# Chapter 5

## Road Dust, Tire Debris, and Organometallic Brake Lining Dust— Roads as Sources and Sinks —

### Introduction

A recent inventory of fine particulate ($d_p \leq 2.0\ \mu m$) organic carbon (OC) emissions to the Los Angeles area atmosphere suggests that fine particulate paved road dust is the third largest source of fine organic carbon particle emissions to that urban atmosphere, following vehicular exhaust and meat cooking emissions (*1*). Traffic on the roads not only contributes particulate emissions from the tailpipes of vehicles, but also particles worn from tires and brake linings, and some of these particles are deposited onto the road surface. Dirt is tracked onto the roads, for example by trucks leaving unpaved construction sites or simply by the wind blowing garden soil particles onto the streets. Leaves and other plant materials accumulate in gutters or on the street surface and can be pulverized by the passing traffic. Hence, fine particulate road dust is an agglomeration of multiple source contributions. Virtually any anthropogenic and biogenic source emissions to the urban atmosphere can via atmospheric removal processes (e.g., dry deposition) contribute to the road dust composite. This road dust can be resuspended into the atmosphere by the passing traffic or wind, followed by redeposition of some of that material back onto the streets. Consequently, road

---

Reference: Rogge, W.F.; Mazurek, M.A.; Hildemann, L.M.; Cass, G.R.; Simoneit, B.R.T. *Environ. Sci. Technol.*, 1993, 27, in press.

dust bears a dynamic relationship to the airborne fine particulate matter as will be shown later in this study.

In the present study, the solvent extractable organic compounds found in fine particulate road dust, brake lining wear, and tire attrition particles are characterized using gas chromatography/mass spectrometry (GC/MS). The chemical composition of road dust will be related to that of the brake lining wear and tire debris, and to the organic compound signatures found in motor vehicle exhaust and vegetative detritus. Using molecular tracer methods, lower or upper limits can be placed on the contribution of these fine particle emission sources to the paved road dust examined here. Finally, the organic chemical composition of this complex road dust mixture will be compared to the composition of atmospheric fine particulate samples.

## Experimental Methods

### Sample Collection

Paved road dust samples were collected using a small vacuum sweeper truck (Tennant 255, 36HP) from several streets within a residential area in Pasadena, California, during May 1988 (*1*). Fine particulate matter ($d_p \leq 2$ $\mu$m) was subsequently collected by placing a portion of the road dust in a clean Teflon bag and agitating the bag to resuspend the particulate matter. Filtered laboratory air was blown into the bag to maintain it at a slight positive pressure, and particle laden air was withdrawn from the bag through cyclone separators (AIHL, 50% cutoff at 2 $\mu$m aerodynamic particle diameter) that removed the coarse road dust particles. The remaining fine particles then were collected on quartz fiber filters (Pallflex 2500 QAO) and Teflon filters (Gelman Teflo, 2.0 $\mu$m pore size).

All quartz fiber filters were annealed at 750°C for 2–4h before use to ensure low contamination levels for organic substances.

To sample the chemical composition of tire debris particles, a used radial tire (195/60R-15 Toyo, 7200 miles) was run on a rolling resistance testing machine at a tire–testing laboratory for several days. The tire wear particles accumulated on the horizontal surfaces of the tire–testing machine were collected as a grab sample. When resuspended, tire debris became electrically charged and adhered to the walls of the sampling equipment. As a result, the attempt to resuspend and collect only fine tire debris particles had to be abandoned. Instead, total particle samples were collected directly consisting mainly of coarse debris particles. Because tire tread is a well mixed industrial material it will be assumed that there are no compositional differences between the fine and coarse particle fractions.

Fine particle brake dust was collected by resuspending and then filtering the brake dust grab sample by the same methods as described for the road dust sample. The organometallic brake dust was brushed from the inside of the rear drum brakes of a late–model light truck. Further details of the road dust, tire debris and brake dust source sampling program are given by Hildemann et al. (*1*).

## Bulk Chemical Analysis

The bulk chemical composition of the source samples discussed here, including organic carbon (OC), elemental carbon (EC), ionic species, and trace metals content has been determined, and these results are published elsewhere (*1*).

## Sample Extraction

The extraction procedure applied to these source samples has been presented in detail elsewhere (*2-8*) and only a brief description will be given here. Prior to extraction a measured amount of perdeuterated tetracosane ($\underline{n}$-$C_{24}D_{50}$) was spiked onto the filter samples. The amount added was predetermined for each sample based on the amount of organic carbon present in that sample according to the OC-data gained from EC/OC–combustion analysis. The samples collected on quartz fiber filters were extracted successively in hexane (2 × 15 ml), followed by benzene/2-propanol (2:1 mixture, 3 × 15 ml). After each extraction step, the extracts were filtered and combined. A specially designed extract transfer and filtering line was used as described by Mazurek et al. (*2*). Using rotary evaporation and gentle high purity $N_2$–stream evaporation, the total sample extract was reduced to 200 – 500 $\mu$l. The sample extract was divided into two aliquots. One aliquot was then derivatized by adding freshly produced diazomethane to convert organic acids to their methyl ester analogues and hydroxy compounds to their methoxy derivatives. Until analysis by GC/MS, the sample extracts were stored at –21°C.

## Sample Analysis

The compound identification and quantification was conducted using a Finnigan 4000 quadrupole mass spectrometer interfaced to a gas chromatograph. The mass spectrometer data generated were stored and processed with an INCOS data system. The mass spectrometer was operated in the electron impact mode (electron energy of 70 eV). Sample extracts were injected onto the GC equipped with a conventional Grob splitless injector which was operated at 300°C. Compound separation was performed using a 30-m fused-silica DB-1701 column (J &

W Scientific, Rancho Cordova, CA). Sample chromatography was accomplished using the following temperature program: (1) isothermal hold at 65°C for 10 min, (2) temperature increase at 10°C/min for 21 min, and (3) isothermal hold at 275°C for another 49 min. Supplemental analyses were performed using a Varian 4600 high-resolution gas chromatograph (HRGC) with a FID-detector (*9*). More extensive descriptions of this analytical procedure can be found elsewhere (*2, 3, 6, 7*).

## Compound Identification and Quantification

The identification and quantification process for particle-bound organics is explained in previous and companion papers that also describe the quality assurance procedures applied to these samples (*6-8*). Compound identification was labeled accordingly: (a) *positive*, when the sample mass spectrum, authentic standard compound mass spectrum and their retention times agreed well; (b) *probable*, same as above except no standards were available, but the sample mass spectrum agreed very well with the National Institute of Standards and Technology (NIST) Library accessed by the INCOS data system; (c) *possible*, same as above except that the sample spectrum contained information from other compounds but with minor overlap; and (d) *tentative*, when the sample spectrum contained additional information from possibly several compounds (noise) with overlap.

The compound quantification process was based on the application of n-$C_{24}D_{50}$ as internal standard and 1-phenyldodecane as coinjection standard. To correct for detector response to compounds of different structures and retention times, sets of known standard compounds were injected onto the analytical system to monitor their specific MS-response.

### Standard Compounds

Confirmation and quantification of organic compounds was obtained through the use of more than 150 authentic standards, as described by Rogge et al. (*8*). The following standard mixtures were injected onto the GC/MS-systems: (1) normal alkanes ranging from n–$C_{10}$ to n–$C_{36}$; (2) normal alkanoic acids as methyl esters ranging from n–$C_6$ to n–$C_{30}$; (3) unsaturated aliphatic acids such as oleic acid and linoleic acid as methyl esters; (4) normal alkanols ranging from n–$C_{10}$ to n–$C_{30}$; (5) several phenolic compounds, benzaldehydes and substituted aromatic acids; (6) a suite of 39 aromatic and polycyclic aromatic hydrocarbons (PAH); (7) 10 polycyclic aromatic ketones and quinones; (8) a set of 8 aromatic and polycyclic aromatic N– and S–substituted compounds; (9) steroids including cholesterol and cholestane; (10) a set of 4 phytosterols; (11) several natural resins; (12) plasticizers; (13) a suite of 11 aliphatic dicarboxylic acids ($C_3$ – $C_{10}$) as methyl esters; (14) one suite of 7 aromatic di- and tricarboxylic acids, all as their methyl esters; and (15) other compounds.

## Results and Discussion

In the following sections, the organic composition of the tire wear and brake dust particles collected here will be examined first. Then, the chemical composition of fine road dust will be discussed and related to direct and indirect contributions from other sources. Finally, it will be demonstrated that contributions from certain anthropogenic and biogenic sources to the fine particulate road dust can be traced using organic markers or groups of marker compounds.

## Mass Balance for Elutable Fine Organic Matter

For all three traffic related particle sources, material balances were constructed that describe the chemical composition of the elutable organic mass as detected by GC/MS and are shown in Figures 5.1a-c. For the tire wear sample 44-49% of the organic matter as determined by EC/OC–combustion analysis was extracted by the solvents used and eluted from the GC column. For the fine road dust sample 21-30% of the EC/OC determined organic mass could be extracted and eluted from the column used. For brake dust, the fraction of organic matter that could be extracted and detected is uncertain because EC/OC delineation by the thermal-optical method used was affected by light absorption due to inorganic brake dust materials with a dark pastel-reddish color. Therefore, only a lower bound of 2.7% can be placed on the fraction of the organic matter that was extracted and eluted from the GC column used (*9*). Because brake linings have to withstand excessive mechanical and heat stress and must be resistant to possible leaking brake fluid, organic fibers and binders are used that show high boiling points and resistance to solvents. Hence, it is not surprising that only a small fraction of the brake lining dust can be examined by the methods used here. Nevertheless, tracer compounds may still be sought in this solvent extractable fraction.

The extractable and elutable organic mass can be subdivided into resolved and unresolved organic compounds. For the sources examined here, the chromatographically-unresolved organic mass or unresolved complex mixture (UCM) (*10*) comprises 65.6% (brake dust) to 77.2% (tire wear debris) of the elutable organic mass. Of the chromatographically-resolved single compound peaks, 77.3% (road dust) to 80.4% (brake dust) by mass could be identified as specific organic

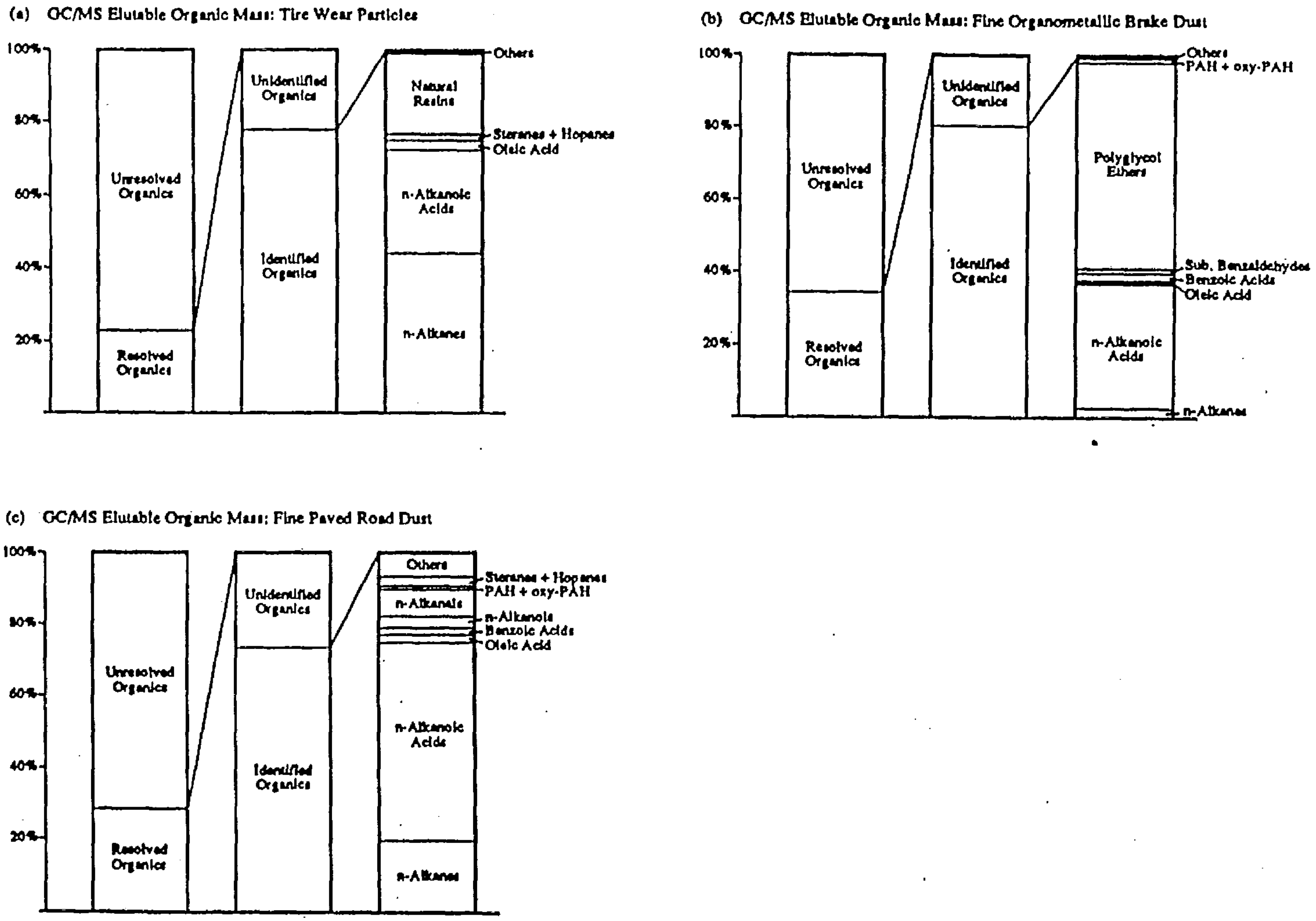


Fig. 5.1: Mass balance for elutable organic matter from (a) tire wear particles, (b) fine brake lining wear particles, and (c) fine paved road dust.

compounds. For the tire wear particles, the main portions of the identifiable elutable mass consist of n-alkanes (43.7%), n-alkanoic acids (28.3%), and natural resins (22.1%). Because sandpaper was used on the rolling resistance testing machine to wear down the tire tread, it cannot be ruled out that at least portions of the natural resins found originate from the sandpaper. The identifiable portion of brake dust organics on the other hand consists mainly of n-alkanoic acids (34.3%) and polyalkylene glycol ethers (56.9%), the latter being typical of brake fluid blending stocks. The resolved compounds present in the fine road dust consist mainly of n-alkanoic acids (54.8%), n-alkanes (19.0%), and higher molecular weight n-alkanals together with n-alkanols (10.1%).

## Tire Dust

Tire tread, a source of airborne particles, is commonly composed of copolymers of natural rubber (NR), polyisoprene rubber (IR), butadiene rubber (BR), and styrene-butadiene rubber (SBR). Which rubbers or combination of rubbers are blended together to produce the tire tread is usually dictated by the required qualities, such as physical strength, driving and road behavior, and wear resistance. Because natural rubber (NR) has a lower heat buildup, high elasticity, resilience, and tackiness, it is a preferable ingredient in the treads of tires used for buses, trucks, and racing cars (*11*). For less demanding vehicles, SBR and BR are commonly used. The polymer fraction of passenger car tires comprises 40 – 60% of the tire stock solution (*11-16*).

Depending on the type of rubbers used and quality demanded, a variety of chemicals are added to the stock formula to obtain the desired plasticity, elasticity, softness, resistance to abrasion, etc. In addition, vulcanization and acceleration agents are necessary during the production process. Typically up to 1% of the processing stock mass consists of vulcanization accelerators such as thiazoles, sulphenamides and others (*11, 14, 15*). In order to accelerate the curing process further, organic activators such as zinc salts of a mixture of fatty acids, primary fatty amines, organic and inorganic acetates and other accelerators are added to the stock solution (*11*). Rubber scorching can occur during the curing process when fast accelerators are used. To prevent such side effects, retarders also can be added. Common retarder additives are terpene-resin acid blends, benzoic acid, N-nitrosodiphenylamine, and many more (*11*). Pigments such as carbon black are used as filling and reinforcing agents, providing the necessary stability of the tire. About 20 – 30% of the tire stock formula is made up of carbon black particles having average diameters ranging from 10 to 500 nm (*11, 16, 17*). In order to adjust the materials' viscosity to the degree necessary for the dispersion of fillers and to insure lubrication during molding, softeners are commonly added. Usually, a wide variety of pitches, oils, coal tars, pine tars, and also synthetic organic materials are added to reach the desired workability of the rubber compounding. Fatty acids (e.g., stearic acid) are added (0.5 – 2.0%) as dispersing agents and softeners. Extenders such as aromatic and naphthenic oils are used to substitute for part of the more costly rubber material, and constitute 10 – 20% of the stock formula. Truck tires, exposed to tougher physical conditions, usually contain small amounts of such organic extender oils (*12, 14, 15*). Plasticizers, which are primarily used to reduce the viscosity during milling of the uncured stock rubber, are added in low amounts (*11*). To protect the rubber material during storage and shipment, antioxidants and stabilizers are needed; depending on the rubbers blended, their concentration levels range from 1.0 – 2.5%.

Ozone is an effective oxidant that can cause severe cracking, especially in tire rubber under stress. To protect rubber from ozone attack, antiozonants (e.g., diamines, waxes, etc.) have to be added to the rubber material. Waxes, consisting of higher n-alkanes (sunproof waxes) are used in quantities ranging from 0.5% to 1.0% of the rubber material and serve both as softeners and as UV– and ozone–protecting agents (*11, 14, 15*). Together with the aromatic and naphthenic type compounds added as extenders, additional n-alkanes are introduced into the rubber stock (*16*).

Due to changing operating temperatures, mechanical wear, oxidant and radical attack combined with the loss of protective rubber ingredients, the tire rubber is gradually altered during use (*18, 19*). Therefore, the chemical composition of tire wear particles depends not only on the recipe of the rubber stock, but also might depend on the age and the physical and chemical stress conditions to which the tire was exposed during use.

Tire wear particles are generated during the rolling shear of the tire tread against the road surface. Depending on the turbulence (traffic density, wind speed) within the air column above the street, some of the tire debris is entrained into the atmosphere where its removal rate depends among other factors on the particle size, which influences the particle settling velocity. It has been reported that the average tread wear rate for a single passenger tire is between 0.006 g/km and 0.09 g/km, depending on the road conditions (e.g., asphalt vs concrete), driving conditions (acceleration, abrupt decceleration, speeding etc.), and tire conditions (tire type, tire pressure, retreaded vs new tires, vehicle load etc.) (*20-23*). Recently, Kim and co-workers (*24*) showed that 30% of the mass concentration of tire wear particles measurable just above the street surface was still found at 86 m height over a heavily-trafficked area. Although only 10% of the tire tread particles (by mass) are smaller than 3 $\mu$m in aerodynamic diameter (*22*), it was estimated that for the heavily urbanized region of Los Angeles (representing 6400 km$^2$), fine particulate tire tread organic carbon (OC) is emitted to the atmosphere at about 0.4 metric tons per day (*1*).

Particulate tire tread in urban air has been evaluated by previous investigators, who have used characteristic tire pyrolysis products such as benzothiazole to trace tire wear debris in the urban atmosphere (*12, 24, 25*). Pierson and Brachaczek (*22*) traced the presence of tire rubber particles in the atmosphere by measuring SBR with infrared absorption spectroscopy. Such analysis techniques do not provide any further information about the chemical composition of the tire wear particles released into the environment. But to study the atmospheric interplay of particulate emissions from different urban sources, it is useful to determine the chemical composition of solvent extracts of the most important urban sources, so that comparisons can be drawn between source and ambient samples that are processed identically by GC/MS techniques. Here, tire debris collected from a Toyo passenger car tire (195/65R-15 Toyo, 7200 miles) has been analyzed using GC/MS techniques. Despite the fact that tires are produced by different companies using their own rubber stock recipes, Kim et al. (*24*) have shown that different tire brands display similar pyrolysis product distributions. Truck tires revealed a different composition and additional pyrolysis products when compared to passenger car tires, but within the class of truck tires variations were also minimal (*24*). Nonetheless, care should be taken in applying the results found in this study because tire formulations can vary between manufacturers, and in particular the abrasion products of truck tires are expected to differ from the single passenger car tire studied here.

Considering a tire wear particle as a whole, it consists to an appreciable extent of styrene and butadiene polymers which can be analyzed by the method of Pierson and Brachaczek (*22*) but not by the solvent extraction method used here. Hence, the following discussion of the chemical composition of extractable organic matter from such rubber particles is mainly concerned with organic compounds that have been added to the rubber stock or that are formed from agents that were originally blended with the polymer stock.

## Organic Composition of Tire Dust

The chemical composition of the tire wear particle extract is shown in Table 5.1. The main compound class identified in particulate tire wear extract consists of n-alkanes ranging from $C_{19}$ to $C_{41}$. n-Alkanes (sunproof waxes) are added to the tire stock solution as a protective agent against oxidants and UV-light induced cracking and hence have a function similar to that of natural leaf surface waxes. As can be seen from Figure 5.2a, the n-alkane mass concentration profile shows increased concentrations for higher molecular weight n-alkanes ($\geq C_{30}$; peak concentration at $C_{37}$) with no evidence of the odd-to-even carbon number predominance that is observed for plant waxes, garden soil or even biogenically influenced airborne particles (*4, 7, 26, 27*). The n-alkane distribution in fossil fuels also does not show any odd-to-even carbon number predominance and generally no enrichment of homologues > n-$C_{35}$ (*10, 29, 30*). Hence, the n-alkanes added to the tire material are most likely derived from the refined paraffin wax fraction of crude oils.

Besides wax components such as n-alkanes, n-alkanoic acids — labeled as

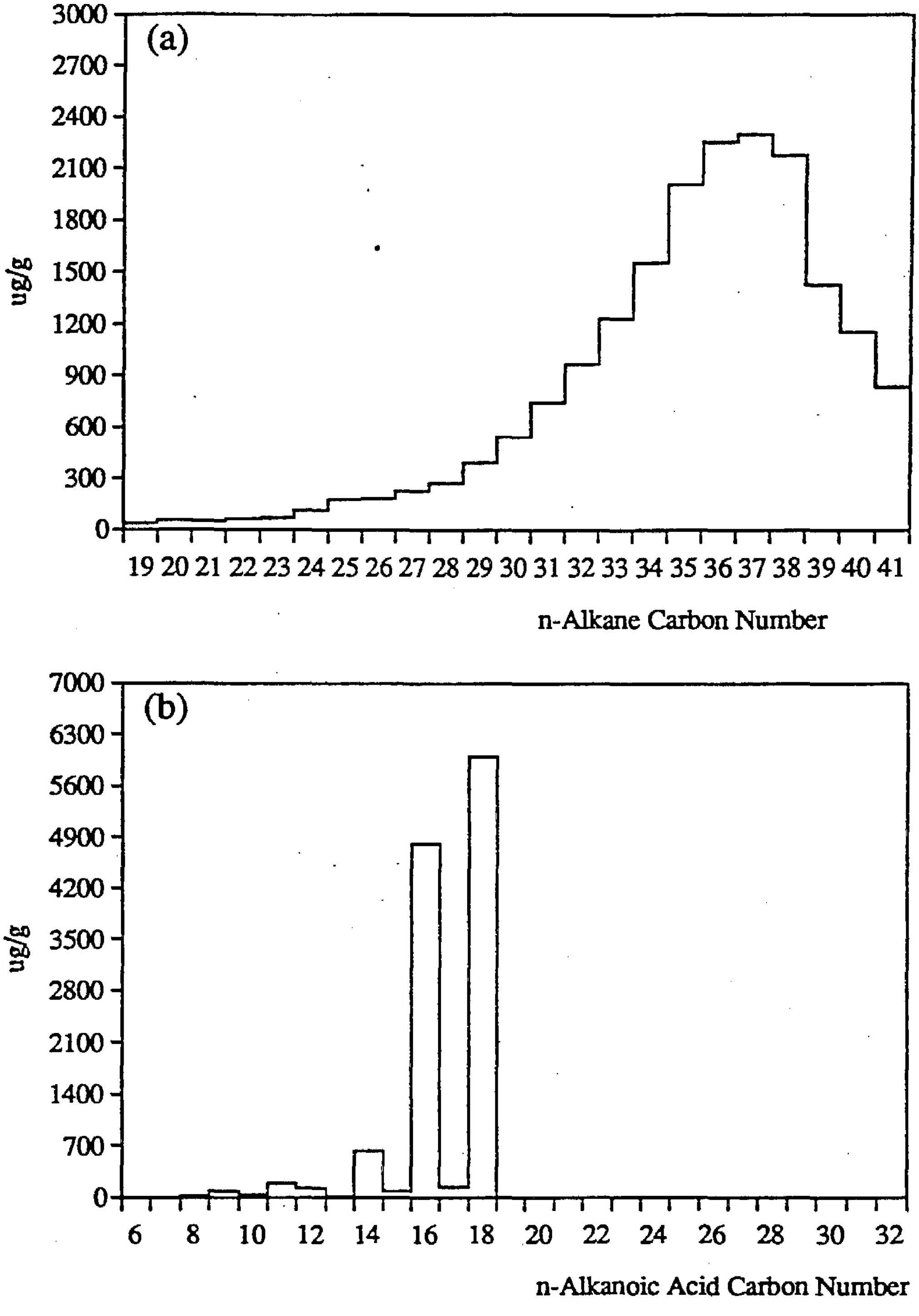


Fig. 5.2.: Mass concentration distributions for tire wear organic constituents in $\mu g\ g^{-1}$ of total (fine plus coarse) tire wear debris for (a) n-alkanes and (b) n-alkanoic acids.

'stearic acid' by the manufacturing trade — also are added to the rubber stock formula (*12, 15, 31*). According to the Merck Index (eleventh edition, (*32*)), commercially used acids labeled as 'stearic acid' under United States Pharmacopoeia (U.S.P.) consist mainly of stearic acid and palmitic acid. As a mix it is made up of about 45% palmitic acid, 50% stearic acid, and 5% oleic acid (*33*).

In the present tire debris sample, stearic acid is the most abundant n-alkanoic acid (more than 6000 $\mu$g stearic acid per gram of tire wear debris), followed by palmitic acid and some myristic acid (see Figure 5.2b). Oleic acid ($C_{18:1}$) and linoleic ($C_{18:2}$) acid, two unsaturated analogues of stearic acid, were also detected in appreciable amounts (see Table 5.1). Other carboxylic acids identified include trace amounts of several benzoic acids and diterpenoid acids. The latter are natural resins (e.g., pine tars) and are added to the formula as softeners and extenders (*17, 33*). Dehydroabietic acid, the partially aromatized product of abietic acid, was the most abundant single organic compound found in this particular tire wear extract (close to 8000 $\mu$g/g of tire wear particles). Abietic acid and related resinous compounds also were identified (see Table 5.1). The detailed composition of those resins would be expected to vary between manufacturers as the resins will depend on the vegetation typical of the area in which the resins were produced.

Another compound class present in tire wear particles consists of polycyclic aromatic hydrocarbons (PAH) totalling over 200 $\mu$g/g tire dust. Compounds of this type could have been introduced into the tire tread, either directly from organic additives derived originally from fossil fuels (such as extender oils) or as contaminants contained in the carbon black addition. PAH have been identified both in fossil fuels (*34, 35*) and in carbon black products (*36, 37*). Pyrene, fluoranthene, and phenanthrene are the dominant unsubstituted PAH found in the tire debris extract studied here. Similar results for PAH contained in tire wear particles have been reported by Wakeham et al. (*38*). Alkyl-PAH, intermediates that can be formed during combustion and manufacturing processes, where aromatization and soot formation is ongoing (*39*), show mass concentrations in the tire debris extract that are comparable to the unsubstituted PAH.

Benzothiazole is one of the many other compounds identified and listed in Table 5.1. It originates from the pendant groups of vulcanization accelerators classified as thiazoles and sulphenamides (*11, 14, 33*). Applying pyrolysis–gas chromatography to tire wear particles and ambient samples, Kim and co-workers (*24*) showed that benzothiazole is a suitable tracer for tire wear contributions to the ambient aerosol. Because benzothiazole is of a semi-volatile nature it must be trapped as a thiazole-type compound within the tire wear particle to actually serve as a particle-phase tracer. Using chemical extraction techniques, a benzothiazole signal from ambient particle samples could reflect both rubber particle-bound material as well as particle-adsorbed benzothiazole that was originally in the gas-phase.

## Brake Dust

During forced deceleration, motor vehicle brake linings are subject to large frictional heat generation and associated brake lining wear. This mechanically induced wear generates brake lining particles which under normal conditions are introduced into the environment. Most passenger cars are equipped with front disc brakes and rear drum brakes. During the deceleration process, front brakes have to provide most of the braking power. In addition, front disc brakes have a smaller friction lining area when compared to rear drum brakes. Consequently, the friction force per unit area of brake lining material is 5 to 6 times larger for front disc brakes (*40*). Because of the different physical demands (e.g., higher friction induced temperature), brake lining materials for disc and drum brakes differ somewhat in composition (*40, 41*). While basically all of the fine particulate brake dust from disc brakes is released to the environment, small amounts of brake dust (average 11%) are retained in the drum brakes (*40*).

Friction materials used in brake systems are made from a combination of binder resins, fillers, reinforcing agents made of glass, steel, asbestos or organic fibers and friction modifiers of inorganic, organic or metallic composition (*41*). Because brake lining materials are proprietary formulations, detailed compositional characteristics are not reported. Basically, nonasbestos friction materials can be classified as: nonasbestos organic (NAO), resin-bonded metallic (semimetallic), sintered metallic, and carbon-carbon (*40-42*).

## Organic Composition of Brake Dust

Here, the extractable organics found in fine particulate organometallic brake lining dust have been analyzed. The sample examined was collected from the dust retained in the rear drum brakes of a late–model light truck. Because only one brake dust sample was analyzed, care should be taken in generalizing the findings reported here. Nonetheless, the results discussed here provide a first indication of the kind of solvent-soluble organic compounds that are introduced into the urban atmosphere via brake lining attrition. Only small amounts of n-alkanes were found in the extractable portion of the brake lining wear particles, ranging from $C_{19}$ to $C_{36}$ (see Figure 5.3a). The same result holds for n-alkanoic acids. Although palmitic and stearic acids are important homologues found in the brake lining debris (Figure 5.3b), low molecular weight n-alkanoic

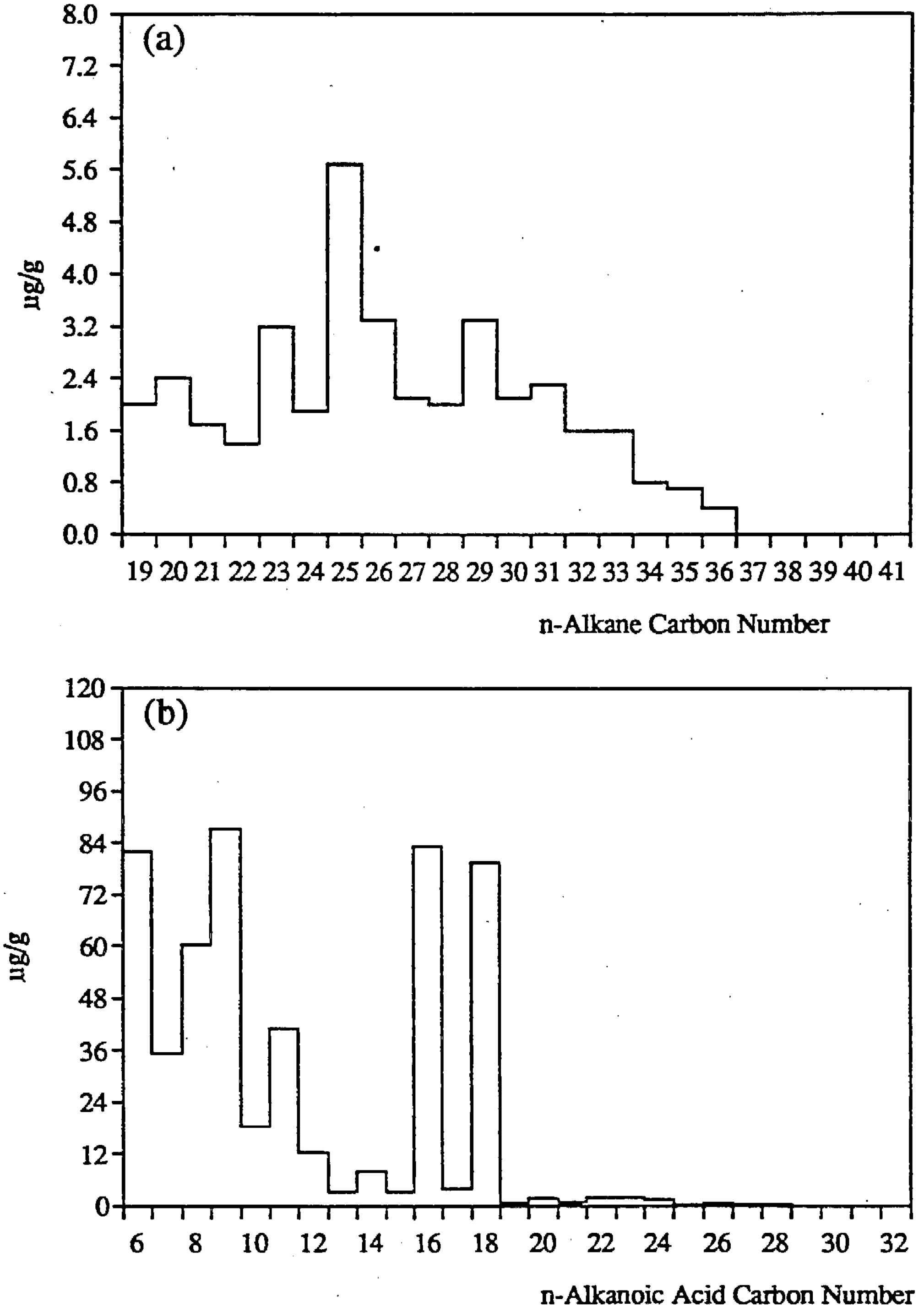


Fig. 5.3.: Mass concentration distributions for brake lining wear organic constituents in $\mu g\ g^{-1}$ of fine brake lining particles for (a) n-alkanes and (b) n-alkanoic acids.

acids ($C_6 - C_9$) are dominant. Trace amounts of PAH were found which might have been formed during the heat build-up that is normal during brake application. Interfacial temperatures of up to 600°C between drum and brake lining have been measured under normal braking conditions, providing the heat necessary to pyrolyze organic brake lining constituents (*41, 43-45*). Polycyclic aromatic ketones (PAK) and quinones (PAQ) also were identified, totalling roughly 3 $\mu$g/g of fine particulate brake debris. Compared to tire wear particles, only minor amounts of fossil petroleum markers such as steranes and hopanes were found. Only one natural resin, dehydroabietic acid, was identified in trace amounts.

By mass, the most abundant solvent-soluble organic compounds identified in brake lining dust are polyalkylene glycol ethers, with triethylene glycol monomethyl ether (2-[2-(2-methoxyethoxy)ethoxy]ethanol) and triethylene glycol monoethyl ether (2-[2-(2-ethoxyethoxy)ethoxy]ethanol) as the most common ones (see Table 5.1). Both compounds are used mainly for hydraulic fluids and to a minor extent as solvents in protective coatings, printing inks, and other chemical specialties (*46, 47*). Additional polyalkylene glycol ethers such as triethylene glycol monobutyl ether (2-[2-(2-buthoxyethoxy)ethoxy]ethanol) and diethylene monobutyl ether (2-(2-buthoxyethoxy)ethanol) are present as well in the brake dust sample, and are also used as components of hydraulic brake fluids but to a smaller extent (*33, 47*). Hence, the findings suggest that the polyalkylene glycol ethers identified here are lost from the hydraulic brake systems to the rear brake drum assembly of the vehicle tested, then find their way onto the brake lining and brake dust. Both triethylene glycol monomethyl ether and triethylene glycol monoethyl ether have been identified recently in urban fine particulate samples collected throughout the greater Los Angeles area (*48*). Annual mean ambient concentrations for 1982 ranged from 7.3 to 9.8 ng $m^{-3}$.

## Paved Road Dust

Urban street surfaces act as repositories for particulate matter. Because streets are usually built for vehicles, particulate automobile exhaust, lubricating oil residues, tire wear particles, weathered street surface particles and brake lining wear particles are direct contributors to the paved road dust. Biogenic material such as leaf detritus (e.g., from street trees, shrubs, lawns), especially epicuticular wax protrusions having micron and submicron dimensions (*49, 50*) and garden soil organics also contribute to the street dust. Indirectly, via atmospheric transport and fallout, practically any anthropogenic or biogenic source can add to the dust accumulation on the road surfaces.

Roads and streets also can function as a source of airborne particulate matter and likewise as a source for toxic compounds washed into drainage systems or delivered to aquifers. Resuspended by wind and vehicle induced turbulences, road dust particles are injected into the atmosphere (*51-54*). In fact, resuspension, fallout, street sweeping, rain, and generation of new particles (e.g., vehicle exhaust) drive a dynamic source and sink relationship which can contribute appreciable amounts of particulate matter and toxic substances to the atmosphere and to the hydrosphere. Recent estimates for an 80 × 80 km area centered over the heavily urbanized Los Angeles area showed that fine particulate organic matter contributions from road surfaces to the urban atmosphere corresponded to over 2000 metric tons annually, making road dust the third largest source of fine particle organic emissions to that urban atmosphere (next to vehicular exhaust emissions and meat-cooking operations) (*1*). Likewise, a study concerned with storm runoff via the Los Angeles River estimated an annual discharge of about

5000 metric tons of total extractable organics (*55, 56*). Due to the fact that the metropolitan Los Angeles rain water is mainly drained by surface streets and finally by the Los Angeles River system, an appreciable portion of that organic discharge must have been due to road dust washed off during the rain storms, indicating how significant road deposits can be.

Here, the findings for the fine particulate road dust sample ($d_p \leq 2\mu m$) will be discussed first, then the composition of fine particulate road dust will be compared with the composition of other anthropogenic and biogenic sources that could contribute to the road dust deposits (*6-8, 57*). Because very similar sampling and analytical techniques have been applied to all of these source samples, many of the possible obstacles to a direct comparison of such disparate sources have been excluded.

## Organic Composition of Paved Road Dust

In the Pasadena road dust sample, n-alkanes ranging from $C_{19}$ to $C_{39}$ have been identified, and their mass concentrations are plotted in Figure 5.4a. The highest mass concentrations were determined for higher molecular weight odd carbon numbered n-alkanes (odd: $C_{25} - C_{33}$) resembling the typical n-alkane profiles found in samples of vegetative detritus (*4, 7, 27, 28, 57*). The lower molecular weight range ($C_{19} - C_{25}$) is typical for vehicle exhaust emissions (*8, 10, 58*). For comparison, Figures 5.4b-d show the n-alkane distribution for green and dead leaf abrasion products, vehicular exhaust emissions, and ambient fine particulate matter. n-Alkanoic acids found in the road dust sample range from $C_6$ to $C_{32}$ ( see Table 5.1) and have a distribution very similar to that found in airborne samples (*7*). Stearic acid and palmitic acid are the dominant homologues and a pronounced even-to-odd carbon number predominance is evident; for the higher

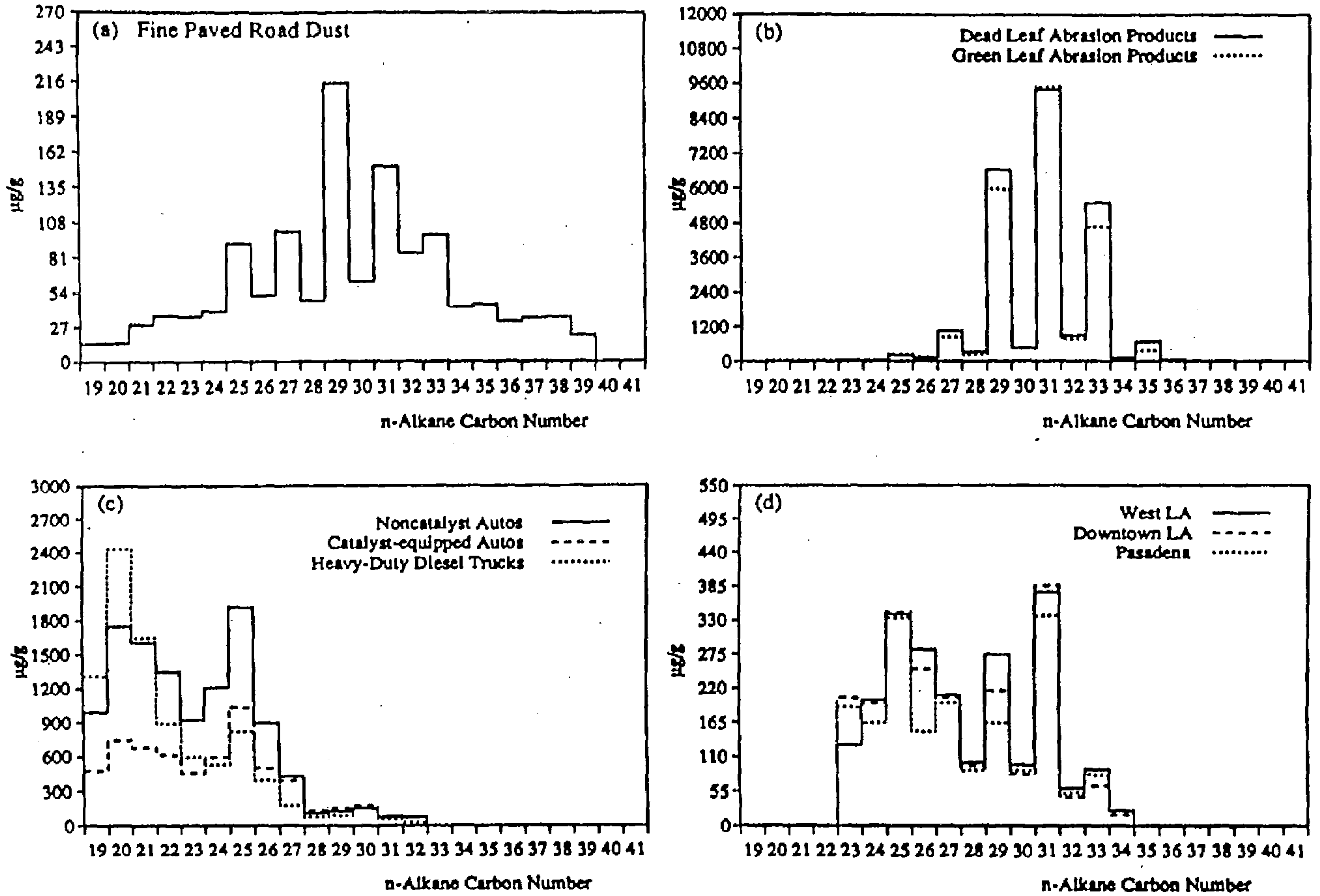


Fig. 5.4: n-Alkanes mass concentration distributions (in $\mu$g g$^{-1}$ of particulate matter) for (a) fine paved road dust, (b) fine particulate dead and green leaf surface abrasion products, (c) fine particulate exhaust emissions from noncatalyst and catalyst-equipped autos and heavy-duty diesel trucks, and (d) ambient fine particulate matter, annual averages for West Los Angeles, downtown Los Angeles, and Pasadena in 1982.

molecular weight n-alkanoic acids, this predominance is characteristic of vegetative detritus (*7, 28, 48*). n-Alkanals ($C_{28}$, $C_{30}$, $C_{32}$) and n-alkanols ($C_{26}$, $C_{28}$) are likewise found in the road dust sampled. As plant wax constituents, they are most likely lost from nearby trees and plants or from garden soil to the road surface. Unsaturated fatty acids found in the fine road dust sample have a myriad of possible sources, including meat cooking, tire wear, brake lining abrasion, plant material, and vehicular exhaust emissions (*4, 6-8, 28*). Benzoic acid and its alkyl substituted homologues also have been found in substantial concentrations in the road dust (see Table 5.1). In addition to the emissions from tire tread abrasion and brake lining wear that have been discussed earlier, benzoic acid type compounds are emitted in the exhaust from gasoline and especially diesel powered vehicles and might subsequently be deposited onto the road surface (*8, 58-60*). Polycyclic aromatic hydrocarbons, such as PAH and oxy-PAH also have been identified in the road dust sample.

