Molecular Tracers for Sources of Atmospheric Carbon Particles: Measurements and Model Predictions

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Abstract

Carbonaceous compounds are the largest contributor to the fine particulate matter in the atmosphere of urban areas. However, little is known about the concentrations, seasonal patterns, ambient chemical formation/destruction and source/receptor relationships that govern the individual compounds present in this complex organic mixture. The objective of the present research is to characterize the particulate organic compounds present in source emissions and in ambient air and to use those data to evaluate methods for computing source contributions to ambient pollutant concentrations.

Airborne fine particulate matter samples collected at 4 urban sites within the Los Angeles basin during 1982 were analyzed by gas chromatography/mass spectrometry. More than 100 individual organic compounds were identified. Primary organic aerosol constituents including n-alkanes, n-alkanoic acids, polycyclic aromatic hydrocarbons, hopanes, and steranes reveal a seasonal pattern with high winter and low summer concentrations. Aliphatic dicarboxylic acids possibly formed by atmospheric reactions show a reverse pattern, with high concentrations in late spring/early summer.

Next, fine particulate emissions from major urban sources were characterized. The sources tested were responsible for more than 80% of the fine carbonaceous aerosol emitted to the Los Angeles atmosphere. The identification of organic compounds that act as markers for the presence of effluents from particular source types was emphasized. It was found that fossil petroleum compounds such as hopanes and steranes can be used to trace vehicular fine particulate emissions in the urban atmosphere, *iso*- and *anteiso*-alkanes are useful tracers for cigarette smoke, cholesterol is a likely tracer for meat smoke aerosol, C_{29} –

C_{33} odd carbon number n-alkanes can be used to estimate airborne vegetative detritus concentrations, and certain resin acids can be used to track wood smoke aerosols.

The source emission data have been used along with an atmospheric transport model to calculate primary source contributions to the concentrations of single particle-phase organic compounds in the Los Angeles atmosphere. The predicted and measured concentrations of stable primary organic compounds agree well. This indicates that a nearly complete knowledge of source/receptor relationships for many particle-phase primary organic compounds has been achieved for the first time. The model predictions indicate that aliphatic dicarboxylic and aromatic polycarboxylic acids measured in the urban atmosphere are indeed the products of atmospheric chemical reactions.

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Chapter 1

Introduction

Motivation

Organic compounds associated with airborne fine particulate matter (particle diameter, $d_p \leq 2\mu m$) are of environmental concern in highly industrialized and urbanized areas as well as in rural regions. Fine particulate matter is known to be easily inhalable and has been considered responsible, together with gaseous pollutants, for the possible health effects connected with air pollutants (*1-4*). Elevated concentrations of organic compounds in fine respirable particles measured in many urbanized areas are of considerable concern because many of the organics present in the atmosphere are known mutagens (*4-8*) and carcinogens (*1-3*). Fine carbon aerosols also play an important role in the severe visibility deterioration observed in urban areas like Los Angeles (*9-11*), and at rural sites like Grand Canyon National Park where visibility obstruction can mask the beauty of the scenery (*12*).

In cities such as Los Angeles, for example, typically 30% of the airborne fine aerosol mass is composed of organic compounds (*13*). Carbonaceous particles are produced by combustion (pyrogenic), synthetic (anthropogenic products), geological (fossil fuels), natural (biogenic), and secondary (atmospheric radical and photochemistry) sources, which upon dispersion admix depending on the emission strength of each of these sources. Given the large number of contributing sources, it has not been at all obvious which sources should be controlled in order to bring carbon particle concentrations downward.

The existing ambient particle composition data that are available for some groups of organic compounds (e.g., PAH, nitro–PAH, normal alkanes, dicarboxylic acids, pesticides, etc.) were acquired using a wide variety of different sampling devices under different sampling conditions (high–volume samplers, low–volume samplers, cascade impactors, cyclone separators, dichotomous samplers, different filter types, etc). Also, the laboratory procedures used to extract and analyze the organic matter present in past sampling studies differ from investigator to investigator. At present, there exists no consistent data set for airborne material which includes a relatively complete characterization of the organic aerosol over different seasonal situations and at a representative number of sampling sites, spread over the area of investigation. The same is true for most of the important anthropogenic and biogenic sources. Only a limited number of source test data are available which were actually taken under appropriate conditions. Most of the source tests performed in the past either underestimated particle-phase organics by filtration at elevated stack temperatures or alternatively overestimated the particle phase organics by cold trapping compounds that under atmospheric conditions would remain in the vapor phase.

Due to the severe limitations of the available ambient data sets and source testing results, detailed source apportionment studies that explain the molecular character of ambient carbonaceous aerosols simply have not been conducted. New data sets suitable for comparison of source and ambient aerosol samples are needed that are designed to describe the source/receptor relation adequately. This demand can be satisfied by using the same particle size separation devices, the same filter materials, and by sampling at about the same temperature, at both sources and receptor sites. The latter requirement invokes the need for a dilution source testing device that simulates the real atmosphere by diluting the source emissions with pre–cleaned air and allowing the condensation processes that would occur as the source effluent enters the atmosphere from a hot stack to happen within the source testing device. In addition, the same laboratory extraction and analytical procedures have to be used, on both source and ambient samples, followed by identical compound identification and quantification protocols.

Research Objectives

The major objectives of the present research are: to provide a detailed molecular characterization of the primary fine carbonaceous aerosols emitted from the major urban air pollution sources; to provide parallel data on the concentrations of organic compounds found in ambient particulate matter; to identify and verify source-specific organic tracer compounds that are suitable to trace source emissions in the urban atmosphere; and finally, to evaluate the predictions of a mathematical model for primary (e.g., directly emitted) aerosol organic compounds that calculates transport from the sources to community receptor air monitoring sites. Air quality model predictions will be tested against ambient organic aerosol concentrations observed in the Los Angeles area month by month during the year 1982.

If these objectives are met, we will be able for the first time to determine single compound contributions from each major pollutant source type to the ambient organic aerosol complex. This study further provides the opportunity to identify and quantify secondary organic aerosol products formed from atmospheric gas-phase oxidation reactions by examining the differences between the actual atmospheric aerosol and the contributions from known primary aerosol sources. The fate of reactive organic compounds such as low molecular weight polycyclic aromatic hydrocarbons (PAH) also can be examined in the course of this work.

Approach

To overcome the limitations of the previously existing ambient organic compound data sets, ambient fine particulate samples collected during an extensive one year long study (*14*) at four urban and one offshore remote sampling site (San Nicolas Island) were chosen to be analyzed using gas chromatography/mass spectrometry (GC/MS). The results of this study are described in Chapter 2.

Next, samples collected during a prior source testing program that was designed to characterize the major carbon particle sources in Southern California were utilized. The source sampling campaign was conducted by Hildemann et al. (*15*). The source types tested were chosen after reviewing the only currently available detailed inventory of carbon particle sources present in a major metropolitan area (compiled for the Los Angeles area by Cass, Boone, and Macias (*16*), revised by Gray (*14*) and further revised by Hildemann (*15*)). The source types tested account for about 80% of the aerosol carbon emissions in Los Angeles.

Source emissions of organics that have moderate vapor pressures are difficult to sample accurately because these compounds are present in both the gas phase and aerosol phase. The partitioning of organic compounds between the two phases is dependent on the temperature and the partial pressure of the compounds in the gas phase, so the partition ratio changes as the source emissions are cooled and diluted in the atmosphere. In order to draw valid comparisons between the composition of organic aerosols at their source and the composition of organic aerosols in ambient air, both the source and ambient samples have to be collected by comparable methods and analyzed by the same technique. To overcome these difficulties a dilution source sampling device was used (*17*) which cools the emissions withdrawn from hot combustion sources down to ambient temperature and provides supersaturated organic vapors enough time to condense onto preexisting particles before sampling. Fine particulate matter was then collected downstream of cyclone separators that were identical to those used for the ambient sampling campaign conducted in 1982 by Gray et al. (*13*).

Micro–methods specifically developed for the quantitative recovery of extractable organic matter contained in the atmospheric fine aerosol fraction were used to extract the collected organic aerosol from both source and ambient samples (*18-20*).

In the current study, the organic chemical composition of the particulate emissions from eighteen source types has been measured. These chemical descriptions of the relevant sources together cover more than 400 organic compounds. Special attention was directed towards the identification of source-specific organic compounds that are suitable for use as tracers for the fine particulate emissions from particular source types in the urban atmosphere. The following sources were characterized: charbroiling and frying of extra-lean and regular hamburger meat, noncatalyst automobiles, catalyst-equipped autobiless, heavy-duty diesel trucks, road dust, tire debris, brake lining dust, particulate abrasion products from the leaf surfaces of urban plants, natural gas home appliances, cigarette smoke, roofing tar pot fumes, oil-fired boilers, and fireplace combustion of oak, pine, and synthetic logs. Chapters 3 through 11 of this work describe the detailed emission profiles for each source type on a compound by compound basis and relate these emissions to the atmospheric concentrations of key compounds that act as source-specific tracers.

Finally in Chapter 12, ambient fine particle-associated organic compound concentrations are predicted using the molecular source profiles acquired here together with the emissions to air quality model proposed by Gray (*14*) and the emission inventory for fine particulate organic carbon (OC) (*14, 15*) that has been complied for an 80 km × 80 km area centered over Los Angeles. The model predictions are compared with the monthly average organic compound concentrations measured throughout 1982 at West Los Angeles, downtown Los Angeles, and Pasadena, as reported in Chapter 12. Besides determining the contributions of specific sources of primary organic compound emissions to the atmospheric aerosol complex, this study allows estimation of the amount of certain atmospheric secondary aerosol reaction products, such as aliphatic dicarboxylic acids and aromatic polycarboxylic acids, that have been added to the urban aerosol burden.

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Chapter 2

Quantification of Urban Organic Aerosols at a Molecular Level: Identification, Abundance and Seasonal Variation

Introduction

Carbonaceous compounds are the largest contributor to the fine particulate matter in the atmosphere of many highly industrialized and urban areas (Wolff and Klimisch, 1982). In Los Angeles, for example, typically 30% of the fine aerosol mass is composed of organic compounds (Gray et al., 1986). However, relatively little is known about the concentrations, seasonal patterns, and source/receptor relationships that govern the individual compounds present in this complex organic mixture. Existing ambient data sets that describe organic aerosol composition either are limited to certain compound classes (e.g., polycyclic aromatic hydrocarbons) or have been collected over short time periods during peak photochemical smog conditions (Appel et al., 1980; Cronn et al., 1977; Grosjean, 1983; Grosjean et al. 1978; Hauser and Pattison, 1972; Schuetzle et al., 1973, 1975). Under heavy photochemical smog conditions in Los Angeles in the early 1970's such studies showed that secondary organic compound concentrations (e.g., dicarboxylic acids) were elevated during daytime when compared to primary organic compound concentrations. Characterization of the organic aerosol over a complete annual cycle has yet to be achieved. As a result, it has not been possible to examine the seasonal changes in aerosol composition or

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

long term relationships between upwind and downwind monitoring sites. Corresponding data that describe the composition of the organic aerosol emitted from a nearly complete set of the important anthropogenic and biogenic sources likewise have not been available.

In the present paper, atmospheric aerosol samples representing a complete annual cycle, collected at four urban locations in Southern California, are analyzed to quantify single compounds in the organic aerosol by high resolution gas chromatography (HRGC) and gas chromatography/mass spectrometry (GC/MS). Seasonal patterns for over 80 organic compounds found in the particulate matter are determined, and their spatial concentration changes are evaluated. Additional samples collected at an offshore island are used to establish pollutant concentrations upwind of the city.

In companion studies (Hildemann et al., 1991a, 1991b; Rogge et al., 1991), primary organic aerosol emitted from the most important sources in the Los Angeles area are analyzed by comparable methods. It has been observed that the inventory of primary emissions of organic aerosol in Los Angeles consists of over 40% contemporary (non-fossil) carbon, which is also consistent with radiocarbon dating of the Los Angeles aerosol (Berger et al., 1986; Currie, 1982; Currie et al., 1983; Hildemann et al., 1991a). Using molecular marker analyses and air quality modeling techniques, it is possible to compare the ambient data set described in the present paper to the results of related studies of primary aerosol sources. Such studies will provide an understanding of the cause and effect relationships that connect primary fine organic particulate matter emissions to ambient concentrations. Through simultaneous sampling at multiple sites over an extended period of time, the present study serves to define temporal and spatial patterns that must be reproduced by a successful air quality model for organic aerosol in Southern California.

Experimental Methods

Field Sampling Program

In 1982, field experiments were conducted to acquire an extensive set of ambient fine particle samples (Gray et al. 1986). Ten stationary sampling sites were chosen extending from the western shoreline of the Pacific Ocean to the eastern end of the greater Los Angeles area. One offshore site, San Nicolas Island, was selected to provide background concentration data necessary to determine the pollutant concentrations present in the atmosphere before air masses enter the Los Angeles area. Monthly averaged aerosol concentrations were constructed by combining samples collected for 24 hour periods at six day intervals for the entire calendar year 1982 at each site. The sampling equipment consisted of low volume (25.9 lpm) cyclone separators which removed particles with an aerodynamic diameter larger than 2.1 μm (John and Reischl, 1980). The sampled air was drawn through four parallel filter assemblies, at preset flow rates (Gray et al., 1986). The first three filter holders contained substrates that were analyzed for 34 trace elements, elemental carbon (EC), organic carbon (OC), and ionic species. The fourth filter holder was operated at 10 lpm and was loaded with quartz fiber filters (Pallflex Tissuquartz 2500 QAO, 47-mm diameter). The quartz filters were preheated prior to use at 600 °C for more than 2 h to reduce the carbon blank associated with new filters. The sampled quartz fiber filters from the West Los Angeles, Downtown Los Angeles, Pasadena, Rubidoux, and San Nicolas Island monitoring sites (shown in Figure. 2.1) were designated for organic compound identification and quantification by means of HRGC and GC/MS.

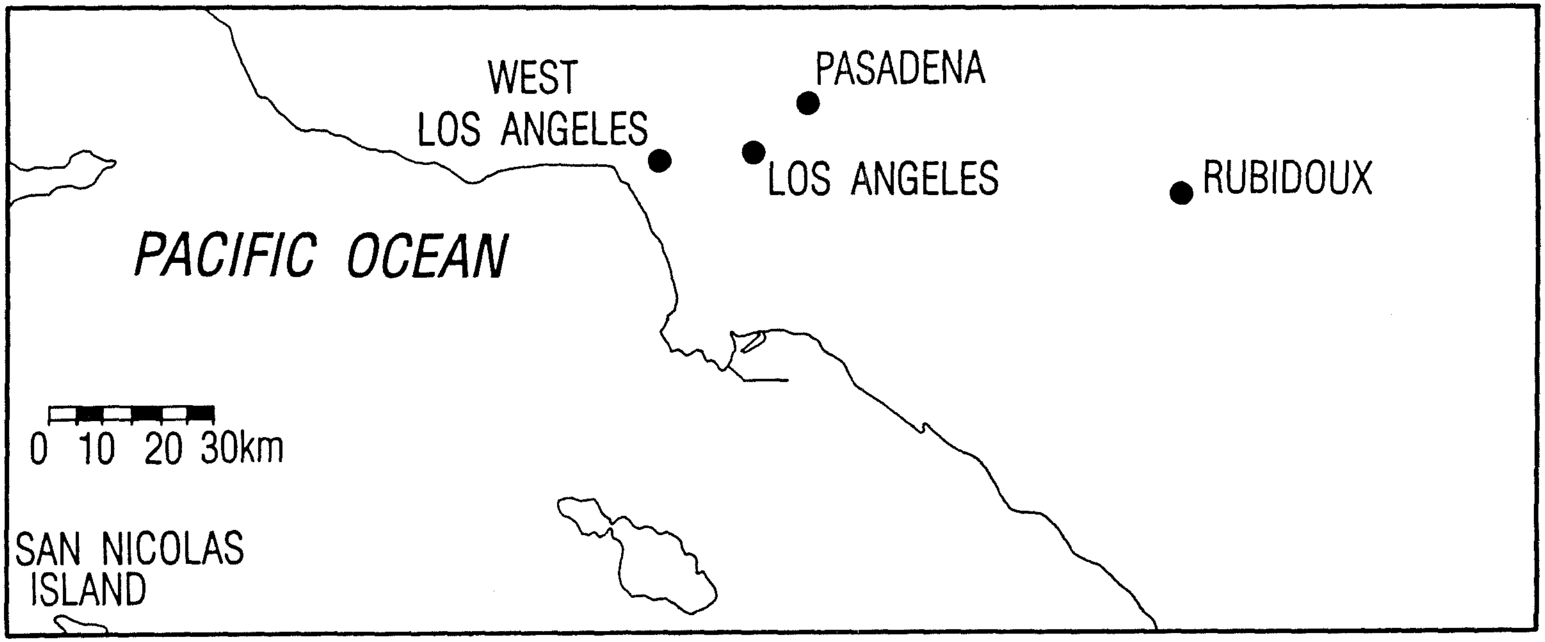

Figure 2.1: Sampling sites used throughout Southern California during the present study.

Extraction Protocol for Ambient Samples

All glassware used for sample extraction was annealed at 550 °C for at least 8 hours. Fittings and transfer lines were made of TFE or PTFE Teflon, and were cleaned with distilled-in-glass grade methanol and dichloromethane solvents. Prior to extraction, the ambient aerosol filter samples were grouped according to calendar month for each monitoring site, forming monthly composites that contained typically 5 sampled filters. The composited filters were placed in annealed borosilicate bottles for subsequent extraction. Each composite was spiked with a predetermined amount of perdeuterated tetracosane ($\underline{n}$-$C_{24}D_{50}$) as recovery standard (Mazurek et al., 1987, 1989, 1990). The amount added was calculated using the OC data obtained by Gray et al. (1986) that were collected in parallel with the present samples. In this manner, the recovery standard was added to the filter composites in relation to the known organic aerosol masses collected. As a result, the recovery standard was added at levels similar to that of the individual compounds present in the samples, which facilitates high quantification accuracy by flame ionization detection (FID) and mass spectrometric (MS) detection methods.

A sequential extraction protocol was followed to optimize the removal of nonpolar and polar compounds from the quartz fiber filters (Mazurek et al., 1987, 1989, 1991). Hexane (2 × 15 ml) and then benzene/isopropanol (2:1 mixture; 3 × 15 ml) were added sequentially to the filter composites. During each of these single extraction steps the extraction process was supported by mild ultrasonic agitation for 10 min at room temperature. After each sonic agitation, the extract was filtered and combined into a single flask using a custom designed transfer line assembly (Mazurek et al., 1987). The combined sample extract then was reduced to a volume of 3 to 5 ml by rotary vacuum distillation (27°C and pressure of 640-mm Hg). The total extract was reduced further by gentle solvent evaporation with a stream of high purity N_2 to a final volume of 300 to 500 μl. Following volume determination using a 500μl syringe (± 10μl units), the concentrated extract was divided into two aliquots. One aliquot was reacted with freshly produced diazomethane to convert organic acids to their methyl ester analogues and acidic hydroxy compounds to their methoxy analogues. After this derivatization, both sample aliquots were stored at -21 °C until analysis by HRGC and GC/MS.

