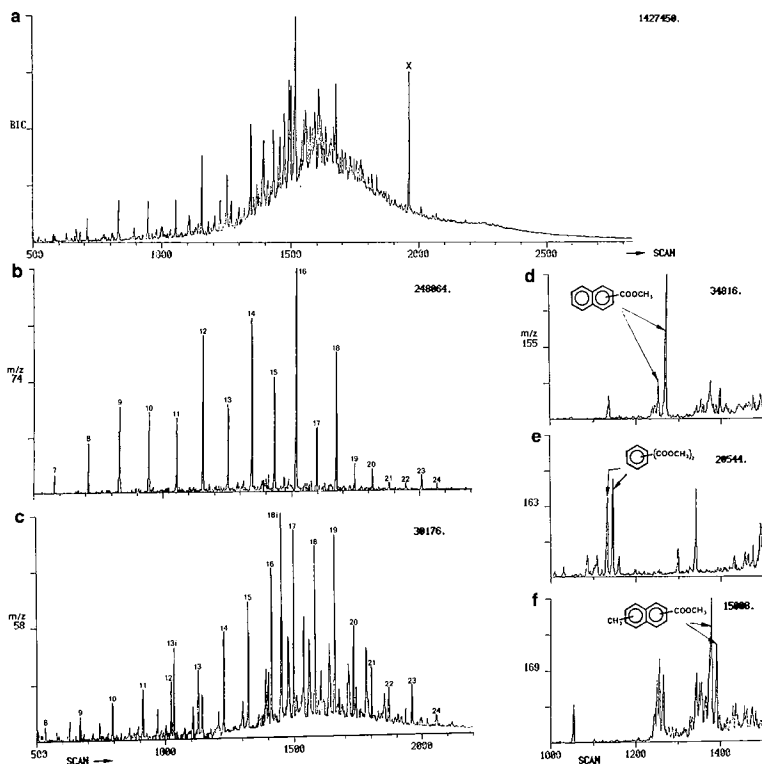


FIGURE 9 Salient features of the GC-MS data for the total carboxylic acid (as methyl esters) and ketone fraction from diesel engine exhaust (Opel 2.3D auto) (the homologous carbon chain lengths are indicated by the numerals):

- Total ion current trace (peak labeled X is a dioctyl phthalate plasticizer contaminant);
- m/z 74 mass chromatogram, indicator for *n*-carboxylic acids (as methyl esters);
- m/z 58 mass chromatogram indicator for *n*-alkan-2-ones, isoprenoidal ketones (13i and 18i) and alkan-1-ones (i.e. aldehydes, lesser peaks adjacent to the alkan-2-ones);
- m/z 155 mass chromatogram, indicator for naphthoic acids (XI);
- m/z 163 mass chromatogram, indicator for benzenedioic acids (XII);
- m/z 169 mass chromatogram, indicator for methylnaphthoic acids (XI).



reflect the admixture of major partial thermal combustion products with minor volatilized primary wax components. Low temperature smoke (brush fire) exhibits the full range ( $C_{10}$ – $C_{32}$ ) of homologs, whereas higher temperature smoke exhibits homologs skewed to the lower molecular weight range (Figure 4j versus p). Unsaturated carboxylic acids from primary biological detritus (e.g. lipids, wax, etc.) are not detectable in smoke aerosols and  $\alpha,\omega$ -dicarboxylic acids are present in minor amounts ranging from  $>C_8$  to  $C_{12}$ . The source of the unsaturated carboxylic acids in aerosols<sup>65</sup> appears to be direct injection from biogenic detritus. The  $\alpha,\omega$ -dicarboxylic acids identified in aerosols,<sup>65</sup> seem to be derived from combustive processes using either fossil or biomass fuels.