In addition to biogenic, synthetic and combustion generated compounds, fossil petroleum markers also have been identified in the road dust sample. Fossil petroleum markers such as steranes and triterpanes are geologically matured organic compounds derived from steroids and triterpenoids that were originally biosynthesized and subsequently deposited in sediments millions of years ago (*35, 61-63*). During diagenesis and catagenesis, these biogenic compounds have been transformed yielding hydrocarbons such as steranes and triterpanes which are found in crude oils (*35, 61*), engine oils, and consequently in auto exhaust aerosol emissions (*8, 10, 58*). Recently, Rogge et al. (*8*) used a set of steranes and pentacyclic triterpanes (hopanes) to trace fine particulate vehicle exhaust in the greater Los Angeles ambient air. It was shown that these fossil petroleum markers released from noncatalyst autos, catalyst-equipped autos, and diesel vehicles contribute about 85% of the fossil petroleum markers emitted to the Los Angeles atmosphere. In the present study, the same set of fossil petroleum markers were quantified in the road dust, tire wear, and brake lining dust samples (see Table 5.1). In Figure 5.5a, the mass concentrations of these fossil petroleum markers are shown for tire wear particles and road dust.

In addition to the compounds already discussed, one insecticide (iridomyrmecin) and one herbicide (simazine) have been found in the paved road dust. These chemicals were most likely applied to gardens bordering the residential streets swept here. Furthermore, also monoterpenoids such as isopulegol, $\alpha$-terpineol, $\beta$-citronellol released from trees and flowers (*33, 64*) were identified in this road dust sample.

In the next section, the organic composition of the fine particulate paved road dust collected will be compared to the composition of related sources that add to the road dust deposits. A method will be illustrated for estimating source contributions to a particular road dust sample utilizing molecular marker compounds that are characteristic for each of the sources.

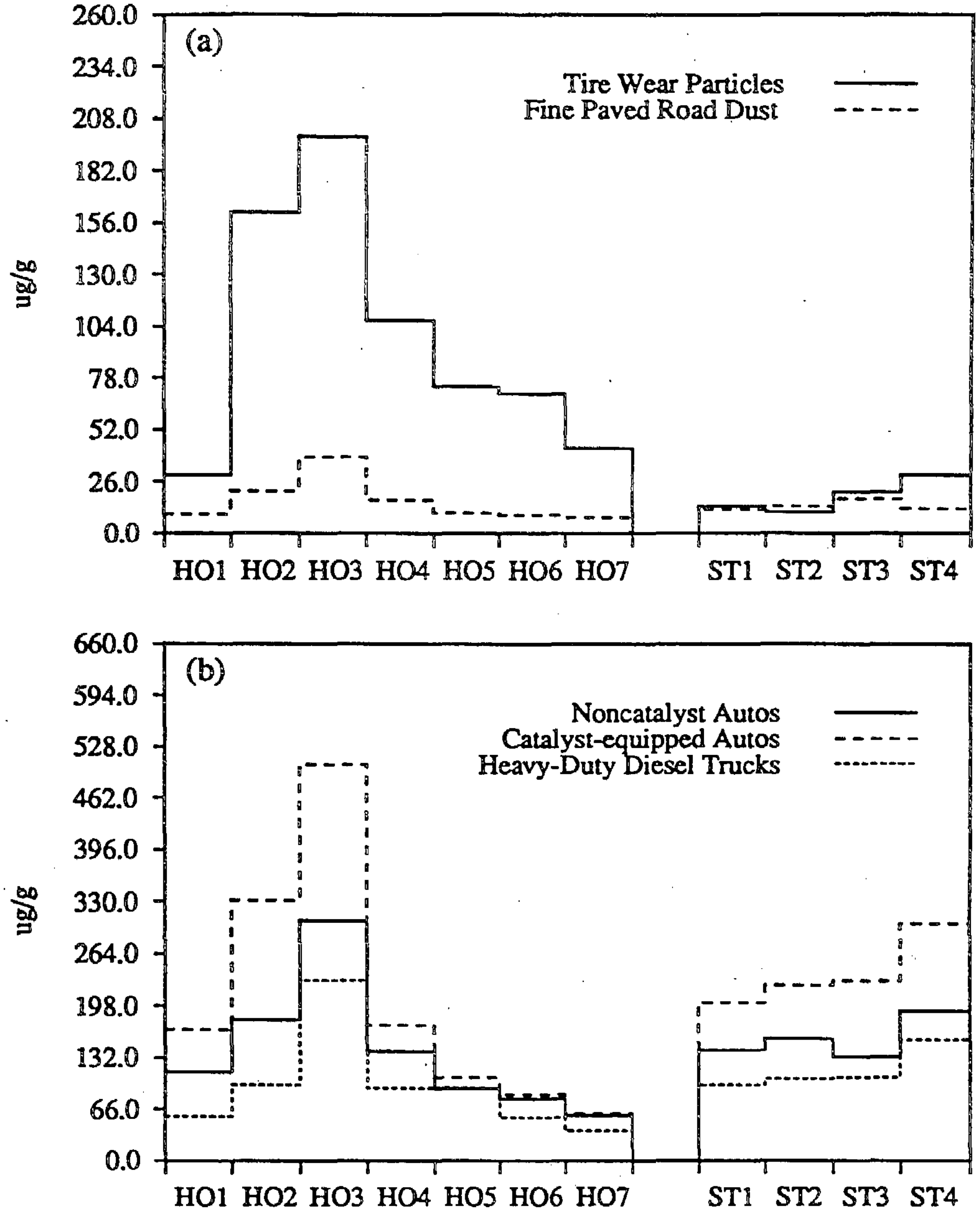


Fig. 5.5.: Fossil fuel marker mass concentrations for (a) tire wear particles and fine paved road dust and (b) noncatalyst and catalyst-equipped autos and heavy-duty diesel trucks. HO1: 22,29,30–trisnorneohopane; HO2: 17α(H),21β(H)-29-norhopane; HO3: 17α(H),21-β(H)-hopane; HO4: 22S–17α(H),21β(H)-30-homohopane; HO5: 22R–17α(H),21β(H)-30-homohopane; HO6: 22S–17α(H),21β(H)-30-bishomohopane; HO7: 22R–17α(H),21β(H)-30-bishomohopane; ST1: 20S&R–5α(H),14β(H), 17β(H)–cholestanes; ST2: 20R–5α(H), 14α(H),17α(H)–cholestane; ST3: 20S&R–5α(H),14β(H),17β(H)–ergostanes; ST4: 20S&R–5α(H),14β(H),17β(H)–sitostanes.

## Source Contributions to Paved Road Dust

Airborne particles that are released on or near the road surface can be expected to contribute to road dust accumulations. Several obvious sources include contributions from tire wear debris, deposited motor vehicle exhaust particles, plant fragments from nearby vegetation, and deposited soil dust. The soil dust contribution to road dust samples can be calculated by comparing the mineral content of pure soil dust to that of a road dust sample, a problem that has been addressed previously by others. Here, we wish to concentrate on organic tracers for the remaining road dust material.

n-Alkanes $\geq C_{35}$ are found in appreciable amounts in tire wear particles (see Figure 5.2a) and in the fine particulate road dust (Figure 5.4a), but are below the detection limit in ambient samples (*6-8, 48*), which suggests that there are few other urban emission sources. The contribution from tire wear to the fine road dust samples can be estimated approximately. Even if all of the n-alkanes that range from $C_{35}$ to $C_{39}$ in the road dust are contributed by tire dust, no more than 1.6% of the fine road dust ($d_p \leq 2.0\ \mu m$) could be derived from fine tire wear particles. Correspondingly, no more than 4.3% of the organics in fine road dust could originate from tires. The actual tire debris contributions will be lower than that if asphalt particles removed from the road itself contain any n-alkanes $\geq C_{35}$. This estimate assumes that the tire dust sample investigated here contains amounts of n-alkanes that are typical of tire tread wear debris in general.

Another possible marker compound for tire wear debris is benzothiazole as discussed earlier. Using the benzothiazole detected in the road dust as a marker for tire wear particles, the fractional contribution of tire wear particles to that road dust sample would be estimated to be 3.5%, which is in the neighborhood of the estimate obtained when using n-alkanes $\geq C_{35}$ only. Because benzothiazole has a fairly high vapor pressure, we believe that it is a less reliable marker in this case than the high molecular weight n-alkanes.

Our upper limits of 1.6% to 3.5% for the tire tread contribution to the road dust sample can be used to show that the PAH in road dust are not dominated by the PAH content of tire wear particles. Instead, the largest quantity of these PAH probably comes from airborne aerosols that deposit onto the streets and that originate from the many types of combustion processes typically found in urban areas (*8*, *65*, *66*).

Hopanes and steranes are measured in the road dust sample. Such compounds have been used previously to trace vehicular emissions to the urban Los Angeles atmosphere (*8*). Comparing Figure 5.5a with 5.5b, it can be seen that the concentration patterns for fossil petroleum markers in the road dust and vehicle exhaust show remarkable similarities, with the peak concentration found for $17\alpha$(H),$21\beta$(H)-hopane (HO3) and concentrations of single steranes comparable to that of single hopanes. The same is true for ambient aerosol samples (*8*). In contrast, the tire attrition particles show much higher concentrations for single members of the hopane series than for the sterane series. This indicates that the crude oil products used in the manufacture of the tire tested here are of different composition than the petroleum products used for fuels in Southern California. The fossil petroleum marker concentration levels in the brake lining particles are very low, suggesting that either only trace amounts of crude oil distillation fractions that contribute these markers are used for brake lining manufacturing or that the hopanes and steranes detected are carried over from other sources emitting in close proximity to the vehicle brakes (e.g., vehicle exhaust aerosol emissions). It is possible to roughly estimate the vehicle exhaust contributions to the street dust considered here by assuming that at the maximum 1.6% of the fine particulate road dust is derived from tire wear, and by observing that nearly all of the remaining hopanes and steranes deposited onto the Los Angeles area streets are contributed from motor vehicle exhaust (*8*). Based on these conditions it is found that at the maximum, about 7.6% of the fine particulate road dust mass collected (both organic and inorganic) originates from vehicular exhaust particles. Considering the organic portion of the road dust sample (16.2% organics), no more than 32.7% of that organic material is derived from vehicular emissions. Because some of the road dust hopanes and steranes might come directly from asphalt abraded off the roads swept, the actual fine particulate exhaust contributions from vehicles to the road dust collected might be somewhat lower.

Marker compounds that indicate the presence of plant fragments in the fine road dust sample likewise can be identified. The organic composition of waxy leaf surface abrasion products released to the atmosphere by leaves as they brush against each other has been documented (*57*). These samples were collected from a composite of 62 plant species weighted according to their abundance in the Los Angeles area. Figure 5.4b shows the mass concentrations of n-alkanes per unit of fine particulate leaf surface matter collected ($\mu$g g$^{-1}$). That figure shows the typical odd carbon number predominance characteristic of plant wax n-alkanes. In the fine road dust sample (Figure 5.4a), n-nonacosane ($C_{29}$) is the dominant n-alkane, while in the leaf abrasion samples $C_{31}$ is the dominant n-alkane. Obviously, the Pasadena area roads swept here are influenced by somewhat different plant communities than are found on the average within the Los Angeles basin. It has been reported that the composition of leaf waxes can differ greatly from tree species to tree species (*67, 68*). Garden soil, the decomposition product of plant material and mineral soil, contains an n-alkane distribution similar to that of the epicuticular plant waxes, with a pronounced odd-to-even carbon number predominance (*69*). Thus, leaf material plus garden soil organics would appear to make major contributions to the road dust n-alkanes. In contrast, the signature for fine particulate n-alkanes emitted from the exhaust of different vehicle types shows no obvious carbon number predominance, with the highest concentrations found for n-alkanes in the range of $C_{19}$ to $C_{25}$ as seen in Figure 5.4c (*8*). Comparing the vehicle exhaust n-alkane distribution to that of the road dust sample, it is seen that relatively small amounts of the n-alkanes found in road dust are in the lower molecular weight range found in vehicle exhaust aerosols.

If all $C_{29}$, $C_{31}$, and $C_{33}$ n-alkanes found in the fine particulate road dust samples originated from deposited airborne dead or green fine particulate leaf abrasion products (see Figure 5.4b), then an estimate for such biogenic contributions to the fine road dust could be made based on the n-alkanes content of vegetation source samples reported by Rogge et al. (*57*). About 2.2 to 2.3% (dead vs green fine leaf abrasion products) of the fine particulate road dust collected here could be derived from deposited airborne leaf surface debris, which translates to 5.3 to 5.5% of the organic compound mass found in the paved road dust sample.

Unfortunately, such an approach does not consider the likely contribution from leaves collected on the street surface that are partially pulverized by the passing vehicles, producing finely ground particulate plant material that contains not only epicuticular plant wax particles, but also higher concentrations of cutin-and suberin-like leaf fragments than would be found in our airborne leaf surface abrasion products samples. In addition, the above approach does not separate plant fragment contributions coming directly from garden soil, instead it considers only the contributions from ambient fallout. To simultaneously estimate the biogenic source contributions to the road dust from deposited airborne leaf abrasion products, ground up plant material, and garden soil, one has to model three source/sink interactions simultaneously. The plant mix that is ground up by passing traffic and garden soil contain additional organic and inorganic debris beyond that found in airborne vegetation fragments. Hence, the overall vegetative detritus contributions to the road dust sample considered here should be higher than estimated solely from airborne leaf surface abrasion n-alkanes. Thus the estimate given above provides a lower limit for vegetative contributions to the fine particulate road dust collected.

Table 5.1 Mass Concentrations for Organic Compounds found in Tire Wear Particles[†], Fine Organometallic Brake Lining Wear Particles, and Fine Paved Road Dust Particles.

| PART A | Concentrations[‡] in $\mu g\ g^{-1}$ of Particle Sample | | | |
|---|---|---|---|---|
| | Tire Wear Particles | Brake Lining Particles | Road Dust Particles | Compound ID[§] |
| | — n-Alkanes— | | | |
| nonadecane | 40.7 | 2.0 | 14.3 | a |
| eicosane | 58.3 | 2.4 | 15.0 | a |
| heneicosane | 47.7 | 1.7 | 28.8 | a |
| docosane | 62.5 | 1.4 | 35.7 | a |
| tricosane | 70.7 | 3.2 | 34.9 | a |
| tetracosane | 114.0 | 1.9 | 39.5 | a |
| pentacosane | 175.1 | 5.7 | 90.7 | a |
| hexacosane | 185.9 | 3.3 | 51.1 | a |
| heptacosane | 227.0 | 2.1 | 100.8 | a |
| octacosane | 268.5 | 2.0 | 47.1 | a |
| nonacosane | 389.3 | 3.3 | 214.7 | a |
| triacontane | 546.0 | 2.1 | 61.9 | a |
| hentriacontane | 742.9 | 2.3 | 150.7 | a |
| dotriacontane | 969.0 | 1.6 | 84.3 | a |
| tritriacontane | 1229.8 | 1.6 | 98.5 | a |
| tetratriacontane | 1556.2 | 0.80 | 42.7 | a |
| pentatriacontane | 2005.8 | 0.67 | 44.1 | a |
| hexatriacontane | 2253.9 | 0.42 | 31.3 | a |
| heptatriacontane | 2301.5 | n.d. | 34.2 | b |
| octatriacontane | 2181.2 | n.d. | 34.4 | b |
| nonatriacontane | 1428.0 | n.d. | 20.5 | b |
| tetracontane | 1157.7 | n.m. | n.m. | b |
| hentetracontane | 831.1 | n.m. | n.m. | b |
| Total class mass concentration: | 18842.3 | 38.47 | 1275.2 | |
| | —n-Alkanoic Acids[¶]— | | | |
| hexanoic acid | 122.0 | 82.1 | 71.4 | a |
| heptanoic acid | 3.0 | 35.4 | 28.6 | a |
| octanoic acid | 31.1 | 60.5 | 57.7 | a |
| nonanoic acid | 90.9 | 87.4 | 135.4 | a |
| decanoic acid | 37.8 | 18.4 | 55.4 | a |
| undecanoic acid | 187.4 | 41.1 | 146.9 | a |
| dodecanoic acid | 136.5 | 12.5 | 105.3 | a |
| tridecanoic acid | 11.6 | 3.2 | 33.6 | a |
| tetradecanoic acid (myristic acid) | 634.5 | 8.1 | 171.8 | a |
| pentadecanoic acid | 86.0 | 3.2 | 64.4 | a |
| hexadecanoic acid (palmitic acid) | 4818.4 | 83.3 | 1216.7 | a |

**Table 5.1 (continued)**

| PART B | Concentrations[‡] in $\mu g\ g^{-1}$ of Particle Sample | | | |
|---|---|---|---|---|
| | Tire Wear Particles | Brake Lining Particles | Road Dust Particles | Compound ID[§] |
| heptadecanoic acid | 150.6 | 4.1 | 61.3 | a |
| octadecanoic acid (stearic acid) | 6009.0 | 79.5 | 689.0 | a |
| nonadecanoic acid | 16.6 | 0.83 | 27.0 | a |
| eicosanoic acid | 127.0 | 1.8 | 119.0 | a |
| heneicosanoic acid | n.d. | 0.87 | 20.9 | a |
| docosanoic acid | n.d. | 2.1 | 70.2 | a |
| tricosanoic acid | n.d. | 1.9 | 23.6 | a |
| tetracosanoic acid | n.d. | 1.6 | 116.2 | a |
| pentacosanoic acid | n.d. | 0.34 | 21.9 | a |
| hexacosanoic acid | n.d. | 0.69 | 93.4 | a |
| heptacosanoic acid | n.d. | 0.36 | 20.6 | a |
| octacosanoic acid | n.d. | 0.55 | 124.0 | a |
| nonacosanoic acid | n.d. | n.d. | 21.5 | a |
| triacontanoic acid | n.d. | n.d. | 120.3 | a |
| hentriacontanoic acid | n.d. | n.d. | 12.5 | a |
| dotriacontanoic acid | n.d. | n.d. | 48.9 | a |
| Total class mass concentration: | 12197.3 | 529.74 | 3677.4 | |
| —n-Alkenoic Acids[¶]— | | | | |
| *cis*-9–octadecenoic acid (oleic acid) | 1115.5 | 10.7 | 130.9 | a |
| 9,12-octadecadienoic acid (linoleic acid) | 163.7 | n.d. | 129.1 | a |
| 9,12,15-octadecatrienoic acid (linolenic acid) | n.d. | n.d. | 17.3 | b |
| Total class mass concentration: | 1279.2 | 10.7 | 277.3 | |
| — *n*-Alkanals— | | | | |
| octacosanal | n.d. | n.d. | 144.4 | a |
| triacontanal | n.d. | n.d. | 232.2 | a |
| dotriacontanal | n.d. | n.d. | 85.9 | a |
| Total class mass concentration: | | | 462.5 | |
| — n-Alkanols— | | | | |
| hexacosanol | n.d. | n.d. | 61.7 | a |
| octacosanol | n.d. | n.d. | 152.9 | a |
| Total class mass concentration: | | | 214.6 | |

Table 5.1 (continued)

| PART D | Tire Wear Particles | Brake Lining Particles | Road Dust Particles | Compound ID[§] |
|---|---|---|---|---|
| | Concentrations[†] in $\mu$g g$^{-1}$ of Particle Sample | | | |
| **— Benzoic Acids[¶] —** | | | | |
| benzoic acid | 74.8 | 31.9 | 114.1 | b |
| 4-methylbenzoic acid | n.d. | 2.6 | 5.2 | a |
| 3,4-dimethoxybenzoic acid | n.d. | n.d. | 5.5 | a |
| Total class mass concentration: | 74.8 | 34.5 | 129.8 | |
| **—Substituted Benzaldehydes—** | | | | |
| 2–methylbenzaldehyde | 4.1 | 0.48 | n.d. | b |
| 3–methylbenzaldehyde | 1.4 | 0.11 | n.d. | b |
| 4–methylbenzaldehyde | 2.3 | 0.30 | n.d. | a |
| 3–methoxybenzaldehyde | n.d. | 13.0 | n.d. | b |
| 3,4–dimethoxybenzaldehyde | n.d. | 0.45 | n.d. | a |
| 2-hydroxybenzaldehyde | n.d. | 4.7 | n.d. | b |
| Total class mass concentration: | 7.8 | 19.04 | | |
| **—Polyalkylene Glycol Ethers—** | | | | |
| 2-(2-butoxyethoxy)ethanol | n.d. | 45.7 | n.d. | a |
| 2-[2-(2-methoxyethoxy)ethoxy]ethanol | n.d. | 248.1 | n.d. | b |
| 2-[2-(2-ethoxyethoxy)ethoxy]ethanol | n.d. | 403.6 | n.d. | b |
| 2-[2-(2-butoxyethoxy)ethoxy]ethanol | n.d. | 181.7 | n.d. | b |
| Total class mass concentration: | | 879.1 | | |
| **—Thiazole—** | | | | |
| Benzothiazole | 124.3 | n.d. | 4.4 | a |
| Total class mass concentration: | 124.3 | | 4.4 | |
| **—Polycyclic Aromatic Hydrocarbons (PAH)—** | | | | |
| phenanthrene | 11.8 | 0.97 | 3.9 | a |
| anthracene | n.d. | n.d. | 0.84 | a |
| methyl–(phenanthrenes, anthracenes) | 23.6 | 0.67 | 1.5 | b |
| dimethyl–(phenanthrenes, anthracenes) | 38.5 | 0.66 | 3.1 | b |
| fluoranthene | 11.1 | 0.69 | 6.9 | a |
| pyrene | 54.1 | 1.1 | 9.4 | a |
| benzacenaphthylene | n.d. | n.d. | 0.23 | b |
| 2–phenylnaphthalene | n.d. | n.d. | 0.16 | b |
| 2–benzylnaphthalene | n.d. | n.d. | n.d. | b |
| methyl–(fluoranthenes, pyrenes) | 24.4 | 0.89 | 2.1 | b |
| benzo[a]fluorene/benzo[b]fluorene | 1.3 | 0.26 | 0.37 | a |

Table 5.1 (continued)

| PART E | Concentrations† in $\mu$g g$^{-1}$ of Particle Sample | | | |
|---|---|---|---|---|
| | **Tire Wear Particles** | **Brake Lining Particles** | **Road Dust Particles** | Compound ID§ |
| benzo[ghi]fluoranthene | 6.3 | 0.34 | 1.3 | a |
| benz[a]anthracene | n.d. | 1.5 | 1.2 | a |
| chrysene/triphenylene | 8.2 | 1.7 | 7.7 | a |
| methyl–(benz[a]anthracenes, chrysenes, triphenylenes) | 18.7 | 2.2 | 1.3 | b |
| dimethyl–(fluoranthenes, pyrenes) | 19.0 | n.d. | n.d. | b |
| benzo[k]fluoranthene | n.d. | 0.62 | 5.5 | a |
| benzo[b]fluoranthene | n.d. | 0.42 | 4.4 | a |
| benzo[e]pyrene | 5.2 | 0.84 | 2.7 | a |
| benzo[a]pyrene | 3.9 | 0.74 | 2.3 | a |
| perylene | n.d. | n.d. | 0.48 | a |
| indeno[1,2,3-cd]fluoranthene | n.d. | n.d. | 1.2 | a |
| benzo[ghi]perylene | n.d. | 2.6 | 2.1 | a |
| Total class mass concentration: | 226.1 | 16.16 | 58.68 | |
| **—Polycyclic Aromatic Ketones (PAK) and Quinones (PAQ)—** | | | | |
| 9H–fluoren-9-one (fluorenone) | n.d. | 0.82 | 0.72 | a |
| 9,10–phenanthrenedione (phenanthrenequinone) | n.d. | 0.31 | 0.41 | a |
| 9,10–anthracenedione (anthraquinone) | n.d. | 0.48 | 1.1 | a |
| phenanthrone/anthrone | n.d. | 0.46 | n.d. | a |
| 9H–xanthen-9-one (xanthone) | n.d. | 0.45 | n.d. | a |
| 4–cyclopenta[def]phenanthren-4-one | n.d. | n.d. | 0.62 | b |
| 7–H–benz[de]anthracen-7-one | n.d. | 0.58 | 0.98 | a |
| 6H–benzo[cd]pyren-6-one (benzo[cd]pyrenone) | n.d. | 0.36 | n.d. | b |
| Total class mass concentration: | | 3.46 | 3.83 | |
| **—Regular Steranes—** | | | | |
| 20S&R-5$\alpha$(H),14$\beta$(H),17$\beta$(H)-cholestanes | 13.5 | 0.30 | 12.1 | b |
| 20R-5$\alpha$(H),14$\alpha$(H),17$\alpha$(H)-cholestane | 10.7 | 0.26 | 13.8 | a |
| 20S&R-5$\alpha$(H),14$\beta$(H),17$\beta$(H)-ergostanes | 20.7 | 0.99 | 17.3 | b |
| 20S&R-5$\alpha$(H),14$\beta$(H),17$\beta$(H)-sitostanes | 29.3 | n.d. | 12.5 | b |
| Total class mass concentration: | 74.2 | 1.55 | 55.7 | |

Table 5.1 (continued)

| PART G | Concentrations[‡] in µg $g^{-1}$ of Particle Sample | | | |
|---|---|---|---|---|
| | **Tire Wear Particles** | **Brake Lining Particles** | **Road Dust Particles** | Compound ID[§] |
| | **—Pentacyclic Triterpanes—** | | | |
| 22,29,30–trisnorneohopane | 29.6 | 0.35 | 10.1 | b |
| 17α(H),21β(H)-30-norhopane | 161.6 | 0.69 | 21.2 | b |
| 17α(H),21β(H)-hopane | 199.2 | 1.2 | 38.3 | b |
| 22S–17α(H),21β(H)-homohopane | 107.4 | 0.41 | 16.7 | b |
| 22R–17α(H),21β(H)-homohopane | 73.9 | 0.18 | 10.3 | b |
| 22S–17α(H),21β(H)-bishomohopane | 69.8 | 0.13 | 9.5 | b |
| 22R–17α(H),21β(H)-bishomohopane | 42.9 | 0.10 | 8.3 | b |
| Total class mass concentration: | 684.4 | 3.06 | 114.4 | |
| | **—Natural Resins[¶]—** | | | |
| dehydroabietic acid | 7970.3 | 10.1 | 6.8 | a |
| abietic acid | 69.6 | n.d. | n.d. | b |
| 7-oxodehydroabietic acid | 10.1 | n.d. | n.d. | a |
| e.g. 13β-ethyl-13-methyl-podocarp--8-en-15-oic acid | 291.3 | n.d. | n.d. | b |
| e.g. 13α-isopropyl-13-methyl-podocarp--8-en-15-oic acid | 255.8 | n.d. | n.d. | b |
| e.g. 13β-isopropyl-13-methyl-podocarp--8-en-15-oic acid | 916.2 | n.d. | n.d. | b |
| Total class mass concentration: | 9513.3 | 10.1 | 6.8 | |
| | **—Amides—** | | | |
| 4-phenylbenzenamine | 12.9 | n.d. | n.d. | b |
| Total class mass concentration: | 12.9 | | | |
| | **—Pesticides—** | | | |
| iridomyrmecin (insecticide) | n.d. | n.d. | 18.4 | b |
| simazine (herbicide) | n.d. | n.d. | 22.6 | b |
| Total class mass concentration: | | | 41.0 | |
| | **—Chorinated Organics—** | | | |
| α-chloroindane | 3.4 | n.d. | n.d. | b |
| 2,4,5'-trichlorobiphenyl | 1.9 | n.d. | n.d. | b |
| Total class mass concentration: | 5.3 | | | |

Table 5.1 (continued)

| PART H | Concentrations[‡] in $\mu g\ g^{-1}$ of Particle Sample | | | |
|---|---|---|---|---|
| | **Tire Wear Particles** | **Brake Lining Particles** | **Road Dust Particles** | Compound ID[§] |
| | **—Pesticides—** | | | |
| iridomyrmecin (insecticide) | n.d. | n.d. | 18.4 | b |
| simazine (herbicide) | n.d. | n.d. | 22.6 | b |
| Total class mass concentration: | | | 41.0 | |
| | **—Chorinated Organics—** | | | |
| α-chloroindane | 3.4 | n.d. | n.d. | b |
| 2,4,5'-trichlorobiphenyl | 1.9 | n.d. | n.d. | b |
| Total class mass concentration: | 5.3 | | | |
| | **—Other Compounds—** | | | |
| hydroxymethylphthalimide | 54.5 | n.d. | n.d. | b |
| p-octylphenol | 17.6 | n.d. | n.d. | b |
| isopulegol | n.d. | n.d. | 296.1 | b |
| α-terpineol | n.d. | n.d. | 27.4 | a |
| β-citronellol | n.d. | n.d. | 71.3 | b |
| Total class mass concentration: | 72.1 | | 394.8 | |

[†] Total (fine plus coarse) tire wear particles; it is assumed that fine wear particles have the same composition.

[‡] n.d. = not detected; n.m. = not measured, GC/MS-analysis was stopped prior to compound elution.

[§] for more details see text. a, positive: authentic std. verification; b, probable: library spectrum verification;
c, possible; d, tentative.

[¶] detected as methyl ester.

### Comparison of Road Dust and Ambient Particulate Matter

Figure 5.4d shows the annual average mass concentrations of airborne fine particulate n-alkanes collected throughout 1982 at 3 urban sites within the greater Los Angeles area (*7*). The ambient n-alkane signature over the range $C_{29}$ to $C_{33}$ follows closely that of the leaf abrasion aerosol samples (compare Figures 5.4b with 5.4d), except that $C_{33}$ is less significant. Compared to the road dust sample, the ambient aerosol samples are enriched in n-alkanes in the range contributed by vehicle exhaust (compare Figures 5.4a, 5.4c-d). If one thinks of both road dust and the ambient aerosol as containing a mixture of plant-derived n-alkanes and vehicle exhaust n-alkanes, then this relative enrichment of vehicle exhaust particles in the atmosphere vs plant-derived organics in road dust can be explained by particle size considerations that are important to particle deposition from the atmosphere. Exhaust aerosol is emitted primarily in submicron particle sizes centered on particles of 0.1 to 0.2 $\mu$m in diameter (*70*) that deposit very slowly from the atmosphere (*71*). Mechanically-generated leaf dust and soil dust particles are larger in size, and hence deposit more readily by gravitational sedimentation or impaction. Thus it is not surprising that the road dust deposits are enriched in organics characteristic of the mechanically-generated fine particle sources while the atmospheric samples are more enriched in combustion-generated organics.

## Conclusion

The chemical composition of the solvent-extractable organics present in fine particulate road dust, fine particulate organometallic brake lining wear, and particulate tire debris has been evaluated using GC/MS techniques. The mass concentrations of more than 100 individual organic compounds have been determined for several compound classes and include the n-alkanes, n-alkanoic acids, n-alkenoic acids, n-alkenoic acids, n-alkanols, n-alkanals, benzoic acids, substituted benzaldehydes, polyalkylene glycol ethers, PAH, oxy-PAH, steranes, hopanes, natural resins, pesticides, and others. n-Alkanes and n-alkanoic acids were the dominant solvent extractable compound classes identified in both tire wear particles and road dust. Natural resins were found in substantial amounts in tire debris, and in trace amounts in brake lining dust. Petroleum markers, e.g., steranes and hopanes, were found in all samples, although brake lining wear contained only small amounts. Polyalkylene glycol ethers, including triethylene glycol monomethyl- and monoethyl ethers, commonly used in brake fluids, were the dominant extractable organic compounds identified in the brake dust samples. While none of these glycol ethers could be detected in the residential paved road dust samples, annual average ambient concentrations in the Los Angeles area atmospheric fine aerosol (1982) ranged from 7.3 to 9.8 ng $m^{-3}$. Benzothiazole, a product of thiazoles that are used as vulcanization accelerators in rubber materials, was measured in tire wear particles and also in road dust that contains tire wear debris.

Molecular concentration patterns found in particulate vehicular exhaust emissions, green and dry vegetative detritus, road dust, brake lining wear particles, and tire debris were compared, and compound classes such as steranes, hopanes, and higher molecular n-alkanes were used to estimate the contribution of tire dust, vegetative detritus and vehicle exhaust aerosol to the road dust sample analyzed here. It was found that a maximum of 7.6% of the fine road dust is derived from vehicular exhaust emissions, which amounts to 32.7% of the organic compound mass found in the road dust sample. Even if all of the higher n-alkanes in the fine road dust sample were present due to tire dust, comparison to our tire dust sample shows that no more than 1.6% of the road dust mass corresponding to 4.3% of the fine organics mass in road dust could be contributed by tire dust.

A lower limit can be placed on biogenic source contributions to the paved road dust sample, utilizing the odd versus even carbon number predominance of n-alkanes ranging from $C_{29}$ to $C_{33}$, as found in leaf surface abrasion products and in the paved road dust sample. Vegetative detritus coming from nearby plants and trees, garden soil, and atmospheric fallout combined was estimated to contribute at the minimum 2.2% to the mass of fine particulate road dust collected here. Restated, at least 5.3% of the organic portion of that fine particulate road dust sample was derived from vegetative detritus.

It can be concluded that paved road dust represents an accumulation of contributions from a variety of urban source types including vehicle exhaust, tire dust and vegetative plant fragments, garden soil, and others. The relative contribution of these source types to the paved road dust complex can be studied by organic molecular marker techniques. Road dust is in many respects chemically similar to the primary portion of the atmospheric aerosol and indeed bears a dynamic relationship to the atmospheric aerosol through resuspension into and redeposition from the atmosphere.

## REFERENCES

(1) Hildemann, L.M.; Markowski, G.R.; Cass, G.R. Chemical composition of emissions from urban sources of fine organic aerosol. *Environ. Sci. Technol.* 1991, 25, 744–759.

(2) Mazurek, M.A.; Simoneit, B.R.T.; Cass, G.R.; Gray, H.A. Quantitative high-resolution gas chromatography and high-resolution gas chromatography/mass spectrometry analysis of carbonaceous fine aerosol particles. *Intern. J. Environ. Anal. Chem.* 1987, 29, 119–139.

(3) Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Interpretation of high-resolution gas chromatography and high-resolution gas chromatography/mass spectrometry data acquired from atmospheric organic aerosol samples. *Aerosol Sci. Technol.* 1989, 10, 408–419.

(4) Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Biological input to visibility-reducing aerosol particles in the remote arid Southwestern United States. *Environ. Sci. Technol.* 1991, 25, 684–694.

(5) Mazurek, M.A.; Hildemann, L.M.; Cass, G.R.; Simoneit, B.R.T.; Rogge, W.F. Methods of analysis for complex organic organic aerosol mixtures from urban sources of particulate carbon. In *Sampling and Analysis of Airbone Pollutants*; Winegar, E.D., Keith, L.H., Eds.; Lewis Publisher: Boca Raton, FL, 1993; pp 178–190.

(6) Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Sources of Fine Organic Aerosol: 1. Charbroilers and Meat Cooking Operations. *Environ. Sci. Technol.* 1991, 25, 1112-1125.

(7) Rogge, W.F.; Mazurek, M.A.; Hildemann, L.M.; Cass, G.R.; Simoneit, B.R.T. Quantification of Urban Organic Aerosols at a Molecular Level: Identification, Abundance, and Seasonal Variations. *Atmos. Environ.* 1993, *in press.*

(8) Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Sources of fine organic aerosol: 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. *Environ. Sci. Technol.* 1993, 27, 636–651.

(9) Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Quantitative characterization of urban sources of fine organic aerosol by high-resolution gas chromatography. *Environ. Sci. Technol.* 1991, 25, 1311–1325.

(10) Simoneit, B.R.T. Organic matter of the troposphere—III. Characterization and sources of petroleum and pyrogenic residues in aerosols over the Western United States. *Atmos. Environ.* 1984, 18, 51–67.

(11) Chi, C.T.; Hughes, T.W.; Ctvrtnicek, T.E.; Horn, D.A.; Serth, R.W. Source assessment: Rubber processing, state of the art. Environmental Protection Technology Series: EPA-600/2-78-004j, U.S. Environmental Protection Agency, Cincinati, OH, 1978, 118 pp.

(12) Cardina, J.A. The determination of rubber in atmospheric dusts. *Rubber Chem. Technol.* 1973, 46, 232–241.

(13) Funazukuri, T.; Takanashi, T.; Wakoa, N. Supercritical extraction of used automotive tire with water. *J. Chem. Engineering of Japan* 1987, 20, 23–27.

(14) Fraser, D.A.; Rappaport, S. Health aspects of the curing of synthetic rubbers. *Environ. Health Perspec.* 1976, 17, 45–53.

(15) Rappaport, S.M.; Fraser, D.A. Gas chromatographic-mass spectrometric identification of volatiles released from a rubber stock during simulated vulcanization. *Anal. Chem.* 1976, 48, 476–481.

(16) Storey, E.B. Oil-extended rubbers. *Rubber Chem. Technol.* 1961, 34, 1402–1484.

(17) Kirk-Othmer *Encyclopedia of Chemical Technology*, 3rd Ed., Vol. 24, John Wiley & Sons, Inc., New York, NY, 1985, 1028–1038.

(18) Kaidou, H.; Ahagon, A. Aging of tire parts during service. II. Aging of belt–skim rubbers in passenger tires. *Rubber Chem. Technol.* 1990, 63, 698–712.

(19) Ahagon, A.; Kaidou, H. Aging of tire parts during service. I. Types of aging in heavy-duty tires. *Rubber Chem. Technol.* 1990, 63, 683–697.

(20) Dannis, M.L. Rubber dust from the normal wear of tires. *Rubber Chem. Technol.* 1974, 47, 1011–1037.

(21) Fwa, T.F.; Ang, B.W. Tire–wear characteristics of public buses. *J. of Transportation Engineering-ASCE* 1991, 117, 298–310.

(22) Pierson, W.R.; Brachaczek, W.W. Airborne particulate debris from rubber tires. *Rubber Chem. Technol.* 1974, 47, 1275–1299.

(23) Schuring, D.J.; Clark, J.D. Load, speed, and pressure effects on passenger car tire rolling-loss distribution. *Rubber Chem. Technol.* 1988, 61, 669–687.

(24) Kim, M.G.; Yagawa, K.; Inoue, H.; Lee, Y.K.; Shirai, T. Measurement of tire tread in urban air by pyrolysis–gas chromatography with flame photometric detection. *Atmos. Environ.* 1990, 24A, 1417–1422.

(25) Thompson, R.N.; Nau, C.A.; Lawrence, C.H. Identification of vehicle tire rubber in roadway dust. *J. of Ameri. Ind. Hyg. Assoc.* 1966, 27, 488–495.

(26) Douglas, A.G.; Eglinton, G. The distribution of alkanes. In *Comparative Phytochemistry*, Swain T. Ed., Academic Press, London, 1966, 57-77.

(27) Simoneit, B.R.T. Organic matter of the troposphere—V. Application of molecular marker analysis to biogenic emissions into the troposphere for source reconciliations. *J. Atmos. Chem.* 1989, 8, 251–275.

(28) Simoneit, B.R.T.; Mazurek, M.A. Organic matter of the troposphere—II. Natural background of biogenic lipid matter in aerosols over the rural Western United States. *Atmos. Environ.* 1982, 16, 2139–2159.

(29) Bray, E.E.; Evans, E.D. Distribution of n-paraffins as a clue to recognition of source beds. *Geochim. Cosmochim. Acta* 1961, 22, 2-15.

(30) Garza, M.E. Jr.; Muth, J. Characterization of crude, semirefined and refined oils by gas–liquid chromatography. *Environ. Sci. Technol.* 1974, 8, 248-255.

(31) Spacht, R.B.; Hollingshead, H.L.; Bullard, H.L.; Wills, D.C. Volatility of antioxidants and antiozonants. II. Effect on rubber testing. *Rubber Chem. Technol.* 1965, 38, 134–139.

(32) Merck Index, $11^{th}$ ed.; Merck and Co., Inc.: New York, 1989.

(33) Sax, N.I.; Lewis, R.J., Sr. In *Hawley's Condensed Chemical Dictionary*; Van Nostrand Reinhold, New York; 1987, p. 130.

(34) Blumer, M. Polycyclic aromatic compounds in nature. *Sci. Am.* 1976, 234, 35–47.

(35) Tissot, B.P.; Welte, D.H. In *Petroleum Formation and Occurrence: A New Approach to Oil and Gas Exploration*, Springer Verlag, Berlin, 1978, 538 pp.

(36) Falk, H.L.; Steiner, P.E.; Goldfein, S. Carcinogenic hydrocarbons in processed rubber and in carbon blacks. *Cancer Res.* 1951, 11, 247.

(37) Falk, H.L.; Steiner, P.E. The identification of aromatic polycyclic hydrocarbons in carbon blacks. *Cancer Res.* 1952, 12, 30–39.

(38) Wakeham, S.G.; Schaffner, C.; Giger, W. Polycyclic aromatic hydrocarbons in recent lake sediments—I. Compounds having anthropogenic origins. *Geochim. Cosmochim. Acta* 1980, 44, 403–413.

(39) Haynes, B.S. Soot and hydrocarbons in combustion. In *Fossil Fuel Combustion: A Source Book* Bartock, W. and Sarofim, A.F. Eds., Wiley & Sons, NY., 1991, 261–326.

(40) Lohrer, W.; Mierheim, H. Substitution of asbestos in friction lining – analysis of problems and development trends. *Staub-Reinhalt. Luft* 1983, 43, 78–83.

(41) Jacko, M.G.; Tsang, P.H.S.; Rhee, S.K. Automotive friction materials evolution during the past decade. *Wear* 1984, 100, 503–515.

(42) Fletcher, L.S. Feasibility analysis of asbestos replacement in automobile and truck brake systems. *Mechanical Engineering* 1990, 3, 50–56.

(43) Day, A.J. An analysis of speed, temperature, and performance characteristics of automotive drum brakes. *J. Tribology–Transactions of the ASME* 1988, 2, 298–305.

(44) Liu, T.; Rhee, S.K. High temperature wear of semimetallic disc brake pads. *Wear* 1978, 46, 213–218.

(45) Ramachandra-Rao, V.T.V.S.; Ramasubramanian, H.; Seetharamu, K.N. Modelling of temperature distribution in a brake drum using finite element method. *Indian J. of Technology* 1989, 27, 417–424.

(46) Harvey, J.L.; Milliken, L.T.; Forthofer, R.J. Trends in motor vehicle brake fluids and their standards. *Soc. Automo. Eng. Tech. Pap.* 1971, SAE 710251: 1018–1036.

(47) SRI International. Directory of chemical producers, United States of America, Menlo Park, California, 1989.

(48) Rogge, W.F.; Mazurek, M.A.; Hildemann, L.M.; Cass, G.R.; Simoneit, B.R.T. Quantification of urban organic aerosols at a molecular level: II. Identification, abundance, and seasonal variations. *in preparation* 1993.

(49) Hall D.H.; Donaldson L.A. The ultrastructure of wax deposits on plant leaf surfaces, 1. Growth of wax on leaves of Trifolium Repens. *Nature* 1963, 191, 95-96.

(50) Kolattukudy, P.E. . Plant waxes. *Lipids* 1970, 5, 259–275.

(51) Braaten, D.A.; Paw, U.; Shaw, R.H. Particulate resuspension in a turbulent boundary layer — Observed and modeled. *J. Aerosol Sci.* 1990, 21, 613–628.

(52) Hall, D. The time dependence of particle resuspension. *J. Aerosol Sci.* 1989, 20, 907–910.

(53) Kulmala, M.; Riihiluoma, V.; Raunemaa, T. Particle emission from gasoline powered vehicles: emission, deposition and re-emission under different traffic density situations. *J. Aerosol Sci.* 1986, 17, 973–983.

(54) Nicholson, K.W.; Branson, J.R. Factors affecting resuspension by road traffic. *Sci. of Total Environ.* 1990, 93, 349–358.

(55) Eganhouse, R.P.; Kaplan, I.R. Extractable organic matter in urban stormwater runoff. 1. Transport dynamics and mass emission rates. *Environ. Sci. Technol.* 1981, 15, 310–315.

(56) Eganhouse, R.P.; Simoneit, B.R.T.; Kaplan, I.R. Extractable organic matter in urban stormwater runoff. 2. Molecular characterization. *Environ. Sci. Technol.* 1981, 15, 315–326.

(57) Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Sources of fine organic aerosol: 4. Particulate abrasion products from leaf surfaces of urban plants. *Environ. Sci. Technol.* 1993, *submitted.*

(58) Simoneit, B.R.T. Application of molecular marker analysis to vehicular exhaust for source reconciliations. *Intern. J. Environ. Anal. Chem.* 1985, 22, 203–233.

(59) Kawamura, K.; Ng. L-L.; Kaplan, I.R. Determination of organic acids ($C_1$ – $C_{10}$) in the atmosphere, motor exhausts, and engine oils. *Environ. Sci. Technol.* 1985, 19, 1082–1086.

(60) Simoneit, B.R.T. Characterization of organic constituents in aerosols in relation to their origin and transport: A review. *Intern. J. Environ. Anal. Chem.* 1986, 23, 207–237.

(61) Hunt, J.M. In *Petroleum Geochemistry and Geology.* W.H. Freeman & Co., San Francisco, 1979.

(62) Johns, R.B. ed. In *Biological Markers in the Sedimentary Record.* Elsevier, Amsterdam, 1986, 364 pp.

(63) Mackenzie, A.S.; Brassell, G.; Eglinton, G.; Maxwell, J.R. Chemical fossils: The geological fate of steroids. *Science* 1982, 217, 491–504.