Extracts from the fine carbon particle samples were analyzed using a Varian 4600 high-resolution gas chromatograph fitted with a Grob injector (splitless mode). The injector temperature was set to 300°C. A 30 meter fused silica OV-1701 column was used (bonded 86% dimethyl 14% cyanopropylphenyl polysiloxane, 25-μm film thickness, 0.32 mm i.d.; J & W Scientific, Rancho Cordova, CA). The HRGC was equipped with a flame ionization detector (FID) and was operated at the maximum range of detector sensitivity (10^{-12}mV). Mass spectrometric analyses were conducted using a Finnigan 4000 quadrupole gas chromatograph/mass spectrometer interfaced with an INCOS data acquisition system. The organic compounds were ionized by electron impact (EI) with electron energy of 70 eV. The scanning frequency was set to 0.5 $\sec^{-1}$, ranging from 50 to 550 daltons. The GC column used, temperature programming and time settings were identical to the HRGC-operating conditions.

Data Handling

Compound Identification

Compounds were identified and confirmed by a sequential process. First, compound identification was conducted by comparison of the unknown compound mass fragmentation pattern to the National Institute of Standards and Technology (NIST) mass spectral reference library, contained in the Finnigan INCOS-data system. Further comparison was made if necessary to an updated version of the NIST-library (IBM-AT, version 2, 1990), which provided additional search options. Second, the preliminary identification of compounds was confirmed by comparison of their mass fragmentation patterns and elution times to that of authentic standards which were injected onto the HRGC and GC/MS systems used here. Compound identification was deemed: **(a) positive**, when the sample spectrum, standard spectrum and NIST-library spectrum were identical and also the retention time of the authentic standard and the sample compound were comparable; **(b) probable**, same as above, except no authentic standard was available, but the NIST-library spectrum agreed very well with the sample spectrum; **(c) possible**, same as above, except that the sample mass fragmentation pattern contained additional ions from other compounds having minor peak coelution; **(d) tentative**, when the sample spectrum revealed additional mass fragments from one or more coeluting compounds (noise) with substantial overlap.

Quantification

Identifiable compound peaks were quantified using the HRGC data system, as long as the uncorrected compound mass was above 60 - 80 ng. The HRGC mass determination was based on the response of known amounts of 1-phenyldodecane (coinjection standard) and the recovery of n-$C_{24}D_{50}$ (internal recovery standard). Whenever the identified compound mass was below the above stated limit, even for one monthly sample from our data sets, the entire data set for that compound was quantified by Selective Ion Monitoring (SIM) using the MS-data system. Relative ion counts were converted to compound mass concentrations using relative response factors obtained by injection of external standards that contained the compound of interest. In this manner, two sets of response factors were generated, one for the FID-detector used in connection with the HRGC and another set for the mass spectrometer. Trace compounds like polycyclic aromatic hydrocarbons (PAH), oxygenated polycyclic aromatic hydrocarbons (oxy-PAH) and many other compounds were quantified by GC/MS.

Quality Assurance

A rigorous and comprehensive quality assurance program was followed throughout this study that is described in detail by Mazurek et al. (1987, 1990, 1991). Filters were sealed in sterilized aluminium foil-lined petri dishes before and after use, and were frozen between the time of collection and analysis. All filter materials (quartz fiber filters) and glass components of the extraction apparatus were annealed as described earlier, and the Teflon and stainless steel parts were solvent cleaned prior to use. Distilled-in-glass solvents were used throughout the analytical sequence and for preparation of standard solutions. All solvents were reanalyzed in our laboratory prior to use to assure that any contaminants present were quantified. Procedural blanks were analyzed in conjunction with the monthly composites. These blanks each consisted of two 47-mm quartz fiber filters that had been subjected to identical pretreatment and storage conditions as the fine aerosol samples. The blank filters were spiked with an 8 component perdeuterated recovery standard representing a range of compound volatility and functionality. Sample recovery and potential background contaminants were monitored by subjecting these blank samples to the same HRGC and GC/MS analyses as for the ambient samples. Contaminants introduced during laboratory procedures were found to be minor. 1,1'-Biphenyl was the major solvent contaminant. A number of sampling artifacts, mainly C_2, C_4, C_6, and C_8 phthalate esters, were monitored throughout the study. Further recovery experiments were conducted for 50 compounds present in our suite of authentic standards to determine their individual recovery. The recovery curve developed from these experiments was used to correct for compound recovery relative to the $\underline{n}$-$C_{24}D_{50}$ that was used as an internal standard applied to each sample composite. Accuracy determinations were performed for both polar and nonpolar standard compounds, showing that the relative standard deviation within a group of similar standard compounds was between 4 and 8% depending on the amount of the standard compounds injected.

Results and Discussion

Over 80 individual organic compounds found in the aerosol phase were identified and quantified, including $\underline{n}$-alkanes, $\underline{n}$-alkanoic acids, one $\underline{n}$-alkenoic acid, one $\underline{n}$-alkanal, aliphatic dicarboxylic acids, aromatic polycarboxylic acids, polycyclic aromatic hydrocarbons (PAH), polycyclic aromatic ketones (PAK), polycyclic aromatic quinones (PAQ), diterpenoid acids, and some nitrogen-containing compounds.

Material balances that describe the chemical composition of the ambient aerosol at different sampling sites were constructed as shown in Figures 2.2a-b. On average, the fine particle mass consists of about 20 – 40% carbonaceous material, with about one third of the aerosol carbon present as black elemental carbon and two thirds present as organic compounds (Gray et al., 1986). Of the bulk organic aerosol mass, typically 45 - 60% is extractable and elutable on the chromatographic column used according to the analytical procedures described earlier. HRGC and GC/MS-chromatograms produced from urban aerosol samples usually contain a large number of branched and cyclic hydrocarbons. These hydrocarbons are derived mainly from fossil fuel utilization and elute closely together to produce an unresolved accumulation of compounds in the chromatograms, usually known as the unresolved complex mixture (UCM)(Simoneit, 1989). Hence, the mass of elutable organics can be subdivided further into resolved (individual peaks) and unresolved (UCM) organic components. The resolved portion of the elutable organics comprises about 23 - 29% of the elutable organic mass. From this resolved portion, about 75 - 85% can be identified as single molecular entities, and these are the subject of this study. Figures 2.2a-b show this mass balance for the most western (West Los Angeles) and most eastern (Rubidoux) sampling sites. During the summer photochemical smog season, the prevailing winds are from west to east. Under these meteorological conditions, West Los Angeles is often on the upwind edge of the city while Rubidoux is far downwind of the metropolitan center. The most striking changes seen when comparing the mass balances in Figures 2.2a and 2.2b are (1) the increase in total fine particle mass at Rubidoux by nearly twofold relative to West Los Angeles; (2) the higher proportion of particulate nitrate at Rubidoux (an inorganic secondary formation product); and (3) the pronounced increase in the aliphatic dicarboxylic acids at the Rubidoux site (increasing from about 200 ng m^{-3} on average at West LA to more than 300 ng m^{-3} at Rubidoux).

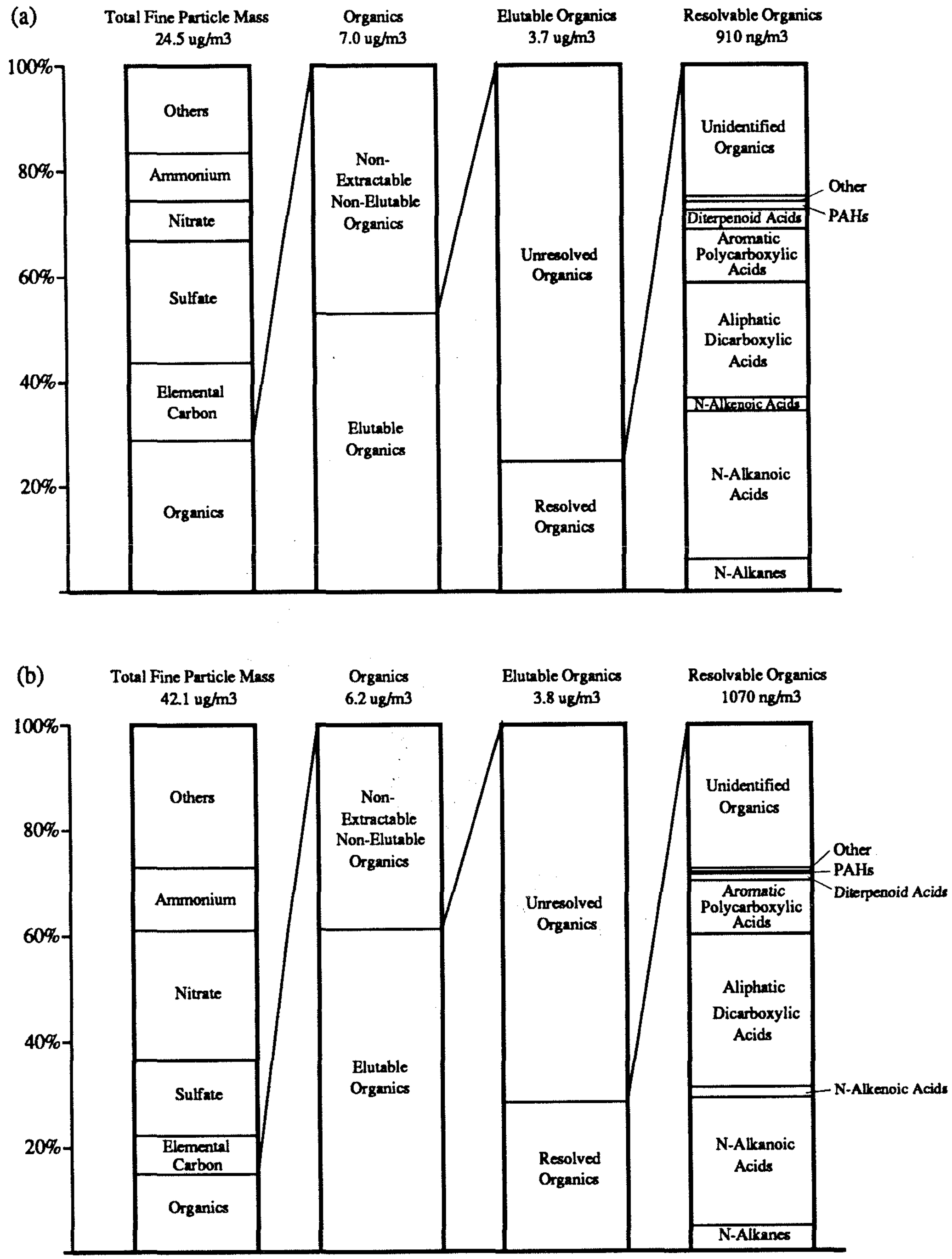

Fig. 2.2: Mass balance on the chemical composition of annual mean fine particle concentrations — 1982 for a) West Los Angeles and b) Rubidoux (Riverside).

In Table 2.1, the annual average material balance on identified organic compounds shown in Figure 2.2 is subdivided further into the ambient mass concentrations of the single compounds present. Because complete data on the relative abundance of these compounds in various source effluents are not available at present, it is not yet possible to calculate source contributions to ambient organic compound concentrations via molecular marker or mathematical modeling methods. However, several important consistency checks on likely source/receptor relationships can be performed. In the sections that follow, the literature on the origin of each of these compound classes will be reviewed briefly and the measured compound concentrations will be described. Then the ambient concentration data will be restated to remove the effects of seasonal changes in atmospheric dilution potential, revealing seasonal changes in source emission rates and atmospheric formation and destruction rates that help to confirm expected source/receptor relationships.

Alkanes

In the industrialized modern world, there are many sources responsible for n-alkanes release into the atmosphere. Anthropogenic sources typically include the combustion of fossil fuels, wood and agricultural debris or leaves. Biogenic sources include particles shed from the epicuticular waxes of vascular plants and from direct suspension of pollen, microorganisms (e.g., bacteria, fungi and fungal spores), and insects (Douglas and Eglinton, 1966; Hallgren and Larsson, 1963; Han and Calvin, 1969; Jackson and Blomquist, 1976; Nilsson et al., 1957; Oró et al., 1966; Simoneit, 1977; Simoneit and Eglinton, 1977; Tulloch, 1976; Weete, 1976). The relative distribution of n-alkanes between homologues of differing molecular weight provides some insight into the likely sources that contribute to an ambient sample. Normal alkanes of higher molecular weight originate from biosynthetic processes which produce homologues that range from C_{12} to C_{40} (Douglas and Eglinton, 1966; Matsumoto and Hanya, 1980; Simoneit, 1989). Biosynthetic n-alkanes exhibit a strong odd carbon number predominance (e.g., C_{29}, C_{31}, C_{33} n-alkanes are more abundant in plant waxes than the C_{28}, C_{30}, and C_{32} homologues). In plants, the most favored route for n-alkane formation is the elongation of C_{16} and C_{18} n-fatty acids, followed by decarboxylation reactions. The n-alkane distribution found in plant waxes shows C_{29} and C_{31} as dominant homologues which often contribute up to 90% of all paraffins found in plant waxes (Kolattukudy, 1970). The impact of mechanical forces such as the wind on biogenic materials is thought to be the principal mechanism for the input of fine plant wax particles into the atmosphere. Electron microscopic studies of leaf surfaces show that epicuticular waxes form a bloom on the surface consisting of wax protrusions that are characteristic of each plant species. The sizes of the wax protrusions range from submicron to micron dimensions and have various morphologies that are formed by different plant species (Hall and Donaldson, 1963; Kolattukudy, 1970). Hall and Donaldson (1963) conducted field experiments to determine epicuticular wax production and loss from leaves. They found in fields after strong winds (15 m sec^{-1} and more) that up to 50% of the leaf surface waxes were lost.

Defining the concentration ratio of odd to even numbered homologues as the Carbon Preference Index (**$\mathbf{CPI}_{odd}$**), organic matter of recent biogenic origin shows a preference for odd carbon numbered n-alkanes with CPI_{odd} values of 6–9 and more (Bray and Evans, 1961; Simoneit, 1978, 1989; Simoneit and Mazurek, 1982). During maturation of sedimentary organic material, the predominance of odd carbon alkanes is reduced drastically. Such fossil petroleum deposits show a CPI_{odd} value near unity and are accompanied by a shift of the most abundant n-alkanes to lower carbon numbers with the most abundant homologues (C_{Max}) in the range C_{22} to C_{25} (Bray and Evans, 1961; Cooper and Bray, 1963; Han and Calvin, 1969; Kvenvolden and Weiser, 1967; Matsuda and Koyama, 1977; Simoneit, 1978). As a result, the emissions from the utilization of fossil fuels exhibit CPI_{odd} values close to 1.0 (Bray and Evans, 1961; Garza and Muth, 1974; Hauser and Pattison, 1972; Jackson et al., 1975; Simoneit, 1984, 1986). When petroleum fuels are burned in internal combustion engines, the n-alkanes and fossil fuel biomarkers in vehicular exhaust condense onto the carbonaceous soot and are derived both from incomplete combustion of fuel and from engine lubricating oil (Simoneit, 1984, 1985). Hauser and Pattison (1972) determined the n-alkane distribution in ambient samples, motor oil, diesel fuel, gasoline, auto exhaust, and diesel soot. The mass median carbon number for n-alkanes was found to be shifted from $\leq C_{19}$ in both diesel and gasoline fuels to C_{24} for auto exhaust and diesel soot. The mass median n-alkane for motor oil was determined to be $\geq C_{26}$. Hence, partial combustion of motor oil may have contributed to the upward shift in the mass median carbon numbers of the n-alkanes in vehicle exhaust as compared to vehicle fuel (Cuthbertson and Shore, 1988; Zinbo et al., 1989).

Normal alkanes ranging from n-tricosane (C_{23}) to n-tetratriacontane (C_{34}) were found in the fine particle samples collected at the four urban sites studied here and also at the remote station at San Nicolas Island. The total n-alkane background concentrations at San Nicolas Island vary only slightly from the Jul. - Sep. composite sample to the Oct. - Dec. composite sample (1.3 ng m^{-3} versus 1.7

ng m^{-3}). The total n-alkane concentrations at the urban sites vary from location to location and between seasons as shown in Figure 2.3a. The highest total n-alkanes concentrations were measured at Downtown Los Angeles (most urbanized site) followed by West Los Angeles and Pasadena, reaching peak monthly average total n-alkane concentrations of 146 ng m^{-3} in winter (December, 1982). The lowest monthly average concentrations (20 ng m^{-3} to 40 ng m^{-3}) were found during the summer months (May through August 1982). As seen in Figure 2.4, the highest single n-alkane concentrations were found for n-pentacosane (C_{25}) and n-hentriacontane (C_{31}). The seasonal variations of the ambient concentrations of all n-alkanes at all urban sites are very similar with the highest concentrations for single homologues found in the wintertime. The same trend can be seen at Rubidoux (downwind and least urbanized site), except that the concentration of n-hentriacontane (C_{31}, which may be dominated by plant wax inputs) is higher in spring and summer than in winter. A strong odd carbon number predominance is seen in Figure 2.4 for the typical plant wax-derived higher n-alkanes (C_{29} – C_{33}), indicating a significant input of recent biogenic origin for this higher molecular weight range.