### Molecular markers

Only isoprenoidal ketones are detectable in vehicular exhausts as oxygenated molecular markers derived from the petroleum biomarkers discussed in the hydrocarbon section. All other molecular markers from vehicular exhaust are extensively degraded or reformed compounds, where a precursor is not easily assigned. Nevertheless, some of these compounds appear to be unique and characteristic for vehicular emissions. Major aromatic acid series and lesser amounts of aromatic ketones, aldehydes and quinones are present in diesel exhaust. The following homologous series are found in order of decreasing concentration: (1) alkylbenzoic acids,  $C_nH_{2n-8}O_2$  for  $n=7-9$ ; (2) alkylnaphthoic acids, XI,  $C_nH_{2n-14}O_2$  for  $n=11-13$  (cf. Figure 9d and f); (3) alkylbenzenedioic acids, XII,  $C_nH_{2n-10}O_4$  for  $n=8-10$  (cf. Figure 9e); (4) alkylphenanthroic acids, XIII,  $C_nH_{2n-20}O_2$  for  $n=15-17$ ; and (5) various minor aromatic ketones, aldehydes and quinones (major component—fluorenone). The same aromatic ketones, aldehydes and quinones have been identified by other workers in diesel exhaust.<sup>1,7,77</sup>

Automobile exhaust contains primarily alkylbenzoic acids,  $C_nH_{2n-8}O_2$  for  $n=7-9$ , alkylbenzenedioic acids,  $C_nH_{2n-10}O_4$  for  $n=8-10$ , fluorenone, anthraquinone and minor amounts of naphthoic acids and other carbonyl compounds. Smoke from both brush and slash fires does not contain dominant aromatic acids, ketones, aldehydes or quinones. Aromatized products from resin acids are, however, present in varying amounts. Two marker compounds,

namely dehydroabietic acid (XIV) and 6,8,11,13-abietatetraen-18-oic acid (XV) have been identified based on their mass spectra and GC retention index.<sup>65</sup>

Aromatic acids and to a lesser degree aromatic carbonyl compounds (oxy-PAH) are characteristic molecular markers for diesel exhaust and to a lesser extent for automobile exhaust (Table IV). The aromatized resin acids (e.g. dehydroabietic acid, XIV) are good molecular markers for combustion emissions using coniferous wood as fuel. All these markers are primary emissions and their stability to secondary reactions and photochemistry needs to be evaluated before they can be utilized as long range tracers.

## CONCLUSIONS

The application of the same sample collection, solvent extraction, chemical derivatization and separation, and instrumental analysis procedures to vehicular emissions, biomass burning and ambient aerosols, allows definitive source reconciliations to be made. Molecular marker analysis provides the supportive evidence for such assessments.

Vehicular exhaust can be distinguished from the natural background (plant wax and resin residues) by presence of petroleum residues (both homologous compounds and geologically mature molecular markers). Hydrocarbon emissions from both diesel and gasoline engines are characterized by a naphthenic hump, some *n*-alkanes with no carbon number predominance and molecular markers characteristic of petroleum (e.g. steranes and triterpanes), with significant amounts of the ubiquitous thermogenic PAH. The sterane and 17 $\alpha$ (H)-hopane distribution signatures are specific for petroleum residues. Secondary molecular markers are found in the oxygenated compound fractions of vehicular exhaust. Oxy-PAH compounds (e.g. alkylbenzenepolycarboxylic acids, alkyl-naphthoic acids, aromatic carbonyl and quinone compounds), isoprenoidal ketones, *n*-alkan-2-ones, *n*-aldehydes and *n*-carboxylic acids have been characterized and they are incomplete combustion products derived primarily from engine fuels and lubricants. Auto exhaust contains lesser amounts of the high weight oxy-PAH than diesel exhaust and in general the

TABLE IV  
Molecular markers of utility for fingerprinting the petroleum residues in vehicular exhausts and in aerosols.