(64) Simonsen, J.L.; Owen, L.N. The Terpenes. Vol. I. The simpler acyclic and monocyclic terpenes and their derivatives. Cambridge University Press, 1953, 479 pp.

(65) Daisey, J.M.; Cheney, J.L.; Lioy, P.J. Profiles of organic particulate emissions from air pollution sources: status and needs for receptor source apportionment modeling. *J. Air Pollut. Control Assoc.* 1986, 36, 17–33.

(66) Grimmer, G.; Hildebrandt, A. Investigation on the carcinogenic burden by air pollution in man. XIII. Assessment of the contribution of passenger cars to air pollution by carcinogenic polycyclic hydrocarbons. *Zbl. Bakt. Hyg., I. Apt. Orig. B* 1977, 161, 104–124.

(67) Rieley, G.; Collier, R.J.; Jones, D.M.; Eglinton, G. The biogeochemistry of Ellesmere Lake, U.K.—I: source correlation of leaf wax inputs to the sedimentary lipid record. *Org. Geochem.* 1991, 17, 901–912.

(68) Eglinton, G.; Gonzalez, A.G.; Hamilton, R.J.; Raphael, R.A. Hydrocarbon constituents of the wax coatings of plant leaves: A taxonomic survey. *Phytochemistry* 1962, 1, 89–102.

(69) Morrison, R.I.; Blick, W. The wax fraction of soils: separation and determination of some components. *J. Sci. Fd. Agric.* 1967, 18, 351–355.

(70) Hildemann, L.M.; Markowski, G.R.; Jones, M.C.; Cass, G.R. Submicrometer aerosol mass distributions of emissions from boilers, fireplaces, automobiles, diesel trucks, and meat-cooking operations. *J. Aerosol Sci.* 1991c, 14, 138–152.

(71) Seinfeld, J.H. In *Atmospheric Chemistry and Physics of Air Pollution.* Wiley-Interscience; New York, 1986, p. 647.

# Chapter 6

# Particulate Abrasion Products from Leaf Surfaces of Urban Plants

## Introduction

In order to model and predict the chemical composition and concentration levels of airborne fine particulate organic compounds ($d_p \leq 2$ $\mu$m) in an urban environment, it is necessary to characterize the source profiles of the major anthropogenic and biogenic sources. It has been observed that appreciable amounts (23 to 52%) of the "fine" ($<$ 1.7 $\mu$m) carbonaceous aerosol consists of contemporary (non-fossil) carbon in the Los Angeles atmosphere (*1-3*). Much of these contemporary carbon emissions are due to anthropogenic activities such as meat cooking (*4*), fireplace combustion of wood, cigarette smoke, road dust, and the natural rubber or resin content of vehicle tire wear debris (*5*). There is also strong evidence that plant leaves contribute an unspecified amount of fine particulate leaf wax protrusions to the atmosphere (*6-18*).

In order to apportion the contributions of primary fine particulate matter released to the atmosphere from urban vegetation, a stable tracer compound or an assemblage of tracer compounds with a distinct pattern is necessary. These tracers must be quantified in both source and ambient aerosol samples so that the fractional contribution of the source material present in the ambient samples can be computed. The first goal of this study is to characterize the organic

---

Reference: Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. *Environ. Sci. Technol.*, 1991, *submitted.*

composition of fine particulate matter released from leaf surfaces, for example due to wind induced-mechanical shear, from rubbing of leaves against each other or due to the aging of the leaves. To accomplish this task and to examine changes in leaf surface composition as leaves age, both green and dead leaves were collected and composited according to the actual vegetation variety prevailing in the Los Angeles basin (*19, 20*). Leaves from 62 different plant species including broadleaf trees, conifers, palms, shrubs and grasses from cultivated and native plant communities collected during the sampling campaign of Hildemann et al. (*5*) were agitated to release particulate matter shed from their surfaces. The resulting aerosol was collected downstream of cyclone separators ($d_p \leq 2\ \mu m$), and the extract was analyzed by gas chromatography/mass spectrometry (GC/MS) to identify and quantify the organic compounds emitted. The second goal of this study is to determine the extent to which specific organic compounds can be used as tracers for fine particulate leaf abrasion products in the urban atmosphere. To achieve that goal, the characteristics of leaf abrasion aerosol will be compared to other important direct and indirect emission sources of vegetative detritus, and then these biogenic source data will be compared to the ambient fine organic aerosol compounds measured in the Los Angeles area atmosphere.

## Experimental Methods

### Sample Collection

To collect a representative sample of leaves from the dominant plant communities of the Los Angeles area, the studies by Winer et al. (*20*) and Miller and Winer (*19*) were used to determine the actual leaf mass for each important plant species growing within the Los Angeles air basin. On the basis of the these studies, leaf samples from 62 individual plant species were collected during the period December 5–8, 1988 (*5*). Both a green leaf sample and a dead leaf sample was collected separately from each plant species. The harvesting campaign occurred following a period of rain which perhaps reduced the amount of anthropogenic particulate matter present due to deposition onto the leaf surfaces (Rainfall totalling 1.76 inches was observed during November 14 and 23–25). The two sample sets (one for fresh green leaves and one for dry dead leaves) included leaves from 51 cultivated ornamental plant types such as broadleaf trees, conifers, shrubs, palms, grasses, and other ground cover and 10 plant species indigenous to the area. Leaves from one agricultural crop (a lemon tree) also were collected. Leaf samples from the cultivated plants were collected in the Los Angeles County Arboretum in Arcadia, CA. Leaves from the plant communities native to the basin were collected from Eaton Canyon Park in Pasadena, CA and from Rancho Santa Ana in Claremont, CA. For more details including the names of the actual plant species collected, their leaf mass per unit area of vegetated land within the Los Angeles basin, and the fractional mass of each species in the composite samples, see Hildemann et al. (*5*).

### Leaf Aerosol Generation

In past studies, leaf surface structures, such as wax protrusions that might under suitable conditions detach and become airborne, have been removed by dipping the complete leaf into solvents such as chloroform or dichloromethane (*12, 16, 21-23*) or by selective solvent extraction of the upper and lower leaf side separately (*24*). However, under natural environmental conditions, these crystalline-like leaf surface waxes are dislodged by the wind and/or by the rubbing motions of leaves against each other. In urban areas, interaction with airborne pollutants may alter leaf wax coatings in a way that affects the emission rate of leaf surface matter (*25*). To acquire a chemical fingerprint representative of leaf surface-derived urban airborne particles, urban leaf material must be sampled and the typical mechanical removal process has to be simulated.

In two separate experiments, first the green leaf and then the dead leaf composites were placed in a Teflon bag. While agitating the leaves, purified laboratory air was blown into the bag through a HEPA filter. Simultaneously, particle laden air was withdrawn from the bag through cyclone separators (50% cutoff at 2 $\mu$m aerodynamic particle diameter) and collected on quartz fiber filters (Pallflex 2500 QAO) and Teflon filters (Gelman Teflo, 2.0 $\mu$m pore size). To ensure that no unfiltered laboratory air could enter the bag it was operated under slight positive pressure. Prior to sampling, the quartz filters used were annealed at 750°C for 2-4 h to guarantee low organic contamination levels. The resuspension and agitation process for both the green and dead leaf mixtures was performed over $\sim$ 2 h periods.

### Sample Extraction

The filter samples collected here were processed according to an extraction procedure initially developed by Mazurek et al. (*26*). Detailed descriptions have also appeared in several subsequent papers, and only a brief discussion will be provided here (*4, 9, 10, 27*). Prior to extraction, a known amount of perdeuterated tetracosane ($\underline{n}$-$C_{24}D_{50}$) was spiked onto the filter samples to serve as an internal standard. The amount added was based on the organic carbon (OC) content of the samples as determined by a separate analysis performed on filters collected in parallel (*5, 28*). The fine particulate dead and green vegetative fragments collected on quartz fiber filters each were extracted successively by mild ultrasonic agitation twice in hexane (2 × 30 ml) and then three times in benzene/2-propanol (2:1 mixture, 3 × 30 ml). After each extraction step, the extracts were filtered and combined using a specially designed transfer and filtering line (*26*). The total sample extract then was reduced to 200 – 500 $\mu$l using rotary evaporation and gentle high purity $N_2$-stream evaporation. In order to improve compound separation and detection, the sample extract was divided into two aliquots. By adding freshly produced diazomethane to one aliquot, the organic acids were derivatized to form their methyl ester analogues and aromatic hydroxy compounds were derivatized to form their corresponding methoxy analogues. Until injection onto the GC/MS system used here, the sample extracts were stored at –21°C.

## Sample Analysis

Compound identification and quantification was conducted using a Finnigan 4000 quadrupole mass spectrometer interfaced with a gas chromatograph and an INCOS data system. For compound fragmentation, the mass spectrometer was operated in the electron impact mode (electron energy of 70 eV). Compound separation was accomplished using a 30-m fused-silica DB-1701 column (J & W Scientific, Rancho Cordova, CA). The chromatographic procedure can be described as follows: (1) sample extract injection in splitless mode at 300°C, (2) isothermal hold at 65°C for 10 min, (3) temperature ramp program at 10°C/min for 21 min, and (4) isothermal hold at 275°C for another 49 min. For parallel analysis, a Varian 4600 high-resolution gas chromatograph (HRGC) with FID-detector system was used (*28*) which was operated with the same temperature programming and physical column used for GC/MS-analysis. Further description of the analytical procedures are available elsewhere (*4, 10, 26, 27*).

## Compound Identification and Quantification

The identification and quantification process for particle-bound organics is explained comprehensively in previous and companion papers that also describe the quality assurance procedures emphasized in the present study (*4, 10, 29*). Confirmation and quantification of the organic compounds present was attained through the use of more than 150 authentic standards (*10, 29*), and by comparison to the mass spectral library maintained by the National Institute of Standards and Technology (NIST). Compound identification was labeled as follows: (a) *positive*, when the sample mass spectrum, authentic standard compound mass spectrum and their retention times agreed well; (b) *probable*, same as above except no standards were available, but the sample mass spectrum agreed very well with NIST Standard Library accessed by the INCOS data system; (c) *possible*, same as above except that the sample spectrum contained information from other compounds but with minor overlap; (d) *tentative*, when the sample spectrum contained additional information from possibly several compounds (noise) with overlap; (e) for *iso-* and *anteiso*-alkanes only: both branched-alkane types can be distinguished from normal alkanes due to differences in the mass fragmentation pattern caused by favored scissions occurring at the C–C-bond adjacent to the tertiary carbon atoms. As a result, major mass spectral peaks at M-43 (*iso*-alkanes) and M-29 (*anteiso*-alkanes) are observed allowing — in addition to the elution time relative to the *n*-alkanes — their positive identification.

The compound quantification process was based on the application of *n*-$C_{24}D_{50}$ as the internal standard and 1-phenyldodecane as the coinjection standard. To correct for detector response, sets of known standard compounds were injected onto the analytical system to monitor their specific MS-response.

## Results and Discussion

### Plant Leaves as Source of Airborne Particulate Matter

The leaf surfaces of vascular plants generally consist of a lipophilic polymer membrane (cuticle) whose monomers are mostly hydroxy fatty acids (*24, 30-32*). Embedded and growing from the cuticular membrane are waxlike lipids forming crystalline structures of micron to submicron dimensions and intercrystalline amorphous zones which together act as a protective barrier between cuticula and the atmosphere (*21, 23, 30, 32, 34-38*). These epicuticular plant waxes along with the stomata (pores for the exchange of $CO_2$, water vapor, $O_2$, etc.) control the aspiration and transpiration of gaseous substances, water, and solutes across the leaf-atmosphere interface. Epicuticular plant waxes consist mainly of aliphatic compounds such as higher molecular weight $n$-alkanes, $n$-alkanals, $n$-alkanols, $n$-alkanoic acids, and wax esters (*16, 21, 23, 24, 30, 32, 39*).

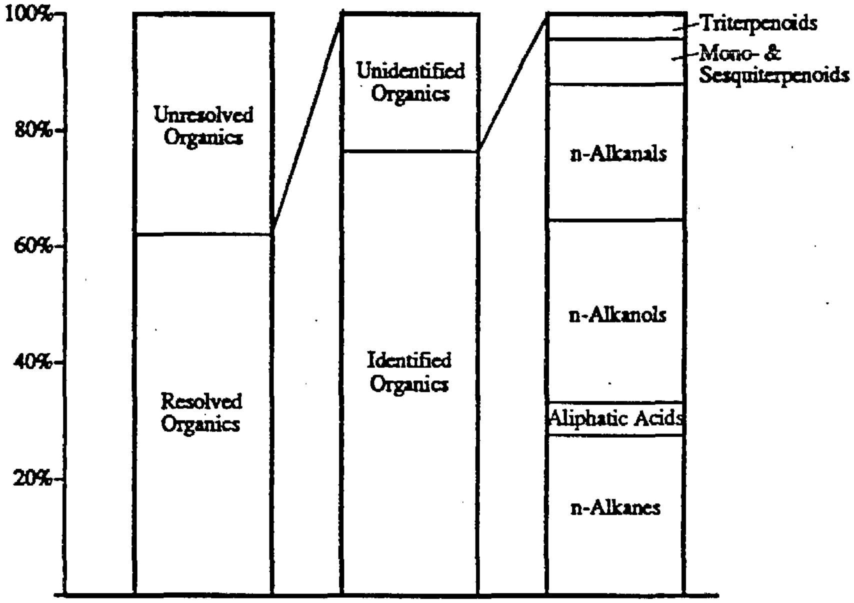
Because plant foliage also hosts microorganisms like bacteria, fungi and fungal spores, plants contribute to the aerial dispersion of such microorganisms (*40-44*). Furthermore, leaves act as a sink for anthropogenic and natural airborne material (e.g., soil particles), which under suitable conditions is reentrained (resuspended) into the atmosphere. Due to wind-induced mechanical shear and rubbing of leaves against each other, such epicuticular wax protrusions and leaf deposits become airborne and have been identified in urban and rural aerosols (*7-11, 14-16, 18, 45-48*).

In the following sections, the organic composition of fine particulate matter collected from the agitation of green and dead leaf composites characteristic of the Los Angeles basin will be discussed. Then these leaf surface emissions will be related to other sources that emit biogenic particulate matter. Finally, comparisons will be made to the organic composition of ambient fine particulate matter collected from the Los Angeles urban atmosphere.

### Mass Balance for Elutable Fine Organic Matter

For both fine particulate green and dead leaf abrasion products, material balances were constructed for the extractable and elutable organics mass as detected by GC/MS (see Figures 6.1a,b). This organics mass can be divided into chromatographically resolved and unresolved organic compounds. The total mass of resolved compounds ranges from 62% (green leaf abrasion products) to 67% (dead leaf abrasion products). From the resolved organic mass, 76% (green leaf abrasion products) to 84% (dead leaf abrasion products) could be identified as individual compounds. The organic compounds identified consist mainly of epicuticular leaf wax constituents such as *n*-alkanes, *n*-alkanoic acids (both as free acids and methyl esters), *n*-alkanols, *n*-alkanals, and other plant wax related compounds. For these identified portions, the relative abundance of each compound class found in the abraded dead and green leaf surface protrusions can be compared as follows (see also Table 6.1): (a) the relative abundance of *n*-alkanes (98.5 to 98.7% of the total alkanes, the remainder are *iso*- and *anteiso*-alkanes) and *n*-alkanals increases only slightly when green leaves die and become brittle; (b) within the aliphatic acid group where *n*-alkanoic acids constitute 92.8 to 98.7% of the mass (the remaining portion is comprised of *n*-alkenoic acids and others, see also Table 6.1), the relative aliphatic acid content in dead leaf abrasion products is nearly tripled compared to green leaf abrasion particles (16.0% vs. 5.7% of the identifiable elutable mass); (c) the relative amount of *n*-alkanol compound mass as a fraction of the whole identified mass is reduced significantly in the dead leaf abrasion products (green: 31.3% vs. dead: 20.6%);

(a) GC/MS Elutable Organic Mass: Green Vegetation Abrasion Products



(b) GC/MS Elutable Organic Mass: Dead Vegetation Abrasion Products

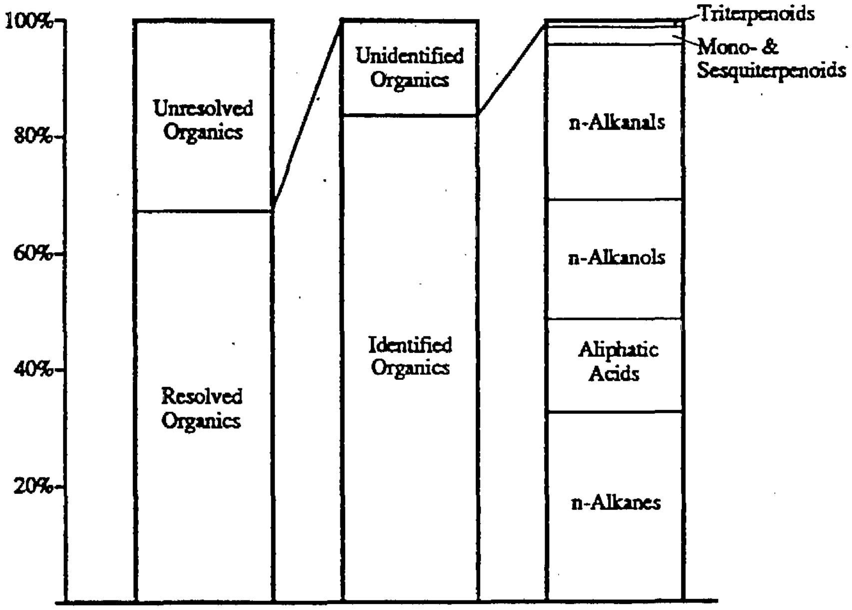


Fig. 6.1: Mass balance for elutable organic matter contained in the fine leaf surface particles shed from: (a) green leaf and (b) dead leaf composites.

(d) mono- and sesquiterpenoids present in leaf abrasion products are reduced more than half in dead leaf versus green leaf samples (green: 7.8% vs. dead: 3.1%); and (e) high molecular weight triterpenoids such as $\beta$-amyrin, ursolic and oleanolic acids are even more drastically depleted in the dead leaf surface abrasion products (green: 4.0% vs. dead: 1.1%).

## Aerosol Composition of Vegetative Origin

The reconstructed total ion current traces for the GC/MS analyses of dead and green leaf abrasion products are shown in Figures 6.2a,b, which identify the major resolved compounds present in the sample extracts. The mass concentrations of the dominant compound classes and their distributions are shown in Figures 6.3a-c. The organic composition of the resuspended vegetative detritus samples can be described as follows.

## Alkanes

Epicuticular waxes containing $n$-alkanes ($C_{20}$ – $C_{40}$) are found on the surfaces of plant leaves, seeds, fruits, stems, pollen, fungi, and also on insects (*12, 21, 30, 33, 39, 45, 49-54*). Waxy $n$-alkanes also have been detected in seed oils (*55*). Biosynthesized leaf wax $n$-alkanes exhibit a strong odd carbon number predominance with the dominant wax $n$-alkanes being $C_{29}$, $C_{31}$, and $C_{33}$ (*16, 21, 23, 30*). Beside normal alkanes, *iso-* (2-methyl) and *anteiso-* (3-methyl) alkanes also have been reported as part of the leaf waxes, especially in tobacco leaves with the highest concentrations for $C_{27}$ to $C_{34}$ branched alkanes (*21, 30, 56-60*). While *iso*-alkanes show a preference for odd carbon number molecules, similar to $n$-alkanes, *anteiso*-alkanes favor even carbon number chain-lengths. Leaf surface wax constituents such as $n$-alkanes and others reveal a characteristic distribution

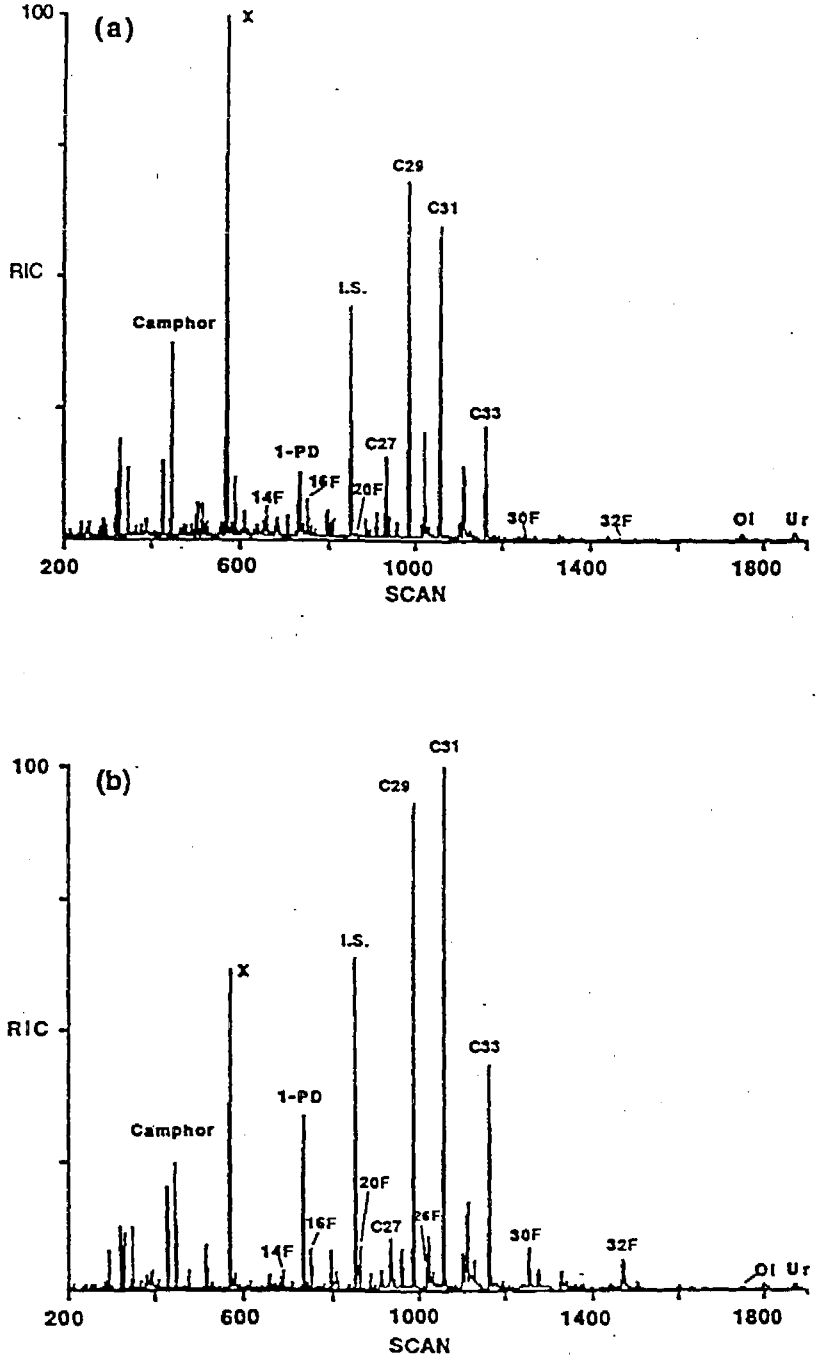


Fig. 6.2: Total reconstructed ion current (RIC) chromatogram (GC/MS) for fine leaf surface particulate matter shed from: (a) green leaf and (b) dead leaf composites. Numbers refer to carbon chain length of compounds: C, *n*-alkanes; F, *n*-alkanoic acids (detected as methyl esters); Ol, oleanolic acid as methyl ester; Ur, ursolic acid as methyl ester; 1-PD, 1-phenyldodecane as coinjection standard; I.S., *n*-$C_{24}D_{50}$ as internal standard; X, contaminant.

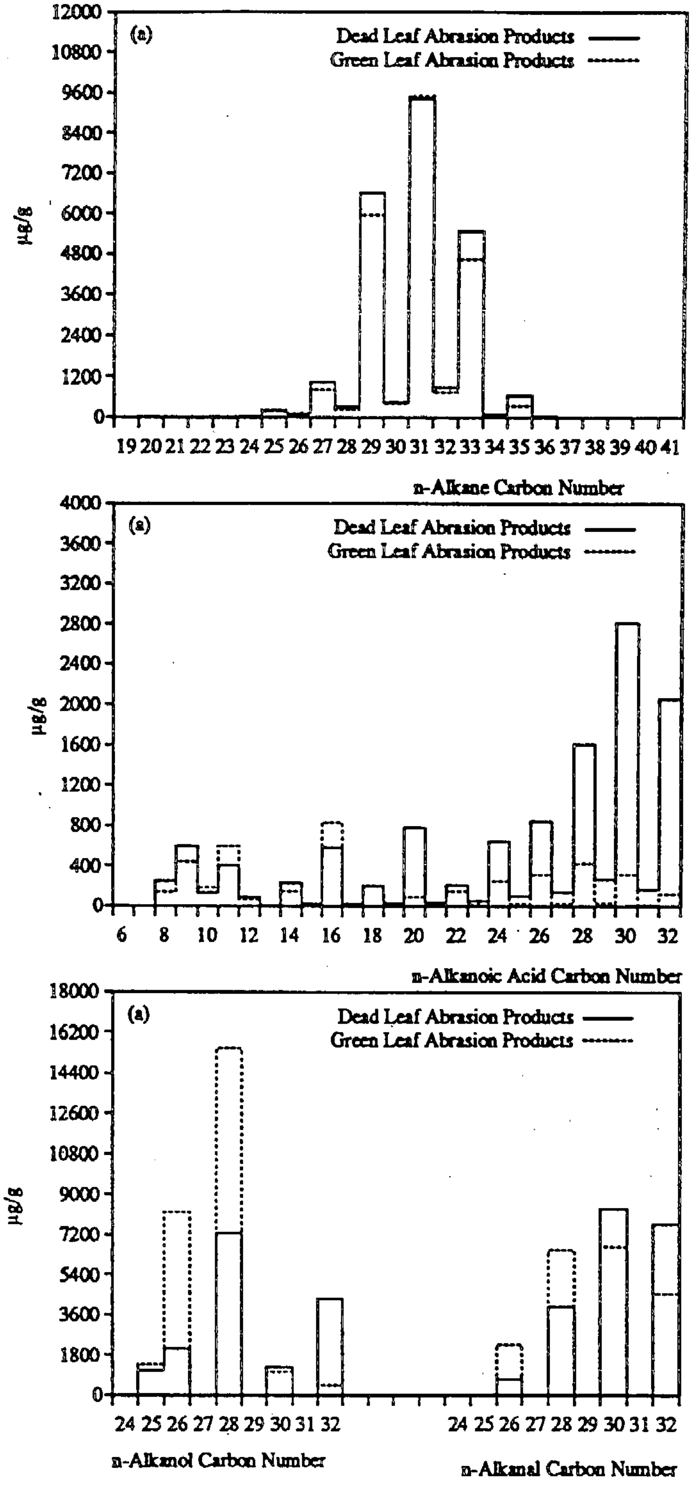


Fig. 6.3: Compound concentrations per gram of fine particulate matter shed from leaf surfaces: (a) *n*-alkanes, (b) *n*-alkanoic acids, and (c) *n*-alkanols and *n*-alkanals.

for each plant species which additionally can be modified to adapt the plants to different climatological and geographic conditions, such as temperature and water supply (*24, 32, 61-65*). Recently, it has been suggested that pollutant exposure also might alter the epicuticular wax composition and accelerate leaf wax erosion (*25, 66-69*).

While pollen, fungi, and insect fragments are much too large ($d_p \gg 2\ \mu m$) to be collected with the methods employed here, some of the fine particulate matter released from the leaf surfaces may contain bacterial microorganisms and fungal spores (*70*). Although bacteria are not known to have a waxlike surface layer, those bacterial lipids that are soluble in organic solvents and distinct from fats and phospholipids are termed "waxes" (*71*). The waxlike lipid fraction of most bacteria consists mainly of fatty acids ($\leq C_{20}$), and usually accounts for less than 5% of the bacterial dry weight (*72*). Microbial "wax" alkanes occur as normal, branched, and monounsaturated homologues. Waxes of photosynthetically active bacteria predominantly contain medium molecular weight hydrocarbons ($C_{14} - C_{20}$), whereas non–photosynthetic bacteria also show small amounts of normal and branched higher molecular weight alkanes ($C_{26} - C_{30}$) (*50, 71, 73*).

Garden soil, a pool for plant degradation, contains *n*-alkanes with an odd carbon number preference in about the same carbon range as epicuticular leaf waxes (*74, 75*). Despite the fact that soil dust consists mainly of coarse particulate matter ($d_p > 2\ \mu m$), waxlike compounds from the soil biota might contribute somewhat to the dead leaves collected from the ground and to a smaller extent to the green leaves, where deposition of airborne soil dust onto the living plants and trees might occur.

In contrast to contemporary biomass, *n*-alkanes found in crude oils and in petroleum-derived products do not show a preference for odd-to-even carbon number *n*-alkanes, having lost this feature during the maturation processes ongoing within the sedimentary organic material. These maturation processes can also be accompanied by a shift of *n*-alkanes to lower carbon numbers, with the most abundant *n*-alkane ($C_{Max}$) in crude oil falling in the range of $C_{22}$ to $C_{25}$ (*76-79*).

In the fine particulate leaf abrasion products investigated here, *n*-alkanes were identified and quantified ranging from $C_{19}$ to $C_{36}$ (Table 6.1). The mass distribution profiles for both green and dead leaf abrasion particles are shown in Figure 6.3a. The odd carbon number *n*-alkanes with 29, 31, and 33 carbon atoms are by far the most prominent wax *n*-alkanes identified in emissions from the vegetation of the leaf composites (see also Figures 6.2a,b). The mass concentrations ($\mu$g $g^{-1}$ of fine particulate leaf surface material emitted) for these hydrophobic and chemically rather stable compounds do not change significantly when comparing green with dead leaf abrasion particle samples. This indicates that most of the *n*-alkanes released during the leaf agitation experiments are in fact derived from epicuticular plant wax protrusions. Besides *n*-alkanes, *iso*- and *anteiso*- alkanes ($C_{29}$ to $C_{34}$) also have been identified in small concentrations. As a group, the identified *iso*- and *anteiso*-alkanes amount only to 1.5 to 1.6% of the $C_{29}$ to $C_{34}$ *n*-alkanes mass.

## Alkanoic and Alkenoic Acids

Another major compound class commonly identified in epicuticular plant waxes is the group of saturated *n*-fatty acids (*12, 14, 16, 23, 30, 32*). Higher molecular weight *n*-fatty acid synthesis includes elongation of low molecular weight homologues yielding predominantly even carbon number *n*-alkanoic acids

(*30*). Whereas the synthesis of higher molecular weight *n*-alkanoic acids is unaffected by light, the synthesis of the short-chain *n*-fatty acids is closely linked to photosynthesis where $C_{16}$ and $C_{18}$ are the major *n*-alkanoic acids produced (*30*).

*n*-Alkanoic acids also have be found in the waxlike extracts of fungi (molds), bacteria, spores, pollen, and algae (*37, 71, 72, 80-83*). The microorganisms mentioned above all favor production of branched, normal, and also hydroxy fatty acids with a carbon length $\leq C_{20}$ (*14, 50, 71, 81, 82, 84*). Recently, Lee and coworkers (*85*) determined the viable bacteria size distribution in the urban atmosphere. The mass median diameter of the airborne bacteria was 7.6 $\mu$m. Only 10% of the bacteria show diameters $\leq 2$ $\mu$m. Molds and their spores show exclusively diameters $> 2$ $\mu$m (*86*). Consequently bacteria and bacterial spores which might be found in the particle size range $d_p \leq 2$ $\mu$m could possibly contribute to the fine particulate matter abraded from the leaf surfaces and would contain *n*-alkanoic acids ($C \leq 20$) that overlap the lower molecular weight range of the *n*-alkanoic acids found in leaf surface waxes.

In this study, *n*-alkanoic acids ranging from octanoic acid ($C_8$) to dotriacontanoic acid ($C_{32}$) have been identified in both green and dead leaf abrasion products (see Figures 6.4a,b). Except for nonanoic acid ($C_9$), which might be an oxidation product of palmitoleic ($C_{16:1}$) and oleic ($C_{18:1}$) acids, a strong even-to-odd carbon number predominance is observed with $C_{26}$, $C_{28}$, $C_{30}$, and $C_{32}$ as the major homologues usually found in leaf waxes of vascular plants (e.g., *24, 32*) (see Figure 6.3b). *n*-Alkanoic acids are often minor compounds in green leaf surface waxes (e.g., *24, 32, 87*) which agrees with the our data, see Table 6.1. Of the total amount of *n*-alkanoic acids quantified, 1.2% (dead leaf abrasion products) to 5.0% (green leaf abrasion products) was found as methyl esters in the

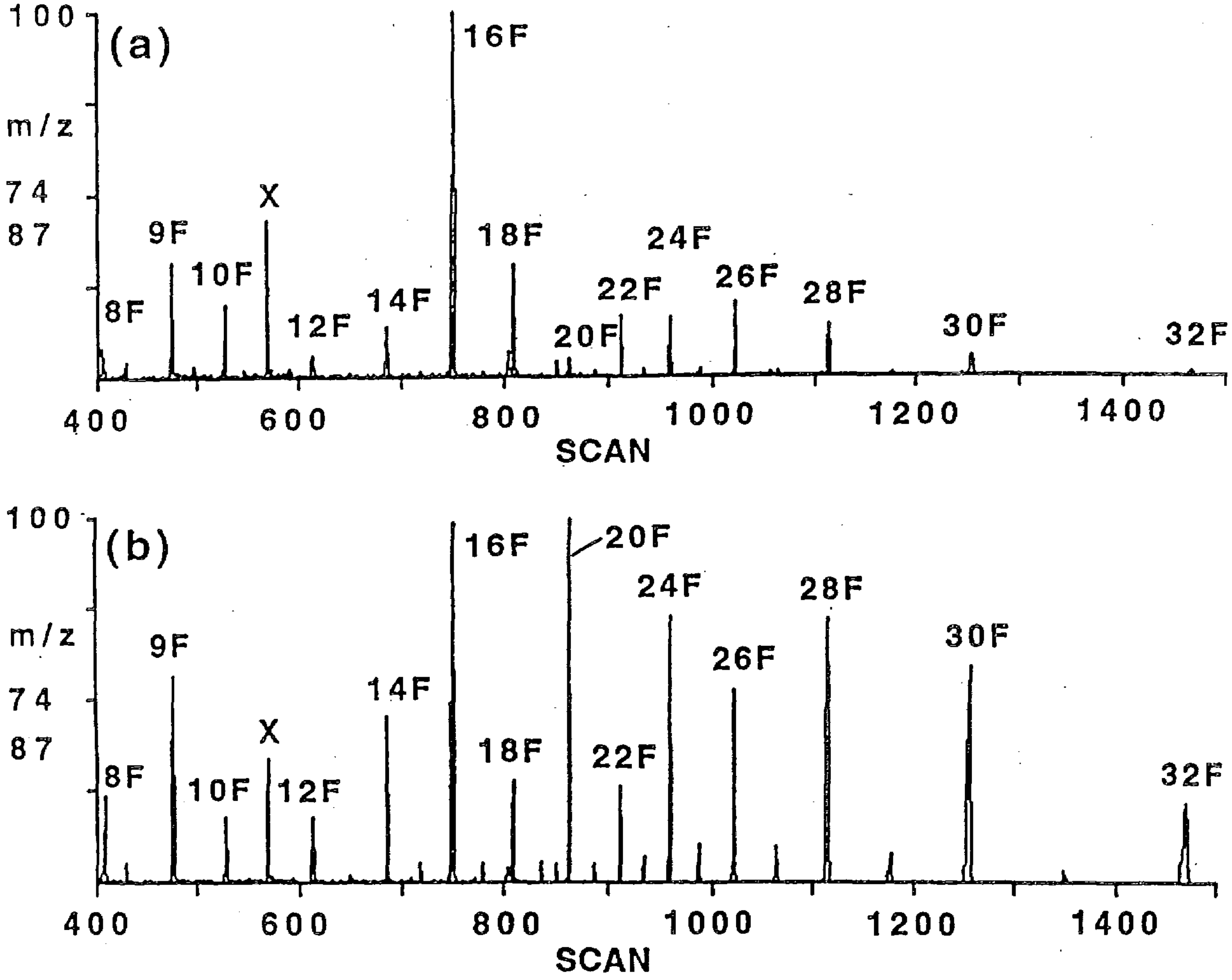


Fig. 6.4: Selected mass fragmentograms for *n*-alkanoic acids as methyl esters (sum: m/z 74 + 87) found in fine particulate leaf abrasion products: (a) green leaf and (b) dead leaf composites. Numbers refer to the carbon chain length of the n-alkanoic acids (detected as methyl esters).

underivatized sample extracts. Hence, most of the *n*-alkanoic acids identified in the range investigated exist as free acids in the plant surface waxes.

A more than four-fold increase in the mass concentration of higher molecular weight *n*-alkanoic acids ($\geq C_{24}$) is observed in dead leaf abrasion products when compared to green leaf abrasion products. Possible explanations include oxidation of *n*-alkanols and *n*-alkanals to form *n*-alkanoic acids in the dead leaf material and/or the effect of environmental growth conditions (e.g., temperature) or leaf age on wax composition (24, 61, 63-65, 88).

Unsaturated *n*-fatty acids also have been identified and quantified in the leaf abrasion products of the present study. Oleic (18:1), linolenic (18:2), and linoleic (18:3) acids are the unsaturated *n*-fatty acids (*n*-alkenoic acids) identified here and are common constituents of the total lipids that can be extracted from broadleaves and conifer needles (*37, 84*). Unsaturated *n*-fatty acids are also found in bacteria, fungal spores, pollen, seeds and seed oils, plant organells and leaf cells (*37, 72, 79, 81, 83, 84*). They are unstable compounds susceptible to radical and oxidant (e.g., ozone) attack (*47, 89, 90*). The *n*-alkenoic acids concentration per mass of abraded fine leaf particles is from 35% to 73% lower in the dead leaf than in the green leaf abrasion products (see Table 6.1), which is consistent with the expected degradation over time of such unsaturated compounds.

## Alkanols and Alkanals

Both compound types are synthetized enzymatically by plants from precursor *n*-alkanoic acids (*30*). Long-chain *n*-fatty acids are more readily utilized in this synthesis than shorter ones. The resulting long-chain *n*-alkanols and *n*-alkanals are often the major compound classes identified in leaf waxes and show a preference for even over odd carbon number homologues (*24, 36*).

Several long-chain primary *n*-alkanols ($C_{25}$, $C_{26}$, $C_{28}$, $C_{30}$, $C_{32}$) and *n*-alkanals ($C_{26}$, $C_{28}$, $C_{30}$, $C_{32}$) have been identified in the present study in both green and dead leaf abrasion detritus (Table 6.1). Even carbon number *n*-alkanols and *n*-alkanals dominate the emissions of these compound classes; with the exception of pentacosanol ($C_{25}$), only the even number homologues were found in this study (see Figures 6.5a,b). The most abundant primary *n*-alkanols in green leaf abrasion products are $C_{26}$ and $C_{28}$ (see Figure 6.3c). On the contrary, $C_{30}$ and $C_{32}$ *n*-alkanols are more abundant in dead than in green leaf abrasion products. A similar trend also was found for *n*-alkanals (see Figure 6.3c). As discussed before, oxidative alterations, environmental growth conditions (e.g., temperature) and/or the effect of leaf age on wax composition might be responsible for the observed compositional differences seen between green and dead leaf abrasion products.

### Mono-, Sesqui-, and Triterpenoids

Several oxygenated acyclic, monocyclic, bicyclic monoterpenoids, sesquiterpenoids, and pentacyclic triterpenoids (terpenols, terpenoid acids and ketones) have been found in both the green and dead leaf abrasion particle samples (see Table 6.1). Mono- and sesquiterpenoids are released from many plant species, and their oxygenated forms are known for their pleasant and distinctive odors (*91-99*). They are synthetized by the plant communities investigated here and adhere to the fine particulate leaf abrasion products. Their mass concentration as a group declines by more than 60% when going from particles abraded from green leaves to those from dead leaves (see Table 6.1). This decline in concentration seen in dead leaf surface matter may be the result of evaporative losses

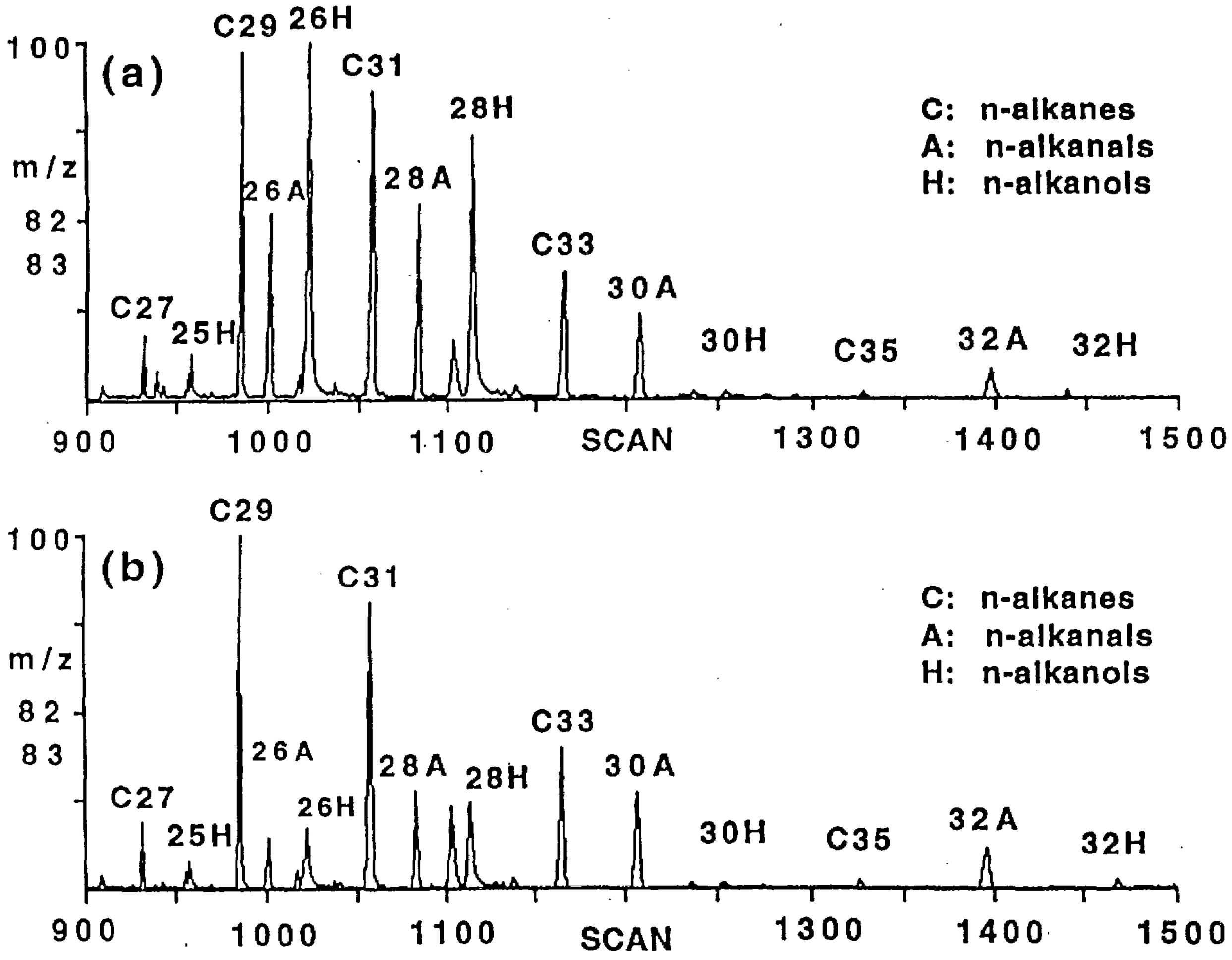


Fig. 6.5: Selected mass fragmentograms typical for *n*-alkanols and *n*-alkanals (sum: m/z 82 + 83) found in fine particulate leaf abrasion products: (a) green leaf and (b) dead leaf composites. Numbers refer to the carbon chain length of the molecules: A, *n*-alkanals; C, *n*-alkanes; H, *n*-alkanols.

as well as possible leaf–atmosphere surface chemical reactions. Camphor, a bicyclic monoterpenone, is the single most abundant terpenoid in both the green ($\sim 3500\ \mu g\ g^{-1}$) and dead ($\sim 1600\ \mu g\ g^{-1}$) fine particulate leaf abrasion product samples studied here.