If the monthly ambient organic aerosol concentrations are divided by a tracer species whose concentration varies according to the atmospheric dilution potential, then the remaining seasonal variability in the organics concentration data reflects mainly changes in other processes such as source emission rates or atmospheric transformation rates. Elemental carbon appears to be the prime candidate for an atmospheric dilution tracer in Los Angeles. It is known that most of the elemental carbon in the Los Angeles atmosphere is emitted by diesel autos and trucks (and also by stationary and off-road diesel engines), which exhibit a

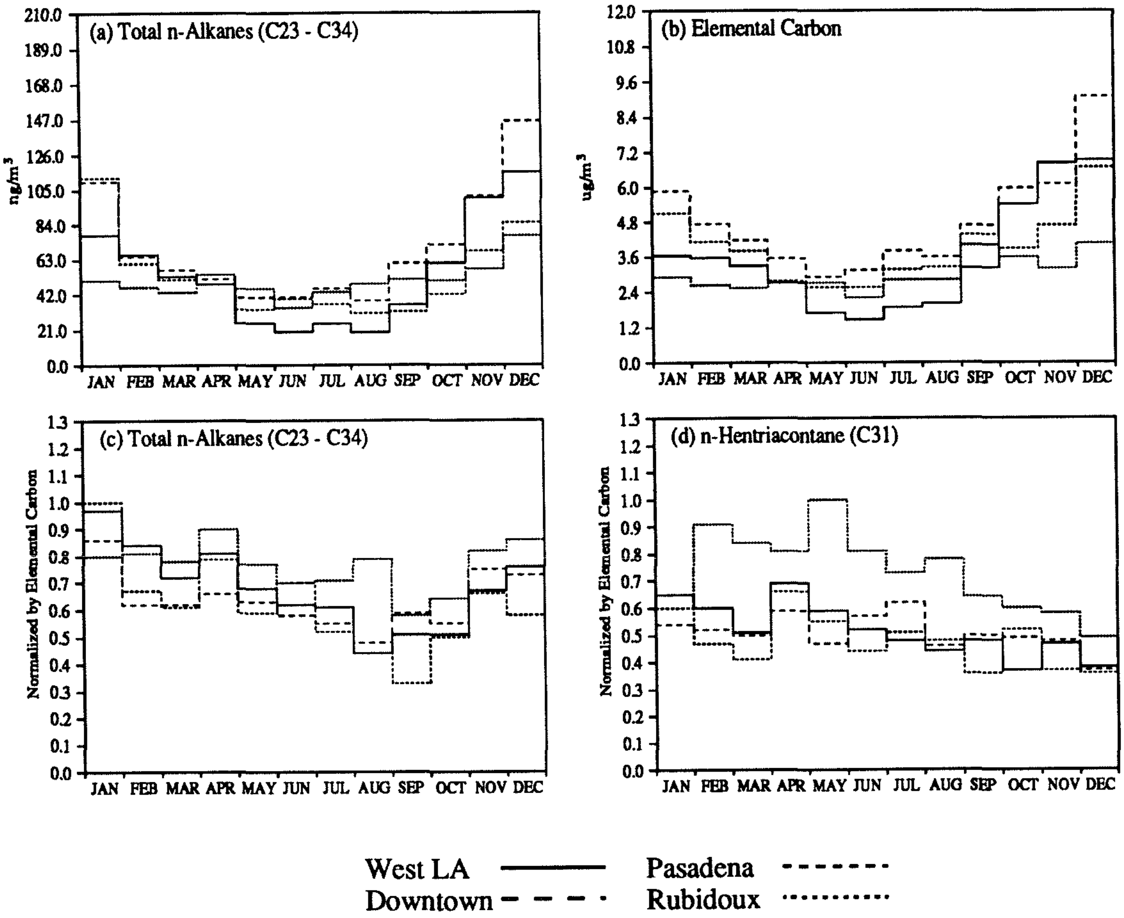

Fig. 2.3: Monthly averaged concentration profiles for (a) total n-alkanes (C_{23} - C_{34}) and (b) elemental carbon; monthly normalized concentration profiles for (c) total n-alkanes (C_{23} - C_{34}), and (d) n-hentriacontane (C_{31}).

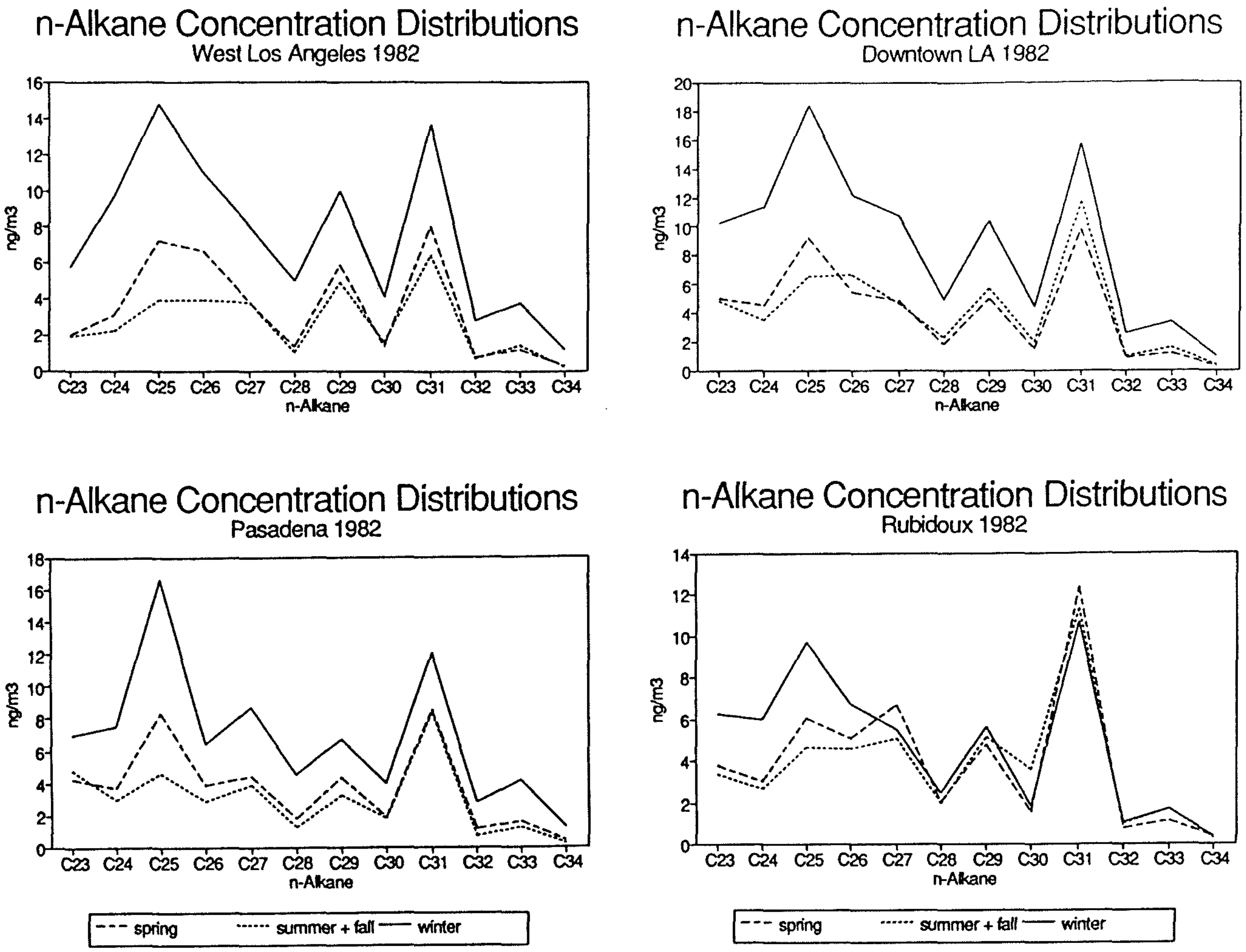

Figure 2.4: Seasonal n-alkane concentration distributions (spring: March - May; summer + fall: June - October; winter: November - February)—1982.

fairly constant emission pattern on a monthly basis throughout the year (Cass et al., 1982; Gray, 1986). Fine elemental carbon particles are chemically inert and are removed very slowly from the atmosphere, at rates comparable to the deposition rates for fine carbonaceous particles as a whole ($d_p \leq 2.1\mu m$).

For this reason, it is possible to use ambient fine elemental carbon particle concentrations to eliminate seasonal meteorological variabilities by dividing the time series of single compound monthly averaged concentrations by the monthly average elemental carbon concentration measured at the same site. To construct these normalized concentration profiles at a monitoring site, the time series of each of the monthly average organic compound concentrations is divided by the time series of monthly average elemental carbon concentrations at that site. As an aid to visualization and comparison, the time series of these non-dimensional normalized concentrations for each compound then are rescaled such that the highest value observed for that compound at any of the monitoring sites is set equal to unity.

Comparing the annual ambient mass concentration profiles for elemental carbon, a steadily emitted and inert primary anthropogenic pollutant, with the respective concentration profiles for total n-alkanes (Figure 2.3a vs. 2.3b) it becomes evident that there is close similarity in the pattern of the monthly averaged concentration changes. When the time series of the total n-alkanes data (C_{23} - C_{34}) is normalized by the time series of the elemental carbon concentrations, these dilution-corrected data suggest a more or less steady total n-alkanes emission rate over the whole year with slight minima in summer (Figure 2.3c). This trend is also seen for single n-alkanes, with the possible exception of n-C_{29} and n-C_{31} at Rubidoux (the least urbanized site) which shows higher dilution-normalized concentrations for these biogenically influenced alkanes in late spring and early summer (Figure 2.3d).

Alkanoic and Alkenoic Acids

Sources contributing saturated n-fatty acids to fine airborne particles are similar to the emission sources of n-alkanes discussed earlier. Anthropogenic sources include the combustion of fossil fuels, wood and organic detritus. Recently, it was shown that meat cooking contributes n-alkanoic acids to the ambient aerosol in Los Angeles (Rogge et al., 1991). The dominant n-alkanoic acids in meat smoke aerosol are C_{14}, C_{16}, and C_{18}, with highest emission rates for C_{16} and C_{18}. The release of n-alkanoic acids from fossil fuel combustion is another important source of the lower molecular weight n-fatty acids, with $C_{Max} = 16$ (Simoneit, 1985, 1986).

Potential biogenic emission sources of n-alkanoic acids are numerous and practically identical to the sources for n-alkanes. Epicuticular plant waxes, fungi, bacteria, spores (from fungi and bacteria), pollen, and algae are considered to be the main biogenic contributors (Brown et al., 1972; Ching and Ching, 1962; Jamieson and Reid, 1972; Kaneda, 1967; Kolattukudy, 1970; Laseter and Valle, 1971; Lechevalier, 1977; Matsumoto and Hanya, 1980; Morrison and Bick, 1967; Shaw, 1974; Simoneit, 1989; Simoneit et al., 1988). Even though the synthesis of n-fatty acids and n-alkanes in plant leaves proceeds via elongation and decarboxylation reactions involving C_{16} and C_{18} n-fatty acids, plant wax acids usually consist of much longer homologues (C_{20} to C_{32}; with strong even carbon number predominance) (Hall and Donaldson, 1963; Kolattukudy, 1970; Simoneit, 1989). Bacterial and some algal detritus mostly favor n-alkanoic acids $\leq$ n-C_{20} (Hitchcock and Nichols, 1971; Kaneda, 1967; Simoneit, 1989). Fungal spores contain n-fatty acids between C_{14} and C_{22} (Laseter and Valle, 1971).

Unsaturated n-fatty acids (alkenoic acids) are emitted to the atmosphere from microbial sources and from the processing, degradation, and combustion of plant and animal constituents. Rogge et al. (1991) showed that meat cooking is an important source of these n-alkenoic acids emissions, mainly for oleic ($C_{18:1}$) and palmitoleic ($C_{16:1}$) acid, and suggested that cooking with seed oils, margarine, or animal fat likewise releases such aerosols to the atmosphere. In contrast to the plant waxes, seeds (and seed oils, e.g., cooking oil), plant organelles, leaf cells, chloroplasts and pollen contain mainly n-C_{16}, n-C_{18}, monounsaturated ($C_{n:1}$), diunsaturated ($C_{n:2}$), and polyunsaturated fatty acids (Ching and Ching, 1962; Hitchcock and Nichols, 1971; Jamieson and Reid, 1972; Laseter and Valle, 1971). Phytoplankton and bacteria also contain a number of unsaturated fatty acids (Hitchcock and Nichols, 1971; Lechevalier, 1977; Shaw, 1974).

Once emitted into the atmosphere, unsaturated fatty acids are likely to be attacked by free radicals, ozone and other oxidants, producing aldehydes, carboxylic acids, and dicarboxylic acids. Kawamura and Gagosian (1987) and Kawamura and Kaplan (1987) proposed that oleic acid, Δ^9-$C_{18:1}$, undergoes photochemically-induced oxidation yielding ω-oxocarboxylic acids, aldehydes, carboxylic acids, and dicarboxylic acids with predominantly C_9 species. Experimental observations of the reaction of oleic acid as its methyl ester with ozone in the liquid phase have demonstrated that aldehydes, carboxylic acids and dicarboxylic acids form the final reaction products (Killops, 1986). The major reaction products were the C_9-aldehyde (nonanal), C_9-ester-aldehyde (9-oxononanoate), and C_9-acid (nonanoic acid), depending on the ozone concentrations used. The extent to which these results can be applied to the atmospheric aerosol is not yet clear. It is speculated that similar reaction pathways also occur in the atmosphere.

Normal alkanoic acids ranging from n-nonanoic acid (C_9) to n-triacontanoic acid (C_{30}) have been identified during the present study at the remote (San Nicolas Island) and urban sampling locations. At the background station on San Nicolas Island, the measured total n-alkanoic acid concentrations summed to 19.5 ng m^{-3} during summer versus 25.6 ng m^{-3} during the October - December time period. The urban total n-alkanoic acid concentrations during the summer season were as low as 150 ng m^{-3} (August, September), whereas during wintertime concentrations were more than tripled (550 ng m^{-3}). As shown in Figure 2.5a, the highest concentrations of single n-alkanoic acids for all sites and seasons were found for the C_{16} acid (100 - 250 ng m^{-3}), followed by C_{18} acid (30 - 100 ng m^{-3}). Both the C_{16} and C_{18} n-fatty acids show relatively constant concentrations throughout the year at the West LA, Downtown LA, and Pasadena sampling sites. Figure 2.5b shows a distinctly different annual concentration profile typical of the higher molecular weight n-alkanoic acids, with n-tetracosanoic acid (C_{24}) as an example, revealing very low summer concentrations with pronounced higher winter concentrations. Trace amounts of the methyl esters corresponding to these alkanoic acids were found in the underivatized atmospheric samples, and show essentially the same even/odd carbon number distribution as found for the derivatized samples.

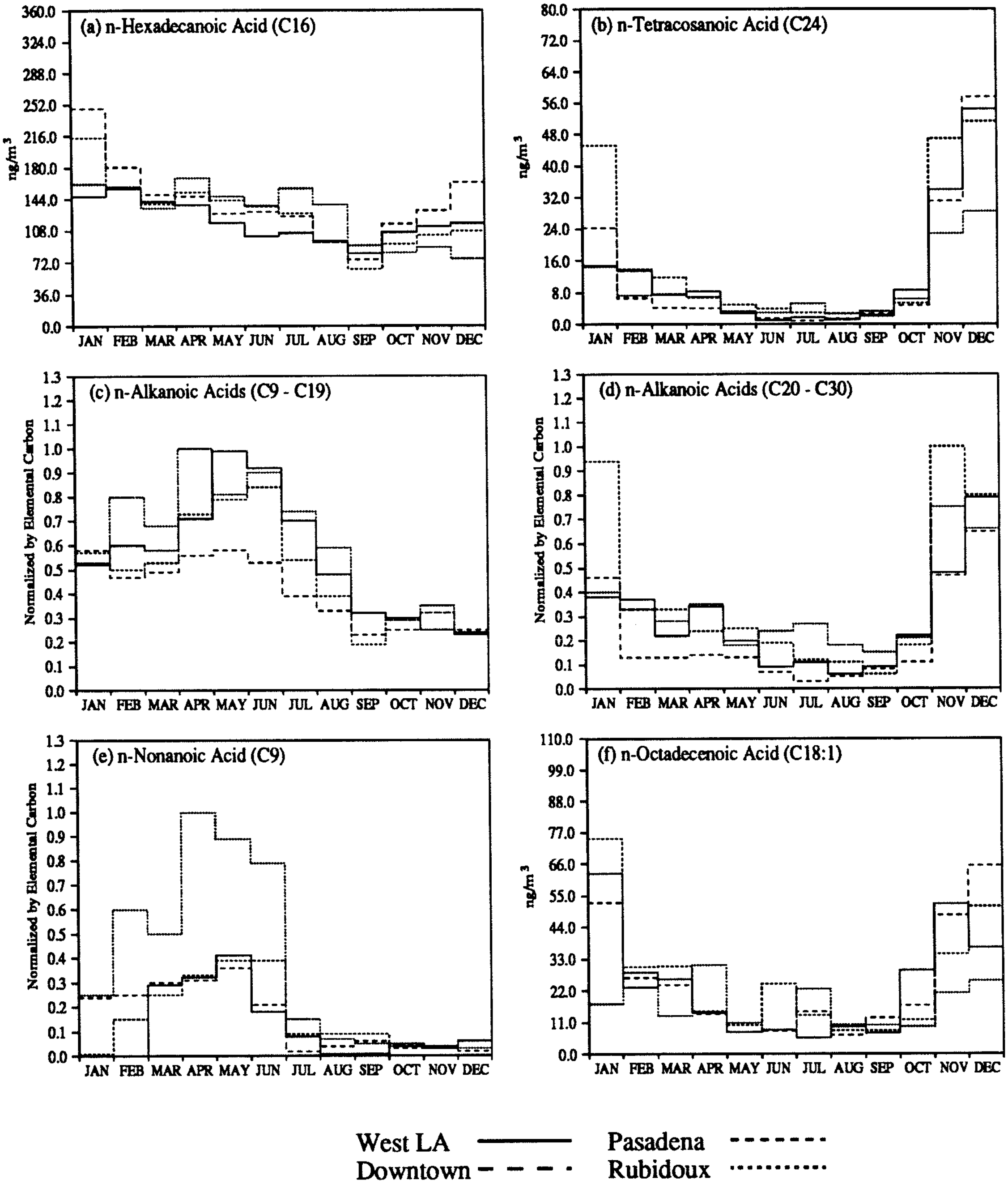

Fig. 2.5: Monthly averaged concentration profiles for a) n-hexadecanoic acid (C_{16}) and b) n-tetracosanoic acid (C_{24}); monthly normalized concentration profiles for c) n-alkanoic acids (C_9 - C_{19}), d) n-alkanoic acids (C_{20} - C_{30}), and e) n-nonanoic acid (C_9); monthly averaged concentration profile for f) n-octadecenoic acid ($C_{18:1}$). (Normalization was achieved by dividing the time series of monthly averaged compound concentrations by the time series of elemental carbon concentrations for each site followed by rescaling as explained in the text.)