Molecular marker compound class	Usual compositional range	Usual major analog or homolog	Concentration range (ng/m <sup>3</sup> )	Occurrence
<i>Hydrocarbons</i>				
Isoprenoid hydrocarbons (pristane, phytane, etc.)	C <sub>10</sub> -C <sub>20</sub>	Pr(C <sub>19</sub> H <sub>40</sub> )	0.1-25	Ubiquitous (not in gasoline)
Alkylcyclohexanes	C <sub>18</sub> -C <sub>29</sub>	C <sub>23</sub> H <sub>46</sub>	0.05-4	Auto exhaust, urban aerosols
Triterpenoid hydrocarbons	C <sub>27</sub> -C <sub>35</sub>	C <sub>30</sub> H <sub>52</sub>	0.04-1.0	Ubiquitous (not in gasoline and diesel fuel)
Tricyclic terpane hydrocarbons	C <sub>19</sub> -C <sub>29</sub> (low C <sub>22</sub> , C <sub>27</sub> )	C <sub>23</sub> H <sub>42</sub>	0.02-0.7	Ubiquitous (not in gasoline)
Steranes and diasteranes	C <sub>27</sub> -C <sub>29</sub>	C <sub>27</sub> H <sub>48</sub>	0.01-0.5	Ubiquitous (not in gasoline and diesel fuel)
Aromatic hydrocarbons (PAH, azaarenes, etc.)	C <sub>14</sub> -C <sub>24</sub>	C <sub>16</sub> H <sub>10</sub>	0.0005-1.0	Ubiquitous (combustion products, limited specificity)
<i>Oxygenated compounds</i>				
Isoprenoid ketones	C <sub>13</sub> , C <sub>18</sub>	C <sub>18</sub> H <sub>36</sub> O		Diesel exhaust, smoke, urban aerosols (combustion products)
<i>n</i> -Alkan-2-ones	<C <sub>10</sub> -C <sub>24</sub>	C <sub>17</sub> H <sub>34</sub> O		Vehicular exhaust, smoke, aerosols (combustion products, limited specificity)
<i>n</i> -Alkanoic acids	<C <sub>10</sub> -C <sub>22</sub>	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>		Vehicular exhaust, smoke, aerosols (combustion products, limited specificity)
$\alpha,\omega$ -Alkanedioic acids	<C <sub>10</sub> -C <sub>22</sub>	C <sub>16</sub> H <sub>30</sub> O <sub>4</sub>		Vehicular exhaust, smoke, aerosols (combustion products, limited specificity)
Alkylbenzoic acids	C <sub>7</sub> -C <sub>9</sub>	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>		Diesel exhaust, urban aerosols (combustion products)
Alkylbenzenedioic acids	C <sub>8</sub> -C <sub>10</sub>	C <sub>8</sub> H <sub>6</sub> O <sub>4</sub>		Diesel exhaust, urban aerosols (combustion products)
Alkylinaphthoic acids	C <sub>11</sub> -C <sub>13</sub>	C <sub>11</sub> H <sub>8</sub> O <sub>2</sub>		Diesel exhaust, urban aerosols (combustion products)
Dehydroabietic acid		C <sub>20</sub> H <sub>28</sub> O <sub>2</sub>		Smoke (brush, slash, wood)

carbonyl compounds are less concentrated in engine emissions than the carboxylic acids.

In contrast, emissions from biomass burning (e.g. slash burns, fire places, wood stoves) contain thermally-altered biomarker compounds. The hydrocarbon fraction of smoke from resin-rich vegetation contains retene as well as the other thermogenic PAH and dehydroabietic and abietatetraenoic acids are major components of the oxygenated compound fractions. The molecular marker compounds identified in vehicular emissions are not found in smoke. Partial combustion products of plant wax are also identifiable as ketones > carboxylic acids.

Thus, vehicular emissions and smoke have characteristic molecular marker signatures. With this information the anthropogenic components of aerosols (i.e. petroleum residues and pyrogenic PAH) can be quantified and distinguished from the natural background of higher plant waxes and resins. Vehicular emissions are a major part of aerosols from urbanized areas and their molecular signatures may be useful and complementary (to the natural background signature and smoke emissions) tracers for air parcels from specific geographic areas.

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