One triterpenol ($\beta$-amyrin) and two triterpenoic acids (oleanolic and ursolic acid) have been identified in the leaf abrasion particle samples studied here. Triterpenoids previously have been identified as common leaf and fruit wax constituents (*30, 47, 87, 88, 100, 101*). Because of their high molecular weights (MW $\geq 426$), oxygenated pentacyclic triterpenoids have very low vapor pressures and exist exclusively in the condensed phase. Nevertheless, the mass concentrations of the three triterpenoids are much lower (by 55 to 75%) in the dead versus green leaf detritus samples, indicating that these compounds are either susceptible to leaf–atmosphere reactions or microbial degradation. Related findings have been reported by Simoneit et al. (*47*) based on direct examination of leaf surface material and total ambient particle samples. They found that triterpenoids were more abundant in composited leaf waxes than were phytosterols, whereas in ambient aerosol samples, triterpenoids were less abundant than phytosterols. Kolattukudy (*30*) reported that certain highly specialized microorganisms (*Pseudomonas* species) can grow on ursolic acid as the sole source of carbon, suggesting that microorganisms could also be responsible for the observed depletion of the triterpenoids in the dead leaf surface abrasion products.

**Table 6.1** **Organic Compounds found in Fine Particulate Abrasion Products from Green and Dead Leaves[a].**

| PART A | Concentrations in $\mu g\ g^{-1}$ of Leaf Abrasion Products[b] | | |
|---|---|---|---|
| | Green Leaf Composite | Dead Leaf Composite | Compound ID[c] |
| | —*n*–Alkanes— | | |
| nonadecane | 9.0 | 4.8 | a |
| eicosane | 13.2 | 4.8 | a |
| heneicosane | 14.0 | 8.6 | a |
| docosane | 15.3 | 8.0 | a |
| tricosane | 33.8 | 21.4 | a |
| tetracosane | 44.9 | 29.6 | a |
| pentacosane | 220.4 | 199.9 | a |
| hexacosane | 93.5 | 125.5 | a |
| heptacosane | 821.9 | 1035.4 | a |
| octacosane | 234.4 | 328.8 | a |
| nonacosane | 5958.4 | 6616.6 | a |
| triacontane | 433.8 | 445.2 | a |
| hentriacontane | 9493.3 | 9395.8 | a |
| dotriacontane | 758.7 | 880.7 | a |
| tritriacontane | 4635.8 | 5480.3 | a |
| tetratriacontane | 90.3 | 91.9 | a |
| pentatriacontane | 359.8 | 651.0 | a |
| hexatriacontane | 49.0 | 13.2 | a |
| Total class mass concentration: | 23279.5 | 25341.5 | |
| | —*iso*- and *anteiso*–Alkanes— | | |
| *iso*-nonacosane | 18.4 | 20.7 | e |
| *iso*-triacontane | 7.7 | 5.4 | e |
| *iso*-hentriacontane | 65.7 | 67.3 | e |
| *iso*-tritriacontane | 123.0 | 140.4 | e |
| *anteiso*-triacontane | 19.7 | 19.3 | e |
| *anteiso*-hentriacontane | 15.9 | 15.9 | e |
| *anteiso*-dotriacontane | 42.7 | 36.3 | e |
| *anteiso*-tritriacontane | 7.2 | 5.5 | e |
| *anteiso*-tetratriacontane | 44.8 | 28.1 | e |
| Total class mass concentration: | 345.1 | 338.9 | |
| | —*n*–Alkanoic Acids[d]— | | |
| octanoic acid (caprylic acid) | 143.4 | 249.7 | a |
| nonanoic acid (pelargonic acid) | 444.7 | 596.8 | a |
| decanoic acid (capric acid) | 183.8 | 133.0 | a |
| undecanoic acid | 597.6 | 403.1 | a |
| dodecanoic acid (lauric acid) | 64.5 | 91.4 | a |

Table 6.1 (continued)

**Concentrations in $\mu$g g$^{-1}$ of Leaf Abrasion Products[b]**

| PART B | Green Leaf Composite | Dead Leaf Composite | Compound ID[c] |
|---|---|---|---|
| tridecanoic acid | 6.7 | 9.6 | a |
| tetradecanoic acid (myristic acid) | 147.8 | 237.4 | a |
| pentadecanoic acid | 15.2 | 25.4 | a |
| hexadecanoic acid (palmitic acid) | 835.4 | 589.9 | a |
| heptadecanoic acid | 9.8 | 25.0 | a |
| octadecanoic acid (stearic acid) | 210.2 | 200.9 | a |
| nonadecanoic acid | 11.2 | 30.2 | a |
| eicosanoic acid (arachidic acid) | 91.7 | 780.5 | a |
| heneicosanoic acid | 12.5 | 38.4 | a |
| docosanoic acid (behenic acid) | 152.2 | 212.4 | a |
| tricosanoic acid | 18.9 | 47.9 | a |
| tetracosanoic acid | 256.6 | 646.9 | a |
| pentacosanoic acid | 24.2 | 100.8 | a |
| hexacosanoic acid | 321.3 | 840.2 | a |
| heptacosanoic acid | 26.7 | 145.6 | a |
| octacosanoic acid | 430.8 | 1610.2 | a |
| nonacosanoic acid | 32.9 | 266.1 | a |
| triacontanoic acid | 322.9 | 2812.9 | a |
| hentriacontanoic acid | 15.9 | 170.6 | a |
| dotriacontanoic acid | 127.7 | 2062.0 | a |
| Total class mass concentration: | 4504.6 | 12326.9 | |
| —*n*–Alkenoic Acids[d]— | | | |
| *cis*–9–octadecenoic acid (oleic acid) | 62.1 | 28.2 | a |
| 9,12–octadecadienoic acid (linoleic acid) | 110.8 | 71.8 | a |
| 9,12,15–octadecatrienoic acid (linolenic acid) | 150.1 | 39.7 | b |
| Total class mass concentration: | 323.0 | 139.7 | |
| — Other Aliphatic Acids — | | | |
| 3,7–dimethyl–6–octenoic acid (citronellic acid)[d] | 59.9 | 4.7 | b |
| 2,6,10–trimethylundecanoic acid methyl ester[e] | 170.5 | 14.0 | b |
| Total class mass concentration: | 230.4 | 18.7 | |
| — *n*-Alkanols— | | | |
| pentacosanol | 1377.5 | 1093.7 | a |
| hexacosanol | 8224.4 | 2069.4 | a |
| octacosanol | 15484.4 | 7293.9 | a |

**Table 6.1 (continued)**

**Concentrations in $\mu$g g$^{-1}$ of Leaf Abrasion Products[b]**

| PART C | Green Leaf Composite | Dead Leaf Composite | Compound ID[c] |
|---|---|---|---|
| triacontanol | 1060.3 | 1248.9 | b |
| dotriacontanol | 443.3 | 4324.9 | b |
| Total class mass concentration: | 26589.9 | 16030.8 | |
| **— *n*-Alkanals—** | | | |
| hexacosanal | 2279.0 | 736.3 | b |
| octacosanal | 6522.0 | 3980.7 | b |
| triacontanal | 6658.4 | 8376.2 | b |
| dotriacontanal | 4537.0 | 7687.4 | b |
| Total class mass concentration: | 19996.4 | 20780.6 | |
| **—Mono- and Sesquiterpenoids —** | | | |
| eucalyptol | 233.9 | 49.4 | b |
| camphor | 3569.6 | 1654.3 | a |
| borneol acetate | n.d. | 567.6 | b |
| linalool | 35.1 | 16.3 | b |
| citral (geranaldehyde) | 462.0 | 1.4 | b |
| citronellol | 869.2 | 13.3 | b |
| geranyl isobutyrate | 31.6 | n.d. | b |
| isopulegol (p-menth-8-en-3-ol) | 86.9 | n.d. | b |
| 4–terpineol (p-menth-1-en-4-ol) | 59.0 | 19.8 | b |
| α–terpineol (p-menth-1-en-8-ol) | 132.7 | 29.9 | a |
| *cis*-terpin hydrate | 830.3 | 25.4 | b |
| β–ionone | 95.4 | 13.6 | b |
| β–cadinene | 60.5 | 8.5 | b |
| Total class mass concentration: | 6466.2 | 2399.5 | |
| **— Triterpenoids —** | | | |
| β-amyrin (olean-12-en-3-ol) | 47.7 | 22.0 | b |
| oleanolic acid (3–oxo-olean-12-en-28-oic acid)[d] | 1544.1 | 379.5 | b |
| ursolic acid (3–hydroxy-urs-12-en-28-oic acid)[d] | 1778.7 | 477.7 | b |
| Total class mass concentration: | 3370.5 | 879.2 | |

Table 6.1 (continued)

**Concentrations in $\mu g\ g^{-1}$ of Leaf Abrasion Products**[b]

| PART D | Green Leaf Composite | Dead Leaf Composite | Compound ID[c] |
|---|---|---|---|
| **—Polycyclic Aromatic Hydrocarbons (PAH)—** | | | |
| fluoranthene | 1.2 | 0.47 | a |
| pyrene | 2.0 | 1.1 | a |
| chrysene/triphenylene | 2.9 | 1.9 | a |
| Total class mass concentration: | 6.1 | 3.47 | |
| **—Others—** | | | |
| dihydroactinidiolide | 75.6 | 12.8 | b |
| Total class mass concentration: | 75.6 | 12.8 | |

[a] fine particulate matter ($d_p \leq 2\mu m$) released from the leaves by by resuspension and agitation of the leaf composites.

[b] n.d. = not detected.

[c] for more details see text. a, positive: authentic std. verification; b, probable: library spectrum verification; c, possible; d, tentative; e, iso- and anteiso-alkanes are positively identified by monitoring their major ions at M-43 and M-29 respectively.

[d] detected as methyl esters in the derivatized sample aliquot.

[e] compound detected as methyl ester in the underivatized sample aliquot.

## Deposition of Airborne Particles onto Vegetational Foliage

Leaf surfaces are considered to be an important sink for airborne particulate matter originating from anthropogenic sources (*102-104*). Assuming that all elemental carbon (EC) determined in the fine particulate leaf abrasion products (*5*) originates from dry deposited fine airborne particulate matter and that the EC/OC ratio found in Los Angeles ambient fine particulate matter is on the average 2:1 (*105*) then the organic fraction in the leaf abrasion particles contributed from airborne particle fallout can be estimated. From those calculations it is found that less than 5% of the abraded organic matter is due to dry deposited airborne fine particles.

Given the small contributions from dry deposited aerosol, it is not surprising that only small amounts of PAH such as fluoranthene, pyrene or chrysene and triphenylene have been found in the fine particles abraded from the leaf composites. No fossil fuel markers (e.g., steranes, hopanes) characteristic for petroleum products have been detected (*29*). Investigations of the organic composition of fine particulate emissions from diesel and gasoline powered vehicles, road dust and other traffic-related sources have been completed recently by Rogge et al. (*29, 106*). Vehicular *n*-alkane emissions are most pronounced for *n*-alkanes $\leq C_{27}$ with no odd to even carbon number predominance. Although the *n*-alkane profiles of ambient fine particle samples reflect such vehicular-derived emissions (*10*), the *n*-alkane profiles of green and dead leaf abrasion products studied here do not reflect significant contributions from motor vehicle exhaust.

### Molecular Tracers for Vegetative Detritus

To trace the emissions and fate of organic fine particulate leaf abrasion products in the urban atmosphere, a stable and distinct molecular marker or an assemblage of such organic compounds is necessary. When using a group of single organic compounds or a series of homologues (e.g., *n*-alkanes, *n*-alkanoic acids, hopanes, etc.) it must be shown that these compounds have a concentration pattern that is characteristic of the source under consideration. Furthermore, the potential for interfering contributions to these ambient tracer concentrations due to other sources must be assessed.

The group of *n*-alkanes ($C_{27}$ – $C_{33}$ with their strong odd carbon number predominance) might serve as a marker assemblage that could be used to trace fine particulate vegetative detritus released to the urban atmosphere. For this to constitute a useful tracer for leaf abrasion products, the extent to which the biogenic preference for odd carbon number *n*-alkanes can be found in the fine particulate emissions of other sources must be determined. The *n*-alkanoic acids ($C_{20}$ – $C_{32}$ with their strong even carbon number predominance) might also be examined for use as tracers, although their variability between dead and green leaf abrasion products is greater.

Because gasoline and diesel fuel powered vehicles emit *n*-alkanes mainly in the carbon range $\leq C_{27}$ with small amounts of *n*-alkanes $> C_{28}$ and virtually no odd/even carbon number predominance, no interference is expected from these sources with the plant wax odd/even *n*-alkane pattern (*29, 106, 107*). Likewise, vehicular exhaust emissions contain only *n*-alkanoic acids $< C_{22}$ with no preference for odd or even carbon numbers (*29, 106, 107*). Similar results for *n*-alkanoic acids have been found for tire wear particles and brake lining abrasion products

(*106*). Although tire wear *n*-alkanes have been identified that range from $C_{19}$ to $C_{40}$ and possibly higher, no odd/even carbon number predominance is observed for that series (for more details see Rogge et al., *106*). Other important sources releasing fine organic particulate matter to the urban Los Angeles atmosphere include meat cooking operations (e.g., hamburger frying and charbroiling; *4*, *5*). However, meat cooking releases only small amounts of *n*-alkanes that do not show a pronounced odd/even carbon number dominance over the range $C_{27}$ to $C_{29}$, and virtually no *n*-alkanoic acids $> C_{18}$ have been found in these fine particulate emissions (*4*). Seed oils used for food preparation also contain small amounts of *n*-alkanes that have been dissolved from the waxlike coating of seed hulls during the oil extraction process (*55*) and that could become airborne during cooking with such oils. Refined seed oils consist mostly of fatty acids, but also contain 0.01–0.5% hydrocarbons by mass, including *n*-alkanes, *iso*-alkanes, plus multi-branched (e.g., squalene), and cyclic hydrocarbons (*55*). The *n*-alkane distributions for many seed oils show the typical plant wax odd/even carbon number predominance ($C_{27}$ to $C_{33}$), which constitutes a potential source of interference with the use of higher molecular weight *n*-alkanes as a tracer for airborne plant debris.

Cigarette smoke, a combustion product from tobacco leaves, exhibits a distribution pattern for higher molecular weight *n*-alkanes that is similar to that found for green and dead leaf abrasion products, as shown by comparing Figure 6.3a with 6.6a (*108*). Likewise, the *n*-alkanoic acids from cigarette smoke exhibit an even/odd carbon number predominance similar to that observed for the leaf abrasion samples (compare Figures 6.3b with 6.6b); however palmitic ($C_{16}$) and stearic ($C_{18}$) acids are relatively more abundant in cigarette smoke

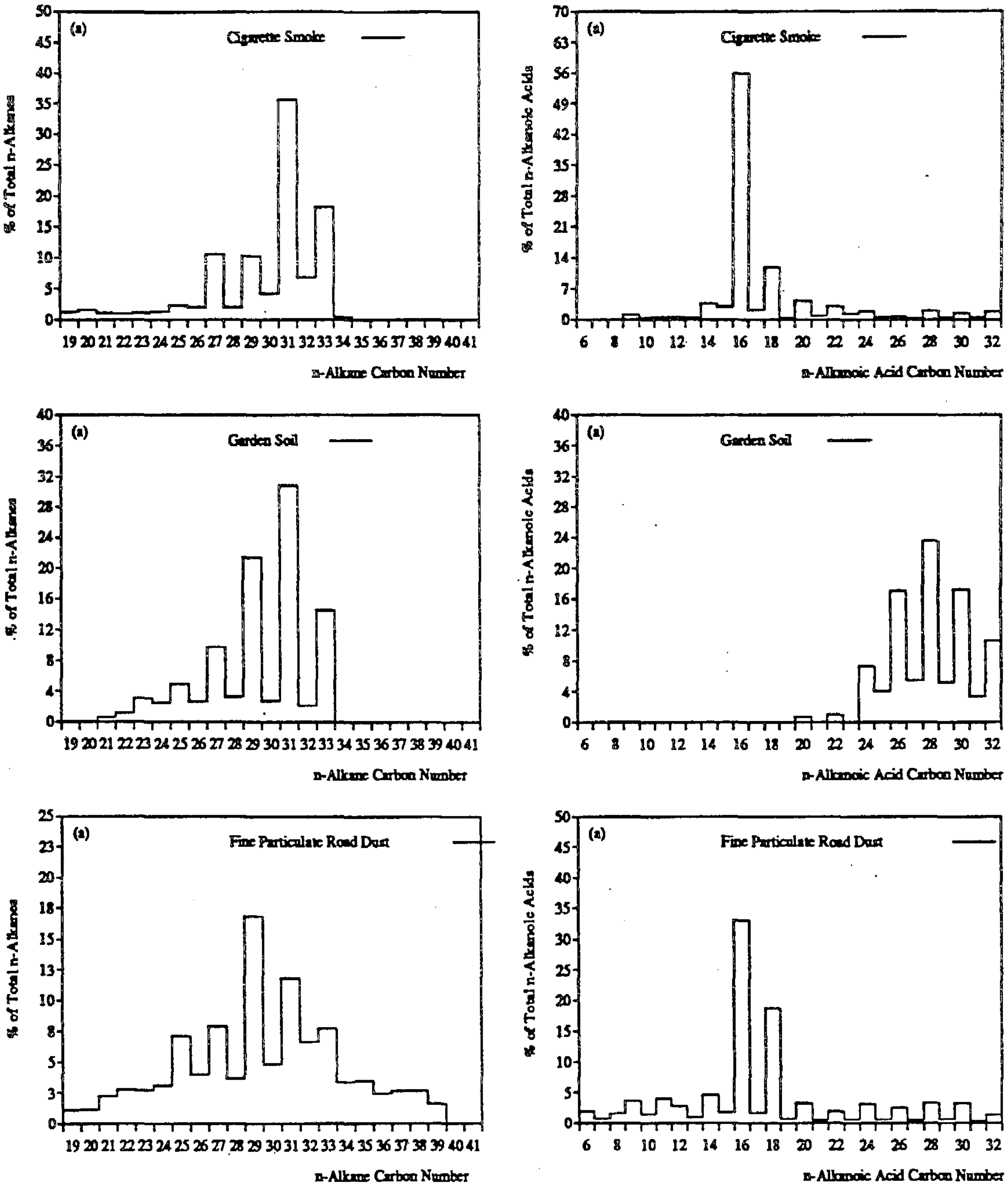


Fig. 6.6: Relative mass concentration expressed as % of that compound class present in fine particles: (a) *n*-alkanes from cigarette smoke; (b) *n*-alkanoic acids from cigarette smoke; (c) *n*-alkanes from garden soil (from Morrison and Blick, 1967); (d) *n*-alkanoic acids from garden soil (from Morrison and Blick, 1967); (e) *n*-alkanes from fine particulate paved road dust; and (f) *n*-alkanoic acids from fine particulate paved road dust.

than in the leaf abrasion samples, and *n*-alkanoic acids $\geq C_{22}$ are less pronounced in the cigarette smoke.

In urban areas, much of the leaf material produced during an annual growing cycle is deposited in nearby gardens and along streets. In this manner, leaf waxes may be added to garden soil and to road dust. Wind or traffic-induced turbulence can resuspend garden soil and road dust, thus entraining vegetative detritus particles into the atmosphere. As a consequence, sources of this kind also have to be investigated in the course of determining the contribution of plant material to the atmosphere.

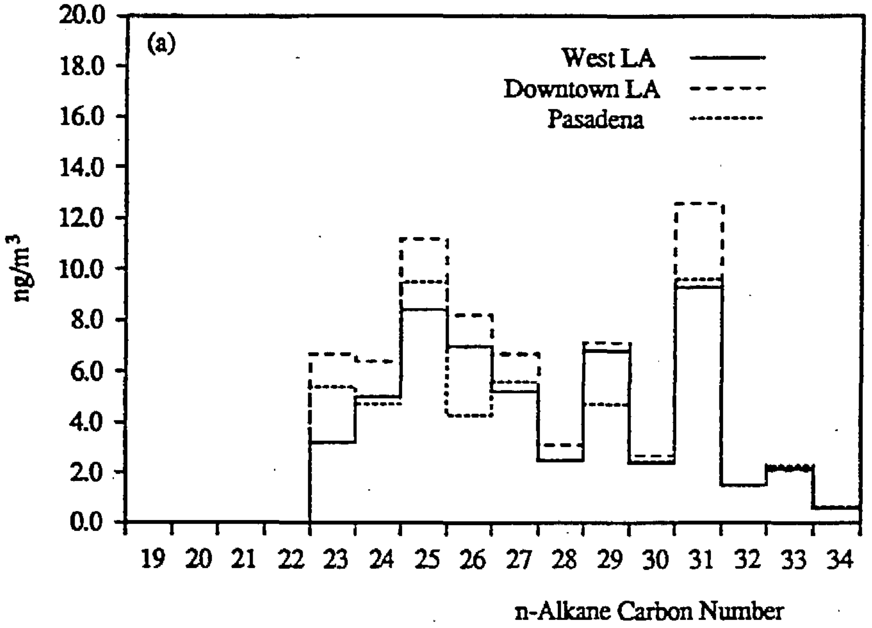
Morrison and Blick (*75*) analyzed garden soil for several compound classes including *n*-alkanes ($C_{21} - C_{33}$) and *n*-alkanoic acids ($C_{20} - C_{34}$). Their results for both compound classes are shown in Figures 6.6c,d and compare well with the green and dead leaf abrasion product samples studied here (Figures 6.3a,b).

Fine particulate road dust, which is a composite of atmospheric fallout, deposited vehicular emissions, soil, and plant detritus, was collected in a residential area in Pasadena, California during spring 1989 (*5, 106*). The road dust *n*-alkanes distribution shows an odd/even carbon number preference over the range from $C_{25}$ to $C_{33}$, with $C_{29}$ as the major homologue. By comparison, the leaf abrasion particle samples have $C_{31}$ as the major homologue (compare Figure 6.6e with 6.3a). Because the *n*-alkane distribution can differ substantially from one plant species to another and between seasons, as discussed previously, a combination of seasonal changes and locally differing vegetational composition might be responsible for the observed difference. The *n*-alkanoic acid distribution pattern for the higher molecular weight homologues found in the road dust closely resembles the pattern found for the green leaf samples, suggesting that the road dust collected in springtime is influenced especially by green vegetative detritus and garden soil material (compare Figures 6.6d,f with 6.3b).

From the anthropogenic and biogenic source types discussed, it seems promising that odd carbon number *n*-alkanes as a group ranging from $C_{27}$ to $C_{33}$ can serve as a molecular tracer assemblage for biogenic-derived *n*-alkane emissions, but the material being traced in this way includes both the direct and indirect (resuspension of soil and road dust) release of green, dead, and degraded plant wax material and may include some processed plant waxes such as are found in cooking oil. Cigarette smoking, an anthropogenically controlled source of biogenically derived leaf waxes, cannot be discriminated from the other biogenic source contributions mentioned without using additional modeling tools or cigarette smoke specific tracers to apportion the emissions from cigarette smoking to the atmospheric fine particulate organic compound concentrations.

### Comparison of Source and Ambient Samples

The organic composition of atmospheric fine particulate samples collected from the greater Los Angeles area atmosphere throughout the year 1982 recently has been quantified (*10*). The sampling technique and analytical protocol used for processing those ambient samples is closely aligned with the procedures used to analyze the leaf abrasion particle samples discussed here, and the results from both studies can be compared directly. Many of the compounds identified in the fine particulate leaf abrasion products also have been quantified in the ambient samples. Figures 6.7a and 6.7b show the ambient concentration distributions for the homologous series of *n*-alkanes and *n*-alkanoic acids. The ambient *n*-alkane concentrations of the higher odd carbon number *n*-alkanes ($C_{27}$ - $C_{33}$) show a pattern that is both similar to that of the leaf abrasion samples (Figure 6.3a)



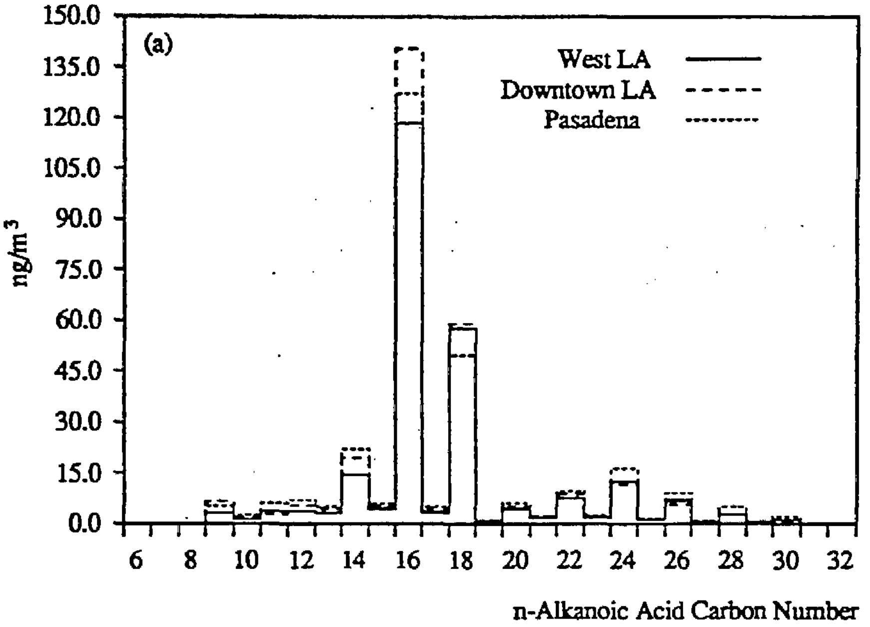


Fig. 6.7: Annual average concentration profiles for fine airborne particulate matter in 1982: (a) *n*-alkanes and (b) *n*-alkanoic acids.

and to the other direct and indirect vegetation-related sources just discussed (road dust, garden soil, cigarette smoke) (see Figures 6.6a,c,e). Hentriacontane ($C_{31}$) is the dominant *n*-alkane in all of the biogenic sources mentioned above, and $C_{29}$ shows a lower concentration relative to $C_{31}$ in all these aerosol sources (except for road dust). Similar trends are seen for the *n*-alkanes found in airborne particulate matter (Figure 6.7a). These observations suggest that the distributions of higher molecular weight *n*-alkanes ($C_{27} - C_{33}$) found in ambient fine particulate matter are indeed consistent with releases from plant material being superimposed on a fossil fuel background. Apart from that, the concentrations of the $C_{33}$ *n*-alkane in airborne particulate matter are depleted compared to the vegetative source samples. As mentioned before, local differences in vegetational composition surrounding the sampling sites might be reflected in the observed *n*-alkane pattern.

Comparing the ambient higher molecular weight *n*-alkanoic acid ($\geq C_{24}$) concentration distribution (Fig. 6.7b) with that of the vegetation-related sources (see Figures 6.6b,d,f and 6.3b), a similar even/odd carbon number predominance exists. While the road dust, green leaf abrasion detritus, cigarette smoke aerosols, and garden soil show a maximum for the $C_{28}$ *n*-alkanoic acid within the higher molecular weight range ($C_{24}$ to $C_{32}$), the ambient *n*-alkanoic acids in that range instead peak at $C_{24}$. Because $C_{24}$ is the dominant higher molecular weight *n*-alkanoic acid observed throughout the year at all three ambient sampling sites shown in Figure 6.7b it has to be assumed that another yet to be investigating source of fine particles might emit higher molecular weight *n*-alkanoic acids with a preference for the $C_{24}$ member of this homologous series.

Focusing on vegetation-specific terpenoid compounds such as mono-, sesqui-, and triterpenoids, only small amounts of some monoterpenoids (camphor, 4-terpineol, $\alpha$-terpineol) have been found at our remote offshore sampling site (San Nicolas Island) during the summer and autumn months. At the urban sampling sites only camphor, the most abundant terpenoid compound identified in this study, was found and then only in trace amounts during the winter season.

## Conclusions

Fine particle leaf abrasion products shed from dead and green leaf composites representative of the dominant vegetation found in the greater Los Angeles area have been characterized using GC/MS techniques. Surface leaf wax compounds such as *n*-alkanes, *n*-alkanoic acids, *n*-alkanals, *n*-alkanols, and triterpenoids have been identified and quantified. In addition to waxy leaf surface constituents, semi-volatile compounds such as mono- and sesquiterpenoids also have been found.

While the relative *n*-alkane content ($\mu$g g$^{-1}$ of leaf surface abrasion products) of fine particulate dead and green leaf abrasion particles is more or less invariant, the relative *n*-alkanoic acid content, especially for higher molecular weight homologues, is drastically increased in the dead leaf abrasion products. In contrast, all terpenoid compounds, independent of molecular weight, are depleted in the dead leaf abrasion products indicating their chemically labile nature relative to the waxy molecular constituents.

In the present work, it has been shown that the concentration pattern of the higher molecular weight *n*-alkanes ($C_{27}$ – $C_{33}$), with its pronounced odd/even carbon number predominance, is a characteristic tracer for those fine particulate emission sources which redistribute plant waxes including leaf surface fragments, garden soil, road dust, cigarette smoke, and possibly vegetable cooking oils. Likewise, the *n*-alkanes measured in atmospheric samples show a pronounced odd/even carbon number predominance within the same *n*-alkane range. The *n*-alkane series ($C_{29} - C_{33}$) can be used to identify the presence of biogenic material in the atmosphere from the source types just discussed. Both natural sources and anthropogenic activities (e.g., smoking, cooking, gardening) together are responsible for the observed ambient concentration levels. To apportion leaf surface abrasion particles in ambient air separately from accompanying road dust, garden soil, cooking oil and cigarette smoke contributions, more advanced modeling tools will be needed.

# REFERENCES

( 1) Berger, R.; McJunkin, D.; Johnson, R. Radiocarbon concentration of California aerosols. *Radiocarbon* 1986, 28, 661-667.

( 2) Currie, L.A. Contemporary particulate carbon .In *Particulate Carbon: Atmospheric Life Cycle*; Wolff, G.T., Klimisch, R.L., Eds.; Plenum Press: New York, 1982, pp 245-260.

( 3) Currie, L.A.; Klouda, G.A.; Continetti, R.E.; Kaplan, I.R.; Wong, W.W.; Dzubay, T.G.; Stevens, R.K. On the origin of carbonaceous particles in American cities: Results of radiocarbon dating and chemical characterization. *Radiocarbon* 1983, 25, 603-614.

( 4) Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Sources of fine organic aerosol: 1. Charbroilers and meat cooking operations. *Environ. Sci. Technol.* 1991, 25, 1112-1125.

( 5) Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Quantitative characterization of urban sources of organic aerosol by high-resolution gas chromatography. *Environ. Sci. Technol.*, 1991b, 25, 1311–1325.

( 6) Arpino, P.; Van Dorsselear, A.; Sevier, K.D.; Ourisson, G. Cires aériennes dans une forêt de pins. *C.R. Acad. Sc. (Paris)*, 1972, 275D, 2837–2840.

( 7) Doskey, P.V.; Andren, A.W. Particulate- and vapor-phase n-alkanes in the northern Wisconsin atmosphere. *Atmos. Environ.* 1986, 9, 1735–1744.

( 8) Gagosian, R.B.; Zafiriou, O.C.; Peltzer, E.T.; Alford, J.B. Lipids in aerosols from the tropical North Pacific: temporal variability. *J. Geophys. Res.* 1982, 87, 11133–11144.

( 9) Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Biological input to visibility-reducing particles in the remote arid southwestern United States. *Environ. Sci. Technol.* 1991, 25, 684-694.

(10) Rogge, W.F.; Mazurek, M.A.; Hildemann, L.M.; Cass, G.R.; Simoneit, B.R.T. Quantification of urban organic aerosols at a molecular level: I. Identification, abundance, and seasonal variations. *Atmos. Environ.* 1993, *in press.*

(11) Sicre, M.-A.; Marty, J.-C.; Saliot, A. n-Alkanes, fatty acid esters, and fatty acid salts in size fractionated aerosols collected over the Mediterranean Sea. *J. Geophys. Res.* 1990, 95, 3649–3657.

(12) Simoneit, B.R.T. Organic matter in eolian dusts over the Atlantic Ocean. *Mar. Chem.* 1977, 5, 443-464.

(13) Simoneit, B.R.T. Characterization of organic constituents in aerosols in relation to their origin and transport. A review. *Int. J. Environ. Anal. Chem.* 1986, 23, 207-237.

(14) Simoneit, B.R.T. Organic matter of the troposphere—V. Application of molecular marker analysis to biogenic emissions into the troposphere for source reconciliations. *J. Atmos. Chem.* 1989, 8, 251-275.

(15) Simoneit, B.R.T.; Cardoso, J.N.; Robinson, N. An assessment of the origin and composition of higher molecular weight organic matter in aerosols over Amazonia. *Chemosphere* 1990, 21, 1285–1301.

(16) Simoneit, B.R.T.; Mazurek, M.A. Organic matter of the troposphere—II. Natural background of biogenic lipid matter in aerosols over the rural Western United States. *Atmos. Environ.* 1982, 16, 2139-2159.

(17) Standley, L.J.; Simoneit, B.R.T. Characterization of extractable plant wax, resin, and thermally matured components in smoke particles from prescribed burns. *Environ. Sci. Technol.* 1987, 21, 163-169.

(18) Wils, E.R.J.; Hulst, A.G.; Hartog, J.C. The occurrence of plant wax constituents in airborne particulate matter in an urban area. *Chemosphere* 1982, 11, 1087–1096.

(19) Miller, P.R.; Winer, A.M. Composition and dominance in Los Angeles basin urban vegetation. *Urban Ecology* 1984, 8, 29–54.

(20) Winer, A.M.; Fitz, D.R.; Miller, P.R. Investigation of the Role of Natural Hydrocarbons in Photochemical Smog Formation in California. Final report to the California Air Resources Board, Sacramento, CA, under Agreement no. A0-056-032; Statewide Air Pollution Research Center, University of California, CA, 1983.

(21) Eglinton, G.; Gonzalez, A.G.; Hamilton, R.J.; Raphael, R.A. Hydrocarbon constituents of the wax coatings of plant leaves: A taxonomic survey. *Phytochemistry* 1962, 1, 89–102.

(22) Mazurek, M.A.; Simoneit, B.R.T. Characterization of biogenic and petroleum-derived organic matter in aerosols over remote, rural and urban areas. In *Identification and Analysis of Organic Pollutants in Air*, ACS Symp., Woburn, MA: Ann Arbor Science/Butterworth Publishers, 1984: 353–370.

(23) Rieley, G.; Collier, R.J.; Jones, D.M.; Eglinton, G. The biogeochemistry of Ellesmere Lake, U.K.—I: source correlation of leaf wax inputs to the sedimentary lipid record. *Org. Geochem.* 1991, 17, 901–912.

(24) Riederer, M. and Schneider, G. The effect of the environment on the permeability and composition of *Citrus* leaf cuticles. II. Composition of soluble cuticular lipids and correlation with transport properties. *Planta* 1990, 180, 154–165.

(25) Simoneit, B.R.T.; Mazurek, M.A. Natural background of biogenic organic matter in aerosols over rural areas. In *Proceedings of the Fifth International Clean Air Congress*; Rispoli, J.A, Rodriguez, R.M., Torti, D.D., Eds.; Assoc. Argentine contra la Contam. del Aire, Buenos Aires, Vol. I, 1982, 332-340.

(26) Mazurek, M.A.; Simoneit, B.R.T.; Cass, G.R.; Gray, H.A. Quantitative high-resolution gas chromatography and high-resolution gas chromatography/mass spectrometry analysis of carbonaceous fine aerosol particles. *Intern. J. Environ. Anal. Chem.* 1987, 29, 119-139.

(27) Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Interpretation of high-resolution gas chromatography and high-resolution gas chromatography/mass spectrometry data acquired from atmospheric organic aerosol samples. *Aerosol Sci. Technol.* 1989, 10, 408-419.

(28) Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Quantitative characterization of urban sources of organic aerosol by high-resolution gas chromatography. *Environ. Sci. Technol.*, 1991b, 25, 1311–1325.

(29) Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Sources of fine organic aerosol: 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. *Environ. Sci. Technol.* 1993, 27, 636–651.

(30) Kolattukudy, P.E. Plant waxes. *Lipids* 1970, 5, 259–275.

(31) Kolattukudy, P.E. Biopolyester membranes of plants: cutin and suberin. *Science* 1980, 208,990–1000.

(32) Riederer, M. Die Kutikula als Barriere zwischen terrestrischen Pflanzen und der Atmosphäre. *Naturwissenschaften* 1991, 78, 201–208.

(33) Douglas, A.G.; Eglinton, G. The distribution of alkanes. In *Comparative Phytochemistry*, Swain T. Ed., Academic Press, London, 1966, 57-77.

(34) Hall, D.H.; Donaldson, L.A. The ultrastructure of wax deposits on plant leaf surfaces, 1. Growth of wax on leaves of *Trifolium repens*. *Nature* 1963, 191, 95–96.

(35) Gülz, P.-G.; Müller, E.; Moog, B. Epicuticular leaf waxes of *tilia tomentosa* Moench. and *Tilia times europaea* L.,tiliaceae. *Z. Naturforsch.* 1988, 43C, 173–176.

(36) Gülz, P.-G.; Müller, E.; Prasad, R.B.N. Organ-specific composition of epicuticular waxes of beech leaves and seeds. *Z. Naturforsch.* 1989, 44C, 731–734.

(37) Jamieson, G.R.; Reid, E.H. The leaf lipids of some conifer species. *Phytochemistry* 1972, 11, 269–275.

(38) Schreiber, L.; Schönherr J. Uptake of organic chemicals in conifer needles: surface adsorption and permeability of cuticles. *Environ. Sci. Technol.* 1992, 26, 153–159.

(39) Tulloch, A.P. Chemistry of waxes of higher plants. In *Chemistry and Biochemistry of Natural Waxes*, Kolattukudy, P.E. Ed., Elsevier, Amsterdam, 1976, 235–287.

(40) Baxter, L.J.; Cookson, J.T. Natural atmospheric microbial conditions in a typical suburban area. *Appl. Environ. Microbiol.* 1982, 45, 919–934.

(41) Kolattukudy, P.E.; Podila, G.K.; Mohan, R. Molecular basis of the early events in plant–fungus interaction. *Genome* 1989, 31, 342–349.

(42) Lindemann, J.; Constantinidou, H.A.; Barchet, W.R.; Upper, C.D. Plants as sources of airborne bacteria, including ice nucleation–active bacteria. *Appl. Environ. Microbiol.* 1982, 44, 1059–1063.

(43) Lindemann, J.; Upper, C.D. Aerial dispersion of epiphytic bacteria over bean plants. *Appl. Environ. Microbiol.* 1985, 50, 1229–1232.

(44) Bovallius, Å.; Bucht, B.; Roffey, R.; Ånäs, P. Three-year investigation of natural airborne bacterial flora at four locations in Sweden. *Appl. Environ. Microbiol.* 1978, 35, 847–852.

(45) Simoneit, B.R.T. Biogenic lipids in eolian particulates collected over the ocean. In *Proceedings Carbonaceous Particles in the Atmosphere*, Novakov, T. Ed., NSF and Lawrence Berkeley Laboratory, LBL-9037, 1979, pp. 233-244.

(46) Simoneit, B.R.T; Cox, R.E.; Standley, L.J. Organic matter of the troposphere—IV. Lipids in Harmattan aerosols of Nigeria. *Atmos. Environ.* 1988, 22, 983-1004.

(47) Simoneit, B.R.T.; Crisp, P.T.; Mazurek, M.A.; Standley, L.J. Composition of extractable organic matter of aerosols from the Blue Mountains and southeast coast of Australia. *Environ. Internat.* 1991, 17, 405–419.

(48) Van Vaeck, L.; Van Cauwenberghe, K. Cascade impactor measurements of the size distribution of the major classes of organic pollutants in atmospheric particulate matter. *Atmos. Environ.* 1978, 12, 2229–2239.

(49) Hallgren, B.; Larsson, S. Long-chain hydrocarbons in the pollen of rye. *Acta. Chem. Scand.* 1963, 17, 1822-639.

(50) Han, J.; Calvin, M. Hydrocarbon distribution of algae, bacteria, and microbiological activity in sediments. *Proc. Natl. Acad. Sci. USA* 1969, 64, 436-443.

(51) Jackson, L.L.; Blomquist, G.J. Insect waxes. In *Chemistry and Biochemistry of Natural Waxes*, Kolattukudy P.E. Ed., Elsevier, Amsterdam, 1976, 201-233.

(52) McClain, E.; Kok, C.J.; Monard, L.A.G. Reflective wax blooms on black Namib desert beetles enhance day activity. *Naturwissenschaften* 1991, 78, 40–42.

(53) Oró, J.; Laseter, J.L.; Weber, D. Alkanes in fungal spores. *Science* 1966, 154, 399-440.

(54) Weete, J.D. Algal and fungal waxes. In *Chemistry and Biochemistry of Natural Waxes*, Kolattukudy P.E. Ed., Elsevier, Amsterdam, 1976, 349-418.

(55) Kuksis, A. Hydrocarbon composition of some crude and refined edible seed oils. *Biochemistry* 1964, 3, 1086–1093.

(56) Carruthers, W.; Johnstone, R.A.W. *Nature* 1959, 184, 1131–1132.

(57) Mold, J.D.; Stevens, R.K.; Means, R.E., Ruth, J.M. The paraffin hydrocarbons of tobacco; normal-, iso-, and anteiso-homologues. *Biochemistry* 1963, 2, 605–610.

(58) Stedman, R.L. The chemical composition of tobacco and tobacco smoke. *Chem. Rev.* 1968, 68, 153–207.

(59) Severson, R.F.; Arrendale, R.F.; Chortyk, O.T.; Snook, M.E. A method for determining the transfer of lipids from tobacco to smoke. *Tob. Sci.* 1978, 22, 130–133.

(60) Spears, A.W.; Lassiter, C.W.; Bell, J.H. Quantitative determination of alkanes in cigarette smoke. *J. Gas Chromatogr.* 1963, 1, 34–37.

(61) Baker, E.A. The influence of environment on leaf wax development in *Brassica oleracea* var. *Gemmifera*. *New Phytologist* 1974, 73, 955–966.

(62) Gülz, P.-G.; Müller, E.; Prasad, R.B.N. Developmental and seasonal variations in the epicuticular waxes of *Tilia tomentosa* leaves. *Phytochemistry* 1991, 30, 769–773.

(63) Prasad, R.B.N.; Gülz, P.-G. Development and seasonal variations in the epicuticular waxes of beech leaves *Fagus sylvatica* L., *Z. Naturforsch.* 1990a, 45C, 805–812.

(64) Schütt, P.; Schuck, H.J. Jahreszeitliche Schwankungen in der Zusammensetzung der Cuticularwachse von *Pinus sylvestris*. *Flora*, 1973, 162, 206–214.

(65) Schuck, H.J. Quantitative Variation der Wachsauflage und der cuticulären Kohlenwasserstoffe bei *Picea abies*–Nadeln. *Flora*, 1976, 165, 303–314.

(66) Gullvåg, B.M.; Østensen, H. Wax layer in spruce needles — an indicator of air-borne pollution. *J. Ultrastructure & Molecular Structure Research* 1986, 3, 280–280.

(67) Sauter, J.J; Kammerbauer, H.; Pambor, L.; and Hock, B. Evidence for the accelerated micromorphological degradation of epistomatal waxes in Norway spruce by motor vehicle emissions. *Eur. J. For. Path.* 1987, 17, 444–448.

(68) Tulloch, A.P. Chemistry of waxes of higher plants. In *Chemistry and Biochemistry of Natural Waxes*, Kolattukudy, P.E. Ed., Elsevier, Amsterdam, 1976, 235–287.

(69) Turunen, M.; Huttunen, S. A Review of the response of epicuticular wax of conifer needles to air pollution. *J. Environ. Qual.* 1990, 19, 35–45.

(70) Pasanen, A.L.; Pasanen, P.; Jantunen, M.J.; Kalliokoski, P. Significance of air humidity and air velocity for fungal spore release into the air. *Atmos. Environ.* 1991, 25A, 459–462.

(71) Albro, P.W. Bacterial Waxes. In *Chemistry and biochemistry of natural waxes*; Kolattukudy, P.E, Ed.; Elsevier, Amsterdam, New York, Chap. 10, 1976, 419–445.

(72) Lechevalier, M.F. Lipids in bacterial taxonomy—a taxonomist's view. *CRC Crit. Rev. Microbiol.*, 1977, 5, 109-210.

(73) Shiea, J.; Brassell, S.C.; Ward, D.M. Comparative analysis of extractable lipids in hot spring microbial mats and their component photosynthetic bacteria. *Org. Geochem.* 1991, 17, 309–319.

(74) Meinschein, W.G.; Kenny, G.S. Analyses of a chromatographic fraction of organic extracts of soils. *Anal. Chem.* 1957, 29, 1153–1161.

(75) Morrison, R.I.; Blick, W. The wax fraction of soils: separation and determination of some components. *J. Sci. Fd. Agric.* 1967, 18, 351-355.

(76) Bray, E.E.; Evans, E.D. Distribution of n-paraffins as a clue to recognition of source beds. *Geochim. Cosmochim. Acta* 1961, 22, 2–15.

(77) Cooper, J.E.; Bray, E.E. (1963) A postulated role of fatty acids in petroleum formation. *Geochim. Cosmochim. Acta* 1963, 27, 1113–1127.