By investigating the dilution-normalized ambient distribution pattern for each single n-alkanoic acid, it is seen that fatty acids fall into two groups. n-Alkanoic acids $< C_{20}$ show typical dilution-normalized maxima in spring and summer. In contrast, higher n-alkanoic acids $\geq C_{20}$ show increased dilution-normalized concentrations in winter. These results suggest enhanced emission rates for n-alkanoic acids $< C_{20}$ during spring and summer and enhanced emission rates for n-alkanoic acids $\geq C_{20}$ during the winter of that year (see Figures 2.5c-d). It is not clear at present whether the increased dilution-normalized concentrations of the lower molecular weight acids in spring and summer are due to (1) secondary formation by atmospheric reactions, or (2) increased bioactivity, or (3) emissions from unidentified anthropogenic sources that vary seasonally. Some of the n-alkanoic acids (especially C_9, C_{10}, C_{12}, and C_{14}) show enhanced dilution-normalized concentration patterns at Rubidoux (during spring and early summer) that are similar to those of the aliphatic dicarboxylic acids. These similarities in dilution-normalized concentrations at Rubidoux suggest that secondary formation of these lower n-alkanoic acids homologues by atmospheric reactions is plausible, particularly for n-nonanoic acid (C_9) which was discussed earlier as one of the likely major products in the ozone and $C_{18:1}$-fatty acid reaction system (Figure 2.5e).

Although a number of unsaturated fatty acids are known to be emitted into the atmosphere, only the dominant $C_{18:1}$ (oleic acid) has been identified to date in the fine particle samples analyzed during the present study. No palmitoleic acid (Δ^9-$C_{16:1}$) acid was identified. Because substantial emissions of palmitoleic acid to the atmosphere have been identified in smoke from meat cooking (Rogge et al., 1991), the non-detection of this unsaturated organic acid in the ambient samples studied here indicates that atmospheric chemical reactions are a likely sink for mono- and polyunsaturated fatty acids. Urban concentrations of oleic acid were highest in wintertime (nearly 80 ng m^{-3}), and were lowest during the summer season (6 ng m^{-3}), see Figure 2.5f. The winter maxima and extended summer minima in concentrations of oleic acid are more pronounced than is seen for elemental carbon, suggesting enhanced atmospheric oxidation of this unsaturated fatty acid during summer months.

Aliphatic Dicarboxylic and Aromatic Polycarboxylic Acids

Aliphatic dicarboxylic acids found in airborne fine carbon particles are an important compound class due to their possible formation by chemical reaction in the atmosphere (Grosjean, 1977; Grosjean and Seinfeld, 1989; Tao and McMurry, 1989). A number of smog chamber experiments have been conducted in the past to identify the gaseous precursor compounds, reaction mechanisms and rates for reactions that lead to linear, branched, and substituted dicarboxylic acids (Grosjean, 1977; Grosjean and Friedlander, 1980; Hatakeyama et al., 1985, 1987).

The direct emission of aliphatic dicarboxylic acids from aerosol sources has not been investigated heavily in the past. Dicarboxylic acids ranging from C_2–C_{10} have been identified in gasoline and diesel engine exhaust (Kawamura and Kaplan, 1987). The highest emission rates of particle phase dicarboxylic acids ($\geq C_3$) originating from gasoline combustion engines were found for methylmaleic acid (2-methyl-2-Z-butenedioic acid), followed by succinic acid (butanedioic acid) and maleic acid (2-Z-butenedioic acid). For diesel exhaust, the highest particle phase emissions were found for maleic acid, methylmaleic acid, and succinic acid. Meat cooking has proven to be an emission source of C_4–C_8 dicarboxylic acids to the atmosphere, with the highest emission rates for hexanedioic acid (adipic acid) (Rogge et al., 1991). Pyrolysis of plants, trees, and organic soil constituents can result in a large number of organic compounds in airborne ash including aliphatic dicarboxylic acids ranging from C_4 to C_9 (Pereira et al., 1982). Higher molecular weight α,ω-dicarboxylic acids (C_{10}–C_{24}) have been reported present in rural aerosol particles and their source may be oxidation products of ω-hydroxy acids from vegetation (Simoneit and Mazurek, 1982).

Aromatic polycarboxylic acids are comprised of the benzoic acid type and also similar compounds that have additional substituents on the aromatic ring system which include methyl, hydroxy, methoxy, and/or carboxyl groups. Hydroxy-substituted benzoic acids and aromatic di- and tricarboxylic acids have been reported in airborne particulate matter (Cautreels and Van Cauwenberghe, 1976; Matsumoto and Hanya, 1980; Satsumabayashi et al., 1989; Wauters et al., 1979; Yokouchi and Ambe, 1986) and also in the rainwater of urbanized areas (Kawamura and Kaplan, 1983; Simoneit and Mazurek, 1989). Mono- and polyhydroxysubstituted benzoic acids (phenolic and polyphenolic acids) are believed to be mainly of biogenic origin, such as from vascular plants, pollen, fungi, and bacteria (El-Basyouni et al., 1964; Hillis and Inoue, 1968; Ratledge, 1964; Smith, 1955; Strohl and Seikel, 1965).

Simoneit (1985) identified phthalic acids in particulate automobile exhaust emissions. Kawamura and Kaplan (1987) reported the presence of phthalic and methylphthalic acids in particulate samples taken from a gasoline and a diesel powered automobile exhaust system, from the air inside a greenhouse and from soil samples. Phthalic acids have been isolated in particulate emissions from tobacco smoke (Graham, 1973; Johnstone and Plimmer, 1959). Another possible source of phthalic acids to the urban atmosphere is the industrial production of phthalate esters (ester group is $R = (CH_2)_n–CH_3$, where n =1 to 7), which are used as plasticizers in the manufacture of plastics (about 500,000 kg of phthalate esters were manufactured in 1972 in the USA (Graham, 1973)). An additional route for the formation of phthalic acids and their introduction into the urban atmosphere may involve the aging of plastic materials in the environment where the ester groups are hydrolyzed to form the parent phthalic acids (Allara, 1975).

Phthalic acid and related compounds also could be produced by atmospheric chemical reactions involving directly emitted PAH. Grosjean et al. (1987) conducted several experiments to identify the mechanism for the reaction of ozone with the colorants alizarin and alizarin crimson (calcium-aluminum lake of alizarin). The most prominent degradation product of these anthraquinone derived compounds was found to be phthalic acid. Moriconi and coworkers (1961, 1963) investigated reactions of benzo[a]pyrene and of 3-methylcholanthrene with ozone in CH_2Cl_2 and CH_2Cl_2-MeOH. They concluded that the test PAH were converted via polycyclic aromatic quinones (PAQ) into polycarboxylic aromatic acids (ring-opening products), including aromatic di-, tri-, and tetracarboxylic acids. Thus it may be possible that ambient reactions involving ozone and PAH could lead via PAQ as intermediates, to polycarboxylic aromatic acids as the major degradation products.

Up to the present time, only Wauters et al. (1979) have reported the presence of benzenetricarboxylic acids in airborne particulate matter. There exists no

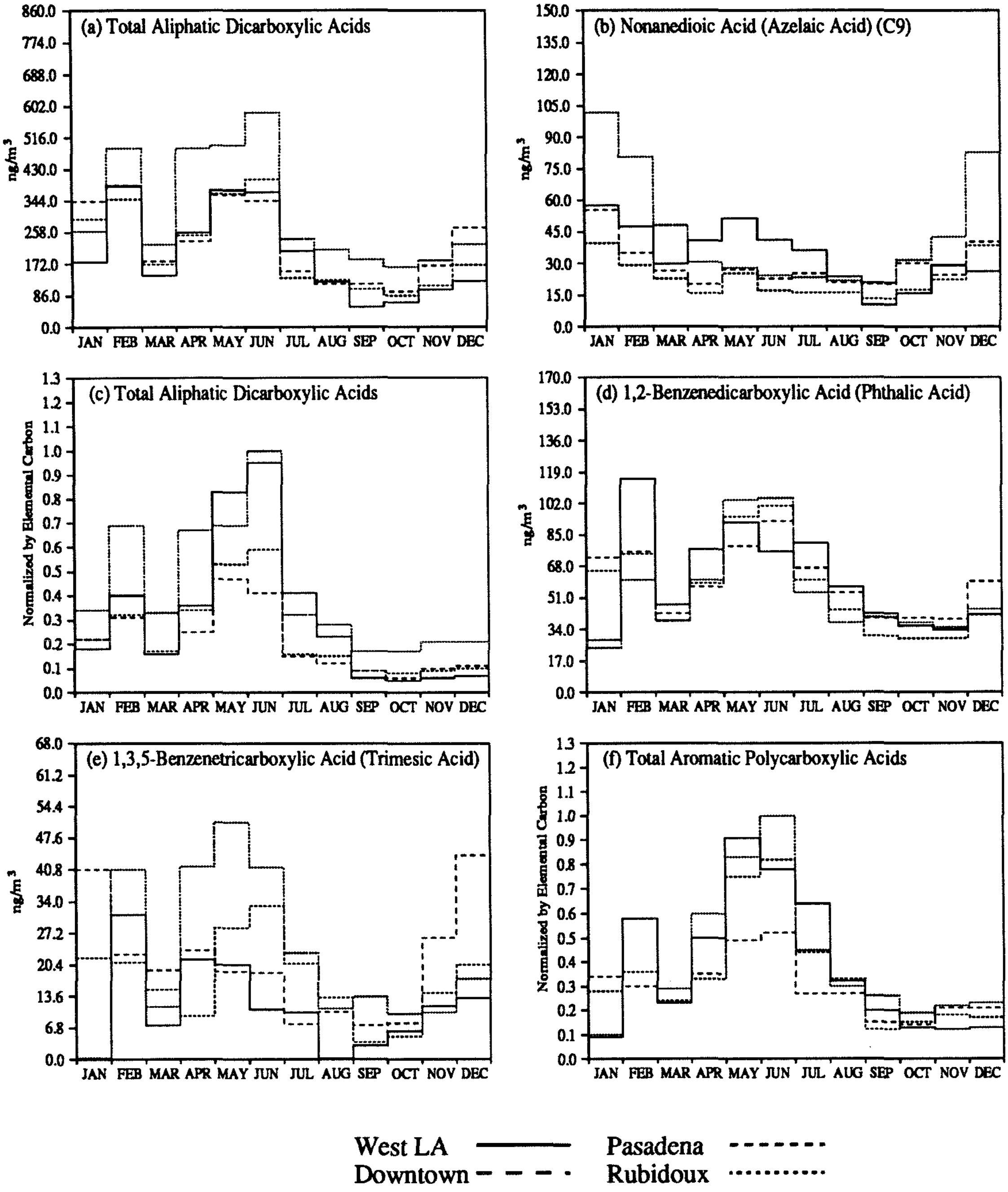

Fig. 2.6: Monthly averaged concentration profiles for a) total aliphatic dicarboxylic acids and b) nonanedioic acid (azelaic acid); monthly normalized concentration profile for c) total aliphatic dicarboxylic acids; monthly averaged concentration profiles for d) 1,2-benzenedicarboxylic acid (phthalic acid) and e) 1,3,5-benzenetricarboxylic acid (trimesic acid); monthly normalized concentration profile for f) total aromatic polycarboxylic acids. (Normalization was achieved as described in Figure 2.5.).

current evidence that benzenetri- or benzenetetracarboxylic acids are emitted from primary anthropogenic or biogenic activities.

The major aliphatic dicarboxylic acids identified in fine carbon particles in the present study range from C_3-C_9, including branched and substituted dicarboxylic acids (see Table 2.1). The highest dicarboxylic acid concentrations are found for succinic acid (C_4), followed by malonic (C_3) and glutaric acid (C_5). The monthly averaged concentration profiles for C_3–C_6 dicarboxylic acids generally reveal more or less the same pattern: high ambient concentrations from April until August and often also for February 1982 (see Figure 2.6a). This contrasts with the concentration profiles for n-alkanes and higher n-alkanoic acids, which peak during the winter months as seen in Figures 2.3a, 2.5b and 2.5d. Azelaic acid (C_9) shows a different seasonal distribution pattern with low summer and higher winter concentrations, except for West Los Angeles, which shows a second concentration peak in the late spring and early summer (Figure 2.6b). The highest total dicarboxylic acid concentration was found at the site farthest downwind (Rubidoux) with 580 ng m^{-3} in June. The lowest total concentration among the urban sites studied was found at the furthest upwind site (West Los Angeles) during the month of September with 63.5 ng m^{-3} (Figure 2.6a). Normalization relative to elemental carbon concentrations further emphasizes the mid-year enrichment in dicarboxylic acid concentrations (Figure 2.6c). This seasonal enrichment is consistent with the behavior expected if significant quantities of dicarboxylic acids are produced by atmospheric photochemical reactions.

Eight aromatic di-, tri- and tetracarboxylic acids were identified in the ambient fine particulate matter samples collected at the four urban sites in the Los Angeles area (Table 2.1). None of the aromatic polycarboxylic acids mentioned here could be found at the remote station on San Nicolas Island. The major aromatic acid identified in airborne fine particles was phthalic acid with monthly averaged ambient concentrations of up to 120 ng m^{-3} (Figure 2.6d), followed by trimesic acid (1,3,5-benzenetricarboxylic acid) (Figure 2.6e) and 4-methylphthalic acid, each showing monthly averaged ambient concentrations of up to about 50 ng m^{-3} during summertime. All aromatic acids except isophthalic acid (1,3-benzenedicarboxylic acid) and terephthalic acid (1,4-benzenedicarboxylic acid) show highest concentrations from May to July and also for February 1982. The ambient concentration profiles and dilution-normalized concentration profiles for the aromatic polyacids (see Figures 2.6d-f) closely resemble the total aliphatic dicarboxylic acid concentration profiles (Figures 2.6a,c), indicating that aromatic di-, tri-, and tetracarboxylic acids may well be the products of atmospheric chemical reactions.

Alkanals

Nonanal was recently identified in fine particulate matter emitted from meat cooking operations (Rogge et al., 1991). Oleic and palmitoleic acids are the most common unsaturated fatty acids in animal and vegetable oils and also in meat fat, each having a Δ^9-double bond (Baines and Mlotkiewicz, 1983; Lovern, 1965; Rogge et al., 1991). Table 2.1 shows that oleic acid is present in the Los Angeles area atmosphere at substantial concentrations. Oxidation reactions in the atmosphere involving oleic acid may produce nonanal as a product. So far, this study has identified only one $\underline{n}$-alkanal, nonanal, in the ambient samples. The measured monthly average ambient concentrations of nonanal never exceeded 20 ng m^{-3} during the sampling year 1982. In wintertime, the concentration distributions are very similar for all urban sampling sites, while in summer, two distinct groups of sampling sites emerge: West LA and Downtown LA show slightly enhanced concentrations during spring and early summer; in contrast, Pasadena and Rubidoux show much higher ambient concentrations during spring and the entire summer. Normalization of the ambient nonanal concentrations relative to elemental carbon concentrations shows a pattern similar to that of the secondary aliphatic dicarboxylic acids (see Figure 2.7a).

Polycyclic Aromatic Hydrocarbons, Ketones and Quinones

Due to their mutagenic and carcinogenic potential, polycyclic aromatic hydrocarbons (PAH) have been extensively investigated in the past. These compounds are considered to be the pyrolysis products of incomplete combustion of organic matter (Alsberg et al., 1985; Grimmer et al., 1983; Tong and Karasek, 1984). Produced during combustion processes, PAH are introduced into the atmosphere in the fine particle mode ($d_p \leq 2.5\mu m$) and are attached to fine carbon

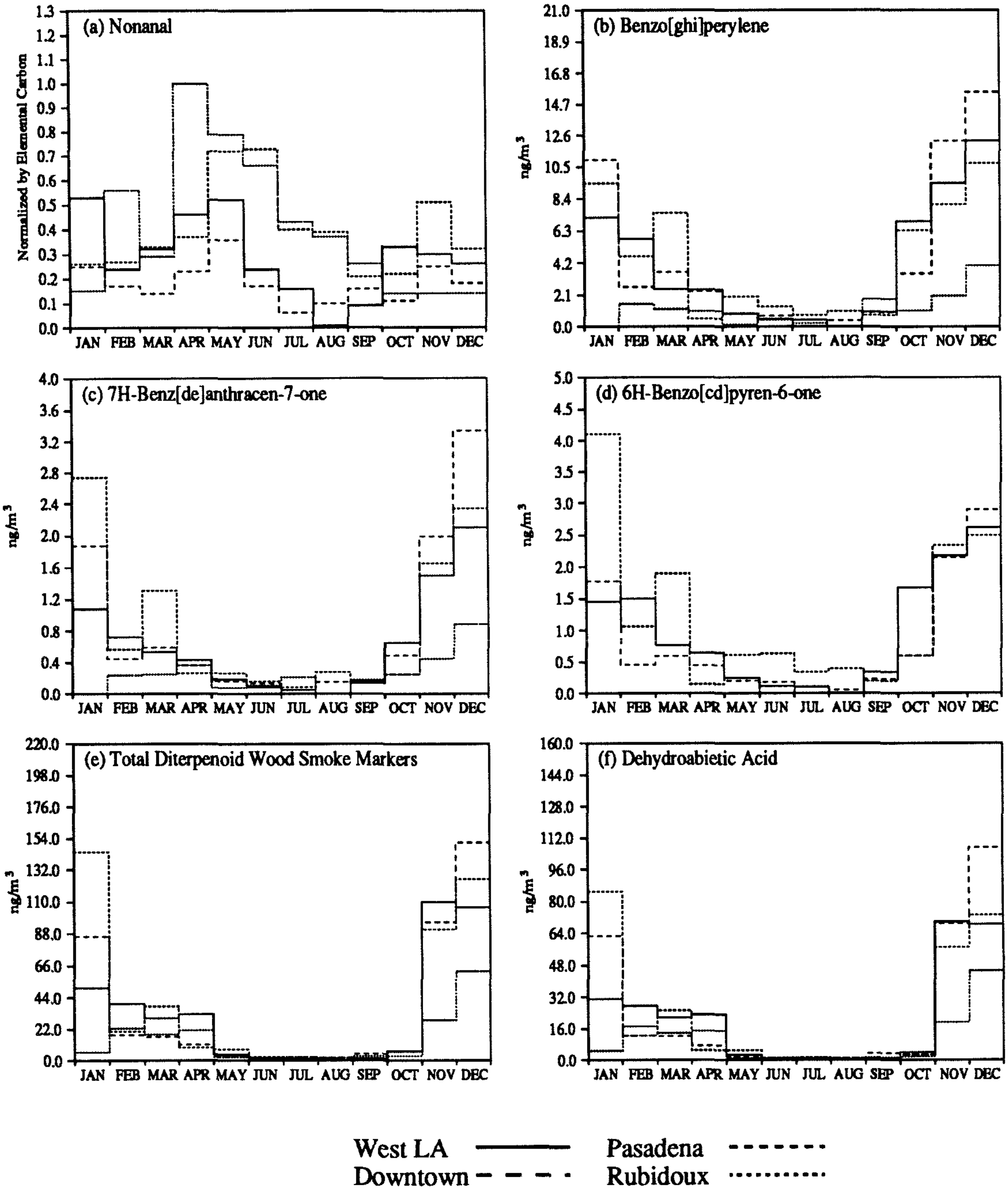

Fig. 2.7: Monthly normalized concentration profile for a) nonanal; monthly averaged concentration profiles for b) benzo[ghi]perylene, c) 7H-benz[de]anthracen-7-one, d) 6H-benzo[cd]pyrene-6-one, e) total diterpenoid wood smoke markers, and f) dehydroabietic acid. (Normalization was achieved by dividing the time series of monthly averaged compound concentrations by the time series of elemental carbon concentrations for each site followed by rescaling as explained in the text.)

particles (Daisey et al., 1986; Leuenberger et al., 1988; Miguel and Friedlander, 1978). When exposed to O_3, NO_2, N_2O_5, and other oxidants, PAH react in the atmosphere slowly, yielding oxygenated polycyclic aromatic hydrocarbons, nitro-PAH (Brorström et al., 1983; Kamens et al., 1990; Nielson, 1988; Pitts et al., 1978, 1985) and possibly aromatic polycarboxylic acids. Further, the interaction of PAH with UV solar radiation or O_3 has been found to yield polycyclic aromatic ketones (PAK) and polycyclic aromatic quinones (PAQ) during photooxidation experiments (Kahn et al., 1967; Kummler et al., 1969; Lane and Katz, 1977; Pitts et al., 1969, 1980; Van Cauwenberghe, 1983).