(78) Kvenvolden, K.A.; Weiser, D. A mathematical model of a geochemical process: normal paraffin formation from normal fatty acids. *Geochim. Cosmochim. Acta* 1967, 31, 1281–1309.

(79) Simoneit, B.R.T. The organic chemistry of marine sediments. In *Chemical Oceanography*; Riley, J.P., Chester, R. Eds.; Academic Press, NY, Vol. 7, Chap. 39, 1978, 233–311.

(80) Ching, T.M.; Ching, K.K. Fatty acids in pollen of some coniferous species. *Science* 1962, 138, 890-891.

(81) Kaneda, T. Fatty acids in the Genus Bacillus. *Journal of Bacteriology* 1967, Mar., 894–903.

(82) Laseter, J.L.; Valle, R. Organics associated with the outer surface of airborne urediospores. *Environ. Sci. Technol.* 1971, 5, 631–634.

(83) Shaw N. Lipid composition as a guide to the classification of bacteria. *Adv. Appl. Microbiol.* 1974, 17, 63–108.

(84) Hitchcock, C.; Nichols, B.W. The lipid and fatty acid composition of specific tissues. In *Plant Lipid Biochemistry*, Academic Press, London, 1971, 59-80.

(85) Lee, R.E.; Harris, K.; Akland, G. Relationship between viable bacteria and air pollutants in an urban atmosphere. *J. Am. Ind. Hyg. Assoc.*, 1973, 34, 164–170.

(86) Owen, M.K.; Ensor, D.S. Airborne particle sizes and sources in indoor air. *Atmos. Environ.*, 1992, 26A, 2149–2162.

(87) Gülz, P.-G.; Hemmers, H.; Bodden, J.; Marner, F.J. Epicuticular leaf waxes of *Euphorbia dendroides* L., euphorbiaceae. *Z. Naturforsch.* 1987, 42, 191–196.

(88) Prasad, R.B.N.; Gülz, P.-G. Surface structure and chemical composition of leaf waxes from *Quercus robur* L., *Acer pseudoplatanus* L. and *Juglans regia* L. *Z. Naturforsch.* 1990b, 45C, 813–817.

(89) Kawamura, K.; Gagosian, R.B. Implication of $\omega$-oxocarboxylic acids in the remote marine atmosphere for photo-oxidation of unsaturated fatty acids. *Nature* 1987, 325, 330-332.

(90) Killops, S.D. Action of ozone on methyl octadec-9-enoate in polar solvents. *Water Res.* 1986, 20, 167-171.

(91) Burns, W.F.; Tingey, D.T. GC/MS analysis of biogenic volatile hydrocarbons on a chemically-bonded fused silica column. *J. Chromatogr. Sci.* 1983, 21, 341–345.

(92) Graedel, T.E. Terpenoids in the atmosphere. *Rev. Geophys. Space Phys.* 1979, 17, 937–947.

(93) Holdren, M.W.; Westberg, H.H.; Zimmerman, P.R. Analysis of monoterpene hydrocarbons in rural atmospheres. *J. Geophys. Res.* 1979, 84, 5083–5088.

(94) Kotzias, D.; Fytianos, K.; Geiss, F. Reaction of monoterpenes with ozone, sulphur dioxide and nitrogen dioxide — gas-phase oxidation of $SO_2$ and formation of sulphuric acid. *Atmos. Environ.* 1990, 24A, 2127–2132.

(95) Lamb, B.; Westberg, H.; Allwine, G.; Quarles, T. Biogenic hydrocarbon emissions from deciduous and coniferous trees in the United States. *J. Geophys. Res.* 1985, 90, 2380–2390.

(96) Rasmussen, R.A. Isoprene: identified as a forest-tpye emission to the atmosphere. *Environ. Sci. Technol.* 1970, 4, 667–671.

(97) Rasmussen, R.A. What do the hydrocarbons from trees contribute to air pollution? *J. Air Pollut. Control Assoc.* 1972, 22, 537–543.

(98) Van Genderen, H.H.; Jaarsma, J. Triterpenes and alkanes in developing variegated and albino leaves of *Ilex aquifolium* L. (Aquifoliaceae). *Plant Science* 1990, 72, 165–172.

(99) Yokouchi, Y.; Okaniwa, M.; Ambe, Y.; Fuwa, K. Seasonal variation of monoter-

penes in the atmosphere of a pine forest. *Atmos. Environ.* 1983, 17, 743–750.

(100) Baker, E.A. Chemistry and morphology of plant epicuticular waxes. In *The Plant Cuticle*; Cutler, D.F., Alvin, K.L, Price, C.E. Eds.; Academic Press, London, 1982, 139–165.

(101) Hemmers, H.; Gülz, P.-G. Triterpenoid compounds in epicuticular leaf waxes of *euphorbia characias* and *Euphorbia dendroides* L., euphorbiaceae. *Plant Lipids* 1988, 369, 15–16.

(102) Hosker, R.P.; Lindberg, S.E. Review: atmospheric deposition and plant assimilation of gases and particles. *Atmos. Environ.* 1982, 16, 889–910.

(103) Shanley, J.B. Field measurements of dry deposition to Spruce foliage and petri dishes in the Black Forest, F.R.G. *Atmos. Environ.*, 1989, 23, 403–414.

(104) Wu, Y.-L.; Davidson, C.I.; Dolske, D.A.; Sherwood, S.I. Dry deposition of atmospheric contaminants: The relative importance of aerodynamic, boundary layer, and surface resistance. *Aerosol Sci.*, 1992, 16, 65–81.

(105) Gray, H.A.; Cass, G.R.; Huntzicker, J.J.; Heyerdahl, E.K.; Rau, J.A. Characteristics of atmospheric organic and elemental carbon particle concentrations in Los Angeles. *Environ. Sci. Technol.*, 1986, 20, 580–589.

(106) Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Sources of fine organic aerosol: 3. Road dust, tire debris, and organometallic brake lining abrasions — roads as sources and sinks. *Environ. Sci. Technol.*, 1993, *in press*.

(107) Simoneit, B.R.T. Organic matter of the troposphere—III. Characterization and sources of petroleum and pyrogenic residues in aerosols over the Western United States. *Atmos. Environ.*, 1984, 18, 51–67.

(108) Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Sources of fine organic aerosol: 6. Cigarette smoke in the urban atmosphere. *in preparation*, 1993.

# Chapter 7

## Natural Gas Home Appliances

### Introduction

To evaluate the origin and fate of airborne fine particulate organic matter, the emissions from common urban sources have to be characterized on a molecular level, and their source emission strengths determined. Natural gas is burned in utility and industrial boilers, in industrial process heaters, and by residential and commercial customers. In the Los Angeles area, residential and commercial natural gas combustion is the largest of these uses; here natural gas is commonly used for space and water heating and for cooking purposes (*1*). Residential sources contribute to indoor and outdoor fine particle concentrations. Several studies have been conducted in the past to evaluate indoor air quality for particulate and gaseous matter released from natural gas-fired home appliances (*2-10*). Fine particle emission rates from natural gas-fired home appliances have been measured for unvented and vented space heaters (6 - 300 ng/kJ), ovens (< 50 ng/kJ), and stovetop burners (240 - 620 ng/kJ) (*4, 6, 8*). Except for fine particulate organic matter measured in the indoor air that includes source emissions from other activities, no chemical characterization of the fine particulate organic matter emitted from natural gas-fired home appliances has been reported to date (*11-13*).

---

Reference: Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; ; Cass, G.R.; Simoneit, B.R.T. *Environ. Sci. Technol.*, 1993, *submitted*.

In order to evaluate the chemical composition and emission strength of particulate emissions formed during natural gas combustion in residential appliances, exhaust emissions must be sampled under near ambient conditions. In this study, a vented natural gas-fired space heater and a water heater that were ducted together were tested to characterize the organic matter formed during combustion and to determine emission rates for individual organic compounds. The results of this study can be used to estimate the release of such emissions to the urban atmosphere, and also may be useful in guiding future studies of indoor air pollution.

## Experimental Methods

### Sources Tested

Fine particulate emissions ($d_p \leq 2$ μm) released from a natural gas-fired water heater (American Standard, Model G-531-H: 44,000 Btu/hr) and a natural gas-fired space heater (Western Gravity Heat, Model 8G100; 100,000 Btu/hr) were collected from a common exhaust duct using a dilution sampling system.

### Dilution Sampling

The dilution source sampling device used in this study also has been used to test several other anthropogenic sources (*14-17*). Since it is described in detail by Hildemann et al. (*18*), only a short description will be provided here. The dilution sampling device is designed to collect fine particulate matter ($d_p \leq 2$ μm), including vapor-phase organic compounds that naturally would condense onto preexisting particulate matter in the atmosphere as the plume downwind of the source is diluted and cooled to ambient temperatures. During fine particle sampling, hot particle-laden exhaust emissions are drawn via a cyclone separator

(10 μm size-cut) into a dilution tunnel. To dilute and cool the emissions as would occur in the atmosphere, precleaned and cooled dilution air (activated carbon-filtered and HEPA-filtered) is mixed with the exhaust emissions in the dilution tunnel. From the dilution tunnel, a constant fraction of the diluted exhaust is then diverted into a residence time chamber (residence time about 2 min) to allow gas phase constituents — which under ambient conditions would condense onto preexisting particles — to condense onto the available exhaust particles. From the chamber, suspended particulate matter is continually withdrawn through six AIHL-design cyclone separators. The cyclone separators are operated in parallel at a flow rate of 27.9 ± 0.3 L/min each with an aerodynamic cut off diameter of 2.0 μm. Fine particulate matter is collected downstream of each cyclone separator using three 47-mm-diameter filter holders. Of the 18 separate fine particle samples acquired per experiment, 16 are collected on quartz fiber filters (Pallflex 2500 QAO), and the remaining 2 on Teflon filters (Gelman Teflo, 2.0-μm pore size). All quartz fiber filters are annealed at 750°C for 2–4h before use to ensure low contamination levels for organic substances.

## Source Testing Procedure

The source sampling experiments were conducted in a vacant single family home located in Pasadena, northeast of Los Angeles. The exhaust ducts of both the space and water heater tested were connected to a single square 23 x 23-cm duct. The exhaust duct from the water heater was an open design so that ambient air could be entrained into the duct. Exhaust emissions were withdrawn from five different horizontal positions within the common exhaust duct. The gas velocity in the duct was measured using a hot wire anemometer, to facilitate isokinetic sampling and to determine flow rates. Stack gas temperatures ranging on the average from 69 to 78°C were measured. Because only a small amount of particulate matter is generated during natural gas combustion, each of the three sampling experiments was conducted for 8 to 12-h. To simulate cyclic operation, the heaters were turned off for 1 to 3-min approximately twice per hour. In order to monitor gas phase adsorption or desorption of organic compounds on the filters (front filter set), quartz fiber backup filters were placed behind each of the 18 front filters for the third experiment.

Although the dilution air of the dilution sampling system was filtered using both activated carbon and a HEPA filtering system, the filtered dilution air was tested to ensure that the dilution air was clean and that any contaminants could be traced. This precaution is especially crucial when conducting experiments involving sources with low emission rates.

### Bulk Chemical Analysis

The bulk chemical characterization of the source emissions included ionic species, trace metals, organic carbon (OC), and elemental carbon (EC). The results, which have been reported elsewhere by Hildemann et al. (*14*), show that most of the fine aerosol emissions consists of organic matter.

### Sample Extraction

The sample extraction procedure followed was developed by Mazurek et al. (*19*), and also has been described in several subsequent publications (*16, 20-22*). Briefly, the extraction protocol can be described as follows: immediately prior to sample extraction, a predetermined amount of perdeuterated tetracosane (n-$C_{24}D_{50}$) used as an internal standard was spiked onto the filter composites. To ensure that the amount of n-$C_{24}D_{50}$ added was in a concentration range comparable to the organic compound concentrations in the sample, the amount to be added was estimated based on the OC concentrations measured by EC/OC-combustion analysis. The particle samples collected on 39 quartz fiber filters (13 filters from each experiment) were composited and sequentially extracted using hexane (2 × 80 ml) followed by benzene/2-propanol (2:1 mixture, 3 × 80 ml). Each of the five extraction steps was assisted by mild ultrasonic agitation for 10 min. The sample extracts were filtered and combined using a specially designed transfer and filtering device (*19*). The combined sample extract volume then was reduced to 200 - 500 $\mu$l using (1) a two step rotary evaporation scheme, followed by (2) gentle high purity $N_2$-stream evaporation. One aliquot of the sample extract was exposed to freshly produced diazomethane to convert organic acids to their methyl ester analogues and other susceptible hydroxy functionalities to their methoxy analogues. The sample extracts were stored in the dark at -21°C until GC/MS analysis.

### Sample Analysis

A Finnigan 4000 quadrupole mass spectrometer coupled with a gas chromatograph and interfaced with an INCOS data system was used for compound identification and quantification. Sample extracts were injected onto a conventional Grob splitless injector (300°C) which was connected to a 30-m fused-silica DB-1701 column (J & W Scientific, Rancho Cordova, CA). Gas chromatography of the injected sample extract was conducted using the following temperature program: (1) isothermal hold at 65°C for 10 min, (2) temperature increase at 10°C/min for 21 min, and (3) isothermal hold at 275°C for another 49 min. The mass spectrometric data were acquired while operating the mass spectrometer in the electron impact mode (electron energy of 70 eV). For a related study of the same samples, a Varian 4600 high-resolution gas chromatograph (HRGC) with FID-detector was used that was operated with the identical capillary column and temperature program as used during GC/MS-analysis (*15*). Additional information describing the analytical procedure can be found elsewhere (*16, 19-22*).

### Quality Assurance

A series of quality control and monitoring steps were followed. The major steps included field and laboratory blank testing, solvent testing to monitor possible contaminants, recovery experiments for a large set of polar and nonpolar standard compounds, and dilution air testing. For a detailed discussion, the reader is referred to accompanying source and ambient fine organic particle studies published earlier (*16, 17, 19-22*).

### Compound Identification and Quantification

Compound identification was conducted using the National Institute of Standards and Technology (NIST) mass spectral library accessed by the INCOS Data System, the NIST/EPA/NIH mass spectral database (PC Version 4.0) distributed by NIST, and by reference to authentic standards injected onto the GC/MS system used here. Compound identification was conducted accordingly: (a) *positive* — sample mass spectrum and authentic standard mass spectrum compared well and showed comparable retention times; (b) *probable* — same as before, except no authentic standards were available, but the NIST or NIST/EPA/NIH library mass spectrum and the sample mass spectrum agreed very well; (c) *possible*, same as above except that the sample spectrum contained information from other compounds but with minor overlap; and (d) *tentative*, when the sample spectrum contained additional information from possibly several compounds (noise) with overlap.

The compound quantification process was based on the application of n-$C_{24}D_{50}$ as internal standard and 1-phenyldodecane as coinjection standard. To correct for varying detector response to compounds having different structures and retention times, sets of known standard compounds were injected onto the analytical system to monitor their specific GC retention and MS-response. For more information, the interested reader is referred to Rogge et al. (*16*, *22*).

## Standard Compounds

Confirmation and quantification of organic compounds was obtained through the use of more than 150 authentic standards, see Rogge et al. (*17*). The following standard mixtures were injected onto the GC/MS-system: (1) normal alkanes ranging from n–$C_{10}$ to n–$C_{36}$; (2) normal alkanoic acids as methyl esters ranging from n–$C_6$ to n–$C_{30}$; (3) unsaturated aliphatic acids such as oleic acid and linoleic acid as methyl esters; (4) normal alkanols ranging from n–$C_{10}$ to n–$C_{30}$; (5) several phenolic compounds, benzaldehydes and substituted aromatic acids; (6) a suite of 39 aromatic and polycyclic aromatic hydrocarbons (PAH); (7) 10 polycyclic aromatic ketones and quinones; (8) 8 aromatic and polycyclic aromatic N– and S–substituted compounds; (9) steroids including cholesterol and cholestane; (10) a set of 4 phytosterols; (11) several natural resins; (12) plasticizers; (13) a suite of 11 aliphatic dicarboxylic acids ($C_3$ – $C_{10}$) as metyl esters; (14) a suite of 7 aromatic di- and tricarboxylic acids, all as methyl esters; and (15) other compounds.

## Results and Discussion

The results of the natural gas home appliance source tests are shown in Table 7.1. Three data sets are presented: (1) HEPA-filtered dilution air sample, (2) the fine particle sample collected on the first series of filters within the samplers, and (3) a sample collected on the backup filters downstream of the particle filters. Samples (1) and (3) listed above are of specific importance for the natural gas source tests. Because the fine particle emissions from natural gas combustion are very low, the sampling experiments have to be conducted for 8 to 12-h. For such low emission rates, the knowledge of the HEPA-filtered dilution air quality is crucial. The backup filter samples also are of particular interest because the combustion of natural gas leads to extremely low emissions of solid particulate matter. Instead semi-volatile compounds are emitted that partition between the gas phase and the particle phase.

Under typical operational conditions, the hot exhaust from the natural gas combustion is released to the atmosphere and upon atmospheric dilution and cooling, organic compounds having a low vapor pressure condense onto preexisting particulate matter, while gaseous organic compounds having somewhat higher vapor pressures partition between the vapor and particle phase (*23-25*). This gas/particle phase partitioning can be disturbed during filter sampling with the result that a second filter placed behind a prefilter will still collect some organic material even after aerosol removal on the upstream prefilter. This collection on the second filter is either due to adsorption of gaseous semi-volatile compounds onto the second filter, or due to volatilization of aerosol material collected on the front filter followed by adsorption onto the backup filter (*26-28*). The backup filter results are presented such that the magnitude of these effects can be judged approximately.

### Mass Balance for Elutable Fine Organic Matter

A material balance for the elutable organic matter as collected on the front filters and detected by GC/MS has been constructed and is shown in Figure 7.1. The extractable and elutable organic mass can be divided into chromatographically resolved and unresolved organic mass. The unresolved organic mass (unresolved complex mixture: UCM) comprises 46.8% of the elutable organic mass. Of the mass fraction that is chromatographically resolved as single peaks, 67.3% can be identified, which then accounts for 26.4% of the gravimetrically determined aerosol mass emitted. The overwhelming majority of the elutable organic mass that can be identified as single compounds consists of polycyclic aromatic hydrocarbons (PAH) plus oxygenated PAH (oxy-PAH) such as polycyclic aromatic ketones (PAK) and polycyclic aromatic quinones (PAQ). Smaller amounts of aza- and thia-arenes, n-alkanes, and n-alkanoic acids also are found, as shown in Figure 7.1. A quantitative assessment of individual compounds and compound classes is given in Table 7.1.

### Exhaust Aerosol Composition

Figures 7.2a,b show the total reconstructed ion current (RIC) plots for (a) front filter particle samples, and (b) backup filter samples. From the RIC-plots it can be seen that PAH and oxy-PAH dominate the identified organic compound mass released from the natural gas home appliances. A discussion of each of the compound classes found in the emissions from the residential space and water heaters follows, including comparisons of the front vs backup filter measurements.

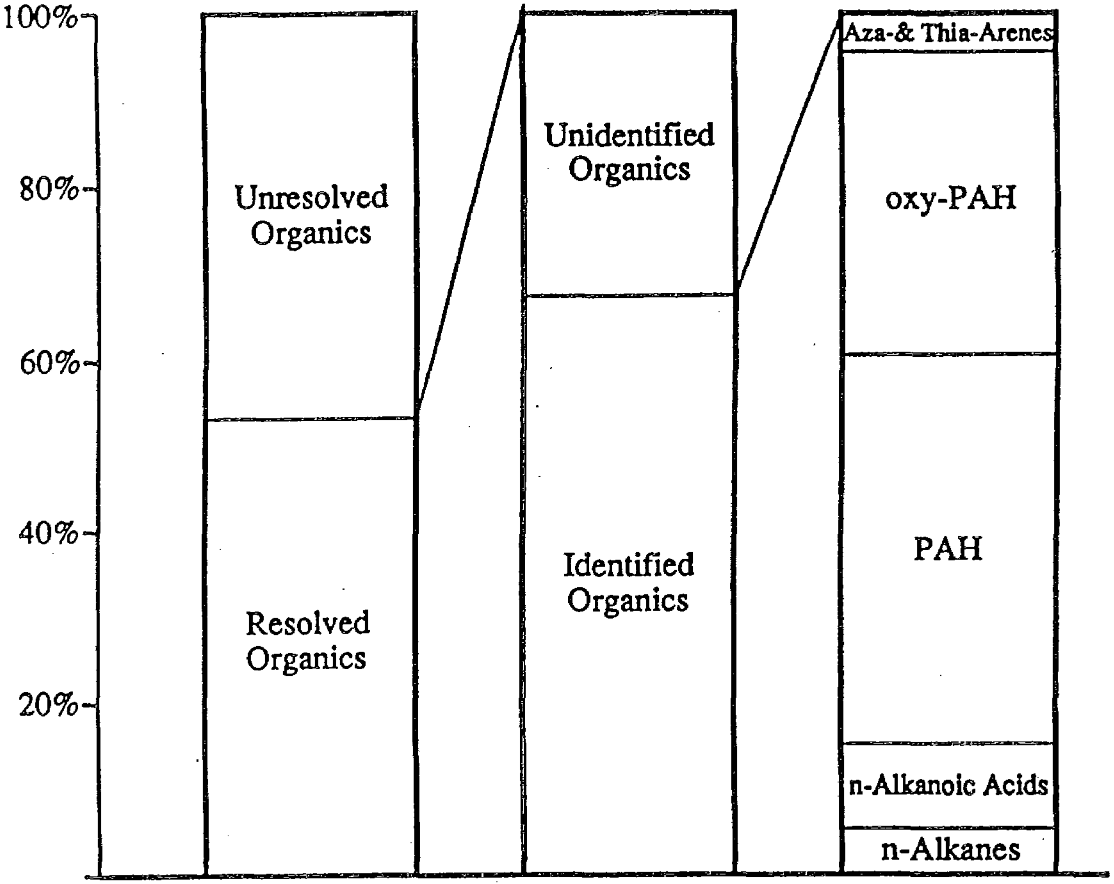


Fig. 7.1: Mass balance for elutable organic matter in the fine particle emissions (front filters only) of natural gas-fired home appliances.

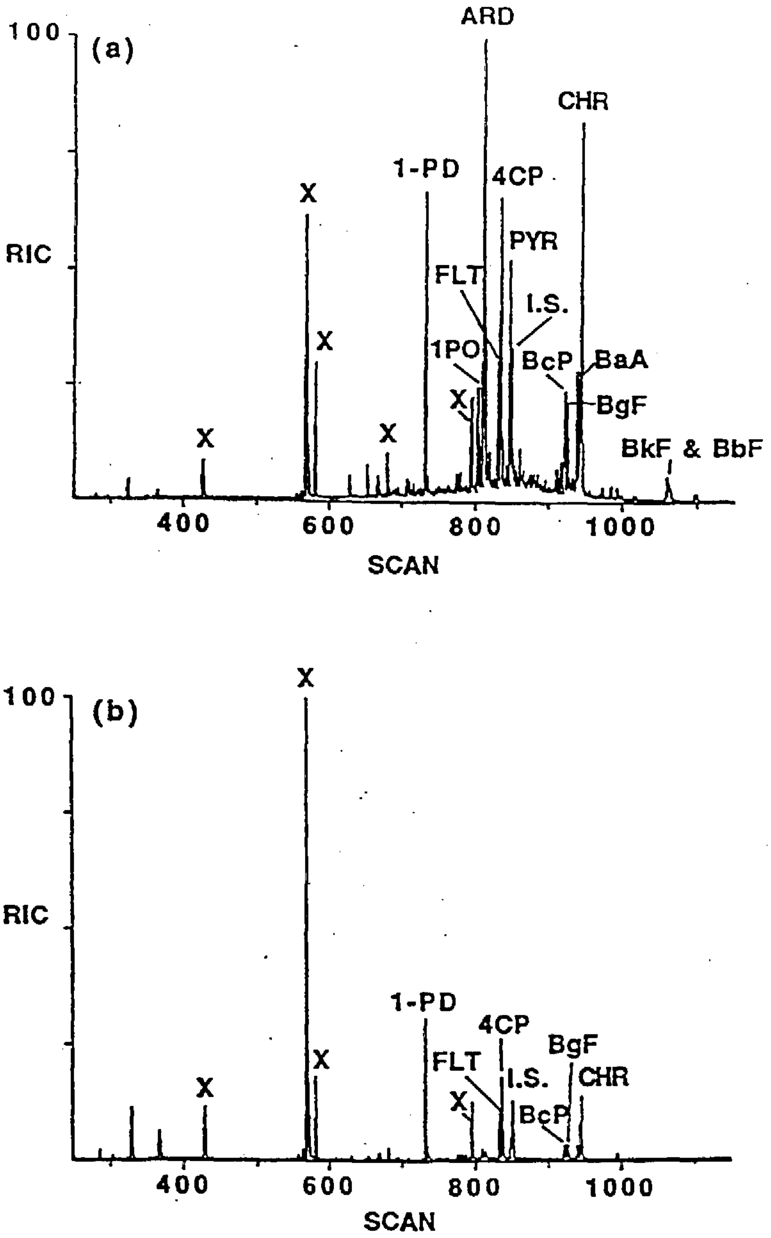


Fig. 7.2: Total reconstructed ion current (RIC) for exhaust emissions from natural gas-fired home appliances: (a) fine particle front filter samples, (b) backup filter samples. I.S.: internal standard ($\underline{n}$-$C_{24}D_{50}$); 1-PD: coinjection standard; 1PO: 1H-phenalen-1-one; FLT: fluoranthene; ARD: 9,10-anthracenedione; 4CP: 4-cyclopenta[def]phenanthren-4-one; PYR: pyrene; BcP: benzo[c]phenanthrene; BgF: benzo[ghi]fluoranthene; BaA: benz[a]anthracene; CHR: chrysene/triphenylene; BkF: benzo[k]fluoranthene; BbF: benzo[b]fluoranthene; X: contaminant.

## Alkanes

Although natural gas does not contain any higher molecular weight n-alkanes, compounds of this class have been identified (range $C_{19}$ to $C_{33}$) in the exhaust samples collected from the space and water heater tested here (see Table 7.1). This indicates that either n-alkanes exist as contaminants within the natural gas pipeline system, or are synthesized during the combustion process, or that they are introduced with unfiltered combustion air, or are entrained through the vents in the exhaust duct serving the water heater. Figure 7.3a shows the n-alkane concentrations measured in the dilution air, front particle filter samples, and on the backup filter samples. From Figure 7.3a it can be seen that only small amounts (8.8% compared to the front filter sample) consisting mainly of lower molecular weight n-alkanes (max: $C_{21}$) are introduced into the sampling system with the activated carbon and HEPA-filtered dilution air. Considering the length (8 to 12-h) of the source testing experiments necessary, the dilution air-related artifacts are minor. The backup quartz fiber filters also collected small amounts of semi-volatile n-alkanes with $C_{22}$ as the dominant homologue. Virtually no n-alkanes $\geq C_{27}$ were found on the backup filters, indicating that they are predominantly found in the particle phase collected on the front filter.

From the n-alkane concentration profile ($\geq C_{27}$) found on the front filter set it can be seen that the odd carbon numbered n-alkanes ($C_{27}$, $C_{29}$, and $C_{31}$) dominate compared to the even numbered homologues. Because such an odd carbon number predominance for higher molecular n-alkanes has been found in urban and remote ambient particle samples (*22, 29-31*) and is thought to be contributed from airborne fine particulate vegetative detritus (*31-33*), it can be concluded that at least a portion of the n-alkanes identified in the exhaust

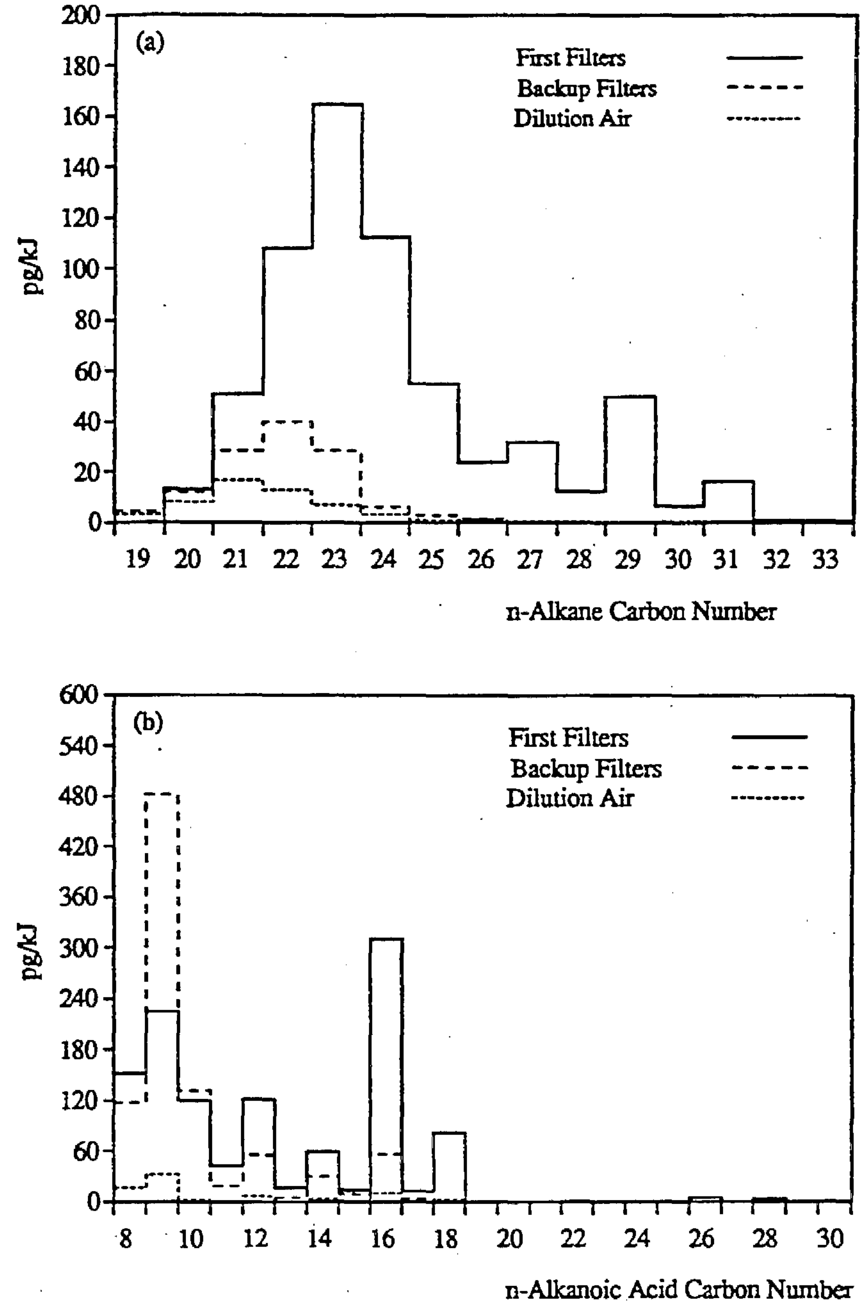


Fig. 7.3: Emission profiles for natural gas-fired home appliances: (a) n-alkanes and (b) n-alkanoic acids.

emissions are contributed from organic matter introduced with either the unfiltered combustion air or with the air entrained through the vent above the water heater. Because the domestic natural gas heaters tested here are operated with unfiltered combustion and entrainment air, such pollutant recycling processes have to be included in source testing experiments because they might be a source for additional newly formed or altered organic compounds emitted to the urban atmosphere. The extent to which the n-alkanes measured in the exhaust emissions are contributed from unfiltered indoor air influenced by outdoor pollutant concentrations will be discussed in a later section.

## Alkanoic Acids

Normal alkanoic acids ranging from $C_8$ to $C_{18}$ have been identified in the emissions of the natural gas home appliances tested with trace amounts of $C_{26}$, $C_{28}$, and $C_{30}$ n-alkanoic acids only found on the front particle filter samples, as shown in Figure 7.3b. In the dilution air sample, only small amounts (6.5% compared to the front filters particle sample) of $C_8$ to $C_{18}$ n-alkanoic acids have been found, with the lower $C_8$ and $C_9$ n-alkanoic acids dominating, again indicating that the HEPA-filtered dilution air is low in contaminants.

In contrast to the n-alkane findings discussed above, semi-volatile n-alkanoic acids ($C_8$ - $C_{18}$) have been found on the backup filter sets that amount to 79% of the n-alkanoic acid mass measured on the front filters. Using the GC-elution time for the n-alkanes and n-alkanoic acids as a measure of their volatility (*34*) (nonadecane elutes close to hexadecanoic acid methyl ester ($C_{16}$-acid)), it is not surprising that for the more volatile n-alkanoic acids $\leq C_{14}$, appreciable amounts are found on the backup filters. From Figure 7.3b it can be seen that nonanoic acid ($C_9$) and to a smaller extent decanoic acid ($C_{10}$) are more pronounced on the backup filters than on the front filters. While the backup filter findings represent the third source test only, the results for the fine particle samples collected on the front filters are the average of three consecutive experiments. Hence, it is possible that the third experiment released higher $C_9$ and $C_{10}$ n-alkanoic acid concentrations then found on average.

The dominant n-alkanoic acids identified in the particle samples are hexadecanoic ($C_{16}$) and octadecanoic ($C_{18}$) acids. In addition, traces of higher molecular weight n-alkanoic acids ($C_{26}$, $C_{28}$, $C_{30}$) have been found on the front filter only. This predominance of even carbon numbered n-alkanoic acids ($\geq C_{16}$) is again attributable to sources of recent biogenic origin (*31-33*), and is typically found in ambient fine particle samples (*22*), suggesting that part of the exhaust emissions are due to uncombusted organic matter introduced into the furnaces or furnace stack vents from ambient air.

## Polycyclic Aromatic Hydrocarbons

During the course of the present study, 18 individual PAH and alkyl-PAH have been quantified in the exhaust emissions from the natural gas home appliances. PAH as a class contribute nearly half of the total elutable organic mass that could be identified as single compounds, with emission rates for individual compounds that range from a few up to nearly 2000 pg/kJ of natural gas burned. Except for trace amounts of lower molecular weight PAH, the HEPA-filtered dilution air is free of any detectable PAH (see Table 7.1). Total PAH found on the backup filters equal 21% of the total PAH collected with the particle sample on the front filters. Figures 7.4a and 4b show the PAH emission rates as determined for the front particle filters and backup filters for low exhaust concentration PAH (Figure 7.4a) and high exhaust concentration PAH (Figure 7.4b).

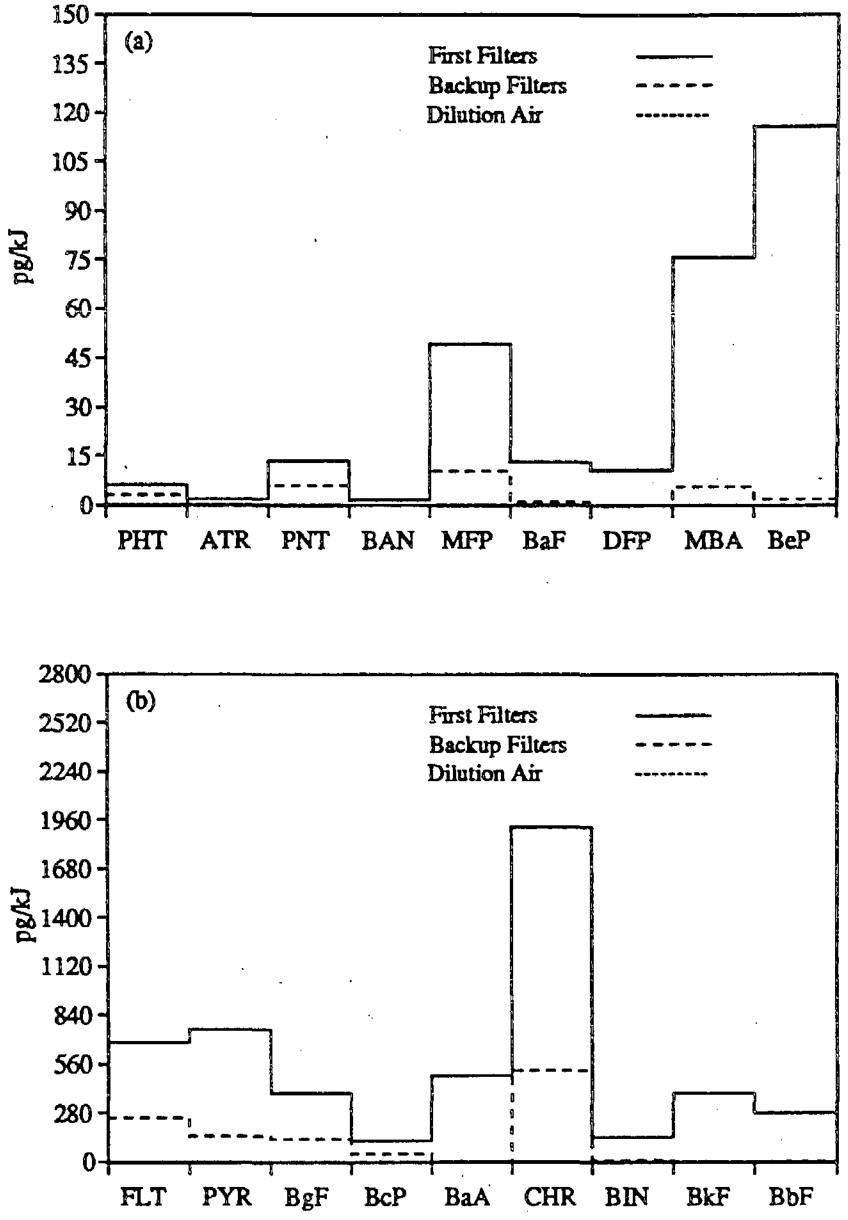


Fig. 7.4: Emission profiles for natural gas-fired home appliances: (a) low concentration PAH and (b) high concentration PAH. PHT: phenanthrene; ATR: anthracene; PNT: 2-phenylnaphthalene; BAN: benzacenaphthylene; MFP: methyl-(fluoranthenes, pyrenes); BaF: benzo[a]fluorene; DFP: dimethyl-(fluoranthenes, pyrenes); MBA: methyl-(benz[a]anthracenes, chrysenes, triphenylenes); BeP: benzo[e]pyrene; FLT: fluoranthene; PYR: pyrene; BcP: benzo[c]phenanthrene; BgF: benzo[ghi]fluoranthene; BaA: benz[a]anthracene; CHR: chrysene/triphenylene; BIN: Binaphthalenes; BkF: benzo[k]fluoranthene; BbF: benzo[b]fluoranthene.

The dominant PAH identified were chrysene and/or triphenylene, which are emitted at a rate of greater than 1900 pg/kJ of fuel burned. These two PAH show identical mass fragmentation patterns and elution times (for the chromatographic conditions used here); therefore, they are reported together. Chrysene/triphenylene, fluoranthene, pyrene, and benzo[ghi]fluoranthene show elevated particle phase concentrations as well as substantial filter adsorbed gas phase concentrations on the backup filters. Higher molecular weight PAH, such as binaphthalenes, benzo[k]- and benzo[b]fluoranthene, and benzo[e]pyrene, were found in smaller amounts and were collected predominantly with the particulate matter on the front filter.

### Polycyclic Aromatic Ketones and Quinones

Oxygenated polycyclic aromatic hydrocarbons (oxy-PAH) are the second important compound class identified in the exhaust emissions of the natural gas-fired combustion sources tested here (see Figure 7.5a). The total amount of oxy-PAH found on the backup filters accounts for 19% of the overall oxy-PAH mass measured on the front filters. Anthraquinone (9,10-anthracenedione), a polycyclic aromatic quinone (PAQ), was emitted at a rate of nearly 2000 pg/kJ of fuel burned, making it the most abundant particle phase compound found on the front filter. The second most abundant oxy-PAH was 4-cyclopenta[def]phenanthren-4-one, emitted at a rate of more than 900 pg/kJ of fuel burned. Although both oxy-PAH show similar retention times for the column used (implying similar vapor pressures) anthraquinone was almost exclusively found on the front filter (front: 1976.8 vs. backup: 39.1 pg/kJ), whereas 4-cyclopenta[def]phenanthren-4-one was relatively enriched on the backup filters (front: 920.2 vs. backup: 501.9 pg/kJ).

In general, not all of the oxy-PAH that show comparable retention times

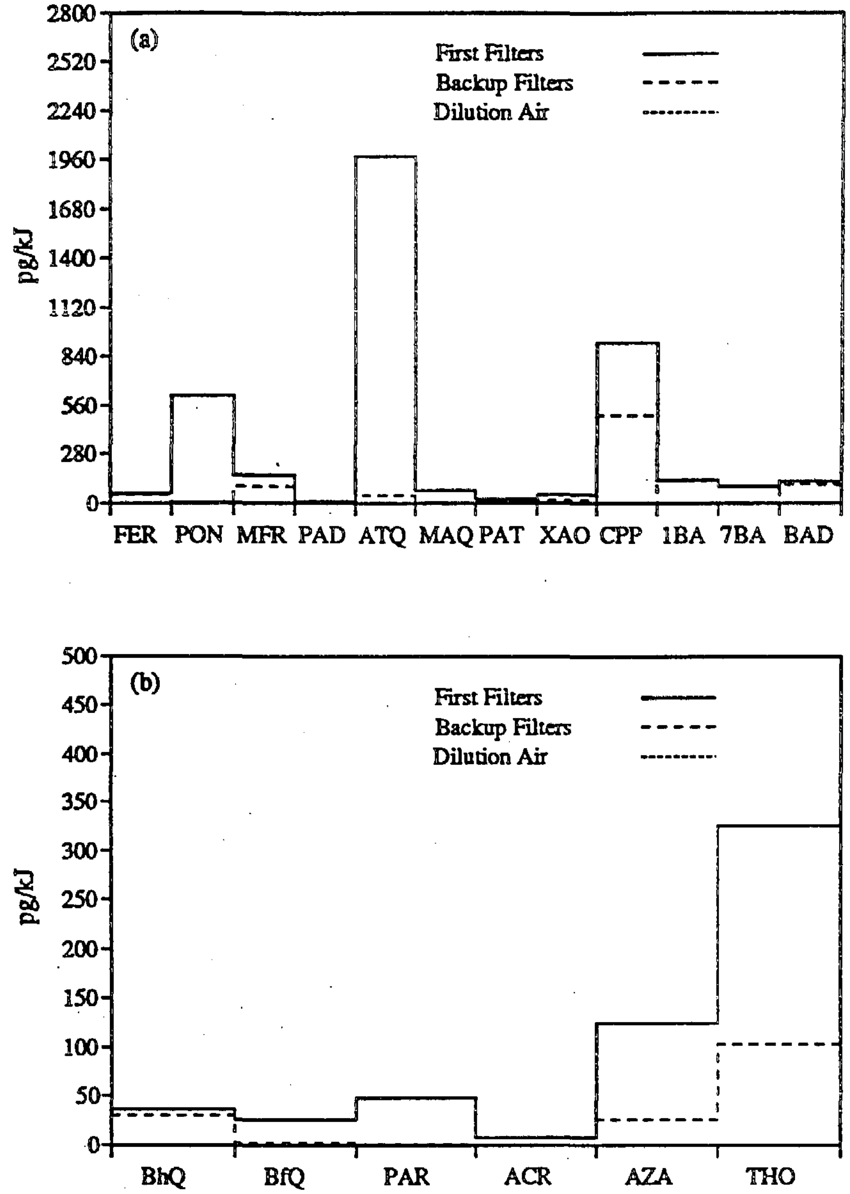


Fig. 7.5: Emission profiles for natural gas-fired home appliances: (a) oxy-PAH and (b) aza- and thia-arenes. FER: 9H–fluoren-9-one; PON: 1H-phenalen-1-one; MFR: methylfluorenones; PAD: phenanthrenequinone; ATQ: anthraquinone; MAQ: 2-methylanthraquinone; PAT: phenanthrone/anthrone; XAO: xanthone; CCP: 4–cyclopenta[def]-phenanthren-4-one; 1BA: 1–H–benz[de]anthracen-1-one; 7BA: 7–H–benz[de]anthracen-7-one; BAD: benz[a]anthracene-7,12-dione; BhQ: benzo[h]quinoline; BfQ: benzo[f]quinoline; PAR: phenanthridine; ACR: acridine; AZA: aza-arenes with MW 203; THO: benzo-[b]naphthothiophenes.

(comparable vapor pressures) show similar front/backup filter concentration ratios. Oxy-PAH such as 1H-phenalen-1-one, anthraquinone, 1-H-benz[de]anthacen-1-one, and 7-H-benz[de]anthracen-7-one show a high front/backup filter concentration ratio, whereas 4-cyclopenta[def]phenanthren-4-one, benz[a]anthracene-7,12-dione show relatively high backup filter concentrations. For benz[a]anthracene-7,12-dione, the oxy-PAH with the highest molecular weight, a nearly equal distribution between the front and backup filters was detected.

It has been observed that nitro-PAH can be converted to oxy-PAH due to photochemical reactions (*35*). Likewise, PAH conversion to oxy-PAH was observed during ozonolysis experiments (*36*). In the present experiments, the fine particulate matter was collected in the dark (sampler), thereby excluding photochemical conversion reactions involving PAH. Although the combustion air was unfiltered, $O_3$ should have been depleted either during combustion or by reaction with NO in the exhaust as well as diluted in the dilution tunnel (24 ×) so that ozonolysis reactions involving the organic matter collected on both filter sets appear unlikely. Should filter substrate specific reactions occur, then these reactions should be similar for front and backup filters. At this point it is not clear what causes the observed differences for compounds with similar molecular mass when comparing front and backup filter concentrations.

## Nitrogen- and Sulfur-Containing Polycyclic Aromatic Hydrocarbons

In addition to PAH and oxy-PAH, nitrogen- (aza-arenes) and sulfur-containing (thia-arenes) heterocyclic polyaromatic hydrocarbons have been identified in the natural gas exhaust emissions (see Figure 7.5b). Compound classes like these have been identified before in the urban atmosphere (e.g., *37-39*) and in the exhaust emissions from several sources (*40, 41*). Aza-arenes as well as thia-arenes have tested positive in Ames bacterial mutagenicity assays and in animal carcinogenicity tests (*42-46*).

Aza- and thia-heterocyclic polyaromatic compounds are formed during the combustion of fossil fuels in a manner similar to PAH formation by incorporating N- and S-atoms into their ring structures. In this study, several aza-arenes and thia-arenes have been identified in the particle samples as well as in the backup filter samples (see Table 7.1). Benzo[h]quinoline, benzo[f]quinoline, phenanthridine, and acridine could be assigned to individual peaks in the reconstructed ion-chromatogram. Three chromatographic peaks also are found that show mass fragmentation patterns very similar to those of indeno[1,2,3-i,j]isoquinoline, acenaphtho[1,2-b]pyridine, and 4-azapyrene. Because the elution order for these aza-arenes on the column used is not known to us, the three peaks are reported together as aza-arenes with a molecular weight of 203 daltons. Likewise, three thia-arene isomers commonly known as benzo[b]naphthothiophenes have been identified. Together, aza-arenes and thia-arenes are present at a mass concentration roughly 10% as high as that of the PAH or oxy-PAH.

**Table 7.1 Fine Particle Emission Rates for Organic Compounds released from Natural Gas Home Appliances[a].**

| PART A | Emission Rates in pg/kJoule<br>HEPA-filtered Dilution Air | Space & Water Heater<br>First Filter | Space & Water Heater<br>Backup Filter | Compound ID[b] |
|---|---|---|---|---|
| | —n–Alkanes— | | | |
| nonadecane | 3.2 | n.d. | 4.6 | a |
| eicosane | 8.4 | 13.3 | 12.0 | a |
| heneicosane | 16.8 | 50.9 | 28.6 | a |
| docosane | 13.1 | 108.4 | 39.8 | a |
| tricosane | 7.1 | 164.6 | 28.8 | a |
| tetracosane | 3.2 | 112.4 | 6.2 | a |
| pentacosane | 1.4 | 55.2 | 2.9 | a |
| hexacosane | 1.2 | 23.8 | 1.5 | a |
| heptacosane | 0.75 | 32.2 | n.d. | a |
| octacosane | 0.84 | 12.7 | n.d. | a |
| nonacosane | 0.61 | 50.2 | n.d. | a |
| triacontane | 0.24 | 6.6 | n.d. | a |
| hentriacontane | 0.26 | 16.6 | n.d. | a |
| dotriacontane | n.d. | 1.1 | n.d | a |
| tritriacontane | n.d. | 0.70 | n.d. | a |
| Total class mass concentration: | 57.1 | 648.2 | 124.4 | |
| | —n–Alkanoic Acids[c]— | | | |
| octanoic acid | 16.2 | 152.0 | 116.9 | a |
| nonanoic acid | 32.6 | 225.2 | 482.6 | a |
| decanoic acid | 2.9 | 119.5 | 131.3 | a |
| undecanoic acid | n.d. | 43.2 | 19.4 | a |
| dodecanoic acid (lauric acid) | 6.9 | 120.7 | 56.2 | a |
| tridecanoic acid | n.d. | 16.0 | 4.8 | a |
| tetradecanoic acid (myristic acid) | 3.7 | 59.6 | 29.9 | a |
| pentadecanoic acid | 0.96 | 14.3 | 8.5 | a |
| hexadecanoic acid (palmitic acid) | 9.7 | 310.4 | 56.8 | a |
| heptadecanoic acid | n.d. | 12.5 | 4.1 | a |
| octadecanoic acid (stearic acid) | 2.6 | 81.8 | n.d. | a |
| nonadecanoic acid | n.d. | n.d. | n.d. | a |
| eicosanoic acid | n.d. | n.d. | n.d. | a |
| heneicosanoic acid | n.d. | n.d. | n.d. | a |
| docosanoic acid | n.d. | n.d. | n.d. | a |
| tricosanoic acid | n.d. | n.d. | n.d. | a |
| tetracosanoic acid | n.d. | n.d. | n.d. | a |
| pentacosanoic acid | n.d. | n.d. | n.d. | a |
| hexacosanoic acid | n.d. | 5.3 | n.d. | a |
| heptacosanoic acid | n.d. | n.d. | n.d. | a |

Table 7.1 (continued)

| PART B | Emission Rates in pg/kJoule<br>HEPA-filtered Dilution Air | Space & Water Heater<br>First Filter | <br>Backup Filter | Compound ID[b] |
|---|---|---|---|---|
| octacosanoic acid | n.d. | 4.0 | n.d. | a |
| nonacosanoic acid | n.d. | n.d. | n.d. | a |
| triacontanoic acid | n.d. | 1.4 | n.d. | a |
| Total class mass concentration: | 75.56 | 1165.3 | 910.5 | |
| **—Polycyclic Aromatic Hydrocarbons (PAH)—** | | | | |
| phenanthrene | 0.20 | 6.3 | 3.2 | a |
| anthracene | 0.22 | 1.9 | 0.26 | a |
| fluoranthene | 0.19 | 685.3 | 251.7 | a |
| pyrene | 0.58 | 759.3 | 146.0 | a |
| benzacenaphthylene | n.d. | 1.6 | n.d. | b |
| 2–phenylnaphthalene | n.d. | 13.6 | 6.1 | b |
| methyl–(fluoranthenes, pyrenes) | n.d. | 49.3 | 10.5 | b |
| benzo[a]fluorene/benzo[b]fluorene | n.d. | 13.3 | 1.1 | a |
| benzo[ghi]fluoranthene | n.d. | 397.7 | 130.7 | b |
| benzo[c]phenanthrene | n.d. | 125.5 | 48.9 | a |
| benz[a]anthracene | n.d. | 497.7 | 6.7 | a |
| chrysene/triphenylene | n.d. | 1922.7 | 524.8 | a |
| methyl–(benz[a]anthracenes, chrysenes, triphenylenes) | n.d. | 75.8 | 5.6 | b |
| dimethyl–(fluoranthenes, pyrenes) | n.d. | 10.6 | n.d. | b |
| 1,2'-; 2,1'-; 2,2'-binaphthalenes | n.d. | 139.7 | 9.0 | b |
| benzo[k]fluoranthene | n.d. | 393.8 | 6.0 | a |
| benzo[b]fluoranthene | n.d. | 284.4 | 5.4 | a |
| benzo[e]pyrene | n.d. | 116.0 | 1.9 | a |
| Total class mass concentration: | 1.19 | 5494.5 | 1157.86 | |
| **—Polycyclic Aromatic Ketones (PAK) and Quinones (PAQ)—** | | | | |
| 9H–fluoren-9-one (fluorenone) | n.d. | 55.1 | 49.2 | a |
| 1H-phenalen-1-one | n.d. | 618.4 | 3.0 | a |
| methylfluorenones | n.d. | 159.5 | 93.9 | b |
| 9,10–phenanthrenedione (phenanthrenequinone) | n.d. | 12.1 | 4.5 | a |
| 9,10–anthracenedione (anthraquinone) | n.d. | 1976.8 | 39.1 | a |
| 2-methyl-9,10–anthracenedione (2-methylanthraquinone) | n.d. | 69.7 | 0.47 | a |
| phenanthrone/anthrone | n.d. | 21.4 | 1.2 | a |

**Table 7.1 (continued)**

**Emission Rates in pg/kJoule**

| PART C | HEPA-filtered Dilution Air | Space & Water Heater First Filter | Space & Water Heater Backup Filter | Compound ID[b] |
|---|---|---|---|---|
| 9H–xanthen-9-one (xanthone) | n.d. | 49.3 | 15.6 | a |
| 4–cyclopenta[def]phenanthren-4-one | n.d. | 920.2 | 501.9 | b |
| 1–H–benz[de]anthracen-1-one | n.d. | 132.0 | 2.9 | b |
| 7–H–benz[de]anthracen-7-one | n.d. | 94.7 | 0.82 | a |
| benz[a]anthracene-7,12-dione | n.d. | 123.7 | 104.1 | a |
| Total class emission rate: | | 4232.9 | 816.69 | |
| — Aza- and Thia-arenes — | | | | |
| benzo[h]quinoline | n.d. | 36.6 | 30.6 | a |
| benzo[f]quinoline | n.d. | 25.9 | 1.7 | b |
| phenanthridine | n.d. | 48.4 | 1.0 | a |
| acridine | n.d. | 7.4 | n.d. | a |
| aza-arenes with MW203[d] | n.d. | 124.3 | 26.6 | b |
| benzo[b]naphthothiophenes | n.d. | 325.4 | 103.5 | b |
| Total class emission rate: | | 568.0 | 163.4 | |

[a] fine particulate matter ($d_p \leq 2\mu m$), samples were collected on two quartz filter sets in series.

[b] for more details see text. a, positive: authentic std. verification; b, probable: library spectrum verification;
c, possible; d, tentative.

[c] detected as methyl ester in the derivatized sample aliquot.

[d] isomers such as indeno(1,2,3-i,i)isoquinoline; acenaphtho(1,2-b)pyridine; 4-azapyrene.

### Influence of Combustion Air or Stack Vent Air on Exhaust Emissions

As mentioned earlier, the concentration distribution found for the higher molecular weight n-alkanes in the natural gas combustion emissions shows an odd-to-even carbon number predominance which is not typical of combustion or fossil fuel derived n-alkanes (*17, 22, 31, 47*) but is typical of urban atmospheric fine particulate matter that contains vegetative detritus (*32*). These higher molecular weight n-alkanes probably entered the gas-fired heaters either with the combustion air or through the air vent above the water heater, and can be used to evaluate the contributions of ambient aerosol to the natural gas source test results.

Figure 7.6 shows the annual averaged n-alkane concentration distribution measured in 1982 at three urban sites within the greater Los Angeles area (*22*). Comparing the ambient n-alkane concentration distributions (Figure 7.6) with the natural gas appliances n-alkane emission profiles (Figure 7.3a), it can be seen that even if all the n-alkanes $\geq C_{27}$ were to have come from ambient air, that most of the lower molecular weight n-alkanes $\leq C_{26}$ in the natural gas exhaust must have been released from the natural gas-fired appliances themselves. Similar arguments hold for the n-alkanoic acids found in the exhaust emissions based on the use of higher molecular weight n-alkanoic acids ($C_{26}$, $C_{28}$, $C_{30}$) as indicators for the presence of entrained urban air.

Fine particle PAH concentrations have been measured throughout 1982 in the Los Angeles area (*22*). Comparing the ambient fine particle PAH concentration distribution with the PAH emissions from the natural gas-fired home appliances tested, it is observed that none of the higher molecular weight PAH (e.g., benzo[ghi]perylene, coronene) found in relatively large amounts in the

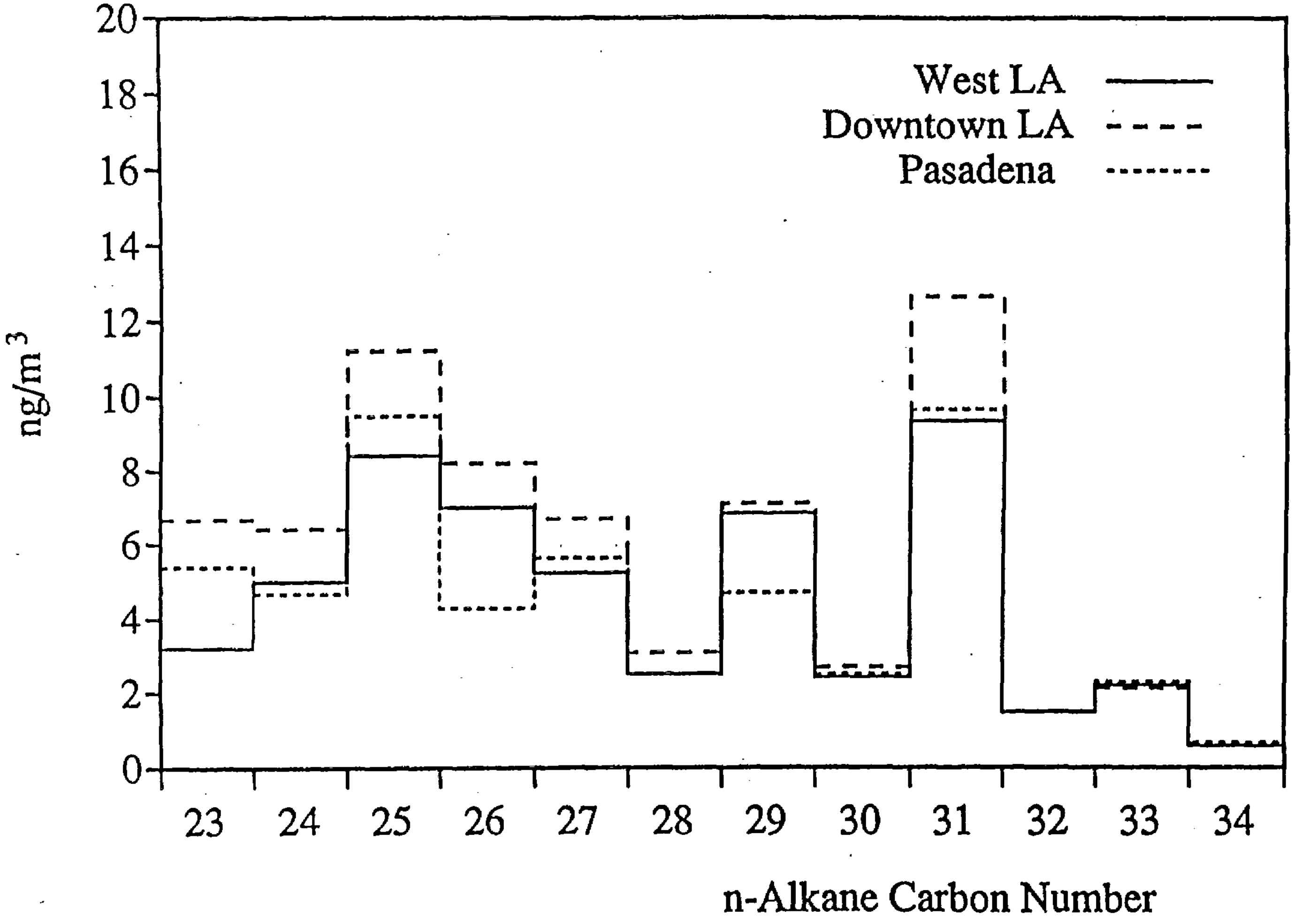


Fig. 7.6: Ambient n-alkane fine particle concentrations; annual averages for West Los Angeles, downtown Los Angeles, and Pasadena in 1982 (from reference *22*).

ambient samples are detected in the natural gas combustion exhaust emissions. Thus, it can be concluded that the PAH measured in the exhaust effluents of natural gas home appliances are almost exclusively due to the natural gas combustion in the space heater and water heater tested and are not dominated by entrained ambient air. Similar arguments hold for oxy-PAH, aza-arenes, and thia-arenes.

### Source Contributions to the Ambient Aerosol

Hildemann et al. (*14*) estimated that natural gas combustion at residences and small commercial establishments within an 80 × 80 km urbanized area centered over Los Angeles emits on the average 30 kg of fine particulate organic carbon (OC) per day, which translates to about 0.1% of the daily total fine particulate organic carbon (OC) mass emitted to that area for the year 1982. At those area-wide emission rates, such natural gas appliances do not contribute significant amounts of particle mass to the urban fine particle burden. Performing a similar calculation for PAH and oxy-PAH compound classes only (the use of natural gas by residential and high priority commercial customers within that 80 × 80 km geographic area has been estimated to be 760 × $10^9$ kJ in 1982 (*1*)) it can be estimated that 4.2 kg/day of PAH and 3.2 kg/day of oxy-PAH may be released from natural gas-fired small combustors (front filter only). Recently, Rogge et al. (*17*) determined fine particle-associated vehicular emissions to the Los Angeles atmosphere for 1982. Compared to the emissions from natural gas-fired home appliances and small commercial natural gas users, catalyst-equipped autos emit about twice as much PAH (7.4 kg/day) and oxy-PAH (6.2 kg/day). PAH and oxy-PAH emissions from all types of diesel vehicles (3.4 kg/day and 3.3 kg/day, respectively) are comparable to the emissions from natural gas-fired home appliances and high priority commercial natural gas users. Hence, natural gas combustion in residential homes and commercial establishments could contribute amounts of PAH and oxy-PAH to the urban atmosphere that are similar to other urban emission sources.

## Conclusions

Organic aerosol compounds present in the combined exhaust from a space heater and a water heater burning natural gas have been measured using a dilution source sampling system. It has been found that the fine particulate mass emission rates are low (45.8 ng/kJ ± 17.4; average of three experiments). The exhaust particles consisted mainly of organic matter. Of the gravimetrically determined particle mass, 26% was attributed to single organic compounds. The overwhelming majority of the identified organic compounds in turn consisted of PAH, oxy-PAH, aza-arenes, and thia-arenes, which together account for 22.5% of the fine aerosol mass. Although the contribution to the outdoor aerosol burden is small, residential and high priority commercial natural gas combustion is estimated to contribute amounts of PAH and oxy-PAH to the Los Angeles area atmosphere in 1982 that are comparable to that emitted from diesel vehicles, and that are about half as much as released from catalyst-equipped automobiles. The emissions of mutagenic organics from motor vehicles have been a matter of intense study in recent years. If regional emissions of PAH and related compounds from natural gas combustion are comparable to those from vehicles, then natural gas combustion aerosol likewise should be examined to determine its mutagenicity.

# REFERENCES

( 1) Gray, H.A. Control of atmospheric fine carbon particle concentrations. Ph.D. Thesis, California Institute of Technology; Pasadena, 1986.

( 2) Bromly, J.H.; Barnes, F.J.; Johnston, R.C.R.; Little, L.H. The effect of vitiation on trace pollutants from domestic gas appliances. *J. Inst. Energy* 1985, 58, 188-196.

( 3) Cote, W.A.; Wade, W.A., III, Yocum, J. In *A study of indoor air quality.* EPA 650/4-74-042, U.S. Environmental Protection Agency: Washington, DC, 1974.

( 4) Girman, J.R.; Apte, G.W.; Traynor, J.R.; Allen, J.R.; Hollowell, C.D. Pollutant emission rates from indoor combustion appliances and sidestream cigarette smoke. *Environ. Int.* 1982, 8, 213-221.

( 5) Himmel, R.L.; Dewerth, D.W. In *Evaluation of the pollutant emissions from gas-fired ranges.* Report No. 1492, American Gas Association Laboratories: Cleveland, OH, 1974.

( 6) Muhlbaier, J.L.; Williams, R.L. In *Particulate Carbon: Atmospheric Life Cycle*; Wolff, G.T., Klimisch, R.L., Eds.; Plenum Press: New York, 1982, pp 185-198.

( 7) Palmes, E.D.; Tomczyk, C.; DiMattio, J. Average $NO_2$ concentration in dwellings with gas or electric stoves. *Atmos. Environ.* 1977, 11, 869-872.

( 8) Traynor, G.W.; Anthon, D.W.; Hollowell, C.D. Technique for determining pollutant emissions from a gas-fired range. *Atmos. Environ.* 1982, 16, 2979-2987.

( 9) Traynor, G.W.; Apte, M.G.; Dillworth, J.F.; Hollowell, C.D.; Sterling, E.M. The effects of ventilation on residential air pollution due to emissions from a gas-fired stove. *Environ. Int.* 1982, 8, 447-452.

(10) Yamanaka, S.; Hirose, H.; Takada, S. Nitrogen oxides emissions for domestic kerosene-fired and gas-fired appliances. *Atmos. Environ.* 1979, 13, 407-412.

(11) Chuang, J.C.; Gregory, A.M.; Kuhlman, M.R. Polycyclic aromatic hydrocarbons and their derivatives in indoor and outdoor air in an eight-home study. *Atmos. Environ.* 1991, 25B, 369-380.

(12) Risner, C.H.; Conner, J.M. The quantification of 4- to 6-ring polynuclear aromatic hydrocarbons in indoor air samples by high-performance liquid chromatography. *J. Liquid Chromato.* 1991, 13, 437-463.

(13) Sexton, K.; Spengler, J.D.; Treitman, R.D. Personal exposure to respirable particles: A case study in Waterbury, Vermont. *Atmos. Environ.* 1984, 18, 1385-1398.

(14) Hildemann, L.M.; Markowski, G.R.; Cass, G.R. Chemical composition of emissions from urban sources of fine organic aerosol. *Environ. Sci. Technol.* 1991, 25, 744–759.

(15) Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Quantitative characterization of urban sources of organic aerosol by high-resolution gas chromatography. *Environ. Sci. Technol.* 1991, 25, 1311-1325.

(16) Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Sources of fine organic aerosol: 1. Charbroilers and meat cooking operations. *Environ. Sci. Technol.* 1991, 25, 1112-1125.

(17) Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Sources of fine organic aerosol: 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. *Environ. Sci. Technol.* 1993, 27, 636-651.

(18) Hildemann, L.M.; Cass, G.R.; Markowski, G.R. A dilution stack sampler for collection of organic aerosol emissions: design, characterization and field tests. *Aerosol Sci. Technol.* 1989, 10, 193-204.

(19) Mazurek, M.A.; Simoneit, B.R.T.; Cass, G.R.; Gray, H.A. Quantitative high-resolution gas chromatography and high-resolution gas chromatography/mass spectrometry analysis of carbonaceous fine aerosol particles. *Int. J. Environ. Anal. Chem.* 1987, 29, 119-139.

(20) Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Interpretation of high-resolution gas chromatography and high-resolution gas chromatography/mass spectrometry data acquired from atmospheric organic aerosol samples. *Aerosol Sci. Technol.* 1989, 10, 408-419.

(21) Mazurek, M.A.; Hildemann, L.M.; Cass, G.R.; Simoneit, B.R.T.; Rogge, W.F. Methods of analysis for complex organic aerosol mixtures from urban emission sources of particulate carbon. In *Proceedings ACS Symposium on Measurements of Airborne Compounds: sampling, analysis, and data interpretation*, August 26-31, 1990, Washington, DC, 1990, Winegar, E., Keith, L.H.; ACS: Washington, DC, 1992, *in press*.

(22) Rogge, W.F.; Mazurek, M.A.; Hildemann, L.M.; Cass, G.R.; Simoneit, B.R.T. Quantification of urban organic aerosols at a molecular level: I. Identification, abundance, and seasonal variations. *Atmos. Environ.* 1993, *in press*.

(23) Bidleman, T.F.; Foreman, W.T. Vapor-particle partitioning of semivolatile organic compounds. In *The Chemistry of Aquatic Pollutants*, Hites, R.A., Eisenreich, S.J., Eds.; ACS Advances in Chemistry Series, ACS: New York, 1987, pp 27-56.

(24) Cautreels W. and Van Cauwenberghe K. Experiments on the distribution of organic pollutants between airborne particulate matter and the corresponding gas phase. *Atmos. Environ.* 1978, 12, 1133-1141.

(25) Pankow, J.F. Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere. Results and Discussion. *Atmos. Environ.* 1987, 21, 2275-2283.

(26) Fitz, D.R. Reduction of the positive organic artifact on quartz filters. *Aerosol Sci. Technol.* 1990, 12, 142-148.

(27) Ligocki, M.P.; Pankow, F. Measurements of the gas/particle distributions of atmospheric organic compounds. *Environ. Sci. Technol.* 1989, 23, 75-83.

(28) McDow, S.R.; Huntzicker, J.J. Vapor adsorption artifact in the sampling of organic aerosol: Face velocity effects. *Atmos. Environ.* 1990, 10, 2563-2571.

(29) Mazurek, M.A.; Cass G.R.; Simoneit, B.R.T. Biological input to visibility-reducing particles in the remote arid southwestern United States. *Environ. Sci. Technol.* 1991, 25, 684-694.

(30) Mazurek, M.A.; Simoneit, B.R.T. Characterization of biogenic and petroleum-derived organic matter in aerosols over remote, rural and urban areas. In *Identification and Analysis of Organic Pollutants in Air*, ACS Symp., Ann Arbor Science/Butterworth Publishers: Woburn, MA, 1984, pp 353–370.

(31) Simoneit, B.R.T.; Mazurek, M.A. Organic matter of the troposphere—II. Natural background of biogenic lipid matter in aerosols over the rural Western United States. *Atmos. Environ.* 1982, 16, 2139-2159.

(32) Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Sources of fine organic aerosol: 4. Particulate abrasion products from leaf surfaces of urban plants. *Environ. Sci. Technol.* 1993, *submitted.*

(33) Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Sources of fine organic aerosol: 3. Road dust, tire debris, and organometallic brake lining dust — roads as sources and sinks. *Environ. Sci. Technol.* 1993, *in press.*

(34) Hinckley, D.A.; Bidleman, T.F.; Foreman, W.T.; Tuschall, J.R. Determination of vapor pressures for nonpolar and semipolar organic compounds from gas chromatographic retention data. *J. Chem. Eng. Data* 1990, 35, 232-237.

(35) Jenkins, P.L.; Phillips, T.J.; Mulberg, E.J.; Hui, S.P. Activity patterns of Californians: Use of and proximity to indoor pollution sources. *Atmos. Environ.* 1992, 26A, 2141-2148.

(36) Chapman, O.L.; Heckert, D.C.; Reasoner, J.W.; Thackaberry, S.P. Photochemical studies on 9-nitroanthracene. *J. Am. Chem. Soc.* 1966, 88, 5550-5554.

(37) Van Cauwenberghe, K.; Van Vaeck, L.; Pitts, J.N.Jr. Chemical transformations of organic pollutants during aerosol sampling. *Adv. Mass Spectrom.*, 1979, 8, 1499-1507.

(38) Cautreels W. and Van Cauwenberghe K. Determination of organic compounds in airborne particulate matter by gas chromatography–mass spectrometry. *Atmos. Environ.* 1976, 10, 447-457.

(39) Dong, M.W.; Locke, D.C.; Hoffmann, D. Characterization of aza-arenes in basic organic portion of suspended particulate matter. *Environ. Sci. Technol.* 1977, 11, 612-618.

(40) Sawicki E., McPherson S.P., Stanley T.W., Meeker J. and Elbert W.C. Quantitative composition of the urban atmosphere in terms of polynuclear azaheterocyclic compounds and aliphatic and polynuclear aromatic hydrocarbons. *Int. J. Air Water Poll.* 1965, 9, 515-524.

(41) Snook, M.E.; Fortson, P.J.; Chortyk, O.T. Isolation and identification of aza-arenes of tobacco smoke. *Beitr. Tabakforsch.* 1981, 11, 67-78.

(42) Sawicki E.; Meeker, J.E.; Morgan, M.J. Polynuclear aza compounds in automotive exhaust. *Arch. Environ. Health* 1965, 11, 773-775.

(43) Adams, E.A.; La Voie, E.J.; Hoffmann, D. Mutagenicity and metabolism of azaphenanthrenes. In *Polynuclear Aromatic Hydrocarbons: Formation, Metabolism and Measurement*; Cooke, M., Dennis, A.J., Eds.; Battelle Press: Columbus, OH, 1982, pp 73-87.

(44) Dutcher, J.S.; Mitchell, C.E. Distribution and elimination of [$^{14}$C]-phenanthridone in rats after inhalation. In *Polynuclear Aromatic Hydrocarbons: Formation, Metabolism and Measurement*; Cooke, M., Dennis, A.J., Eds.; Battelle Press: Columbus, OH, 1982, pp 427-435.

(45) Grimmer, G.; Jacob, J.; Naujack, K.-W.; Dettbarn, G.; Brune, H.; Deutsch-Wenzel, R.; Misfeld, J.; Timm, J. Contribution of polycyclic aromatic compounds to the carcinogenicity of flue gas from hard-coal-fired residential furnaces and characterization of arenes (PAH), azaarenes, oxaarenes, and thiaarenes. In *Polynuclear Aromatic Hydrocarbons: Chemistry, Characterization and Carcinogenesis*; Cooke, M., Dennis, A.J., Eds.; Battelle Press: Columbus, OH, 1984, pp 359-370.

(46) La Voie, E.J.; Shigematsu, A.; Adams, E.A.; Geddie, N.G.; Rice, J.E. Quinolines and benzoquinolines: studies related to their metabolism, mutagenicity, tumor-initiating activity, and carcinogenicity. In *Polynuclear Aromatic Hydrocarbons: A Decade of Progress*; Cooke, M., Dennis, A.J., Eds.; Battelle Press: Columbus, OH, 1985, pp 503-518.

(47) Willey, C; Pelroy, R.A.; Stewart, D.L. Comparative analysis of polycyclic aromatic sulfur heterocycles isolated from four shale oils. In *Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry.*; Cooke, M., Dennis, A.J., Fisher, G.L., Eds.; Battelle Press: Columbus, OH, 1981, pp 907-917.

(48) Simoneit, B.R.T. Organic matter of the troposphere—III. Characterization and sources of petroleum and pyrogenic residues in aerosols over the Western United States. *Atmos. Environ.* 1984, 18, 51-67.

# Chapter 8

## Cigarette Smoke in the Urban Atmosphere

### Introduction

Cigarette smoke has been intensively researched in the last three decades. Studies that focus on the gaseous and particulate smoke constituents have been numerous, and substantial literature is available on both the chemical composition and possible health risks due to tobacco smoke (e.g., Baker, 1981; IARC Monographs, 1986; Johnstone and Plimmer, 1959; Katzenstein, 1992; Repace and Lowrey, 1990; Stedman, 1968; U.S. Dept. of Health and Human Services, 1989).

Previous investigations have developed nicotine, solanesol, *n*-alkanes, polycyclic aromatic hydrocarbons (PAH) and other organic constituents as marker compounds for the presence of cigarette smoke in indoor air (e.g., Benner et al., 1989; Chuang et al., 1991; Eatough et al., 1989; Girman et al., 1982; Grimmer et al., 1977; Hammond et al., 1987; Löfroth et al., 1989; Klus and Kuhn, 1982; Mitra et al., 1992; Ogden and Maiolo, 1989; Ramsey et al., 1990; Tang et al., 1990). The purpose of the present study is not to add additional knowledge to the extensive literature available for cigarette smoke composition and indoor air quality. Instead, in this study, tobacco smoke is viewed as one of the many sources contributing organic fine particulate matter to the outdoor urban atmosphere.

To trace cigarette smoke in outdoor ambient air, cigarette smoke constituents are examined to evaluate their use as possible tobacco smoke markers in the urban atmosphere. To be useful, such tracers must be fairly stable in the atmosphere and must not be confounded by fine aerosol emissions from other anthropogenic or biogenic sources. Likely tracer compounds that appear to meet these requirements first are identified. Then utilizing an emission inventory for fine particulate organic matter released to the Los Angeles area atmosphere from all major urban sources (for 1982), combined with average cigarette consumption data and compound emission rates per cigarette smoked, estimates are made of ambient tobacco smoke marker concentrations. These estimates are then verified by comparison to actual marker concentration levels measured outdoors at several sites within that metropolitan area.

## Experimental Methods

### Cigarettes Tested

Four different cigarette types — including regular (nonfilter), filtertip, light, and menthol cigarettes — have been tested and the resulting aerosol samples composited to closely represent the market share in the U.S. in 1981 for each of these cigarette types. For each cigarette type, one of the five most popular cigarette brands has been employed for this study including products carrying the Camel, Merit, Winston, and Benson & Hedges brand names. For more details see Hildemann et al. (1991a).

### Sampling

A specially designed vertically oriented dilution tunnel was used to collect the exhaled mainstream and sidestream smoke generated by human smokers (Hildemann et al. 1991a). The size of the dilution tunnel and flow rate through the tunnel (residence time of circa 30sec) provided sufficient time for cigarette smoke to cool to ambient temperatures, allowing condensible organic compounds emitted in the vapor phase, to condense onto the smoke particles prior to sampling. Five AIHL-design cyclone separators were mounted at the downstream end of the dilution tunnel. Two of the cyclone separators was operated at a flow rate of 27.9 ± 0.3 L $min^{-1}$, removing particles with an aerodynamic diameter $> 2.0\ \mu m$ from the air stream. Fine particulate matter ($d_p \leq 2.0\ \mu m$) next was collected by filtration downstream of each cyclone separator using three to four parallel 47-mm-diameter filter assemblies per cyclone, for a total of 7 filter samples per cigarette type. The cigarette smoke particles were collected on quartz fiber filters (Pallflex 2500 QAO) and Teflon filters (Gelman Teflo, 2.0-$\mu m$ pore size). All quartz fiber filters were annealed before use (750°C for 2–4h) to guarantee low contamination levels for organic compounds. Additional details of the experimental protocol are elsewhere (Hildemann et al., 1991a).

### Bulk Chemical Analysis

Trace elements, ionic species, organic carbon (OC), and elemental carbon (EC) emission rates have been previously quantified in the cigarette smoke samples (Hildemann et al., 1991a).

### Sample Extraction

Organic compounds present in the cigarette smoke aerosol samples were extracted using the procedure developed for ambient fine particulate matter by Mazurek et al. (1987) that subsequently has been used in several studies concerned with organic aerosol emissions and ambient airquality (Mazurek et al.,

1989, 1991; Hildemann et al., 1991b; Rogge et al., 1991, 1993a-d). The extraction protocol can be best described briefly as follows: Before sample extraction, fine aerosol cigarette smoke samples were composited according to their market share. Perdeuterated tetracosane ($n$-$C_{24}D_{50}$), which serves as an internal standard, next was spiked onto the filter composites. The composited quartz fiber filter samples were extracted in a sequential procedure that utilized with hexane (2 × 30 ml) followed by benzene/2-propanol (2:1 mixture, 3 × 30 ml). Each extraction step was conducted for 10-min and supported by mild ultrasonic agitation. Following each extraction step, the extracts were filtered and combined using a transfer and filtering device that is described in detail by Mazurek et al. (1987). A two step rotary evaporation scheme followed by gentle high purity $N_2$-stream evaporation was employed to reduce the combined sample extract volume to 200-500 $\mu$l. One portion of the sample extract was then processed with freshly produced diazomethane to convert organic acids to their methyl ester analogues and other compounds with susceptible hydroxy functionalities to their methoxy analogues. The sample extracts were stored prior to GC/MS analysis in the dark at -21°C.

### Sample Analysis

A Finnigan 4000 quadrupole mass spectrometer connected to a gas chromatograph and interfaced with an INCOS data system was used for compound identification and quantification. Sample extracts were injected onto a conventional Grob splitless injector (300°C) which was connected to a 30-m fused-silica DB-1701 column (J & W Scientific, Rancho Cordova, CA). Gas chromatography of the injected sample extract was carried out using the following temperature program: (1) isothermal hold at 65°C for 10 min, (2) temperature increase at

To trace cigarette smoke in outdoor ambient air, cigarette smoke constituents are examined to evaluate their use as possible tobacco smoke markers in the urban atmosphere. To be useful, such tracers must be fairly stable in the atmosphere and must not be confounded by fine aerosol emissions from other anthropogenic or biogenic sources. Likely tracer compounds that appear to meet these requirements first are identified. Then utilizing an emission inventory for fine particulate organic matter released to the Los Angeles area atmosphere from all major urban sources (for 1982), combined with average cigarette consumption data and compound emission rates per cigarette smoked, estimates are made of ambient tobacco smoke marker concentrations. These estimates are then verified by comparison to actual marker concentration levels measured outdoors at several sites within that metropolitan area.

## Experimental Methods

### Cigarettes Tested

Four different cigarette types — including regular (nonfilter), filtertip, light, and menthol cigarettes — have been tested and the resulting aerosol samples composited to closely represent the market share in the U.S. in 1981 for each of these cigarette types. For each cigarette type, one of the five most popular cigarette brands has been employed for this study including products carrying the Camel, Merit, Winston, and Benson & Hedges brand names. For more details see Hildemann et al. (1991a).

### Sampling

A specially designed vertically oriented dilution tunnel was used to collect the exhaled mainstream and sidestream smoke generated by human smokers (Hildemann et al. 1991a). The size of the dilution tunnel and flow rate through the tunnel (residence time of circa 30sec) provided sufficient time for cigarette smoke to cool to ambient temperatures, allowing condensible organic compounds emitted in the vapor phase, to condense onto the smoke particles prior to sampling. Five AIHL-design cyclone separators were mounted at the downstream end of the dilution tunnel. Two of the cyclone separators was operated at a flow rate of 27.9 ± 0.3 L $\text{min}^{-1}$, removing particles with an aerodynamic diameter $> 2.0$ $\mu$m from the air stream. Fine particulate matter ($d_p \leq 2.0$ $\mu$m) next was collected by filtration downstream of each cyclone separator using three to four parallel 47-mm-diameter filter assemblies per cyclone, for a total of 7 filter samples per cigarette type. The cigarette smoke particles were collected on quartz fiber filters (Pallflex 2500 QAO) and Teflon filters (Gelman Teflo, 2.0-$\mu$m pore size). All quartz fiber filters were annealed before use (750°C for 2–4h) to guarantee low contamination levels for organic compounds. Additional details of the experimental protocol are elsewhere (Hildemann et al., 1991a).

## Bulk Chemical Analysis

Trace elements, ionic species, organic carbon (OC), and elemental carbon (EC) emission rates have been previously quantified in the cigarette smoke samples (Hildemann et al., 1991a).

## Sample Extraction

Organic compounds present in the cigarette smoke aerosol samples were extracted using the procedure developed for ambient fine particulate matter by Mazurek et al. (1987) that subsequently has been used in several studies concerned with organic aerosol emissions and ambient airquality (Mazurek et al., 1989, 1991; Hildemann et al., 1991b; Rogge et al., 1991, 1993a-d). The extraction protocol can be best described briefly as follows: Before sample extraction, fine aerosol cigarette smoke samples were composited according to their market share. Perdeuterated tetracosane ($n$-$C_{24}D_{50}$), which serves as an internal standard, next was spiked onto the filter composites. The composited quartz fiber filter samples were extracted in a sequential procedure that utilized with hexane (2 × 30 ml) followed by benzene/2-propanol (2:1 mixture, 3 × 30 ml). Each extraction step was conducted for 10-min and supported by mild ultrasonic agitation. Following each extraction step, the extracts were filtered and combined using a transfer and filtering device that is described in detail by Mazurek et al. (1987). A two step rotary evaporation scheme followed by gentle high purity $N_2$-stream evaporation was employed to reduce the combined sample extract volume to 200-500 $\mu$l. One portion of the sample extract was then processed with freshly produced diazomethane to convert organic acids to their methyl ester analogues and other compounds with susceptible hydroxy functionalities to their methoxy analogues. The sample extracts were stored prior to GC/MS analysis in the dark at -21°C.

### Sample Analysis

A Finnigan 4000 quadrupole mass spectrometer connected to a gas chromatograph and interfaced with an INCOS data system was used for compound identification and quantification. Sample extracts were injected onto a conventional Grob splitless injector (300°C) which was connected to a 30-m fused-silica DB-1701 column (J & W Scientific, Rancho Cordova, CA). Gas chromatography of the injected sample extract was carried out using the following temperature program: (1) isothermal hold at 65°C for 10 min, (2) temperature increase at

10°C/min for 21 min, and (3) isothermal hold at 275°C for another 49 min. The mass spectrometric data were acquired while operating the mass spectrometer in the electron impact mode (electron energy of 70eV). For supplemental studies a Varian 4600 high-resolution gas chromatograph (HRGC) with FID-detector was used and operated with the same physical column and temperature program as used during these GC/MS-analyses (Hildemann et al., 1991b). Additional information describing the analytical procedure can be found elsewhere (Mazurek et al., 1987, 1989, 1993; Rogge et al., 1991, 1993a,b).

### Quality Assurance

A series of quality control and monitoring steps were followed. The major steps include: field and laboratory blank testing; solvent testing to monitor possible contaminants; recovery experiments in which a large set of polar and nonpolar standard compounds were spiked onto test filters and then extracted; and dilution air testing. For a more detailed discussion, the reader is referred to accompanying source and ambient fine organic particle studies published elsewhere (Mazurek et al., 1989, 1993; Rogge et al., 1991, 1993a,b).

### Compound Identification and Quantification

Compound identification was labeled using the National Institute of Standards and Technology (NIST) mass spectral library accessed by the INCOS Data System, the NIST/EPA/NIH mass spectral database (PC Version 4.0) distributed by NIST, and by reference to authentic standards injected onto the GC/MS system used here. Compound identification was labeled accordingly: (a) *positive* — sample mass spectrum and authentic standard mass spectrum compared well and showed identical retention times; (b) *probable* — same as before, except no authentic standards were available, but the NIST or NIST/EPA/NIH library mass spectrum and the sample mass spectrum agreed well; (c) *possible*, same as above except that the sample spectrum contained information from other compounds but with minor overlap; (d) *tentative*, when the sample spectrum contained additional information from possibly several compounds (noise) with overlap.

The compound quantification process was based on the application of $n$-$C_{24}D_{50}$ as internal standard and 1-phenyldodecane as coinjection standard. To correct for detector response to compounds having different structures and retention times, sets of known standard compounds were injected onto the analytical system to monitor their specific MS-response. For more information, the interested reader is referred to Rogge et al. (1991, 1993a).

### Standard Compounds

Confirmation and quantification of organic compounds was obtained through the use of more than 150 authentic standards, see Rogge et al. (1993b). The following standard mixtures were injected onto the GC/MS-system: (1) normal alkanes ranging from $n$–$C_{10}$ to $n$–$C_{36}$; (2) normal alkanoic acids as methyl esters ranging from $n$–$C_6$ to $n$–$C_{30}$; (3) unsaturated aliphatic acids such as oleic acid and linoleic acid as methyl esters; (4) normal alkanols ranging from $n$–$C_{10}$ to $n$–$C_{30}$; (5) several phenolic compounds, benzaldehydes and substituted aromatic acids; (6) a suite of 39 aromatic and polycyclic aromatic hydrocarbons (PAH); (7) 10 polycyclic aromatic ketones and quinones; (8) a set of 8 aromatic and polycyclic aromatic N– and S–substituted compounds; (9) steroids including cholesterol and cholestane; (10) a set of 4 phytosterols; (11) several natural resins; (12) plasticizers; (13) a suite of 11 aliphatic dicarboxylic acids ($C_3$ – $C_{10}$); and (14) a suite of 7 aromatic di- and tricarboxylic acids, all as their methyl ester analogues; (15) nicotinic acid, nicotine , myosmine, and other compounds characteristic of cigarette smoke.

## Results and Discussion

### Mass Balance for Elutable Fine Cigarette Smoke Organic Aerosols

A material balance has been constructed for the elutable and extractable portion of the organic matter associated with cigarette smoke particles and is shown in Figure 8.1. Of the extractable and elutable organic mass, 38.3% could be resolved chromatographically as single compound peaks. The remainder is made up of organic compounds eluting closely together forming, an unresolvable accumulation of compounds known as the unresolved complex mixture (UCM) and present in the GC/MS-chromatograms as a "hump" (Simoneit, 1989). Using GC/MS-techniques, 71.6% of the resolved organic mass could be identified and attributed to known single organic compounds. As seen from Figure 8.1, the major portion (35.6%) is made up of N-heterocyclic compounds, especially alkaloids such as pyridines, pyrrolidines, and pyrroles. Nicotine, the most common pyridine alkaloid in cigarette smoke, constitutes close to 69% of the N-heterocyclic compound class (see also Table 8.1). Phytosterols (10.7%), phenolic compounds (8.2%), *n*-alkanols (6.6%), carboxylic acids (19.0%), plus normal (11.6%), branched (6.1%), and isoprenoid (1.7%) alkanes have been identified and quantified in the fine aerosol collected from exhaled main- plus sidestream cigarette smoke.