Directly emitted PAK are considered to be the transformation products of PAH containing a single-bonded carbon atom (methylene PAH) which become oxidized immediately after being transported out of the reductive combustion zone (Ramdahl, 1983a; Van Cauwenberghe, 1983). PAK have been identified in the particulate emissions coming from gasoline and diesel engines (Alsberg et al., 1985; Behymer and Hites, 1984; Choudhury, 1982; Jensen and Hites, 1983; Newton et al., 1982; Schuetzle, 1983; Yu and Hites, 1981) and in emissions from the burning of biomass, such as wood, leaves, cereal straw, etc. (Alsberg and Stenberg, 1979; Ramdahl, 1983a; Ramdahl and Becher, 1982; Sawicki et al., 1965).

Fifteen PAH have been quantified in the fine particle samples studied here, see Table 2.1. The seasonal concentration patterns for all PAH are very similar, with high winter and low summer concentrations. The highest monthly concentrations usually were found for benzo[ghi]perylene (nearly 20 ng m^{-3}), followed by coronene (close to 10 ng m^{-3}). Figure 2.7b shows as an example the annual concentration distribution pattern for benzo[ghi]perylene. Monthly averaged total PAH concentrations in fine particles of up to 40 ng m^{-3} and more were measured during wintertime. It is worth mentioning that the very low summer PAH concentrations not only reflect the increased atmospheric dilution, but probably also the increased degradation rate of PAH as a result of the more active photochemistry prevailing during the summer months and/or lack of winter-specific combustion sources such as wood combustion.

The oxy-PAH identified and quantified in the present study are: 7H-benz-

[de]anthracen-7-one (benzanthrone) (Figure 2.7c), 6H-benzo[cd]pyren-6-one (Figure 2.7d), and benz[a]anthracen-7,12-dione (1,2-benzanthraquinone). All three compounds have been identified as major oxy-PAH in ambient air and combustion sources (e.g., Cautreels and Van Cauwenberghe, 1976; Choudhury, 1982; König et al., 1983; Ramdahl, 1983b). They exhibit enhanced winter and reduced summer concentrations, ranging from about 0.1 ng m^{-3} to more than 4.0 ng m^{-3} depending on the sampling site and the compound considered.

Diterpenoid Acids and Retene

The combustion of wood and ligneous products is considered to be the most relevant input mechanism for resinous organic compounds into the fine mode of suspended airborne particles. Compounds such as diterpenoids, phenols, PAH, and many other natural and thermally-modified natural compounds have been identified in wood smoke aerosol (Hawthorne et al., 1988; Ramdahl, 1983a, 1983b; Ramdahl and Becher, 1982; Simoneit and Mazurek, 1982; Standley and Simoneit, 1987, 1990). Useful tracer compounds identified previously in ambient fine carbonaceous particles originating from resinous wood combustion are dehydroabietic, isopimaric, and pimaric acids, plus retene. In cities where 50% or more of all households use wood for space heating, ambient dehydroabietic acid concentrations were found to range from 48 ng m^{-3} to 440 ng m^{-3} (Standley and Simoneit, 1990) and retene concentrations from 6 to 8 ng m^{-3} (Ramdahl, 1983b). Hildemann et al. (1991a) have shown that woodsmoke is the third largest contributor to the fine primary organic aerosol emission inventory in the Los Angeles area atmosphere. Thus measurable quantities of woodsmoke markers should be found in the present aerosol samples.

The annual concentration pattern for wood smoke markers (7 identified diterpenoid acids and retene) is shown in Figure 2.7e. Concentration changes closely follow the heating season, with highest concentrations during January, November, and December. For example, in winter, dehydroabietic acid concentrations reach 60 - 110 ng m^{-3}, while from February until April the dehydroabietic acid concentrations decline abruptly to about 28 ng m^{-3} (Figure 2.7f). During the summer, the ambient concentrations were typically 1 ng m^{-3} and lower, indicating only minor emissions due to wood combustion. Retene shows a maximum concentration of only 0.55 ng m^{-3} during the heating season. None of the wood smoke compounds could be detected at San Nicolas Island.

Steroids

Recently, it has been suggested that cholesterol can be used as a tracer for the presence of aerosols derived from meat cooking operations in the urban atmosphere (Rogge et al., 1991). Therefore, it is useful to measure ambient cholesterol concentrations. Annual average cholesterol levels measured in the present study range from 2.7 ng m^{-3} to 1.9 ng m^{-3} at West Los Angeles and Pasadena, respectively, while cholesterol concentrations are below their detection limit at central Los Angeles (an industrial neighborhood) and at Rubidoux. The highest monthly average ambient cholesterol concentration was found at West LA during October 1982 reaching 14.6 ng m^{-3}.

Spatial and Seasonal Distribution of Fine Particle Organic Compounds

It is possible to examine differences in the magnitude and spatial distribution of the various major compound classes along an east–west transect across Southern California using the measured organic aerosol compound concentrations. From late spring throughout summer when photochemical processes are at their peak, a sea breeze prevails from west to east. Under such meteorological conditions, aliphatic dicarboxylic acids are the most abundant species, and their concentrations are highest at Rubidoux, downwind of the city (Figure 2.8a). In winter, when the onshore flow is reduced or reversed, the concentrations of many of the primary components are increased and peak over the center of the city where the major sources are located (Figure 2.8b). The increase in $\underline{n}$-alkanoic acid concentrations in winter is dominated by the higher carbon number homologues (C_{20} – C_{30}). The higher molecular weight $\underline{n}$-alkanoic acid (C_{20} – C_{30}) concentrations increase over the center of the city by more than 10-fold in wintertime compared to the summer season (see also Figure 2.5b), a relative increase that is much more pronounced than the seasonal change in elemental carbon concentrations. Thus this increase in ambient concentrations reflects additional emissions of higher molecular weight $\underline{n}$-alkanoic acids (C_{20} – C_{30}) during the winter season.

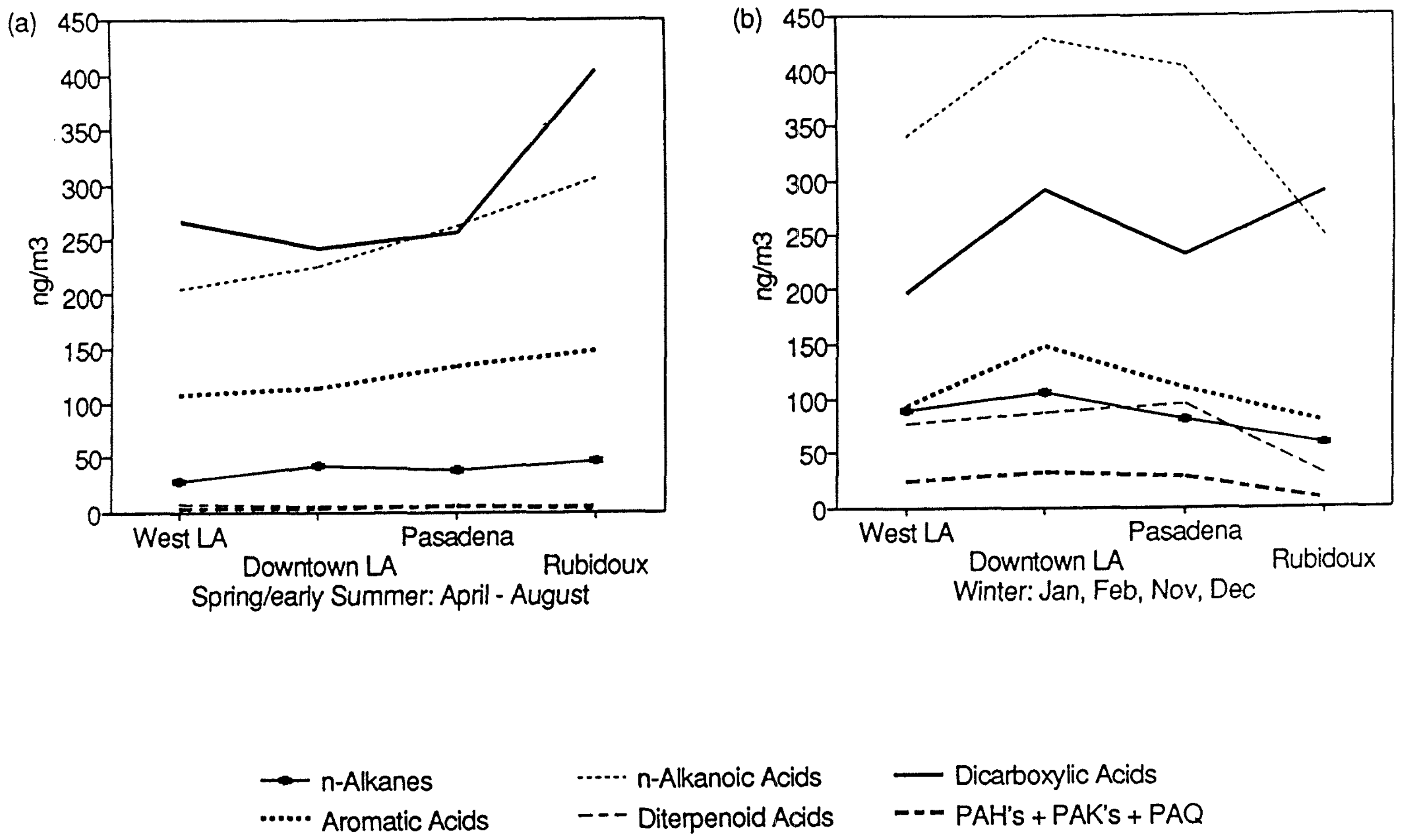

Figure 2.8: Seasonal and spatial concentration patterns of fine particle associated organic compounds for a) April through August and b) January, February, November and December—1982.

Similarities in Ambient Concentration Patterns

Hierarchical cluster analysis was employed to quantitatively evaluate the degree of similarity or difference between the seasonal ambient concentration patterns of the organic compounds identified. To provide a reference for the proximity of each compound group to the behavior of a directly emitted inert aerosol species with a nearly constant emission rate, elemental carbon concentrations were included in the analysis. Because the n-alkanoic acids fall naturally into two distinct groups (C_9 - C_{19} and C_{20} - C_{30}), these two groups were considered separately.

After normalizing all data so that the highest monthly average concentration found within each single compound class has a value of unity at each site, the CLUSTER-routine included in the statistical software package SPSS-X was used to calculate the degree of similarity between the seasonal patterns for each of the compound classes. The squared Euclidean distances between the compound classes in the 12-dimensional space defined by the pattern of concentration values over the months of the year were employed as the measure of proximity. The cluster agglomerative process can be described as follows: the squared Euclidean distances between the single classes in the 12-dimensional space first are calculated, and then the two nearest compound classes in that space are grouped together. The next step is the recomputation of the proximities for the reduced sample set. Again the two closest compound classes are combined according to the average linkage between groups method (Norusis, 1985). This reduction process is continued until all samples are combined into one cluster. An example of the resulting cluster hierarchy formed from the ambient data at Rubidoux is shown in Figure 2.9.

The cluster analysis shows that three subclusters are formed for each sampling site. The first subcluster includes PAH, PAK and PAQ, together with diterpenoid wood smoke markers and higher n-alkanoic acids (n-C_{20} - n-C_{30}). Two explanations are possible for this first cluster grouping. First, some polycyclic aromatic hydrocarbons and also in part higher n-alkanoic acids are released in connection with wood burning (Ramdahl, 1983a, b; Ramdahl and Becher, 1982). Hence, their association with the diterpenoid wood smoke markers is plausible.

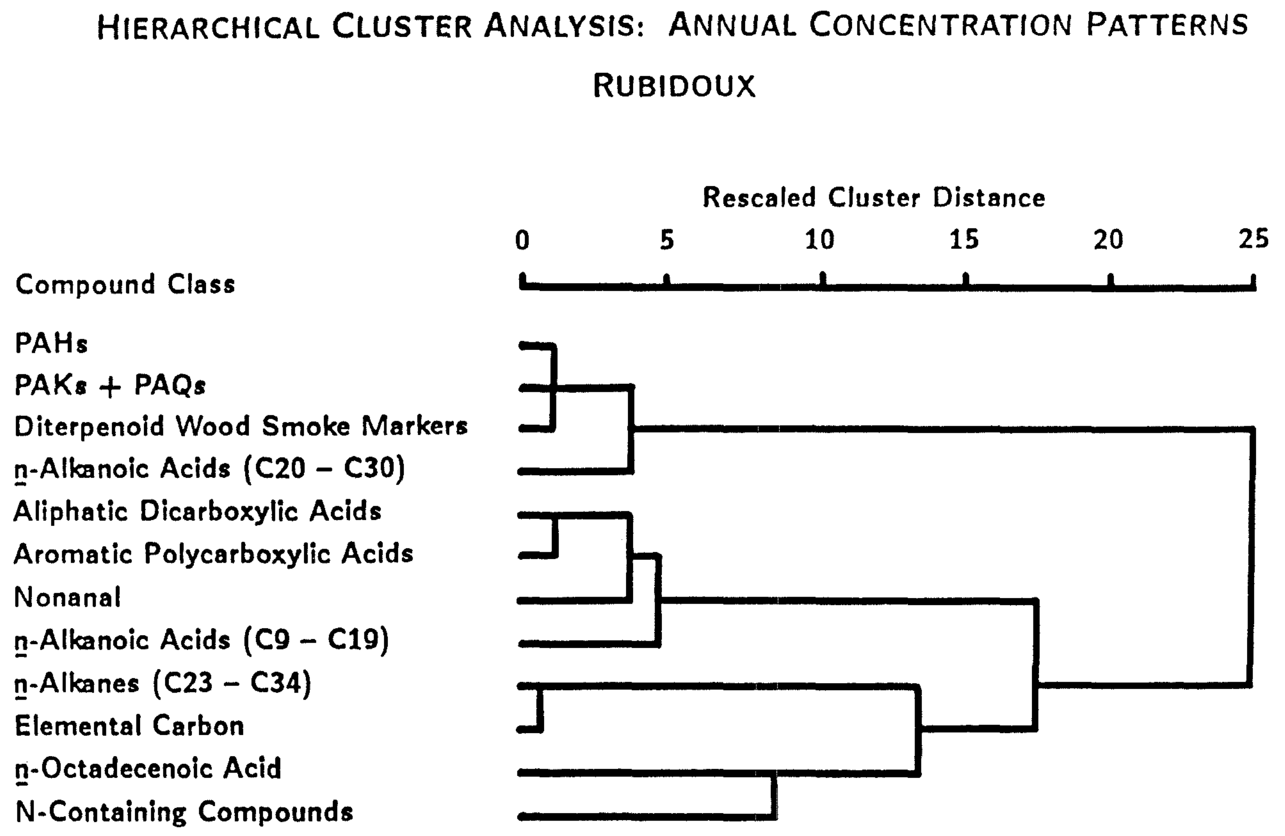

Figure 2.9: Hierarchical cluster analysis to determine similarities in the seasonal variations of monthly average concentrations measured at Rubidoux.

Second, all compound classes of this cluster are subject to depletion in the summer months. Diterpenoid wood smoke markers show very low concentrations during the summer season because wood simply is not burned in a significant quantity in Los Angeles during the summer (Gray, 1986). PAH show the same low summer concentration distributions, in part, because they are more susceptible to photochemical attack during the summer smog season.

The second subcluster consists of elemental carbon and the n-alkanes and occurs at all sites except Pasadena. The elemental carbon acts as an indicator for direct unaltered primary emissions from sources with little seasonal variation in emissions, and the n-alkanes are relatively unreactive compounds that are known to be directly emitted.

The third subcluster contains aliphatic dicarboxylic acids and aromatic polycarboxylic acids, which are due at least in part to secondary aerosol formation and/or transformation in the urban atmosphere. It is worth mentioning that the lower n-alkanoic acids (C_9 - C_{19}) group in reasonable proximity to the subcluster that contains the aliphatic dicarboxylic and aromatic polycarboxylic acids.

Conclusions

The concentrations and seasonal variations of more than 80 organic compounds present in airborne fine particles in the Southern California atmosphere have been determined via HRGC and GC/MS techniques. Material balances constructed for the fine aerosol as a whole show that 22 to 43% of that aerosol is carbonaceous, and that about one third of the carbonaceous matter consists of elemental carbon while approximately two thirds is composed of organic compounds. Of those organics, 40 to 61% are extractable and elute under the GC conditions used here. Resolved compounds comprise 23 to 29% of the elutable organics mass. Single compounds identified in the present study account for 74 to 81% of the resolved organic mass. Normal alkanoic acids, aliphatic dicarboxylic acids, and aromatic polycarboxylic acids are the major constituents of the resolved organic aerosol mass (250 to 300 ng m^{-3}; 200 to 300 ng m^{-3}, and circa 100 ng m^{-3} annual average, respectively). Smaller quantities of n-alkanes, n-alkenoic acids, alkanals, wood smoke markers, PAH, PAK, PAQ, and

N-containing compounds are identified and quantified.

Direct emissions of organic aerosol from sources leads to primary aerosol components that show low summer and high winter concentrations, and resemble closely the annual concentration profiles for inert elemental carbon. Elemental carbon in Los Angeles is emitted throughout the year with nearly a constant emission rate; thus, the variation in primary organic ambient concentration is governed mainly by seasonal variations in atmospheric dilution. n-Alkanes, higher molecular weight n-alkanoic acids (C_{20} - C_{30}), PAH, and diterpenoid acids show a similar seasonal pattern which is characteristic of primary anthropogenic or biogenic emissions. The higher molecular weight n-alkanes (C_{28} - C_{34}) show a strong odd carbon number predominance, indicating recent biogenic emissions into the atmosphere. Diterpenoid wood smoke markers follow closely the seasonal use of wood for space heating, suggesting that they are suitable markers for wood burning contributions to the airborne particulate pollutant complex.