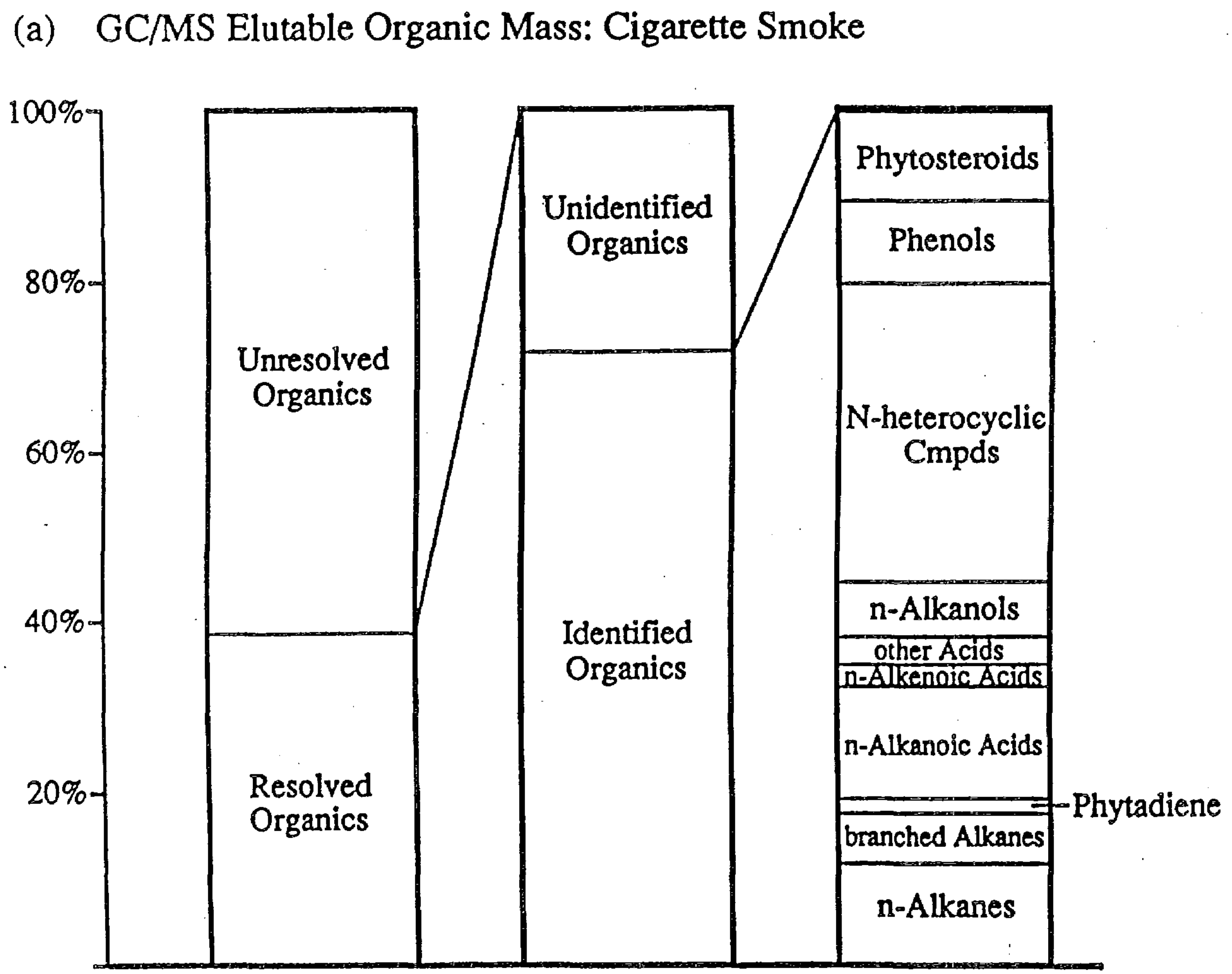

(a) GC/MS Elutable Organic Mass: Cigarette Smoke

Fig. 8.1: Mass balance for elutable organic matter contained in fine cigarette smoke particles.

In the following sections, the organic compound emission rates per cigarette smoked will be discussed first and then compared to previous findings. This approach is crucial to validate our findings before relating cigarette smoke emissions to the urban atmosphere.

## Alkanes and Alkenes

*n*-Alkanes ranging from $C_{20}$ to $C_{35}$ have been identified and quantified (see Table 8.1). The emission rate profile ($\mu$g/cigarette; exhaled mainstream plus sidestream smoke aerosol) reflects the typical leaf surface wax *n*-alkanes distribution commonly found in the leaf surface waxes of vascular plants (Douglas and Eglinton, 1966; Eglinton et al., 1962; Kolattukudy, 1970; Mazurek and Simoneit, 1984; Mazurek et al., 1991; Nishimoto, 1974a; Riederer, 1991; Riederer and Schneider, 1990; Rieley et al., 1991; Rogge et al., 1993a,d; Simoneit and Mazurek, 1982) with a pronounced odd-to-even carbon number predominance as shown in Figure 8.2a. The highest emission rates were found for the $C_{27}$, $C_{29}$, $C_{31}$, and $C_{33}$ *n*-alkanes with $C_{31}$ as the dominant *n*-alkane, closely resembling results from prior studies (Mold et al., 1963; Severson et al., 1978; Spears et al., 1963; Ramsey et al., 1990; Wynder and Hoffmann, 1967); see Table 8.1 for the comparison.

*iso*- (2-methyl-) and *anteiso*- (3-methyl-) Alkanes are leaf wax constituents that are preferentially found in tobacco leaf surface waxes (Carruthers and Johnstone, 1959; Mold et al., 1963; Newell et al., 1978; Stedman, 1968; Severson et al., 1978; Spears et al., 1963; Wynder and Hoffmann, 1967). They are also found to a much lesser degree in leaf waxes typical of urban vegetation, as will be shown in a later section (Baker, 1982; Eglinton and Hamilton, 1967; Eglinton et al., 1962; Kolattukudy, 1970; Rogge et al., 1993d; Simoneit and Mazurek, 1982;

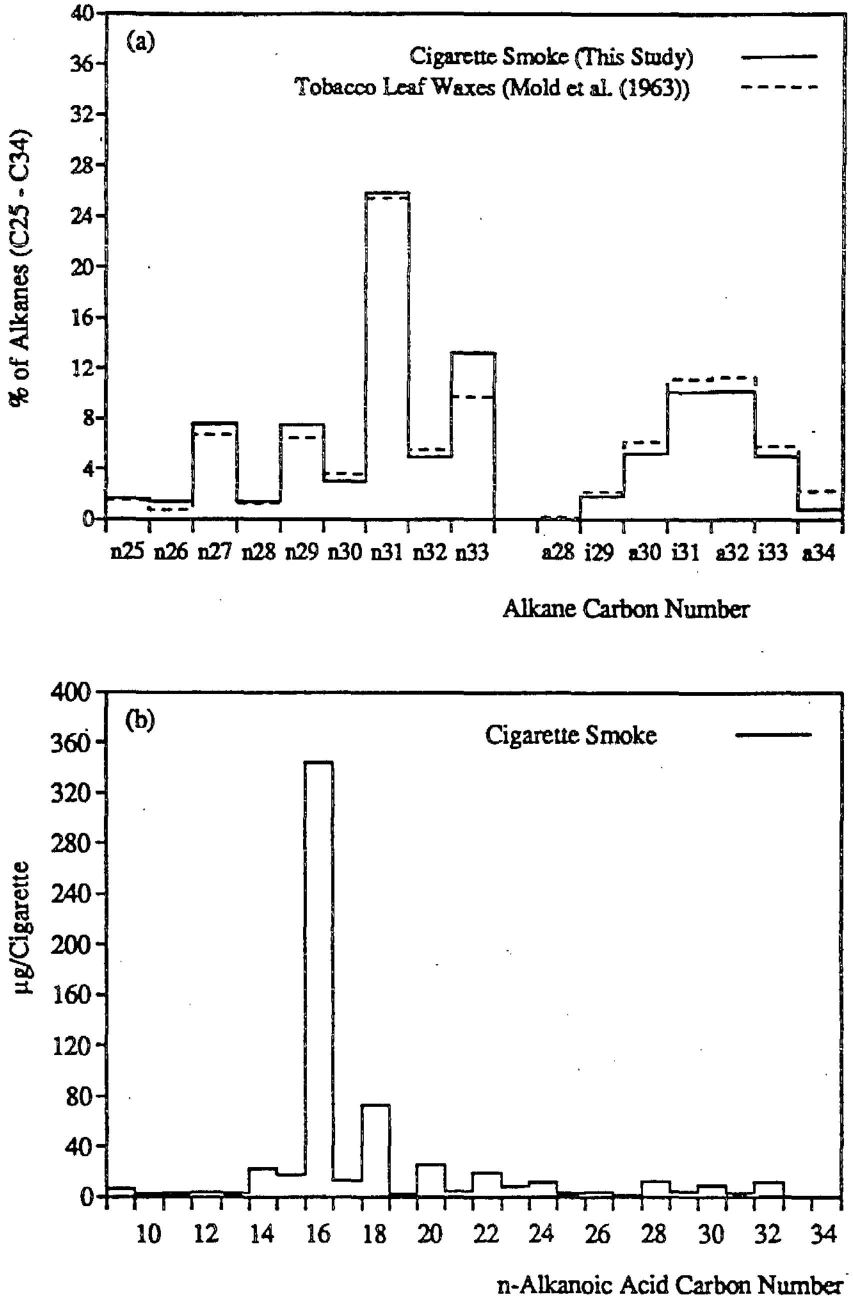


Fig. 8.2: Concentration distributions for cigarette smoke constituents: (a) *n*-alkanes in cigarette smoke (this study) compared to the tobacco leaf wax data of Mold et al. (1963) (in mass % relative to total alkanes in the range from $C_{25}$ to $C_{36}$), and (b) *n*-alkanoic acids in cigarette smoke (this study).

Nishimoto, 1974a,b). *iso*-Alkanes found in the cigarette smoke aerosol show a preference for odd carbon numbered homologues, whereas *anteiso*-alkanes are present at the highest concentrations for even numbered homologues, a result that is closely linked to the route of their biosynthesis in the plant leaves (Kolattukudy, 1970; Mold et al., 1963). In Figure 8.2a, the normal and branched alkane profiles ($C_{25}$ – $C_{34}$) obtained from cigarette smoke during the present study are compared to the results published by Mold et al. (1963) for direct extraction of leaf waxes from unburned tobacco leaves. The *n*-alkane, *iso*-, and *anteiso*-alkane concentration profiles of both studies agree rather well indicating that each alkane-type compound is transferred at about the same rate from the tobacco leaf waxes into the cigarette smoke aerosol. This observation concurs with prior studies in which the transfer of these and other organic tobacco constituents into the cigarette smoke aerosol has been investigated (Carruthers and Johnstone, 1959; Mold et al., 1963; Severson et al. 1978; Stedman, 1968).

Acyclic isoprenoid-type alkenes (unsaturated and branched) constitute another compound class commonly found in tobacco and tobacco smoke (IARC, 1986; Matsushima et al., 1979; Sakuma et al., 1984a; Severson et al., 1978; Stedman, 1968). Several isoprenoid compounds are tobacco-specific and often are also found in cigarette smoke (IARC, 1986; Stedman, 1968; Wynder and Hoffmann, 1967). Here, neophytadiene (a diunsaturated and branched alkene) has been identified, and its concentration is comparable to that found in earlier studies, see Table 8.1 (Sakuma et al., 1984a; Severson et al., 1978).

### Carboxylic Acids

*n*-Alkanoic acids and their unsaturated homologues are found in the leaf surface waxes of vascular plants, including tobacco leaves (Douglas and Eglinton, 1966; Elmenhorst, 1972; Jamieson and Reid, 1972; Kolattukudy, 1970; Mazurek and Simoneit, 1984; Mazurek et al., 1991; Riederer, 1991; Riederer and Schneider, 1990; Simoneit and Mazurek, 1982; Rieley et al., 1991; Rogge et al., 1993a,d). As a result of their biosynthesis, *n*-alkanoic acids show a preference for even carbon numbered homologues, as shown in Figure 8.2b. In this study aerosol-phase, *n*-alkanoic acids have been identified ranging from $C_8$ to $C_{34}$. In contrast to leaf surface waxes of other vascular plants that typically show increased concentrations of the higher molecular weight *n*-alkanoic acids $> C_{20}$, cigarette smoke is exclusively enriched in lower molecular weight $C_{14}$, $C_{16}$, and $C_{18}$ *n*-alkanoic acids (Johnstone and Plimmer, 1959; Rogge et al., 1993d; Simoneit and Mazurek, 1982; Kolattukudy, 1970; Mold et al., 1966; Van Duuren and Kosak, 1958). Of the three unsaturated fatty acids identified, linolenic acid ($C_{18:3}$) is most abundant, which agrees with prior published data (Carruthers and Johnstone, 1959; Hoffmann and Woziwodzki, 1968).

Dicarboxylic acids also have been identified in our cigarette smoke samples, of which succinic acid is most abundant. Likewise, cyclic acids such as furancarboxylic acids, phenylacetic acid, and nicotinic acid have been quantified. For comparison to the results of other researchers, see Table 8.1.

### Alkanols

Several acyclic alcohols have been identified in the exhaled mainstream plus sidestream tobacco smoke particles investigated here, and the results are included in Table 8.1. *n*-Alkanols are often the major compound class identified in leaf waxes and commonly show a preference for even carbon number homologues (Gülz et al., 1989; Kolattukudy, 1970; Mazurek and Simoneit, 1984; Riederer and Schneider, 1990; Rogge et al., 1993d; Simoneit, 1989; Simoneit et al., 1990).

However, Severson et al. (1978) have reported that the *n*-alkanols content in tobacco smoke is low because the *n*-alkanols content of tobacco leaf waxes is lower than for many other plants. In this study, the *n*-alkanols range from $C_{15}$ to $C_{26}$ with no obvious carbon number predominance.

### Phenols

A great number of phenols and polyphenols are known to be present in cigarette smoke (IARC, 1986; Johnstone and Plimmer, 1959; Sakuma et al., 1983; Stedman, 1968). Here, only a few have been quantified in the fine cigarette smoke particles. *p*-Cresol and *o*-cresol, two rather volatile phenols, have been found in traces in the particulate cigarette smoke. One of the prominent phenols quantified in Table 8.1, hydroquinone (1,4-benzenediol), is emitted at a rate of 283.5 μg/cigarette, comparable to that found by Sakuma et al. (1983).

### Phytosterols

Tobacco plants, similar to other higher plants, contain $C_{28}$- and $C_{29}$- phytosterols such as campesterol, stigmasterol, and β-sitosterol as the major sterols. Cholesterol ($C_{27}$), a typical zoosterol (from animals, especially vertebrates) that is commonly found only in traces in plant materials, is somewhat more pronounced in tobacco leaf waxes when compared to the typical phytosterols than is the case for most other plants (Schmeltz et al., 1975; Severson et al., 1978). Stigmasterol, emitted at a rate of more than 250 μg/cigarette, was the most abundant phytosterol, followed by β-sitosterol. Data drawn from the literature on main- and sidestream cigarette smoke phytosterols show concentration ranges similar to our data, and are included in Table 8.1 for comparison (Schmeltz et al., 1975; Severson et al., 1978).

### N-containing Compounds

When burning a cigarette, about 60% of the nicotine in tobacco undergoes degradation and conversion (Schmeltz et al., 1979). Portions of the tobacco alkaloids are converted to pyridines, indoles, quinolines, arylnitriles, aromatic hydrocarbons, and other compounds (Schmeltz and Hoffmann, 1977; Baker , 1981; Johnstone and Plimmer, 1959; Stedman, 1968). Due to its volatility, nicotine is mainly found in the gas-phase and then primarily in sidestream smoke (Browne et al., 1980; Eatough et al., 1989; Matsushima et al., 1979; Nelson et al., 1992; Sakuma et al., 1984a,b). Nonetheless, the most abundant single compound identified in the fine particle-associated cigarette smoke emissions is nicotine, which was emitted at a rate of 1159 $\mu$g/cigarette. Comparable nicotine concentrations in the particle phase also have been measured by Browne et al. (1980) (see also Table 8.1). Besides nicotine, several other alkaloids commonly found in cigarette smoke (Schmeltz and Hoffmann, 1977; Baker, 1981; Johnstone and Plimmer, 1959; Stedman, 1968) have been identified and are summarized in Table 8.1. While most of these N-containing compounds are partitioned between the gas and the particle phase, the N'-acylalkaloids have a high enough molecular weight to be found exclusively in the aerosol phase (Snook et al., 1984) and thus might serve as a potential tracer for particle-phase cigarette smoke. One of the more abundant members of this compound class, N'-*iso*-octanoylnornicotine, was identified in our cigarette smoke samples, but in fairly low concentrations (see Table 8.1).

### Polycyclic Aromatic Hydrocarbons

While most of the compounds discussed so far are released mainly by distillation the tobacco during combustion (with some accompanying partial degradation), the polycyclic aromatic hydrocarbons (PAH) are typical pyrolysis products formed during combustion in zones of relatively low oxygen content (Baker, 1981; Grimmer et al., 1987; Schmeltz et al., 1979; Lee et al., 1976; Severson et al., 1977). In Table 8.1, the PAH identified in this study are listed and compared to results from a study by Grimmer et al. (1987) in which PAH emission rates were reported for the particle and gas phase in main- as well as in sidestream cigarette smoke separately. From their experimental data (see also Table 8.1) Grimmer and coworkers concluded that most of the PAH are formed between puffs and consequently are found primarily in the sidestream smoke aerosol. Total particle-phase PAH concentrations of 13.5$\mu$g/cigarette were measured in this study, which compares well with the measurements of Grimmer et al. (1987).

Table 8.1 Emission Rates for Single Organic Compounds found in Fine Cigarette Smoke Aerosol.

| PART A | Emission Rates in μg/Cigarette<br>This Study[a] exhaled MS + SS | Other Studies[b]<br>SS | <br>MS | Compound ID[c] for this Study |
|---|---|---|---|---|
| | —n–Alkanes— | | | |
| heneicosane | 5.6 | | 6–19[g] | a |
| docosane | 5.3 | | 6–22[g] | a |
| tricosane | 6.7 | | 4–9[g] | a |
| tetracosane | 7.6 | | 3–105[g] | a |
| pentacosane | 13.2 | | 3–31[g] | a |
| hexacosane | 11.1 | | 3–32[g] | a |
| heptacosane | 59.2 | 66–87[f] | 21–131[g] | a |
| octacosane | 11.3 | | 3–23[g] | a |
| nonacosane | 58.0 | 28–39[f] | 30–104[g] | a |
| triacontane | 23.8 | | 37–101[g] | a |
| hentriacontane | 200.6 | 148–197[f] | 164–341[g] | a |
| dotriacontane | 38.3 | | 97–194[g] | a |
| tritriacontane | 102.3 | 44–62[f] | 73–268[g] | a |
| tetratriacontane | 3.2 | | | a |
| pentatriacontane | 2.8 | | | a |
| Total class mass concentration: | 549.0 | | 450.0-1380.0[g] | |
| | — *iso*– and *anteiso*–Alkanes— | | | |
| *iso*-nonacosane | 14.1 | | | e |
| *iso*-triacontane | 4.9 | | | e |
| *iso*-hentriacontane | 78.7 | | | e |
| *iso*-dotriacontane | 7.2 | | | e |
| *iso*-tritriacontane | 39.5 | | | e |
| *iso*-tetratriacontane | 1.8 | | | e |
| *anteiso*-triacontane | 40.7 | | | e |
| *anteiso*-hentriacontane | 10.5 | | | e |
| *anteiso*-dotriacontane | 79.1 | | | e |
| *anteiso*-tritriacontane | 6.2 | | | e |
| *anteiso*-tetratriacontane | 6.5 | | | e |
| Total class mass concentration: | 289.2 | | | |
| | — *isoprenoid*–Alkenes— | | | |
| neophytadiene | 81.6 | 70–421[h] | 61–308[h,i,j] | b |
| Total class mass concentration: | 81.6 | | | |

Table 8.1 (continued)

| | Emission Rates in μg/Cigarette | | | |
|---|---|---|---|---|
| PART B | This Study[a] exhaled | Other Studies[b] | | Compound ID[c] for this Study |
| | MS + SS | SS | MS | |
| —*n*–Alkanoic Acids[d]— | | | | |
| nonanoic acid | 6.9 | | | a |
| decanoic acid | 2.9 | | | a |
| undecanoic acid | 3.6 | | | a |
| dodecanoic acid (lauric acid) | 3.9 | | up to 34[k] | a |
| tridecanoic acid | 3.2 | | | a |
| tetradecanoic acid (myristic acid) | 22.8 | | 4–38[k] | a |
| pentadecanoic acid | 18.0 | | | a |
| hexadecanoic acid (palmitic acid) | 344.4 | | 44–312[j,k,l] | a |
| heptadecanoic acid | 13.7 | | | a |
| octadecanoic acid (stearic acid) | 73.0 | | 9–107[j,k,l] | a |
| nonadecanoic acid | 2.3 | | | a |
| eicosanoic acid | 26.2 | | | a |
| heneicosanoic acid | 5.4 | | | a |
| docosanoic acid | 19.4 | | | a |
| tricosanoic acid | 8.4 | | | a |
| tetracosanoic acid | 11.9 | | | a |
| pentacosanoic acid | 3.6 | | | a |
| hexacosanoic acid | 4.5 | | | a |
| heptacosanoic acid | 2.0 | | | a |
| octacosanoic acid | 12.3 | | | a |
| nonacosanoic acid | 4.0 | | | a |
| triacontanoic acid | 9.4 | | | a |
| hentriacontanoic acid | 3.3 | | | a |
| dotriacontanoic acid | 12.1 | | | a |
| tritriacontanoic acid | 0.12 | | | a |
| tetratriacontanoic acid | 0.19 | | | a |
| Total class mass concentration: | 617.51 | | | |
| —*n*–Alkenoic Acids[d]— | | | | |
| *cis*–9–octadecenoic acid (oleic acid) | 22.3 | | 21–108[l] | a |
| 9,12–octadecadienoic acid (linoleic acid) | 39.8 | | 50–146[l] | a |
| 9,12,15–octadecatrienoic acid (linolenic acid) | 62.0 | | 52–329[l] | b |
| Total class mass concentration: | 124.1 | | | |

Table 8.1 (continued)

| PART C | Emission Rates in μg/Cigarette | | | |
|---|---|---|---|---|
| | This Study[a] exhaled MS + SS | Other Studies[b] SS | Other Studies[b] MS | Compound ID[c] for this Study |
| | **— Dicarboxylic Acids[d] —** | | | |
| butanedioic acid (succinic acid) | 30.7 | 65-70[m] | 112–163[m] | a |
| methylbutanedioic acid (methylsuccinic acid) | 3.6 | 1–13[m] | 4–20[m] | a |
| pentanedioic acid (glutaric acid) | 3.7 | 6-18[m] | 10–58[m] | a |
| 1,2-benzenedioic acid | 0.35 | | | a |
| Total class mass concentration: | 38.35 | | | |
| | **— Other Aliphatic and Cyclic Acids[d] —** | | | |
| 4-oxopentanoic acid | 11.1 | | | b |
| furancarboxylic acid (furoic acid) | 15.5 | 25–60[m] | 44–107[k,m] | b |
| 2-methyl-2-furancarboxylic acid | 1.0 | | | b |
| benzeneacetic acid (phenylacetic acid) | 46.5 | 11–30[m] | 0.6–41[k,m] | b |
| nicotinic acid | 42.6 | | | a |
| Total class mass concentration: | 116.6 | | | |
| | **— n-Alkanols—** | | | |
| pentadecanol | 21.4 | | | b |
| hexadecanol | 24.8 | | | b |
| heptadecanol | 38.8 | | | a |
| octadecanol | 28.3 | | | a |
| nonadecanol | 23.7 | | | a |
| eicosanol | 21.6 | | 1.7–3.7[j] | a |
| heneicosanol | 26.8 | | | b |
| docosanol | 23.8 | | 5.6–12.4[j] | a |
| tricosanol | 12.7 | | | b |
| tetracosanol | 36.7 | | 0.6–1.0[j] | a |
| pentacosanol | 39.4 | | | a |
| hexacosanol | 12.7 | | | a |
| Total class mass concentration: | 310.7 | | | |
| | **— Phenols[e] —** | | | |
| 1-ethenyl-4-hydroxybenzene | 16.3 | | | b |
| 1,2-benzenediol (catechol) | 12.7 | 138–292[m] | 148–362[m] | a |
| 1,4-benzenediol (hydroquinone) | 283.5 | 91–285[m] | 114–300[m] | b |

Table 8.1 (continued)

| PART D | Emission Rates in μg/Cigarette<br>This Study[a] exhaled MS + SS | Other Studies[b]<br>SS | MS | Compound ID[c] for this Study |
|---|---|---|---|---|
| 4-methyl-1,2-benzenediol (4-methylcatechol) | 49.6 | 25–55[m] | 29–80[m] | a |
| 2-methyl-1,4-benzenediol | 21.4 | | | b |
| 4-ethenyl-1,2-benzenediol | 3.1 | | | b |
| Total class mass concentration: | 386.6 | | | |
| | — Phytosterols — | | | |
| cholesterol | 23.3 | 18.8[n] | 8.5–22.0[j,n] | a |
| cholest-5-en-3β-ol acetate | 28.2 | | | b |
| campesterol | 92.8 | 25.8[n] | 42.7[n] | a |
| stigmasterol | 252.2 | 53.6[n] | 78.0[n] | a |
| β-sitosterol | 100.4 | 28.0[n] | 27.1–59.3[j,n] | a |
| Total class mass concentration: | 496.9 | | | |
| | — Triterpenoids — | | | |
| β-amyrin | 8.7 | | | b |
| Total class mass concentration: | 8.7 | | | |
| | —N-containing Compounds — | | | |
| nicotine *(total: gas- + particle-phase)* | | 2987–6588[h,i,o,p] | 799–4229[h,i,p] | |
| nicotine *(particle-phase only)* | 1159.0 | 970–1320[o] | 550–1620[o] | a |
| cotinine | 52.8 | | | b |
| 2,3'-bipyridyl | 34.3 | 35–76[h,p] | 16–22[h,p] | b |
| 3-pyridinol | 57.8 | | | b |
| 1-(2-pyridinyl)-ethanone | 4.6 | | | b |
| 1-(1-methyl-1H-pyrrol-2-yl)-ethanone | 17.2 | | | b |
| 3-hydroxypyridine[e] | 128.6 | 157–172[h] | 90–211[h] | b |
| 1-methyl-2,5-pyrrolidinedione (N-methylsuccinimide) | 30.2 | | | b |
| 1-methyl-2(1H)-pyridione | 7.4 | | | a |
| 4-methylbenzhydrazide | 8.0 | | | b |
| 3-(3,4-dihydro-2H-pyrrol-5-yl)-pyridine, (myosmine) | 177.9 | 73–224[m] | 8.8-53.4[i,m] | a |

Table 8.1 (continued)

| PART E | Emission Rates in μg/Cigarette<br>This Study[a] exhaled MS + SS | Other Studies[b] SS | Other Studies[b] MS | Compound ID[c] for this Study |
|---|---|---|---|---|
| 1-methyl-9H-pyrido[3,4-b]indole (harman) | 4.9 | 1.9–3.5[q] | 1.1–3.1[q] | b |
| N'-*iso*-octanoylnornicotine | 8.5 | | | b |
| Total class mass concentration: | 1691.2 | | | |
| —Polycyclic Aromatic Hydrocarbons (PAH)— | | | | |
| phenanthrene | 2.6 | 2.1[r] | 0.075[r] | a |
| anthracene | 0.76 | 0.67[r] | 0.024[r] | a |
| methyl–(phenanthrenes, anthracenes) | 3.5 | | 0.16[s] | b |
| fluoranthene | 0.95 | 0.67[r] | 0.061[r] | a |
| pyrene | 1.0 | 0.47[r] | 0.043[r] | a |
| benzacenaphthylene | 0.30 | | | b |
| 2–phenylnaphthalene | 0.37 | | | b |
| methyl–(fluoranthenes, pyrenes) | 1.3 | | 0.11[s] | b |
| benzo[a]fluorene/benzo[b]fluorene | 0.54 | 0.20[r] | 0.021[r] | a |
| benz[a]anthracene | 0.27 | 0.20[r] | 0.013[r] | a |
| chrysene/triphenylene | 0.67 | 0.49[r] | 0.020[r] | a |
| methyl–(benz[a]anthracenes, chrysenes, triphenylenes) | 0.69 | | | b |
| dimethyl–(fluoranthenes, pyrenes) | 0.55 | [r]: particle phase only | | b |
| Total class mass concentration: | 13.5 | | | |
| — Others — | | | | |
| 6,7-dihydroxy-2H-1-benzopyran-2-one | 7.3 | | | b |
| Vitamin E | 0.88 | | | b |
| Total class mass concentration: | 8.18 | | | |

---

[a] This study: exhaled MS + SS (exhaled mainstream and sidestream fine particulate matter).

[b] Other studies: if not otherwise indicated the measurements include particle plus gas phase components together (condensate); data for references [j,k,n] are reported in μg per 1 g of tobacco smoked (depending on the cigarette type the tobacco content ranges on average from 0.6 to 1.1g per cigarette).

[c] for more details see text. a, positive: authentic std. verification; b, probable: library spectrum verification; c, possible; d, tentative; e, *iso*- and *anteiso*-alkanes are positively identified by monitoring their major ions at M-43 and M-29 respectively.

[d] detected as methyl ester in the derivatized sample aliquot.

[e] compound detected as methoxy homologue in the derivatized sample aliquot.

[f] Ramsey et al. (1990), sidestream particulate matter of different filter cigarettes was collected using a
dilution sampler.

[g] Spears et al. (1963), mainstream condensate of nonfilter cigarettes.

[h] Sakuma et al. (1984a), main- and sidestream condensate of nonfilter cigarettes.

[i] Matsushima et al. (1979), mainstream particulate matter from nonfilter cigarettes.

[j] Severson et al. (1978), mainstream condensate of nonfilter cigarettes (conc. in $\mu g/g$ of tobacco).

[k] Elmenhorst (1972), mainstream condensate of nonfilter cigarettes (conc. in $\mu g/g$ of tobacco).

[l] Hoffmann and Woziwodzki (1968), mainstream condensate of nonfilter cigarettes.

[m] Sakuma et al. (1983), main- and sidestream condensate of nonfilter cigarettes.

[n] Schmeltz et al. (1975), main- and sidestream condensate of nonfilter cigarettes (conc. in $\mu g/g$ of tobacco).

[o] Browne et al. (1980), main- and sidestream particulate and gaseous nicotine.

[p] Sakuma et al. (1984b), main- and sidestream condensate of nonfilter cigarettes.

[q] Klus and Kuhn (1982), main- and sidestream condensate of filter and nonfilter cigarettes.

[r] Grimmer et al. (1987), main- and sidestream particle samples of nonfilter cigarettes (gas phase PAH also were measured and usually consisted of 1% of the amount was found for the particle phase).

[s] Lee et al. (1976), mainstream condensate of standard cigarettes.

### Tracing Cigarette Smoke Aerosol in Urban Atmospheres

Because people spend on average most of their time indoors (e.g., Jenkins et al., 1992) where restricted airflow limits the indoor/outdoor air exchange, cigarette smoke exposure studies in the past have been concerned mainly with elevated indoor pollutant concentrations caused by cigarette smoking (Brunekreef and Boleij, 1982; Girman et al., 1982; IARC, 1986; Katzenstein, 1992; Repace and Lowrey, 1990; US Dept. of Health and Human Services, 1989). To apportion the tobacco smoke contributions to an indoor environment with several potential indoor air pollution sources, a number of organic marker compounds such as nicotine, 3-ethylenepyridine, solanesol, PAH, and *n*-alkanes have been utilized in the past (Benner et al., 1989; Chuang et al., 1991; Hammond et al., 1987; Leaderer and Hammond, 1991; Ogden and Maiolo, 1989; Mitra and Wilson, 1992; Ramsey et al., 1990; Tang et al., 1990).

In order to trace tobacco smoke particles in a reactive outdoor urban atmosphere that is influenced by a great number of different emission sources, organic marker compounds for tobacco smoke must meet several requirements: The tracer compounds must be (1) source specific; (2) detectable in urban air; (3) exclusively in the particle phase; and (4) chemically stable over transport times between the source and the atmospheric measurement sites.

Nicotine, a possible tobacco smoke tracer, is known to partition between the gas and particle phase. Because nicotine is primarily associated with the gas-phase (Benner et al., 1989; Eatough et al., 1989; Ogden and Maiolo, 1992; Tang et al., 1990) and is susceptible to photodegradation (Eatough et al., 1989), it is not a reliable quantitative tracer for cigarette smoke particles in the urban atmosphere, although it might be useful as a qualitative tracer for whole cigarette smoke if both gas- plus particle-phase constituents were of interest. 3-Ethylenepyridine, a combustion product of nicotine, also is mainly found in the gas phase but is more stable in the presence of UV-radiation than nicotine (Eatough et al., 1989; Heavner et al., 1992; Nelson et al., 1992).

Solanesol, a long chain ($C_{45}H_{74}O$) trisesquiterpenoid alcohol, is characteristic of cigarette smoke and completely in the particle phase under normal conditions; hence it has been suggested as an indoor cigarette smoke tracer (Ogden and Maiolo, 1989; Tang et al., 1990). Because solanesol is an isoprenol with nine double bonds, the probability that it will degrade rapidly in a photochemically reactive atmosphere is high (e.g., due to $O_3$ or photodegradation). Tang and coworkers (1990) have shown that tobacco smoke-associated solanesol reacts rapidly when exposed to UV-light simulating midday solar radiation. Hence, although it may be suitable to trace tobacco smoke in indoor environments, solanesol probably is not suitable as a tobacco smoke tracer in the outdoor urban atmosphere.

PAH have been used as well in indoor environments to assess the contribution of cigarette smoke to indoor air pollution (e.g., Chuang et al., 1991; Grimmer et al., 1977; Mitra and Wilson, 1992; Risner and Conner, 1991). In the absence of indoor heating sources such as wood burning stoves or kerosene heaters, indoor PAH concentrations may track the exposure to tobacco smoke. In the urban atmosphere, PAH are contributed by virtually all combustion sources and are known to degrade photochemically in the presence of UV light (e.g., Rogge et al., 1993a,b,f; Kamens et al., 1990; Pitts et al., 1969, 1980). Consequently, PAH are not suitable as tracers for cigarette smoke in the urban atmosphere.

Higher molecular weight *n*-alkanes ($C_{27}$, $C_{29}$, $C_{31}$, and $C_{33}$) have been used to monitor tobacco smoke particles in indoor environments (Ramsey et al., 1990). While the odd carbon numbered *n*-alkane concentration pattern in a smoker's home might be mainly due to tobacco smoke, the outdoor odd-to-even carbon numbered *n*-alkane concentration pattern found in ambient suspended fine particulate matter is mainly controlled by the release of vegetative detritus in the form of abraded waxy leaf surface particles shed by outdoor plants (Mazurek and Simoneit, 1984; Simoneit, 1989; Simoneit and Mazurek, 1982; Rogge et al., 1993b). Hence, the high molecular weight odd carbon *n*-alkanes cannot be used to identify cigarette smoke in outdoor air.

A more promising compound class that shows properties similar to the *n*-alkanes consists of the branched alkanes such as *iso*- (2-methyl-) and *anteiso*-(3-methyl-) alkanes. These *iso*- and *anteiso*-alkanes show a characteristic concentration pattern in tobacco leaf surface waxes and consequently in tobacco smoke (see Figure 8.2a). To serve as cigarette smoke markers in the urban atmosphere, the *iso*- and *anteiso*-alkane concentration patterns in tobacco smoke aerosol must be distinctly different from those found in the leaf surface abrasion products of urban plants such that tobacco smoke derived *iso*- and *anteiso*-alkanes will dominate the outdoor concentrations of such compounds. The latter requirement, if met, would guarantee that possible interferences due to *iso*- and *anteiso*-alkane release from urban vegetation to the atmosphere are minor.

In order to determine whether cigarette smoke particles dominate the emissions of *iso*- and *anteiso*-alkanes to the urban environment, it is first necessary to characterize the emissions of such compounds from plants growing outdoors.

Release of fine particulate leaf surface abrasion products from plants typical to the Los Angeles area have been characterized on a molecular level by Rogge et al. (1993b). Green and dead leaves from the 62 common plant species growing in the Los Angeles area, including broadleaf trees, conifers, palms, shrubs, and grasses, were collected during a harvesting campaign in 1988 (Hildemann et al., 1991a). The collected green and dead leaves were each composited according to the mass fraction of leaf material attributed to each species in the Los Angeles area as determined by Miller and Winer (1984) and Winer et al. (1983). The green leaf and the dead leaf composites were separately agitated to release particulate matter shed from their surfaces when the leaves brush against each other as would occur naturally by the wind. The abraded waxy leaf surface material was subsequently collected as fine particulate matter on quartz fiber filters downstream of cyclone separators, and the samples then were extracted by the same methods used in the present study (Hildemann et al., 1991b; Rogge et al., 1993b). Additional information on the sampling campaign including the plant species collected is summarized by Hildemann et al. (1991a).

Organic compounds present in these Los Angeles dead and green leaf abrasion product samples were analyzed by GC/MS (Rogge et al., 1993b). It was found that the *n*-, *iso*-, and *anteiso*-alkane concentrations present in the fine particulate leaf surface abrasion products were very similar when comparing green with dead leaf surface abrasion products. This in turn indicates that the wax type alkanes are rather stable in the urban environment, since the dead leaf material had aged for quite some time between the end of wax synthesis by the leaf and the time that particular samples were collected. *iso*- and *anteiso*-Alkanes were found in the leaf abrasion products in the range from $C_{29}$ to $C_{34}$. Comparing the amount of *iso*- and *anteiso*-alkanes to the amount of *n*-alkanes in the same carbon range ($C_{29}$ – $C_{34}$), such *iso*- and *anteiso*-alkanes together only amount to 1.5 to 1.6% of the respective *n*-alkanes found in the dead or green leaf surface abrasion products. Similar results also have been reported by other researchers for several plants species (e.g., Eglinton et al., 1962; Eglinton and Hamilton, 1967; Waldron et al., 1961).

In contrast, the same branched alkanes in the tobacco smoke samples investigated here comprise close to 68% of the respective *n*-alkane mass ($C_{29}$ – $C_{34}$) found in the smoke particles, a 40 times higher abundance than found for the leaf abrasion products of urban vegetation. Similar results have been found for tobacco leaves (Benner et al., 1989; Carruthers and Johnstone, 1959; Mold et al., 1963; Severson et al., 1978; Spears et al., 1963; Stedman, 1968) and tobacco smoke (Carruthers and Johnstone, 1959; Kolattukudy, 1970; Mold et al., 1963; Severson et al. 1978; Stedman, 1968). Typical ion-chromatograms characteristic of the alkanes are shown in Figures 8.3a and 8.3b for green leaf surface abrasion products and tobacco smoke particles. These figures clearly demonstrate enrichment in *iso*- and *anteiso*-alkanes relative to *n*-alkanes in the tobacco smoke samples when compared to Los Angeles green leaf surface abrasion products. Figures 8.4a and 8.4b show the concentration of *iso*- and *anteiso*-alkanes measured in green and dead leaf abrasion products ($\mu$g/g of fine particulate abraded leaf surface material) and fine tobacco smoke particles ($\mu$g/cigarette). On comparing these two graphs it can be seen that: (1) *iso*-hentriacontane (*iso*-$C_{31}$) in the cigarette smoke samples is found at about the same concentration level as *anteiso*-dotriacontane (*anteiso*-$C_{32}$), which differs noticeably from the Los Angeles area vegetative leaf composite surface waxes (*iso*-$C_{31}$ > *anteiso*-$C_{32}$); (2) while *iso*-tritriacontane (*iso*-$C_{33}$) is the dominant branched alkane in the Los Angeles leaf surface wax composites, *anteiso*-dotriacontane (*anteiso*-$C_{32}$) is the dominant alkane in tobacco smoke followed closely by *iso*-$C_{31}$. These characteristic tobacco leaf surface *iso*- and *anteiso*-alkane concentration patterns, preserved in the cigarette smoke particles, might be useful to trace such emissions in the atmosphere of urban areas.

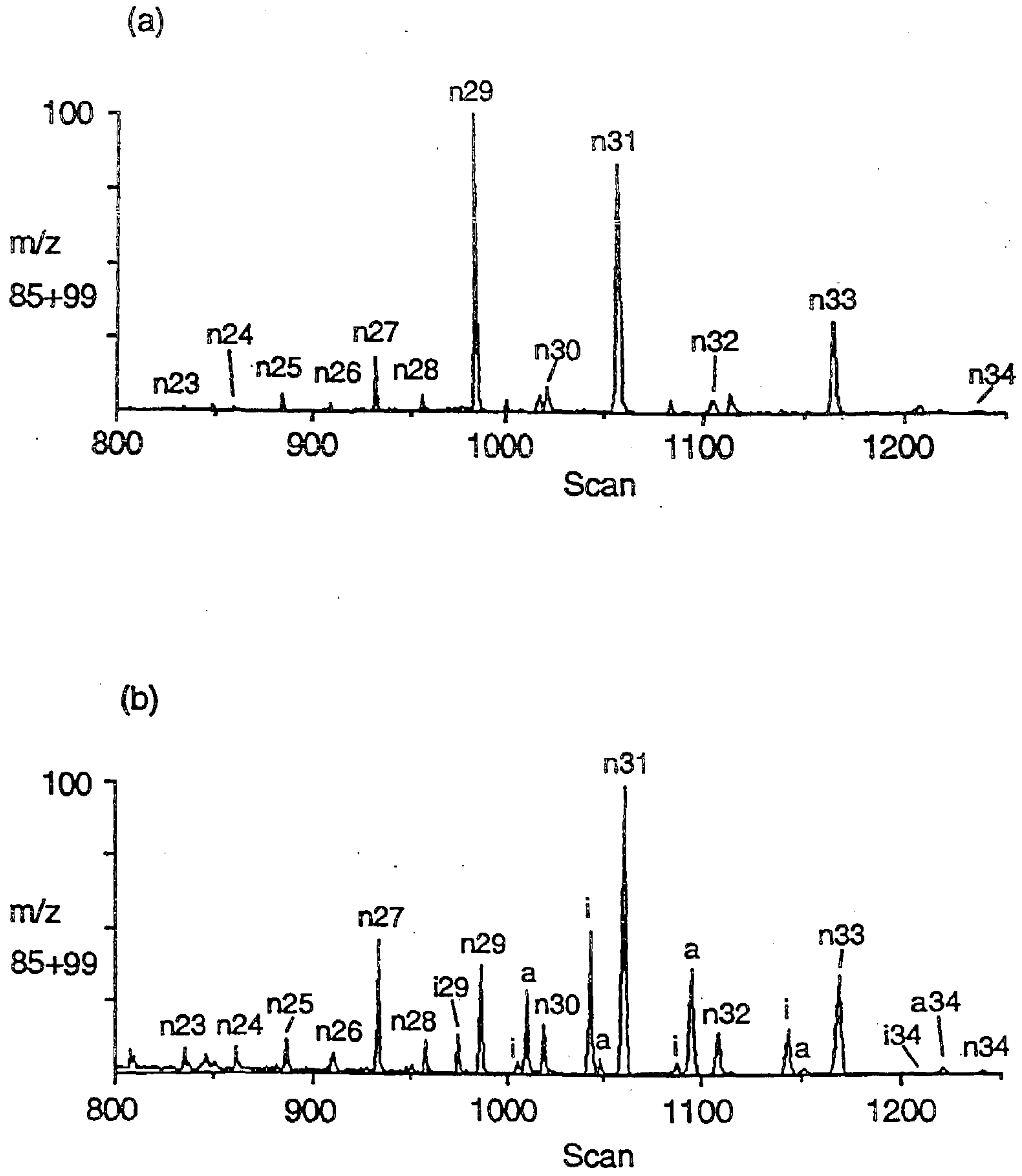


Fig 8.3: Selected mass fragmentograms for *n*-, *iso*-, and *anteiso*-alkanes (sum: m/z 85 + 99) found in: (a) leaf abrasion products from green leaf composites typical of the Los Angeles area, and (b) cigarette smoke aerosol. Numbers refer to the carbon chain length of the molecules: n: *n*-alkanes; i: *iso*-alkanes; a: *anteiso*-alkanes; for simplicity, only the major compound peaks are labeled.