Organic aerosol compounds that are formed at least in part by atmospheric chemical reactions show higher concentrations in late spring and early summer, and these concentrations are highest at Rubidoux which is downwind of metropolitan Los Angeles. Aliphatic dicarboxylic acids, aromatic polycarboxylic acids, and certain of the lower molecular weight n-alkanoic acids, and nonanal (to some extent) show this type of behavior which is evident especially once the ambient concentration data have been corrected to remove the effects of atmospheric dilution. Not all organic compounds revealing higher concentrations in late spring and early summer are of secondary origin. For example, hexadecanoic (C_{16}) and octadecanoic (C_{18}) acid, the greatest contributors to the ambient fatty acid concentrations, have numerous biogenic and anthropogenically modified biogenic sources (e.g., food preparation including meat cooking and the use of seed oils for cooking, plant material, etc.).

When combined with source test data taken by comparable methods, the ambient data set described here can be used to study source contributions to the ambient organic aerosol via molecular marker or air quality modeling techniques.

Table 2.1 Ambient Annual Average Concentrations for Fine Particle Organic Compounds found at West Los Angeles, Downtown Los Angeles, Pasadena, Riverside, and San Nicolas Island for the Year 1982.

Part A

Compound Name	West LA	Downtown LA	Pasadena	Rubidoux	San Nicolas Island[a] (Jul. - Dec.)	Compound Identification[b] a = positive b = probable c = possible d = tentative
	Concentrations in ng m^{-3}					
n-Alkanes						
n-Tricosane	3.2	6.7	5.4	4.5	0.09	a
n-Tetracosane	5.0	6.4	4.7	3.9	0.23	a
n-Pentacosane	8.4	11.2	9.5	6.7	0.25	a
n-Hexacosane	7.0	8.2	4.3	5.4	0.15	a
n-Heptacosane	5.2	6.7	5.6	5.6	0.06	a
n-Octacosane	2.5	3.1	2.5	2.1	0.18	a
n-Nonacosane	6.8	7.1	4.7	5.2	0.26	a
n-Triacontane	2.4	2.7	2.5	2.5	0.22	a
n-Hentriacontane	9.3	12.6	9.6	11.4	0.10	a
n-Dotriacontane	1.5	1.5	1.5	1.0	< 0.03	a
n-Tritriacontane	2.2	2.1	2.3	1.5	< 0.03	a
n-Tetratriacontane	0.59	0.58	0.68	0.36	< 0.03	a
n-Alkanes (C23 - C34)	54.09	68.88	53.28	50.16		
n-Alkanoic Acids						
n-Nonanoic Acid	3.3	6.6	5.3	9.9	0.24	a
n-Decanoic Acid	1.3	2.0	2.4	3.1	< 0.02	a
n-Undecanoic Acid	3.8	2.8	6.0	2.8	0.18	a
n-Dodecanoic Acid	3.7	5.3	7.0	6.3	0.19	a
n-Tridecanoic Acid	3.3	4.3	4.9	3.9	0.13	a
n-Tetradecanoic Acid	14.4	19.7	22.2	22.8	2.73	a
n-Pentadecanoic Acid	4.3	5.3	6.1	5.1	0.67	a
n-Hexadecanoic Acid (Palmitic Acid)	118.3	140.5	127.4	128.1	14.0	a
n-Heptadecanoic Acid	3.4	4.7	5.2	4.0	0.34	a
n-Octadecanoic Acid (Stearic Acid)	57.7	59.2	50.0	41.1	2.46	a
n-Nonadecanoic Acid	0.79	1.1	1.1	0.95	0.07	a
n-Eicosanoic Acid	4.3	5.1	6.1	3.1	0.20	a

Table 2.1 (continued)

Part B

Compound Name	West LA	Downtown LA	Pasadena	Rubidoux	San Nicolas Island[a] (Jul. - Dec.)	Compound Identification[b] a = positive b = probable c = possible d = tentative
	Concentrations in ng m^{-3}					
n-Heneicosanoic Acid	1.7	2.1	2.3	1.4	0.08	a
n-Docosanoic Acid	7.5	8.7	9.9	5.7	0.39	a
n-Tricosanoic Acid	2.0	2.0	2.5	1.5	0.10	a
n-Tetracosanoic Acid	12.5	11.8	16.5	9.2	0.53	a
n-Pentacosanoic Acid	1.4	1.3	1.6	1.1	0.07	a
n-Hexacosanoic Acid	7.1	5.6	9.3	5.3	0.23	a
n-Heptacosanoic Acid	0.66	0.49	0.81	0.47	0.03	a
n-Octacosanoic Acid	2.9	2.7	4.9	3.2	0.15	a
n-Nonacosanoic Acid	0.53	0.33	0.57	0.43	< 0.02	a
n-Triacontanoic Acid	1.2	1.0	2.2	2.2	< 0.02	a
n-Alkanoic Acids (C9 - C30)	256.08	292.62	294.28	261.68		
n-Alkenoic Acids						
n-Octadecenoic Acid	23.6	24.8	26.0	17.3	< 0.02	a
n-Alkanals						
Nonanal	6.9	5.7	9.5	7.5	0.67	b
Aliphatic Dicarboxylic Acids						
Propanedioic Acid (Malonic Acid)	28.0	32.7	44.4	51.0	< 0.02	a
2-Butenedioic Acid	0.58	0.66	1.3	0.84	< 0.02	a
Butanedioic Acid (Succinic Acid)	55.0	66.5	51.2	84.1	< 0.02	a
Methylbutanedioic Acid (Methylsuccinic Acid)	11.6	18.0	15.0	20.3	< 0.02	a
Pentanedioic Acid (Glutaric Acid)	28.4	32.3	28.3	38.7	< 0.02	a
Methylpentanedioic Acid (Methylglutaric Acid)	15.5	19.3	16.6	23.7	< 0.02	a
Hydroxybutanedioic Acid (Hydroxysuccinic Acid)	7.8	14.3	16.0	22.1	< 0.02	a
Hexanedioic Acid (Adipic Acid)	15.0	14.1	14.1	24.3	< 0.02	a
Octanedioic Acid (Suberic Acid)	2.9	3.4	4.1	2.5	< 0.02	a
Nonanedioic Acid (Azelaic Acid)	34.2	29.0	22.8	44.7	< 0.02	a
Aliphatic Dicarboxylic Acids (C_3 - C_9)	198.98	230.26	213.8	312.24		

Table 2.1 (continued)

Part C

Compound Name	West LA	Downtown LA	Pasadena	Rubidoux	San Nicolas Island[a] (Jul. - Dec.)	Compound Identification[b] a = positive b = probable c = possible d = tentative
	Concentrations in ng m^{-3}					
Diterpenoid Acids and Retene[c]						
Dehydroabietic Acid	20.9	23.6	22.6	10.2	< 0.03	a
13-Isopropyl-5α-podocarpa-6,8,11,13-tetraen-16-oic Acid	0.75	0.63	1.2	0.30	< 0.03	b
8,15-Pimaradien-18-oic Acid	1.1	0.44	0.57	0.07	< 0.03	b
Pimaric Acid	3.0	2.3	4.8	0.94	< 0.03	a
Isopimaric Acid	1.2	1.3	2.3	0.71	< 0.03	b
7-Oxodehydroabietic Acid	3.5	3.4	4.1	1.9	< 0.03	a
Sandaracopimaric Acid	1.4	1.6	2.2	0.60	< 0.03	b
Retene	0.10	0.07	0.06	0.01	< 0.01	a
Wood Smoke Markers	31.95	33.34	37.63	14.73		
Aromatic Polycarboxylic Acids						
1,2-Benzenedicarboxylic Acid (Phthalic Acid)	60.6	60.0	55.7	53.5	< 0.03	a
1,3-Benzenedicarboxylic Acid (Isophthalic Acid)	2.1	3.4	2.9	2.1	< 0.03	a
1,4-Benzenedicarboxylic Acid (Terephthalic Acid)	1.3	2.8	1.5	0.88	< 0.03	a
4-Methyl-1,2-benzenedicarboxylic Acid (4-Methylphthalic Acid)	15.2	27.8	28.8	26.3	< 0.03	a
1,2,4-Benzenetricarboxylic Acid (Trimellitic Acid)	0.45	0.52	0.84	0.67	< 0.03	a
1,3,5-Benzenetricarboxylic Acid (Trimesic Acid)	11.3	20.6	17.2	22.6	< 0.03	a
1,2,4,5-Benzenetetracarboxylic Acid (Pyromellitic Acid)	0.67	0.74	0.80	0.40	< 0.03	a
Aromatic Polycarboxylic Acids	91.72	115.86	107.74	106.45		
Polycyclic Aromatic Hydrocarbons						
Fluoranthene	0.09	0.15	0.13	0.07	< 0.01	a
Pyrene	0.12	0.26	0.17	0.14	< 0.01	a
Benz[a]anthracene	0.19	0.29	0.25	0.09	< 0.01	a
Cyclopenta[cd]pyrene	0.20	0.23	0.41	0.04	< 0.01	b
Benzo[ghi]fluoranthene	0.19	0.39	0.30	0.11	< 0.01	b
Chrysene/Triphenylene	0.30	0.61	0.43	0.23	< 0.01	a
Benzo[k]fluoranthene	1.03	1.15	1.20	0.33	< 0.01	a
Benzo[b]fluoranthene	0.77	1.23	0.85	0.68	< 0.01	a

Table 2.1 (continued)

Part D

Compound Name	West LA	Downtown LA	Pasadena	Rubidoux	San Nicolas Island[a] (Jul. - Dec.)	Compound Identification[b] a = positive b = probable c = possible d = tentative
	Concentrations in ng m^{-3}					
Benzo[e]pyrene	0.93	0.97	0.93	0.38	< 0.01	a
Benzo[a]pyrene	0.32	0.42	0.44	0.18	< 0.01	a
Indeno[1,2,3-cd]pyrene	0.43	0.37	0.42	0.07	< 0.01	b
Indeno[1,2,3-cd]fluoranthene	0.85	1.05	1.09	0.26	< 0.01	b
Benzo[ghi]perylene	4.11	4.47	4.43	1.12	< 0.01	a
Coronene	2.41	N.M[d]	N.M[d]	N.M[d]	< 0.01	a
Polycyclic Aromatic Hydrocarbons	11.92	11.59	11.04	3.70		
Polycyclic Aromatic Ketones and Quinones						
7H-Benz[de]anthracen-7-one	0.62	0.81	0.84	0.25	< 0.01	a
Benz[a]anthracene-7,12-dione	0.18	0.21	0.25	0.12	< 0.01	a
Benzo[cd]pyren-6-one	0.97	0.80	1.24	0.02	< 0.01	b
Polycyclic Aromatic Ketones and Quinones	1.77	1.82	2.33	0.39		
Steroids						
Cholesterol	2.7	N.D.[e]	1.9	N.D.[e]	< 0.10	a
N-Containing Compounds						
3-Methoxypyridine	0.50	0.86	1.4	0.46	< 0.03	b
Isoquinoline	0.61	1.1	1.1	0.74	< 0.03	b
1-Methylisoquinoline	1.1	0.27	0.24	0.51	< 0.03	b
1,2-Dimethoxy-4-nitro-benzene	1.0	1.8	3.9	0.22	< 0.03	b
N-Containing Compounds	3.21	4.03	6.64	1.93		

Table 2.1 (continued)

Part E

Compound Name	West LA	Downtown LA	Pasadena	Rubidoux	San Nicolas Island[a] (Jul. - Dec.)	Compound Identification[b] a = positive b = probable c = possible d = tentative
	Concentrations in ng m^{-3}					
Regular Steranes						
20S&R-5α(H),14β(H),17β(H)-cholestanes	0.50	1.18	0.55	0.34	< 0.03	b
20R-5α(H),14α(H),17α(H)-cholestane	0.57	1.23	0.83	0.34	< 0.03	a
20S&R-5α(H),14β(H),17β(H)-ergostanes	0.67	1.75	0.82	0.51	< 0.03	b
20S&R-5α(H),14β(H),17β(H)-sitostanes	0.67	1.67	1.03	0.52	< 0.03	b
Regular Steranes	2.41	5.83	3.23	1.71		
Pentacyclic Triterpanes						
22,29,30-trisnorneohopane	0.35	0.93	0.40	0.32	< 0.01	b
17α(H),21β(H)-29-norhopane	0.88	2.42	0.98	0.66	< 0.01	b
17α(H),21β(H)-hopane	1.32	4.02	1.47	1.32	< 0.01	b
22S-17α(H),21β(H)-30-homohopane	0.58	1.42	0.64	0.52	< 0.01	b
22R-17α(H),21β(H)-30-homohopane	0.40	1.06	0.42	0.36	< 0.01	b
22S-17α(H),21β(H)-30-bishomohopane	0.36	0.84	0.43	0.33	< 0.01	b
22R-17α(H),21β(H)-30-bishomohopane	0.23	0.58	0.27	0.20	< 0.01	b
Pentacyclic Triterpanes	4.12	11.27	4.61	3.71		
***iso*- and *anteiso*-Alkanes**						
anteiso-triacontane	0.23	< 0.03	0.19	< 0.03	< 0.03	b
iso-hentriacontane	1.30	1.50	1.25	0.73	< 0.03	b
anteiso-hentriacontane	0.12	< 0.03	0.12	< 0.03	< 0.03	b
iso-dotriacontane	0.13	< 0.03	0.09	< 0.03	< 0.03	b
anteiso-dotriacontane	1.07	1.31	0.94	0.89	< 0.03	b
iso-tritriacontane	0.30	0.33	0.32	0.30	< 0.03	b
iso- and *anteiso*-Alkanes	3.15	3.14	2.91	1.92	< 0.01	

[a] sample analyses were completed only for July to December 1982; [b] for more detail see text;

[c] wood smoke markers: diterpenoid acids and retene usually were present at measurable concentrations only during heating seasons. Annual average concentrations were calculated considering all 12 months of the year; hence, the average concentrations during heating seasons are higher;

[d] N.M. = not measured; since coronene elutes very late from the column used in this study, coronene data were taken only at West LA; [e] N.D. = not detected.

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Chapter 3

Charbroilers and Meat Cooking Operations

Introduction

Emission inventory data show that fine carbon particles ($d_p \leq 2$ μm) from charbroiling and frying of meat should make a significant contribution to urban concentrations of organic aerosol. Fine organic carbon particle emissions from meat cooking in the greater Los Angeles area for the year 1982 have been estimated to range from 4400 to 4900 kg/day for charbroiling and 1400 kg/day for meat frying (*1*, *2*). Within an 80 x 80 km area including the heavily urbanized and industrialized surroundings of Los Angeles, meat frying and charbroiling together account for approximately 21% of all fine organic particulate matter released into the atmosphere (*2*). The emissions from meat cooking operations depend strongly on the cooking method used, fat content of the meat, and the type of grease eliminator system that may be in operation above the cooking surface. The source tests conducted by Hildemann et al. (*2*) showed that charbroiling regular hamburger meat produced fine aerosol emissions totaling up to 40 g/kg of meat cooked, whereas charbroiling extra-lean meat produced fine aerosol emissions of 7 g/kg of meat cooked. In contrast, frying the same two types of meat generated fine aerosol emissions of only 1 g/kg of meat (*2*).

The detailed organic chemical composition of the fine particulate matter emitted from meat cooking operations has not been determined previously. Once

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comprehensive information on the molecular composition of such emissions is available, it may be possible to estimate the contribution of meat cooking operations to the atmospheric particulate matter burden using molecular tracer techniques. If unique organic compounds or groups of distinct compound assemblages characteristic of meat cooking operations also can be measured in ambient samples, then the fraction of the ambient aerosol derived from meat cooking operations can be traced to its source.

In the present study, the molecular composition of the organic aerosol emissions from meat cooking operations is examined. Source samples collected during the study of Hildemann et al. (*2*) are analyzed by high resolution gas chromatography (HRGC) and gas chromatography/mass spectrometry (GC/MS) techniques in order to identify and quantify those key marker compounds which are emitted as fine aerosol during meat cooking. The emission rates of key marker compounds are related to the bulk quantity of fine organic aerosol and fine aerosol mass emitted. It is found that cholesterol and other related compounds are emitted in significant quantities from cooking meat, and that these compounds also are identifiable in urban atmospheric aerosol samples.

Experimental Methods

Dilution Sampler

The source sampling device used in this study is designed to collect fine organic aerosol ($d_p \leq 2$ μm), including vapor-phase organics that condense onto preexisting solid particles as the plume from the source cools to ambient conditions (*3*). The sampler inlet probe consists of an in–stack stainless steel cyclone separator which removes particles greater than 10 μm in aerodynamic diameter from the source effluents. Both exhaust gases and particles smaller than 10 μm in diameter are drawn through a heated Teflon inlet line into a stainless steel dilution tunnel. In the dilution tunnel, the source effluent is mixed with a much larger volume of purified precooled air. Hot organic vapors that would have condensed into the aerosol phase upon cooling and dilution in the atmospheric plume downwind of the source instead condense at simulated ambient conditions within the dilution tunnel. Fine aerosol samples then are collected from the dilution tunnel by filtration downstream of cyclone separators which have a 50% cutoff at 2 μm aerodynamic particle diameter.

Dilution Sampler Preparation

In order to reduce the possibility of contamination, all parts of the dilution sampler were carefully cleaned prior to use. Large components of the sampling system were vapor-degreased using tetrachloroethylene, with all open ends wrapped with clean aluminum foil immediately after cleaning to prevent recontamination. The smaller parts, including the cyclones and filter holders, were washed with detergent, rinsed with deionized water, and then sonicated first for 5 minutes in glass-distilled methanol, and then for another 5 minutes in glass-distilled hexane.

Source Testing Procedure

A local commercial-scale kitchen was used to conduct the meat cooking experiments. Two types of hamburger meat, regular (approx. 21% fat) and extra-lean (approx. 10% fat), were cooked by the following two methods: charbroiling over a natural gas flame and frying. Four sets of cooking experiments were performed. During each experiment, 80 quarter-pound (113 g) hamburger patties were cooked until they were medium to well-done, eight at a time, over a period of 70 to 80 minutes. The smoke resulting either from frying or charbroiling was withdrawn through a 14,000 cfm (6.6 m^3 sec^{-1}) overhead exhaust hood equipped with a baffle-type grease extractor which has an estimated removal efficiency of about 60% by mass (*4*).

The sampler was located on the roof of the kitchen, and samples were withdrawn at the exit to the exhaust duct. The air flow through the exhaust vent was measured at the start of each experiment to insure isokinetic sampling. The flowrate through each of the filters was measured before and after each experiment using a rotameter that was calibrated to an accuracy of ± 1 %. During each experiment, the flowrates of the dilution air, and of the mixture leaving the dilution tunnel, were measured at regular intervals using in–line orifice plates. The exhaust gas flow through the inlet line was measured using a venturi meter. All flowrates were corrected to standard temperature and pressure (STP). Fine aerosol samples were collected by sampling from the residence time chamber at the downstream end of the sampling system. The particulate samples were taken using six parallel AIHL cyclone separators (*5*) each operated at 27.9 ± 0.3 lpm with a cut–off diameter of 2.0 μm. Further downstream of each of these cyclone separators, three parallel 47 mm diameter filter holders were used to collect the particulate matter at a flowrate of 9.0 to 9.6 lpm, yielding 18 separate fine particle samples. Two of the 18 filter holders contained Teflon filters (Gelman Teflo, 2.0 μm pore size), and the remaining filter holders were loaded with quartz fiber filters (Pallflex 2500 QAO).

All quartz filters were baked at 750 °C for 2 to 4 hours before use in order to insure low concentrations of organic compounds on the blank filter material. For each experiment, the two Teflon filters and one quartz filter were used for the determination of bulk chemical properties, including ionic species, trace metals, and total organic and elemental carbon by combustion. The results of this bulk chemical analysis are reported by Hildemann et al. (*2*). The remaining 15 quartz fiber filters were used for detailed organic compound analysis. All samples were stored at minus 25 °C within 2 hours after completion of the source testing experiment to avoid possible biogenic degradation. Since frying hamburger meat released small amounts of organic material, the filters from frying extra–lean and regular meat were aggregated prior to extraction. Thus, in the following discussion, the samples from the meat frying experiments represent the sequentially fried extra–lean and regular hamburger meat with an averaged fat content of 15.5%.

Sample Extraction

An extraction protocol developed for the quantitative analysis of organic aerosol samples has been presented in detail by Mazurek et al. (*6, 7*). For each source test, 15 quartz fiber filters containing collected source effluents were composited. Prior to extraction, each group of filters was spiked with a known amount of perdeuterated tetracosane (n-$C_{24}D_{50}$) that is used as a recovery standard. The quantity added was calculated based on the amount of organic aerosol present as determined by combustion analysis of a separate quartz fiber filter source sample. This preliminary bulk carbon analysis was needed to estimate the correct amount of recovery standard to be added to each extraction set. Distilled–in–glass, hexane, benzene, and isopropanol were used throughout the analytical procedure (Burdick and Jackson, Muskegon, IL). The filter composites were extracted in heavy–walled flint glass jars which had been annealed at

550 °C for eight hours and were equipped with tightly–fitting Teflon–lined caps. Samples were extracted for 10 minute intervals with hexane (two times) and with benzene/isopropanol (2:1) (three times) using an ultrasonic bath maintained at room temperature. After each extraction step, the extract was transferred to a volumetric flask with a special transfer line, described elsewhere (*6*). The extract volume was reduced to 200 to 500 μl. One aliquot of the extract was derivatized by addition of diazomethane to convert organic acids to their methyl ester analogues. This technique allowed comparison of the neutral (unmethylated) fraction with the acid plus neutral (methylated) fraction by means of HRGC and GC/MS.

Analysis

The meat cooking aerosol extracts were analyzed with a Varian 4600 high–resolution gas chromatograph equipped with a Grob injector (splitless mode) and a 30 m fused–silica DB–1701 column (bonded 86% dimethyl–[14%]–cyanopropyl-phenyl polysiloxane; 0.25 μm film thickness; 0.32 mm i.d.; J & W Scientific, Rancho Cordova, CA) using an FID detector range of 10^{-12}mV. Temperature programming consisted of the following steps: 1) injection at 65 C; 2) isothermal hold at 65 C for 10 min; 3) temperature ramp of 10 C min^{-1} for 21 minutes and 4) an isothermal hold at 275 C for another 49 min. Further details are described elsewhere (*6*, *8*, *9*).

The GC/MS analyses were carried out with a Finnigan 4000 quadrupole mass spectrometer (nominal resolution), interfaced with an INCOS data system. The major organic compounds in the source samples were initially identified by computer matches to standard reference mass fragmentograms in the National Institute of Standards and Technology (NIST) library and were confirmed later by comparison with authentic standards. The GC/MS analyses were performed by electron impact ionization with an electron energy of 70 eV. The chromatographic conditions were identical to those used for the HRGC analyses. The same DB–1701 column was used for both HRGC and GC/MS analyses.

Standard Compounds

Quantification and compound confirmation was achieved using prepared standards. The following standard mixtures were injected onto the HRGC and GC/MS–systems: 1) normal alkanes ranging from $\underline{n}$–C_{10} to $\underline{n}$–C_{36}; 2) normal alkanoic acids as methyl esters from $\underline{n}$–C_6 to $\underline{n}$–C_{30}; 3) a suite of 37 aromatic and polycyclic aromatic hydrocarbons (PAHs): isopropylbenzene; indan; neopentylbenzene; 1,2,3,4–tetramethyl-benzene; 2–methylnaphthalene; 1–methylnaphthalene; 1,1'–biphenyl; 2,6–dimethylnaph-thalene; hexamethylbenzene; acenaphthylene; 2,3,4–trimethylnaphthalene; fluorene; 2–methylfluorene; 3,4'–dimethyl–1,1'–biphenyl; dibenzothiophene; phenanthrene; anthracene; fluoranthene; pyrene; 2,3–benzofluorene; 1,1'–binaphthalene; benz[a]anthracene; chrysene; triphenylene; benzo[k]fluoranthene; benzo[e]pyrene; benzo[a]pyrene; perylene; 9,10–diphenylanthracene; 1,2,5,6–dibenzanthracene; benzo[ghi]perylene; anthanthrene; coronene; 1,2,4,5-dibenzopyrene; naphthalene; 1,3,5–triisopropylbenzene; 3–methyl–1,1'–biphenyl; 4) a suite of 11 dicarboxylic acids as esters; and 5) one marker compound which is an important component of the meat smoke: cholesterol.

Quality Assurance

A well-established quality assurance protocol was followed (*6*, *8*). Briefly, all solvents used were tested for possible contaminants, procedural blanks were extracted and examined to provide a qualitative and quantitative assessment of background contamination introduced by laboratory procedures, and field blanks which were taken from the source sampler during operation likewise were analyzed for contaminants. Only minor amounts of procedural and field contaminants were present as shown by GC/MS analysis of the blanks. In Figures 3.1a-c, contaminants in the meat smoke chromatograms are labeled with an "X" and are either solvent or sampling artifacts. The first four peaks labeled as contaminants are solvent artifacts, identified via routine quality control/assurance procedures involving solvent testing. The largest peak labeled with an "X" is 1,1'–biphenyl, an impurity of the benzene used. The last three contaminant peaks are sampling or analytical artifacts (e.g., phthalates).

Compound Identification and Quantification

Compound identification was performed with the help of the NIST Standard Library accessed by the INCOS Data System and, where available, by comparison with the retention times and/or mass fragmentation patterns of standard reference compounds. Organic compounds that remain undetected include: (a) compounds of molecular weight higher than about 500 (the upper limit of the spectrometer mass scan), e.g., polymeric compounds; (b) organics in very low yields of $\leq 0.1\%$, since the MS-system does not record mass fragments whose intensities are less than 0.1% of that of the base peak; (c) compounds insoluble in the solvents used; and (d) compounds which could not elute from the column used. Within these constraints, compound identification was deemed: (a) ***positive***, when the sample mass spectrum was identical to that of an authentic standard and the library spectrum and also the retention time data for the sample and standard agreed quite well; (b) ***probable***, same as above except that no standards were available; (c) ***possible***, same as above except that the spectrum

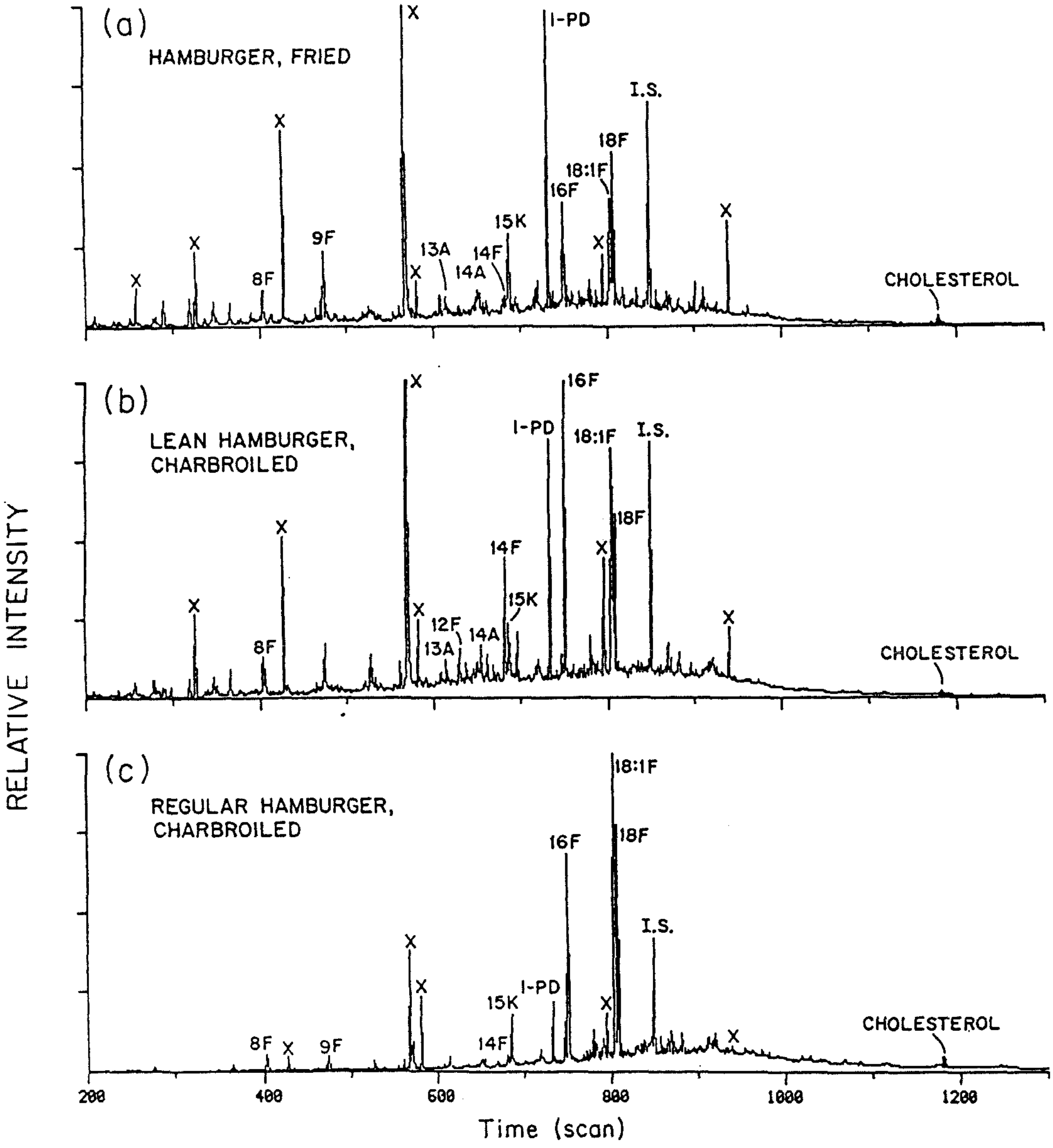

Figure 3.1: Total ion current traces from GC/MS data (equivalent to HRGC traces) for the smoke aerosol from hamburger cooking: (a) frying extra-lean/regular meat 50%/50% (15.5% fat), (b) gas-broiling extra-lean meat (10% fat), (c) gas-broiling regular meat (21% fat). Numbers refer to carbon chain length of compounds: A = aldehyde, K = n-alkan-2-one, F = n-alkanoic acids as methyl esters, 18:1F = oleic acid as methyl ester, 1-PD = 1-phenyldodecane as coinjection standard, I.S. = n-$C_{24}D_{50}$ internal standard, X = contaminant.

obtained contained information from other compounds but with minor overlap; or (d) tentative, when the spectrum revealed additional information from several compounds (noise) with overlap.

Extract quantification was accomplished using the HRGC system, based on the combined use of a coinjection standard (1–phenyldodecane) and the recovery data derived from the applied internal standard ($\underline{n}$–$C_{24}D_{50}$), as described recently (*6*). Peak integration was performed using a Varian Vista 201 data system. Whenever the uncorrected (Relative Response Factor RRF = 1.0) compound mass concentration for a target compound was below 60 – 80 ng per sample nominal, quantification was conducted using selective ion monitoring (SIM) with the MS system, since in this application the detection limit for the mass spectrometer lies between 1.0 and 5.0 pg depending on the nature of the organic molecule and its elution time. Given the low levels of PAHs present in the meat smoke aerosol, these compounds were quantified solely by GC/MS–SIM. The quantification procedure was identical for the HRGC and GC/MS, but relative response factors were determined separately for each compound on HRGC and GC/MS. Single compound masses were computed relative to the coinjection standard and adjusted according to the recovery calculations for each sample.

Sixty to seventy percent of the mass of resolved compounds could be identified, accounting for 10 to 20% of the total complex mixture. The unidentified fraction consists mainly of the unresolved hump seen in Figures 3.1a-c, which can only be studied by using further analytical separation techniques.

Results and Discussion

Cooking Process

Freshly cut meat usually contains about 75% water, 15 to 20% proteins, and about 5 to 10% fat (*10–12*). Hamburger meat is preprocessed deliberately to adjust its fat content. The beef is shredded, while adding fat to bring the fat content to well defined amounts (regular, 21% fat; extra–lean 10%).

Cooking has a drastic effect on the muscle tissue and fat. As soon as meat is heated to between 40 to 50 °C, the muscle fibers lose their myosin protein solubility, which indicates protein denaturation and membrane deterioration in the contractile system (*13, 14*). Between 65 and 75 °C, meat begins to shrink along the muscle fibers due to denaturation of connective tissue proteins and loss of water. The shrinkage for non–shredded meat comprises 25 to 35% with a loss of water of up to 40% (*10, 13*). It can be assumed that the loss of water in hamburger meat is higher, since the water loss depends greatly on the distance between the cut surfaces of the meat. Shredding reduces the muscle fiber length enormously, so that a large amount of the water that is contained in these tissues can be removed easily.

Broiling and frying, the so–called dry cooking methods (in contrast to boiling, steaming, and stewing) can heat the meat to temperatures well above the boiling point of water. This produces a much higher thermal stress on the surface of the dry cooked meat. The temperature distribution within hamburgers during cooking can be divided into three distinct zones. The inner zone, containing a high percentage of water, never reaches temperatures above 100 °C, under normal cooking conditions. Usually, the temperature inside the meat increases slowly with cooking time. In order to cook meat medium to well–done, the internal temperature is allowed to reach 70 to 80 °C for a very short time only (*13, 14*). The outer zone or surface zone, a very thin layer, reaches temperatures well above the boiling point of water during the frying or broiling process. Average temperatures of 160 °C and higher are common on the surface (*12*). Slightly below the surface layer is the transition zone which should be characterized by a constant temperature of 100 °C, the boiling point of water. This temperature is reached shortly after the beginning of the cooking process. The transition zone moves while the cooking process is underway into the bulk of the meat patty. Water from the inner zone enters the transition zone, reaches the boiling point and leaves the hamburger meat through the surface zone as vapor, and that vapor carries with it unaltered organic and inorganic meat constituents.

In addition, compounds are released during meat cooking which are formed by oxidation, decarboxylation, fragmentation, recombination, rearrangement, condensation, and cyclization reactions of the precursor raw meat components (*15–17*). The uncooked fat component of meat contains large amounts of bound unsaturated and saturated fatty acids. The most common fatty acids are palmitic and stearic acids and their unsaturated homologs (*18*). These fatty acids, which have melting points between 12 and 69 °C and boiling points up to 360 °C (*18, 19*), either can leave the frying or charbroiling meat unaltered in the liquid phase or can be vaporized at the outer surface of the hamburger. The emissions to the atmosphere of liquid phase material could be quite different for the frying and charbroiling processes. Only a minor amount of the liquified fatty acids may become airborne when frying on top of a metal grill; instead, the liquid may simply run off of the surface of the grill. In contrast, charbroiling offers a very efficient way to produce aerosol fatty acids. Liquid grease droplets fall into the gas–flame or onto heated briquettes underneath the broiling grill where they can be vaporized or splattered. Oxidative decomposition of the fatty acids, especially unsaturated species, is a further source for many organic compound groups, including aldehydes, ketones, alcohols, hydrocarbons, esters, furans, and lactones as will be described in detail in the following sections.

Smoke Aerosol Composition

Total ion current traces from the GC/MS analyses of the hamburger smoke aerosol are shown in Figures 3.1a-c. The variety of compounds present can be described as follows.

Alkanes

Under ambient conditions, the normal alkanes with carbon numbers C_{21} and higher are found mainly in the particulate phase due to their low vapor pressure. The mass emission rates of these compounds determined for each of the cooking experiments are summarized in Table 3.1. Normal alkanes comprise only a minor fraction of the total organic mass emitted, and the emissions depend greatly on the cooking conditions. Frying meat releases about one third the mass of $\underline{n}$–alkanes that are emitted when charbroiling extra–lean meat (5.5 versus 16.0 mg kg^{-1} meat). The fat content of the raw meat is also important in determining $\underline{n}$–alkane mass emission levels. Charbroiling of regular meat emits about four times more alkanes (65.9 mg kg^{-1}) by mass than broiling extra–lean meat, with significantly increased emission rates for the $\underline{n}$–C_{24} and $\underline{n}$–C_{25} homologs in this particular case. This pattern of increasing release rates for particular homologous compounds as one progresses from frying to charbroiling extra–lean meat, to charbroiling regular meat corresponds to changes observed in the emission rate for the entire fine organic aerosol mass as reported by Hildemann et al. (*2*).