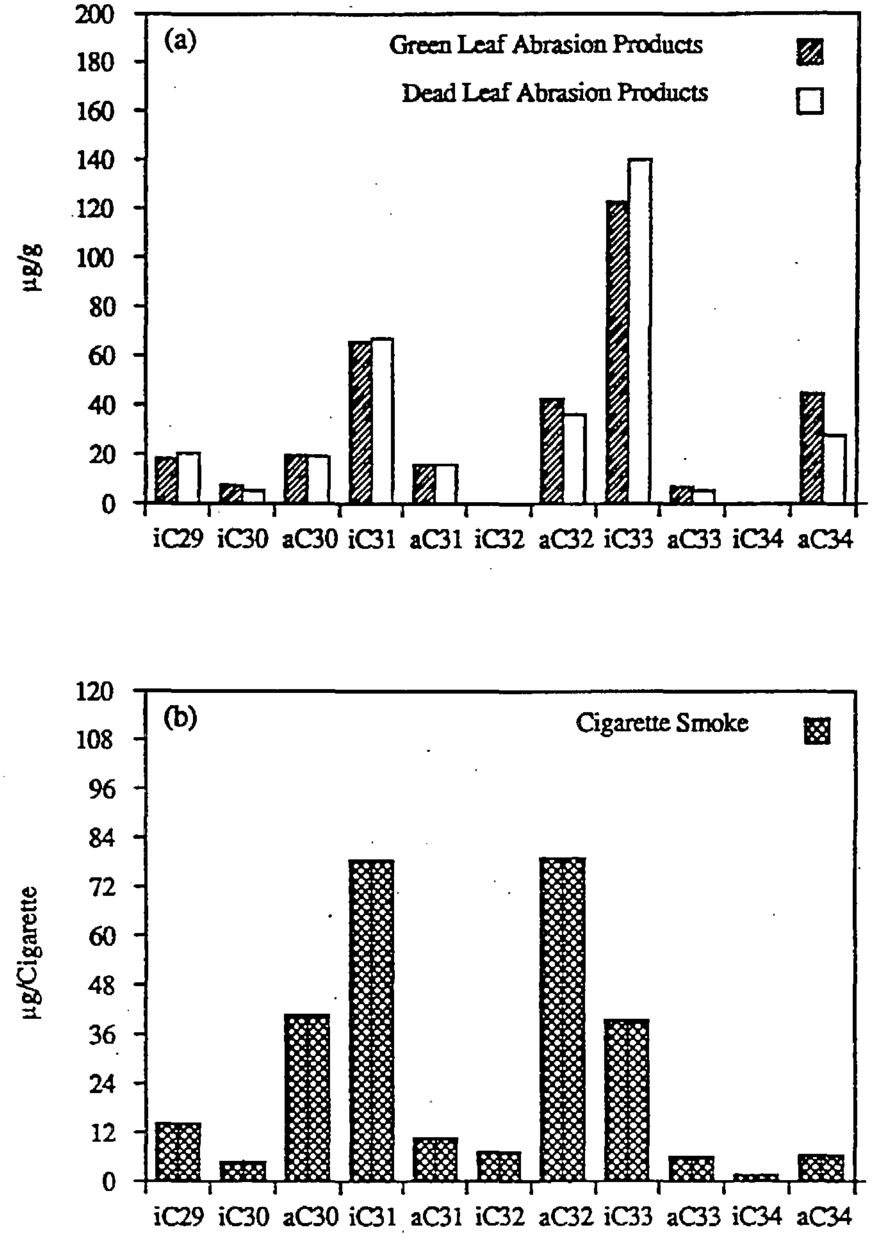


Fig. 8.4: *iso-* and *anteiso-*Alkane concentrations measured in (a) leaf surface abrasion products from green and dead leaf composites typical of the Los Angeles area, and (b) cigarette smoke aerosol collected in this study.

## Emission Source Interferences

Before these characteristic tobacco leaf *iso-* and *anteiso*-alkane concentration patterns can be applied to trace cigarette smoke in the outdoor environment, it must be determined that other sources do not emit such higher molecular weight *iso-* and *anteiso*-alkanes with a similar concentration pattern.

The fine particulate emissions from gasoline and diesel powered vehicles have been characterized by Rogge et al. (1993a) using methods essentially identical to those employed in the present study. None of the *iso-* and *anteiso*-alkanes discussed here could be detected in that or other studies (e.g., Simoneit, 1984). This result agrees well with the observation that long chain alkanes from higher plants are typically not found in crude oils as a result of the diagenic and catagenic processes ongoing during crude oil formation (Albrecht et al., 1976; Tissot and Welte, 1984). Kissin (1987) reported that monomethyl-substituted alkanes found in crude oils are the result of chemical processes occurring during catagenesis, with methyl groups approximately equally substituted in all positions of the alkane molecules, primarily below $C_{20}$. Biogenically-derived or human-controlled biogenic sources, such as meat cooking, wood combustion, aerial dispersion of bacteria or resuspension of insect fragments, likewise need to be examined to see if they interfere with these possible cigarette smoke tracers. Meat cooking (Rogge et al., 1991) does not produce detectable amounts of higher molecular weight branched alkanes. Wood combustion, already very low in *n*-alkane emissions, also does not emit any branched alkane type compounds (Rogge et al., 1993g). Likewise, bacteria that might become airborne and that are smaller than 2.0 $\mu$m in diameter do not contain the higher molecular weight *iso-* and *anteiso*-alkanes studied here ($C_{28}$ – $C_{34}$). Instead such bacteria do contain complex mixtures of unsaturated and branched (*iso-* and *anteiso-*) alkenes in the range from $C_{23}$ to $C_{29}$ (Albro, 1976; Tornabene et al., 1970), and *iso-* and *anteiso*-alkanoic acids ($C_{12} - C_{17}$) (Kaneda, 1967).

The cuticula of insects are usually covered with a thin layer of waxy compounds including *n*-alkanes, and mono-, di-, and trimethylalkanes ranging from $C_{26}$ to about $C_{43}$ (Bonavita-Cougourdan, 1991; Lockey, 1988, 1992; Lockey and Metcalf, 1988; Nelson, 1978; Nelson et al., 1981). The series of *iso-* and *anteiso*-alkanes in the carbon range of interest ($C_{28} - C_{34}$) is typically incomplete. The members of these series are usually minor compared to *n*-alkanes and dimethylalkanes, and typically show a different concentration pattern then is found in tobacco leaf waxes and consequently in cigarette smoke (Bonavita-Cougourdan, 1991; Lockey, 1988, 1992; Lockey and Metcalf, 1988; Nelson, 1978; Nelson et al., 1981). Further, it is unlikely that insect debris contributes much to airborne particulate matter in particle sizes smaller than 2.0 $\mu$m in diameter.

## Estimated Emission Rates for Cigarette Smoking in Los Angeles

Whether or not cigarette smoke particles can be traced in the urban atmosphere depends in part on the total emission rates for cigarette smoke constituents. Consequently, the first step is to estimate the emission rates of particle-associated cigarette smoke constituents that have been released during indoor and outdoor activities combined. Using total cigarette sales data for the entire United States in 1982 (IARC, 1986) together with population data for the same year (U.S. Bureau of the Census, 1991), the average number of cigarettes per capita smoked in the U.S. in 1982 was determined to be 2700. In this study, total cigarette smoke compound emissions during 1982 were estimated for an 80 x 80 km study area centered over downtown Los Angeles (see map in Rogge et al. (1991)). Any subsequent year could have been chosen. However, the present study is part of a larger investigation that encompasses measurements of emission rates from the major primary fine particle emission sources (Hildemann et al., 1991a), creation of emission inventories for primary fine particulate organic carbon (OC) and elemental carbon (EC) (Gray, 1986; Hildemann et al., 1991a), ambient OC and EC data (Gray et al., 1986), ambient fine particulate organic compound concentrations determined at several sites within that Los Angeles area during 1982 (Rogge et al., 1992a,e), and characterization of the organic chemical composition of the source emissions (Rogge et al., 1991, 1993b-d,f). The data base available for testing proposed organic tracer techniques during 1982 is the most advanced data set available.

Fine particle-associated organic compound class emission rates from cigarette combustion during 1982 within our Los Angeles study area as computed from cigarette sales plus the source test data of Table 8.1 are given in Table 8.2. Many of these cigarettes, of course, are smoked inside of buildings. Much of that cigarette smoke, however, reaches the outdoor atmosphere as air is exchanged between buildings and the outdoors. Considerable effort has been expended to characterize the penetration of particulate matter present in the outdoor atmosphere into the indoor air of buildings in Los Angeles (Nazaroff et al., 1990; Ligocki et al., 1993). It has been found that fine particle levels inside Sepulveda House, a well-ventilated former private residence in downtown Los Angeles that lacks any deliberate particle filtration system, are virtually as high as those outdoors (Ligocki et al., 1993). Experiments and modeling calculations that examine the fate of fine particles present in that building show that they are vented back to the outdoor atmosphere with greater than 90% efficiency (Nazaroff et al., 1990). Hence, cigarette smoke would easily escape from such buildings over time.

Buildings with conventional commercial air conditioning systems with low efficiency particle filters (single pass efficiency of roughly 15–35% for removing particles of 0.1–0.5 μm diameter, accompanied by several passes of air recirculated through the filters for each pass of outdoor makeup air) have indoor fine particle levels in the range of 20–60% as high as those outdoors (Ligocki et al., 1993; Nazaroff and Cass, 1991). Only a very small fraction of the fine particles present inside such buildings are collected by deposition on indoor surfaces: instead, nearly all fine particles are either collected by the ventilation system filters or are exhausted to the outdoor atmosphere (Nazaroff and Cass, 1991). For a standard commercial building with 25% of its ventilation system flow contributed by outdoor makeup air and 75% of its air flow contributed by indoor air recirculated through filters with a single pass removal efficiency for fine particles of circa 35% per pass, roughly half of the fine particle cigarette smoke emitted inside that building will be exhausted to the outdoor atmosphere (see Nazaroff and Cass, 1991). If the single pass filtration efficiency for fine particles is only 15%, then approximately two thirds of any fine cigarette smoke particles generated indoors will be exhausted to the outdoor air. The daily compound class emission rates in the Los Angeles study area given in Table 8.2 thus represent upper limits on their release to the outdoor atmosphere, with the actual release being smaller by the amount of cigarette smoke removed by the ventilation system filters in mechanically-vented buildings.

It can be seen from Table 8.2 that the dominant compound class in cigarette smoke emitted to the Los Angeles atmosphere in 1982 consists of semi-volatile pyridine alkaloids (e.g., nicotine) and other N-containing compounds. Because nicotine is rather volatile and unstable in the urban atmosphere, ambient fine particle-associated nicotine concentrations, if measurable, may not be found in the atmosphere in known proportions to whole tobacco smoke particle concentrations. Up to 19 kg of *iso-* and *anteiso*-alkanes were emitted per day to the atmosphere of the 80 × 80km Los Angeles study area from cigarette smoking in 1982. For the two most prominent branched alkanes (*iso*-$C_{31}$, *anteiso*-$C_{33}$) alone, the daily emission rates totaled 10.4 kg $day^{-1}$.

Using the emission inventory for fine particulate organic carbon (OC) for the 80 × 80 km area centered over Los Angeles that was compiled for 1982 (Gray, 1986; Hildemann et al., 1991a), the emissions of primary aerosol organic carbon (OC) from all sources combined was estimated to total 29820 kg $day^{-1}$. Expressed as total organic compound mass (organic compounds $\simeq 1.2 \times$ organic carbon) this amounts to 35800 kg $day^{-1}$ of equivalent organic compound mass. Thus, the two branched alkanes considered, when combined, account for 0.029% of the fine particulate organic compound emissions.

Gray et al. (1986) published annual mean ambient fine particulate OC data for the area of interest. These data can be used to compute the annual mean fine particle-associated total organic compound concentrations, yielding 6.94 $\mu g\ m^{-3}$ at West Los Angeles, 8.63 $\mu g\ m^{-3}$ at downtown Los Angeles, and 8.06 $\mu g\ m^{-3}$ at Pasadena during 1982. If 0.029% of that ambient fine particulate compound mass at each of the three sampling sites were present as the *iso*-$C_{31}$ plus the *anteiso*-$C_{33}$ alkane, then the ambient fine particle concentrations of these two branched alkanes together would account for: West Los Angeles 2.0 ng $m^{-3}$, downtown Los Angeles 2.5 ng $m^{-3}$, and Pasadena 2.3 ng $m^{-3}$ during 1982.

Table 8.2 Daily Cigarette Smoke Aerosol Emissions for Single Compound Classes within the Urbanized (80 × 80 km) Los Angeles Study Area for 1982.

| Compound Class | Emission Rates[a] in kg $day^{-1}$ |
|---|---|
| *n*-Alkanes | 36.2 |
| *iso*- and *anteiso*-Alkanes | 19.1 |
| Isoprenoid alkanes | 5.4 |
| *n*-Alkanoic Acids | 40.7 |
| *n*-Alkenoic Acids | 8.2 |
| Dicarboxylic Acids | 2.5 |
| Other Organic Acids | 7.7 |
| *n*-Alkanols | 20.5 |
| Phenols | 25.5 |
| Phytosterols | 32.8 |
| Triterpenoids | 0.57 |
| N-Containing Compounds (e.g. Alkaloids) | 111.5 |
| Polycyclic Aromatic Hydrocarbons (PAH) | 0.89 |
| Other Identified Compounds | 0.54 |
| Total Identified | 312.1 |

[a] daily compound class emission rates to the metropolitan 80 × 80 km area centered over Los Angeles were estimated as follows: the compound emission rates from Table I were multiplied by the average number of cigarettes sold per capita in the U.S. in 1982 (2700 cigarettes[b]) times the population in the 80 × 80 km study area in 1982 (8,910,400[c]), then divided by 365 days.

[b] determined from the total number of cigarettes sold in the U.S. in 1982 (624 billion, (IARC, 1986)) divided by the U.S. population in 1982 (231 million, (U.S. Bureau of the Census, 1991)).

[c] to estimate the population in the 80 × 80 km study area in 1982, the population data for 1980 for the study area as determined by Gray (1986) was used along with an assumed 1% population growth per year according to the nationwide average (U.S. Bureau of the Census, 1991) to estimate the population in the 80 × 80 km study area in 1982.

## Cigarette Smoke Aerosol in the Los Angeles Atmosphere

Fine aerosol organic compound concentrations during the year 1982 have been measured at sites within the 80 × 80 km greater Los Angeles study area discussed earlier. Sampling techniques, analytical protocols, and compound identification procedures were essentially the same as those applied to the source samples described in the present study, except that samples were drawn directly from the atmosphere. Figures 8.5a,b show the ambient concentration pattern for *iso*- and *anteiso*-alkanes measured at West Los Angeles and Pasadena during October and November 1982. Because the minor *iso*- and *anteiso*-alkanes were below detection limits during the summer months, the annual average ambient concentrations for such branched alkanes were determined only for the more abundant $C_{31}$ *iso*-alkane and for the $C_{32}$ *anteiso*-alkane as shown in Figure 8.5c.

Comparing the ambient *iso*- and *anteiso*-alkane concentration patterns (Figures 8.5a-c) with the concentration pattern found for cigarette smoke (Figure 8.4b), and similarly with green and dead vegetative detritus (Figure 8.4a), the following observations can be made: (1) the relative concentrations of both the *iso*-$C_{31}$ and *anteiso*-$C_{32}$ alkanes in the ambient sample are comparable, which is also the case for cigarette smoke aerosol; (2) *anteiso*-$C_{32} \gg$ *iso*-$C_{33}$ in both cigarette smoke and ambient fine particle samples, whereas *iso*-$C_{33} \gg$ *anteiso*-$C_{32}$ in the vegetative leaf surface abrasion products typically released to the Los Angeles atmosphere. Consequently, the ambient *iso*- and *anteiso*-alkane concentration profile does not match that of leaf surface abrasion products from the plant communities growing in Los Angeles. Instead it compares well to the concentration profile found in cigarette smoke aerosol. Further, the measured ambient annual average concentration of the *iso*-$C_{31}$ plus *anteiso*-$C_{32}$ alkanes during 1982 totals

2.4 ng $m^{-3}$ at West Los Angeles, 2.8 ng $m^{-3}$ at downtown Los Angeles, and 2.2 ng $m^{-3}$ at Pasadena. This is very close to the 2.0 – 2.5 ng $m^{-3}$ concentration range estimated earlier in this paper based on previously published emissions and ambient organic aerosol concentrations. Working backward, an ambient *iso*-$C_{31}$ plus *anteiso*-$C_{32}$ alkane concentration of 2.2 – 2.8 ng $m^{-3}$ would correspond to an ambient fine particle contribution from cigarette smoke of 0.57 to 0.72 $\mu$g $m^{-3}$ (or 2.0 to 2.5% of the total fine ambient particle mass).

To test the hypothesis that urban plants are not the major source of urban atmospheric *iso*- and *anteiso*-alkane concentrations in Los Angeles, the following consistency check can be performed. Assume for a moment that all *iso*- and *anteiso*-alkanes ($C_{29}$ - $C_{34}$) measured in this urban atmosphere were completely due to the leaf surface abrasion products of common vegetation typical of the Los Angeles area. Then it would be possible to estimate from the ambient *iso*- and *anteiso*-alkane concentrations the hypothetical ambient *n*-alkane concentration contributions that must be present from vegetative detritus using the ratio between branched vs. *n*-alkanes found in the leaf surface abrasion product composites discussed earlier. It was found from these calculations (using *iso*-$C_{31}$-alkane plus $C_{29}$–$C_{34}$ *n*-alkane) that the urban $C_{29}$ – $C_{34}$ *n*-alkane concentrations measured on average in the greater Los Angeles area would have to be roughly 20-fold higher than actually observed, if all *iso*- and *anteiso*-alkanes found in the airborne fine particulate matter were solely due to urban vegetation. Conversely, the contribution from urban plant detritus to the measured Los Angeles atmospheric *iso*- and *anteiso*-alkane concentrations must be 5% or less based on the upper limit posed by the ambient $C_{29}$–$C_{34}$ *n*-alkane concentration. Under such circumstances the *iso*- and *anteiso*-alkanes concentration pattern characteristic

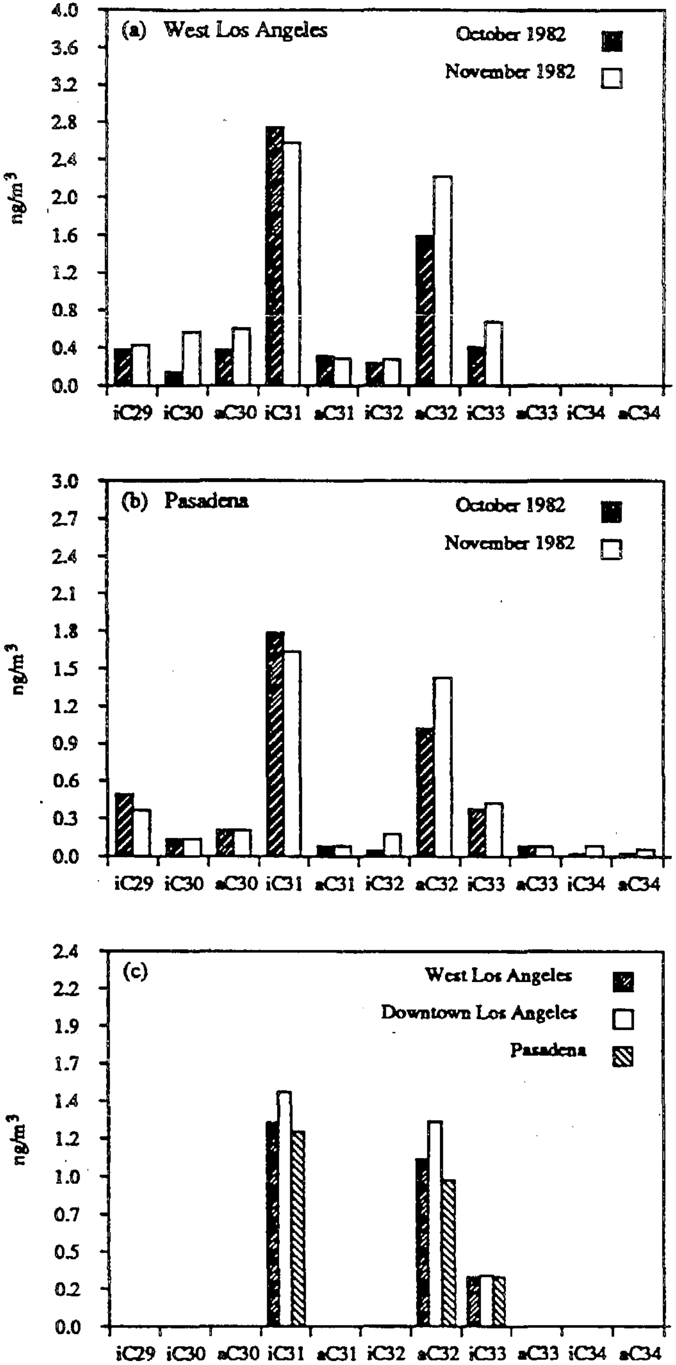


Fig. 8.5: Ambient *iso-* and *anteiso*-alkane concentrations measured at (a) West Los Angeles and (b) Pasadena, both in October and November 1982, and (c) annual average concentrations measured at West Los Angeles, downtown Los Angeles, and Pasadena during 1982.

of cigarette smoke can be used as a marker assemblage to accurately trace cigarette smoke aerosol in the urban atmosphere.

## Conclusions

A study has been conducted to identify marker compounds that can be used to trace cigarette smoke particles in the outdoor Los Angeles urban atmosphere. The organic compounds present in cigarette smoke aerosol samples from exhaled mainstream plus sidestream smoke were examined by gas chromatography/mass spectrometry. The compound emission rates agree with literature values, thereby validating the sampling and analytical methods applied here. It was shown that the *iso-* and *anteiso*-alkanes concentration pattern characteristic of tobacco leaf surface waxes is preserved in cigarette smoke aerosol. To verify whether or not this *iso-* and *anteiso*-alkane concentration pattern found in the cigarette smoke aerosol is sufficiently unique that it can be used to trace cigarette smoke emissions in the urban atmosphere, common anthropogenic and biogenic emission sources likewise have been investigated. Particulate matter dislodged from the waxy leaf surfaces of urban plants by wind and weather show on average an *iso-* and *anteiso*-alkane concentration pattern that is different than that was found for the cigarette smoke aerosol. Other major emission sources ranging from vehicular emissions to meat cooking do not show any detectable amounts of *iso-* and *anteiso*-alkanes in the carbon range from $C_{29}$ to $C_{34}$, when analyzed by the same methods as used for the cigarette smoke and leaf surface waxes.

Using cigarette sales and population data for Los Angeles in 1982, ambient cigarette smoke branched alkane tracer concentrations were estimated that closely resemble concentrations measured in ambient air throughout the greater Los Angeles area. Considering all avenues investigated, the *iso-* and *anteiso-*

alkane concentration pattern found in cigarette smoke aerosol is unique, and is preserved in the urban atmosphere. It can be concluded that cigarette smoke aerosol can indeed be traced in the urban atmosphere and the tracer assemblage can be used to quantitatively etimate the ambient cigarette smoke concentrations outdoors. On average in 1982 in the Los Angeles area, the outdoor ambient fine particle cigarette smoke concentration determined by this technique averaged approximately 0.57 to 0.72 $\mu$g m$^{-3}$.

# REFERENCES

Albrecht, P.; Vandenbroucke, M.; Mandengué, M. Geochemical studies on the organic matter from the Douala Basin (Cameroon)–I. Evolution of the extractable organic matter and the formation of petroleum. *Geochim. Cosmochim. Acta* 1976, 40, 791–799.

Albro, P.W. Bacterial Waxes. In *Chemistry and Biochemistry of Natural Waxes*; Kolattukudy, P.E, Ed.; Elsevier, Amsterdam, New York, Chap. 10, 1976, 419–445.

Baker, E.A. Chemistry and morphology of plant epicuticular waxes. In *The Plant Cuticle.*; Cutler, D.F., Alvin, K.L., Price, C.E., Eds.; Academic Press, London, 1982, pp. 139–165.

Baker, R.R. Product formation mechanisms inside a burning cigarette. *Prog. Energy Combust. Sci.* 1981, 7, 135–153.

Benner, C.L.; Bayona, J.M.; Cake, F.M.; Tang, H.; Lewis, L.; Crawford, J.; Lamb, J.D.; Lee, M.L.; Lewis, E.A.; Hansen, L.D.; Eatough, D.J. Chemical composition of environmental tobacco smoke. 2. Particulate-phase compounds. *Environ. Sci. Technol.* 1989, 23, 688–699.

Bonavita-Cougourdan, A.; Theraulaz, G.; Bagnéres, A.-G.; Roux, M.; Pratte, M.; Provost, E.; Clément, J.-L. Cuticular hydrocarbons, social organization and ovarian development in a polistine wasp: *Polistes Dominulus* Christ. *Comp. Biochem. Physiol.* 1991, 100B, 667–680.

Browne, C.L.; Keith, C.H.; Allen, R.E. The effect of filter ventilation on the yield and composition of mainstream and sidestream smokers. *Beitr. Tabakforsch.* 1980, 10, 81–90.

Brunekreef, B.; Boleij, J.S.M. Long term average suspended particulate concentrations in smokers' homes. *Int. Arch. Occup. Environ. Health* 1982, 50, 299–302.

Carruthers, W.; Johnstone, A.W. Composition of a paraffin wax fraction from tobacco leaf and tobacco smoke. *Nature* 1959, 184, 1131–1132.

Chuang, J.C.; Gregory, A.M.; Kuhlman, M.R. Polycyclic aromatic hydrocarbons and their derivatives in indoor and outdoor air in an eight-home study. *Atmos. Environ.* 1991, 25B, 369-380.

Douglas, A.G.; Eglinton, G. The distribution of alkanes. In *Comparative Phytochemistry*, Swain T. Ed., Academic Press, London, 1966, 57-77.

Eatough, D.J.; Benner, C.L.; Bayona, J.M.; Richards, G.; Lamb, J.D.; Lee, M.L.; Lewis, E.A.; Hansen, L.D. Chemical composition of environmental tobacco smoke. 1. Gas-phase acids and bases. *Environ. Sci. Technol.* 1989, 23, 679–687.

Eglinton, G.; Gonzalez, A.G.; Hamilton, R.J.; Raphael, R.A. Hydrocarbon constituents of the wax coatings of plant leaves: A taxonomic survey. *Phytochem.* 1962, 1, 89–102.

Eglinton, G.; Hamilton, R.J. Leaf epicuticular waxes. *Science* 1967, 156, 1322–1335.

Elmenhorst, H. Säuren and phenole in der "semi-volatile"–fraction des rauches von blend-, virginia-, burley-, und orient-cigaretten. *Beitr. Tabakforsch.* 1972, 6, 182–188.

Girman, J.R.; Apte, G.W.; Traynor, J.R.; Allen, J.R.; Hollowell, C.D. Pollutant emission rates from indoor combustion appliances and sidestream cigarette smoke. *Environ. Int.* 1982, 8, 213-221.

Gray, H.A. Control of atmospheric fine carbon particle concentrations. Ph.D. Thesis, California Institute of Technology, Pasadena, 1986, 317pp.

Gray, H.A.; Cass, G.R.; Huntzicker, J.J.; Heyerdahl, E.K,; Rau, J.A. Characteristics of atmospheric organic and elemental carbon particle concentrations in Los Angeles. *Environ. Sci. Technol.* 1986, 20, 580–589.

Grimmer, G.; Böhnke, H. ; Harke, H.-P. Zum proben des passivrauchens: konzentrationsmessungen von polycyclischen aromatischen kohlenwasserstoffen in innenräumen nach dem machinellen abrauchen von zigaretten. *Int. Arch. Occup. Environ. Hlth.* 1977, 40, 83–92.

Grimmer, G; Naujack, K.-W.; Dettbarn, G. Gas chromatographic determination of polycyclic aromatic hydrocarbons, aza-arenes, and aromatic amines in the particle and vapor phase of mainstream and sidestream smoke of cigarettes. *Toxicol. Lett.* 1987, 35, 117–124.

Gülz, P.-G.; Müller, E.; Prasad, R.B.N. Organ-specific composition of epicuticular waxes of beech leaves and seeds. *Z. Naturforsch.* 1989, 44C, 731–734.

Hammond, S.K.; Leaderer, B.P.; Roche, A.C.; Schenker, M. Collection and analysis of nicotine as a marker for environmental tobacco smoke. *Atmos. Environ.* 1987, 21, 457–462.

Heavner, D.L.; Ogden, M.W.; Nelson, P.R. Multisorbent thermal desorption/gas chromatography/mass selective detection method for the determination of target volatile organic compounds in indoor air. *Environ. Sci. Technol.* 1992, 26, 1737–1746.

Hildemann, L.M.; Markowski, G.R.; Cass, G.R. Chemical composition of emissions from urban sources of fine organic aerosol. *Environ. Sci. Technol.* 1991a, 25, 744–759.

Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Quantitative characterization of urban sources of organic aerosol by high-resolution gas chromatography. *Environ. Sci. Technol.* 1991b, 25, 1311-1325.

Hoffmann, D.; Woziwodzki, H. Chemical studies on tobacco smoke. IV. The quantitative determination of nonvolatile fatty acids in tobacco and tobacco smoke. *Beitr. Tabakforsch.* 1968, 4, 167–175.

*IARC Monographs*; World Health Organization, International Agency for Research on Cancer, Lyon, France, 1986, 38, 421 pp.

Jamieson, G.R.; Reid, E.H. The leaf lipids of some conifer species. *Phytochem.* 1972, 11, 269–275.

Jenkins, P.L.; Phillips, T.J.; Mulberg, E.J.; Hui, S.P. Activity patterns of Californians: Use of and proximity to indoor pollution sources. *Atmos. Environ.* 1992, 26A, 2141-2148.

Johnstone, R.W.; Plimmer, J.R. The chemical constituents of tobacco and tobacco smoke. *Chem. Rev.* 1959, 59, 885–936.

Kamens, R.M.; Guo, J.; Guo, Z.; McDow, S.R. Polynuclear aromatic hydrocarbon degradation by heterogeneous reactions with $N_2O_5$ on atmospheric particles. *Atmos. Environ.* 1990, 24A, 1161-1173.

Kaneda T. Fatty acids in the Genus Bacillus. *J. Bacteriology* 1967, Mar., 894-903.

Katzenstein, A.W. Environmental tobacco smoke and lung cancer risk: epidemiology in relation to confounding factors. *Environ. Int.* 1992, 18, 341-345.

Kissin, Y.V. Catagenesis and composition of petroleum: origin of *n*-alkanes and isoalkanes in petroleum crudes. *Geochim. Cosmochim. Acta* 1987, 51, 2445–2457.

Kolattukudy, P.E. Plant waxes. *Lipids* 1970, 5, 259–275.

Klus, H.; Kuhn, H. Verteilung verschiedener tabakrauchbestandteile auf haupt- und nebenstromrauch (eine übersicht). *Beitr. Tabakforsch.* 1982, 11, 229–265.

Leaderer, B.P.; Hammond, S.K. Evaluation of vapor-phase nicotine and respirable suspended particle mass as markers for environmental tobacco smoke. *Environ. Sci. Technol.* 1991, 25, 770–777.

Lee, M.L.; Novotny, M.; Bartle, K.D. Gas chromatographic/mass spectrometric and nuclear magnetic resonance spectrometric studies of carcinogenic polynuclear aromatic hydrocarbons in tobacco and marijuana smoke condensates. *Analyt. Chem.* 1976, 48, 405–416.

Ligocki, M.P.; Salmon, L.G.; Fall, T.; Jones, M.C.; Nazaroff, W.W.; Cass, G.R. Characteristics of airborne particles inside Southern California Museums *Atmos. Environ.* 1993, *in press.*

Lockey, K.H. Lipids of the insect cuticle: origin, composition and function. *Comp. Biochem. Physiol.* 1988, 89B, 595–645.

Lockey, K.H. Insect hydrocarbon chemotaxonomy: cuticular hydrocarbons of adult and larval *Epiphysa* species blanchard and adult *Onymacris Unguicularis* (Haag) (Tenebrionidae: Coleoptera). *Comp. Biochem. Physiol.* 1992, 102B, 451–470.

Lockey, K.H.; Metcalfe, N.B. Cuticular hydrocarbons of adult *Himatismus* species and a comparison with 21 other species of adult tenebrionid beetle using multivariate analysis. *Comp. Biochem. Physiol.* 1988, 91B, 371–382.

Lõfroth, G.; Burton, R.M.; Forehand, L.; Hammond, S.K.; Seila, R.L.; Zweidinger, R.B.; Lewtas, J. Characterization of environmental tobacco smoke. *Environ. Sci. Technol.* 1989, 23, 610–614.

Matsushima, S.; Ishiguro, S.; Sugawara, S. Composition studies on some varieties of tobacco and their smoke. *Beitr. Tabakforsch.* 1979, 10, 31–38.

Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Interpretation of high-resolution gas chromatography and high-resolution gas chromatography/mass spectrometry data acquired from atmospheric organic aerosol samples. *Aerosol Sci. Technol.* 1989, 10, 408-419.

Mazurek, M.A.; Cass G.R.; Simoneit, B.R.T. Biological input to visibility-reducing particles in the remote arid southwestern United States. *Environ. Sci. Technol.* 1991, 25, 684-694.

Mazurek, M.A.; Simoneit, B.R.T. Characterization of biogenic and petroleum-derived organic matter in aerosols over remote, rural and urban areas. In *Identification and Analysis of Organic Pollutants in Air*, ACS Symp., Woburn, MA: Ann Arbor Science/Butterworth Publishers, 1984: 353–370.

Mazurek, M.A.; Simoneit, B.R.T.; Cass, G.R.; Gray, H.A. Quantitative high-resolution gas chromatography and high-resolution gas chromatography/mass spectrometry analysis of carbonaceous fine aerosol particles. *Int. J. Environ. Anal. Chem.* 1987, 29, 119-139.

Mazurek, M.A.; Hildemann, L.M.; Cass, G.R.; Simoneit, B.R.T.; Rogge, W.F. Methods of analysis for complex organic aerosol mixtures from urban emission sources of particulate carbon. In *Sampling and Analysis of Airborne Pollutants*; Winegar, E.D.; Keith, L.H.; Eds.; Lewis Publishers: Boca Raton, FL, 1993; pp 178–190.

Mitra, S.; Wilson, N.K. Pattern of polynuclear aromatic hydrocarbons in indoor air: exploratory principal component analysis. *Environ. Int.* 1992, 18, 477-487.

Mold, J.D.; Stevens, R.K.; Means, R.E., Ruth, J.M. The paraffin hydrocarbons of tobacco; normal-, iso-, and anteiso-homologues. *Biochemistry* 1963, 2, 605–610.

Mold, J.D.; Means, R.E.; Ruth, J.M. The higher fatty acids of flue-cured tobacco. Methyl and cyclohexyl branched acids. *Phytochem.* 1966, 5,59-66.

Miller, P.R.; Winer, A.M. Composition and dominance in Los Angeles basin urban vegetation. *Urban Ecology* 1984, 8, 29–54.

Nazaroff, W.W.; Cass, G.R. Protecting museum collections from soiling due to the deposition of airborne particles. *Atmos. Environ.* 1991, 25A, 841–852.

Nazaroff, W.W.; Salmon, L.G.; Cass, G.R. Concentration and fate of airborne particles in museums *Environ. Sci. Technol.* 1990, 24, 66–77.

Nelson, D.R. Long-chain methyl-branched hydrocarbons: occurrence, biosynthesis, and function. *Adv. Insect Physiol.* 1978, 13, 1–33.

Nelson, D.R.; Dillwith, J.W.; Blomquist, G.J. Cuticular hydrocarbons of the house fly, *Musca Domestica Insect Biochem.* 1981, 11, 187–197.

Nelson, P.R.; Heavner, D.L.; Collie, B.B.; Maiolo, K.C.; Ogden, M.W. Effect of ventilation and sampling time on environmental tobacco smoke component ratios. *Environ. Sci. Technol.* 1992, 26, 1915–1921.

Newell, M.P.; Heckman, R.A.; Moates, R.F.; Green, C.R.; Best, F.W.; Schumacher, J.N. Isolation and identification of new components in the ether-soluble portion of cigarette smoke condensate. *Tob. Sci.* 1978, 22, 6–11.

Nishimoto, S. A chemotaxonomic study of *n*-alkanes in leaf surface waxes of terrestrial plants. *J. Sci. Hiroshima Univ.*, Ser. A, 1974a, 38, 151–158.

Nishimoto, S. Branched chain alkanes in surface waxes of waxy wheats and nowaxy wheats. *J. Sci. Hiroshima Univ.*, Ser. A, 1974b, 38, 165–174.

Ogden, M.W.; Maiolo, K.C. Collection and determination of solanesol as a tracer of environmental tobacco smoke in indoor air. *Environ. Sci. Technol.* 1989, 23, 1148–1154.

Ogden, M.W.; Maiolo, K.C. Comparative evaluation of diffusive and active sampling systems for determining airborne nicotine and 3-ethenylpyridine. *Environ. Sci. Technol.* 1992, 26, 1226–1234.

Pitts, J.N. Jr.; Khan, A.U.; Smith, E.B.; Wayne R.P. Singlet oxygen in the environmental sciences: singlet molecular oxygen and photochemical air pollution. *Environ. Sci. Technol.* 1969, 3, 241–247.

Pitts, J.N. Jr.; Lockensgard, D.M.; Ripley, P.S.; Van Cauwenberghe, K.A.; Van Vaeck, L.; Schaffer, S.D.; Thill, A.J.; Belser, W.L. Jr. Atmospheric epoxidation of benzo[a]pyrene by ozone: formation of the metabolite benzo[a]-pyrene-4,5-oxide. *Science* 1980, 210, 1347-1349.

Ramsey, R.S.; Moneyhun, J.H.; Jenkins, R.A. Generation, sampling and chromatographic analysis of particulate matter in dilute sidestream tobacco smoke. *Anal. Chim. Acta* 1990, 236, 213–220.

Repace, J.L.; Lowrey, A.H. Risk assessment methodologies for passive smoking-induced lung cancer. *Risk Analysis* 1990, 10, 27–37.

Riederer, M. Die kutikula als barriere zwischen terrestrischen pflanzen und der atmosphäre. *Naturwissenschaften* 1991, 78, 201–208.

Riederer, M. and Schneider, G. The effect of the environment on the permeability and composition of *Citrus* leaf cuticles. II. Composition of soluble cuticular lipids and correlation with transport properties. *Planta* 1990, 180, 154–165.

Rieley, G.; Collier, R.J.; Jones, D.M.; Eglinton, G. The biogeochemistry of Ellesmere Lake, U.K.—I: source correlation of leaf wax inputs to the sedimentary lipid record. *Org. Geochem.* 1991, 17, 901–912.

Risner, C.H.; Conner, J.M. The quantification of 4- to 6-ring polynuclear aromatic hydrocarbons in indoor air samples by high-performance liquid chromatography. *J. Liquid Chromatog.* 1991, 13, 437-463.

Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Sources of fine organic aerosol: 1. Charbroilers and meat cooking operations. *Environ. Sci. Technol.* 1991, 25, 1112-1125.

Rogge, W.F.; Mazurek, M.A.; Hildemann, L.M.; Cass, G.R.; Simoneit, B.R.T. Quantification of urban organic aerosols at a molecular level: I. Identification, abundance, and seasonal variations. *Atmos. Environ.* 1993a, *in press.*

Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Sources of fine organic aerosol: 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. *Environ. Sci. Technol.* 1993b, 27, 636–651.

Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Sources of fine organic aerosol: 3. Road dust, tire debris, and organometallic brake lining dust — roads as sources and sinks. *Environ. Sci. Technol.* 1993c, *in press.*

Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Sources of fine organic aerosol: 4. Particulate abrasion products from leaf surfaces of urban plants. *Environ. Sci. Technol.* 1993d, *submitted.*

Rogge, W.F.; Mazurek, M.A.; Hildemann, L.M.; Cass, G.R.; Simoneit, B.R.T. Quantification of urban organic aerosols at a molecular level: II. Identification, abundance, and seasonal variations. *in preparation*, 1993e.

Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Sources of fine organic aerosol: 5. Natural gas home appliances. *Environ. Sci. Technol.* 1993f, *submitted.*

Rogge, W.R.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. Sources of Fine Organic Aerosol: 9. Fireplace Wood Smoke. *in preparation*, 1993g.

Sakuma, H.; Kusama, M.; Muankata, S.; Ohsumi, T.; Sugawara, S. The distribution of cigarette smoke components between mainstream and sidestream smoke. I. Acidic components. *Beitr. Tabakforsch.* 1983, 12, 63–71.

Sakuma, H.; Kusama, M.; Yamaguchi, K.; Matsuki, T.; Sugawara, S. The distribution of cigarette smoke components between mainstream and sidestream smoke. III. Middle and higher boiling components. *Beitr. Tabakforsch.* 1984a, 12, 251–258.

Sakuma, H.; Kusama, M.; Yamaguchi, K.; Matsuki, T.; Sugawara, S. The distribution of cigarette smoke components between mainstream and sidestream smoke. II. Bases. *Beitr. Tabakforsch.* 1984b, 12, 199–209.

Schmeltz, I.; De Paolis, A.; Hoffmann, D. Phytosterols in tobacco: quantitative analysis and fate in tobacco combustion. *Beitr. Tabakforsch.* 1975, 8, 211–218.

Schmeltz, I.; Hoffmann, D. Nitrogen-containing compounds in tobacco and tobacco smoke. *Chem. Rev.* 1977, 77, 295–311.

Schmeltz, I.; Wenger, A.; Hoffmann, D.; Tso, T.C. Chemical studies on tobacco smoke. 63. On the fate of nicotine during pyrolysis and in a burning cigarette. *J. Agric. Food Chem.* 1979, 27, 602–608.

Severson, R.F.; Schlotzhauer, R.F.; Arrendale, M.E.; Snook, M.E.; Higman, H.C. Correlation of polynuclear aromatic hydrocarbon formation between pyrolysis and smoking. *Beitr. Tabakforsch.* 1977, 9, 23–37.

Severson, R.F.; Arrendale, R.F.; Chortyk, O.T.; Snook, M.E. A method for determining the transfer of lipids from tobacco to smoke. *Tob. Sci.* 1978, 22, 130–133.

Simoneit, B.R.T.; Mazurek, M.A. Organic matter of the troposphere—II. Natural background of biogenic lipid matter in aerosols over the rural Western United States. *Atmos. Environ.* 1982, 16, 2139-2159.

Simoneit, B.R.T. Organic matter of the troposphere—III. characterization and sources of petroleum and pyrogenic residues in aerosols over the Western United States. *Atmos. Environ.* 1984, 18, 51–67.

Simoneit, B.R.T. Organic matter of the troposphere—V. Application of molecular marker analysis to biogenic emissions into the troposphere for source reconciliations. *J. Atmos. Chem.* 1989, 8, 251–278.

Simoneit, B.R.T.; Cardoso, J.N.; Robinson, N. An assessment of the origin and composition of higher molecular weight organic matter in aerosols over Amazonia. *Chemosphere* 1990, 21, 1285–1301.

Snook, M.E.; Fortson, P.J.; Chortyk, O.T. Isolation and identification of N'-acylalkaloids of cigarette smoke. *Beitr. Tabakforsch.* 1984, 12, 227–243.

Spears, A.W.; Lassiter, C.W.; Bell, J.H. Quantitative determination of alkanes in cigarette smoke. *J. Gas Chromatogr.* 1963, 1, 34–37.

Stedman, R.L. The chemical composition of tobacco and tobacco smoke. *Chem. Rev.* 1968, 68, 153–207.

Tang, H.; Richards, G.; Benner, C.L.; Tuominen, J.P.; Lee, M.L.; Lewis, E.A.; Hansen, L.D.; Eatough, D.J. Solanesol: A tracer for environmental tobacco smoke particles. *Environ. Sci. Technol.* 1990, 24, 848–852.

Tissot, B.P.; Welte, D.H. In *Petroleum Formation and Occurrence: A New Approach to Oil and Gas Exploration*, Springer Verlag, Berlin, 2nd ed., 1984, 699 pp.

Tornabene, T.G.; Morrison, S.J.; Kloos, W.E. Aliphatic hydrocarbon contents of various members of the family Micrococcaceae. *Lipids* 1970, 5, 929–937.

U.S. Bureau of the Census, Statistical Abstract of the United States, 1991, ($111^{th}$ edition), Washington, DC, 1991, U.S. Government Printing Office, Washington, DC 20402.

U.S. Dept. of Health and Human Services. Reducing the Health Consequences of Smoking: 25 Years of Progress: A Report to the Surgeon General. Washington, DC, 1989, DHHS publication (CDC) 89-8411.

Van Duuren, B.L.; Kosak, A.I. Isolation and identification of some components of cigarette smoke condensate. *J. Org. Chem.* 1958, 23, 473–475.

Waldron, J.D.; Gowers, D.S.; Chibnall, A.C.; Piper, S.H. Further observations on the paraffins and primary alcohols of plant waxes. *J. Biochem.* 1961, 78, 435–442.

Wynder, E.L.; Hoffmann, D. Eds. In *Tobacco and Tobacco Smoke. Studies in Experimental Carcinogenesis*, New York, Academic Press, 1967, 365–371.

Winer, A.M.; Fitz, D.R.; Miller, P.R. Investigation of the Role of Natural Hydrocarbons in Photochemical Smog Formation in California. Final report to the California Air Resources Board, Sacramento, CA, under Agreement no. A0-056-032; Statewide Air Pollution Research Center, University of California, CA, 1983.