Alkanoic and Alkenoic Acids

The normal fatty acids in raw meat are bound chemically as triglycerides and phospholipids, and are liberated either by bacterial enzymes or by hydrolysis and thermal oxidation during the cooking process (*17*). Table 3.1 shows the emission rates for the normal alkanoic acids ranging from C_7 to C_{18}, along with the unsaturated fatty acids that were detected. Typical mass fragmentograms from the GC/MS data are shown in Figures 3.2a-c. Frying produces the lowest total emissions of these compounds with only 72.8 mg of aerosol n–alkanoic and n–alkenoic acids kg^{-1} of meat cooked. Gas–broiling of extra–lean meat produces a nearly five-fold increase in the total alkanoic and alkenoic acids emission rate (362.1 mg kg^{-1} meat). This enhanced release indicates the importance of grease droplets falling onto the bed of the charbroiler (i.e., onto the charcoal when charcoal–broiling with possible ignition, or into the flame when using a gas–broiler) where they are volatilized. As the fat content of the meat is increased, this effect becomes even more pronounced: gas–broiling regular hamburger meat (1698.7 mg of n–alkanoic and n–alkenoic acids emitted kg^{-1} meat) yields a 23–fold higher emission rate than meat frying. The homolog distribution pattern for the fatty acids is the same for all three cooking methods with a strong even–to–odd carbon number predominance and the highest emission rates for palmitic and stearic acids (Figures 3.2a-c). The two most common unsaturated fatty acids containing a single double bond were palmitoleic (i.e., cis–9–hexadecenoic acid) and oleic (i.e., cis–9–octadecenoic acid) acids. Oleic acid and palmitic acid were found with the highest emission rates of all fatty acids identified. The unsaturated fatty acid results agree with the reported composition data for raw

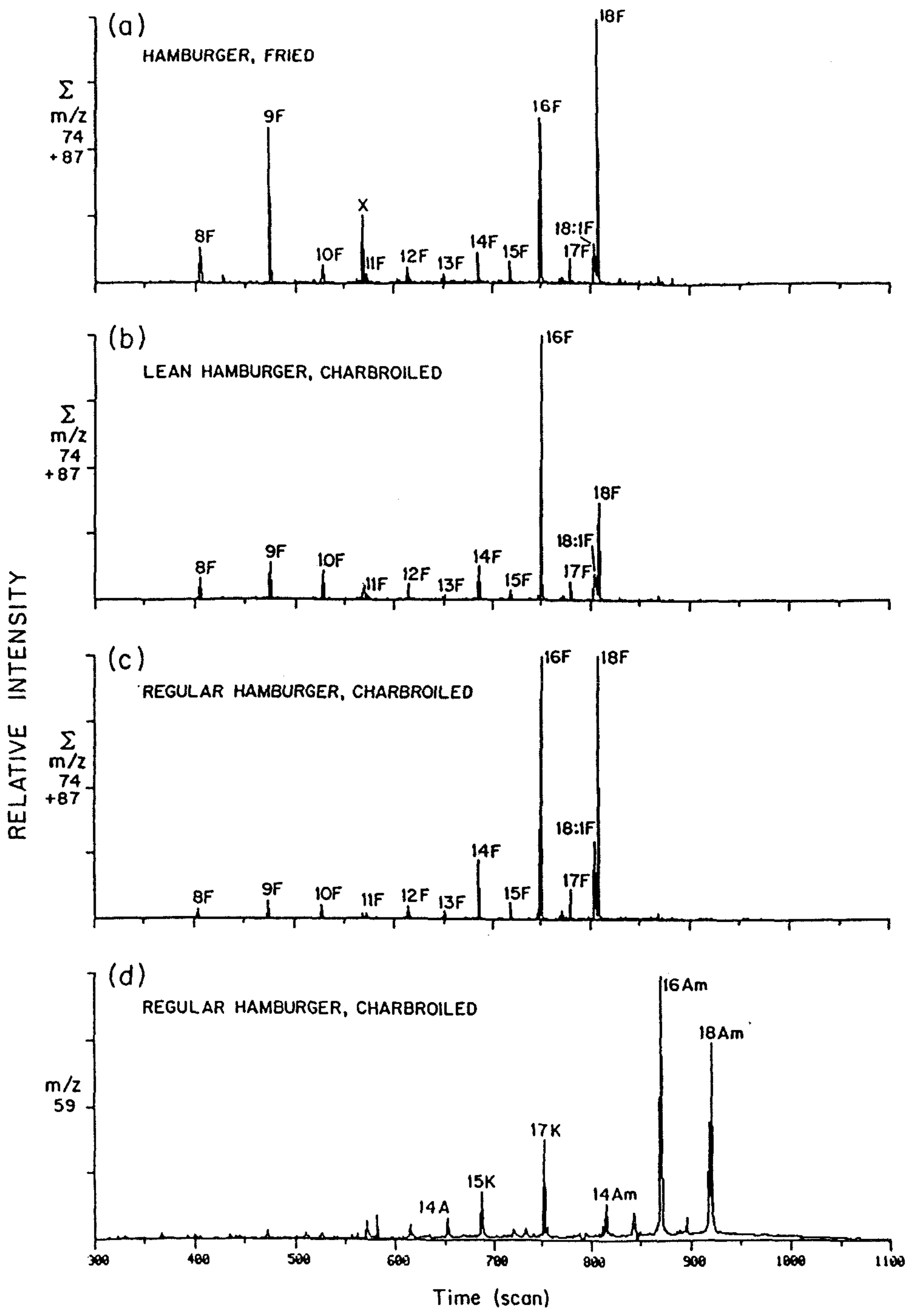

Figure 3.2: Selected mass fragmentograms for n-alkanoic acids as methyl esters (a)–(c), showing summed m/z 74 + 87, and amides (d), showing m/z 59 for the smoke aerosol from hamburger cooking: (a) frying, (b) gas-broiling extra-lean meat, (c) gas-broiling regular meat, (d) gas-broiling regular meat (numbers refer to the carbon chain length of the homologous compounds, Am = amide, K = n-alkan-2-one, A = aldehyde, X = contaminant).

meat, which show large concentrations of palmitoleic and oleic acids versus the concentrations of n–alkanoic and other n–alkenoic acid homologs found in meat (*17, 18*).

Oxidation Products in Meat

Cut meat in the presence of initiators such as heat, metals or light, and unsaturated lipids, forms free radicals (R·) via hydrogen abstraction from the lipids involved. These lipid radicals combine with oxygen to form peroxy radicals (ROO·), which propagate as the peroxy radicals react with additional unsaturated lipids, to form hydroperoxides (ROOH). The subsequent decomposition of these lipid hydroperoxides involves a large set of reactions. These breakdown products form a complex mixture of aldehydes, ketones, alcohols, hydrocarbons, esters, furans, and lactones (*16, 17, 20–22*). MacLeod and Seyyedain–Ardebili (*23*) compiled a table of more than 600 compounds which were found in red meats before and after the cooking process was completed. The same groups of compounds are formed during cooking due to oxidative decomposition of lipid–derived fatty acids, which leads to significant quantities of straight chain aldehydes, ketones, alcohols, and hydrocarbons. The process is catalyzed in meat by traces of transition metals and by haem and haematin compounds which are iron complexes (*17*). Thermal autoxidation of lipids can occur at a temperature of 60 C in the presence of a few free radicals, but most of the degradation occurs at 200 to 300 C. At higher temperatures, about 600 C, pyrolysis occurs (*14*). Sanderson et al. (*24*) reported that heating fat alone does not give significant amounts of carbonyl groups, whereas heating lean beef in fat produces about three times the carbonyl yield as is seen when lean beef is heated without additional fat. A large number of higher boiling organics arising from autoxidation reactions in the meat could be expected to be found in the hamburger aerosol, and are the subject of the following discussion.

Dicarboxylic Acids

Dicarboxyclic acids are the oxidation products of dialdehydes formed during the autoxidation process of unsaturated lipids (*17*). The aerosol emission rates of these compounds from meat cooking are lower than for the alkanoic and alkenoic acids, as seen in Table 3.1. Nevertheless, it is interesting to note that there are direct primary emissions of these substances from aerosol sources, as airborne dicarboxylic acids are often attributed to secondary formation in the atmosphere from gas–phase precursors (*25*). Frying produces the lowest emission rates of dicarboxylic acids. These emissions increase by about five–fold when gas–broiling extra–lean meat, and by almost nine–fold when gas–broiling regular meat.

Alkanals and Alkenals

The n–alkanals and n–alkenals are products of n–alkenoic acid oxidation (*17*). The most commonly observed aldehyde in heated meat is nonanal (*17*) and it is prominent among the list of meat smoke components quantified in the present study. Table 3.1 includes the emission rates calculated for 4 other normal alkanals and one alkenal identified. The unsaturated aldehyde 2–octadecenal is only identifiable in the emissions from the gas–broiled regular meat sample, and this observation may be related to the large emission of oleic acid during that test.

Ketones

Of all identified ketones, the most abundant are the n–alkan–2–ones, formed most likely by the pyrolysis of triglycerides containing a β–keto fatty acid (*17*).

Seven alkan–2–ones ranging from C_9 to C_{18} are identified in the aerosol emissions (Table 3.1). The ketone mass emission rates seen here are comparable to those observed for the aldehydes in many cases.

Alkanols

Only two n–alkanols and one diol are identified, and all occur with low emission rates. The emission rates vary between types of meat and cooking techniques in a manner roughly proportional to the aldehydes and ketones.

Furans

These compounds together with thiophenes are probably the most important flavor constituents of cooked beef (*17, 26*). Furans are mainly formed via two reaction pathways. The most important one involves the interaction of carbohydrates with amino acids (*17, 26*). The second reaction path involves the oxidation of alkanals, the breakdown of 5'-ribonucleotides followed by the intermediate ribose-5-phosphate, and the thermal decomposition of thiamine. Two furan–type compounds are identified in the meat smoke aerosol samples: 2–pentylfuran, which is the major furan found in the non-fatty portion of cooked meat (*17*), and 3–methyltetrahydrofuran, which is found with similar emission rates independent of the type of cooking. Since the furan-type compounds are derived from the non-fatty portion of the beef, it is not surprising that the emission rates of these compounds are roughly the same over the range of fat contents studied in these experiments (90% to 79% non-fatty tissue). 2–Pentylfuran has a relatively high vapor pressure, so the aerosol samples collected here may reflect only a small fraction of the total quantity emitted, with the remainder in the gas phase.

Lactones (Furanones)

Lactones are formed in the lipid fraction by the lactonization of δ– and γ–hydroxy fatty acids, which are normally found in triglycerides (*17*). They also can be created by the oxidation of alkenals and oleic acid. The predominant furanones in meat smoke aerosol are long–chained γ–lactones. Charbroiling extra–lean hamburger meat releases about three times the amount of lactones into the atmosphere when compared to frying (52.4 vs. 15.0 mg kg^{-1} meat), while charbroiling regular hamburger meat increases the emissions by nearly six fold (83.6 mg kg^{-1} meat).

Amides

No information was found in the literature concerning the presence of amides in meat. An example of a mass fragmentogram (m/z 59, base peak) from the GC/MS data on hamburger smoke is shown in Figure 3.2d, and the homolog distribution pattern follows that of the n–alkanoic acids. Palmitamide, stearamide, and oleamide are identified in hamburger smoke aerosol. Another nitrogen containing compound found is N,N–dibutylformamide. Frying hamburgers emits 2.8 mg of amides kg^{-1} meat, whereas gas–broiling extra–lean meat increases the amount released by 13 fold (36.2 mg kg^{-1} meat); doubling the fat content (regular meat) further doubles the amount emitted (69.6 mg kg^{-1} meat).

Nitriles

Two nitriles, palmitonitrile and stearonitrile, are identified in the meat smoke samples (Table 3.1). In contrast to the amides, the emission rates between frying and gas–broiling (extra–lean meat) only differ by a factor of three. Charbroiling regular hamburger meat further enhances the emission rate by a factor of 2.5.

Polycyclic Aromatic Hydrocarbons

Organic substances containing carbon and hydrogen yield PAHs during incomplete combustion or pyrolysis. Doremire et al. (*27*) investigated charcoal–broiled meats to determine the benzo[a]pyrene content of cooked meat. Their findings suggested that the concentrations of benzo[a]pyrene in charbroiled meat are proportional to the fat content of the meat used. Halaby et al. (*28*) exposed meat compounds (fatty acids, triglycerides, cholesterol, and β–carotene) to temperatures between 400 and 700 °C. All the compounds produced PAHs when pyrolyzed. Panalaks (*29*) examined the PAH content of charcoal–broiled steaks, chickens, hamburgers, and frankfurters. The hamburgers appeared to have the highest PAH concentrations found in all four meat products and also the highest fat content. According to Lijinsky and Shubik (*30*) and Lijinsky and Ross (*31*), the rendered fat falls onto the hot charcoals and is pyrolyzed, forming PAHs, which are then volatilized and partly redeposited on the meat surface. Besides the fat content of the meat and cooking temperature, the distance between the grill and the heating source may play an important role in determining the degree of redeposition of PAHs onto the exposed surface of the meat (*30–32*).

The emission rates and the number of PAHs that are found above the detection limits in our experiments differ markedly between various tests. Only 5 PAHs are detected in the aerosol emissions from frying meat, whereas the number of observed PAHs increases to 7 while gas–broiling extra–lean meat, and to 10 while gas–broiling regular meat. Benzo[a]pyrene, a known carcinogen that has been heavily investigated in the past (*33*), is only detected in particulate matter emitted from gas–broiling regular meat. The highest emission rates for PAHs are found for chrysene/triphenylene. Since chrysene and triphenylene have identical

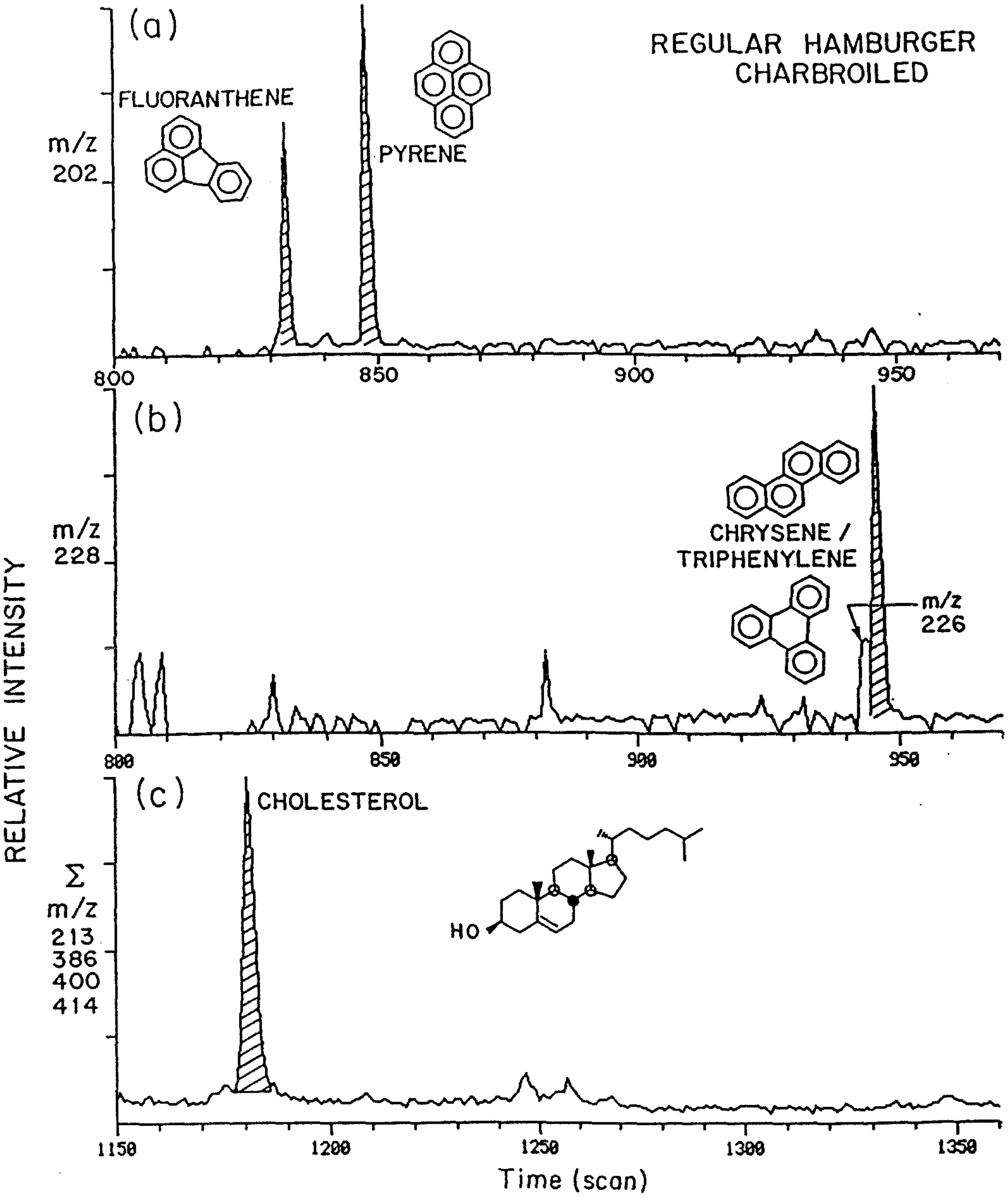

Figure 3.3: Selected mass fragmentograms for PAH ((a) + (b) —m/z 202 and 228, respectively) and sterols ((c) —summed m/z 213, key ion and m/z 386, 400, and 414, molecular ions of C_{27} to C_{29} sterols).

mass spectra and also coelute during the HRGC and GC/MS–techniques applied here, both PAHs are mentioned together, even though chrysene seems to be the more likely compound, based on PAH analyses of cooked meat (*33*). Typical examples of mass fragmentograms (m/z 202, molecular ions of fluoranthene and pyrene; m/z 228, molecular ions of chrysene/triphenylene) from the GC/MS data are shown in Figures 3.3a and b. Additional non–PAH compounds also elute in these retention time regions. When comparing meat frying to gas–broiling of extra–lean meat, the total PAH emission rate increases by nearly five–fold. Gas–broiling regular hamburger meat further increases the PAH emissions two–fold, in agreement with previously published results obtained by analysis of cooked meat itself, which shows that a doubling of the fat content of charbroiled meat doubles the PAH content (*27, 29, 33*).

Pesticides

Diazinon and chlorpyrifos are identified in the hamburger smoke aerosol. Both belong to the group of organophosphorus insecticides and are commonly used (*34*). The emission rates for pesticide residues vary between tests in a manner similar to the fat–derived meat components: the lowest emission rate is 1.5 mg kg^{-1} meat for frying; the highest 5.3 mg kg^{-1} for charbroiling regular hamburger meat. The possibility that these pesticides were used to treat the kitchen being tested rather than being present in the meat cannot be ruled out.

Cholesterol

Cholesterol, belonging to the group of steroids, is biosynthesized by higher animals (*35, 36*). It is found in all body tissues, especially in animal fats and oils (*36*). The biosynthesis starts with the triterpene squalene, which upon enzymatic

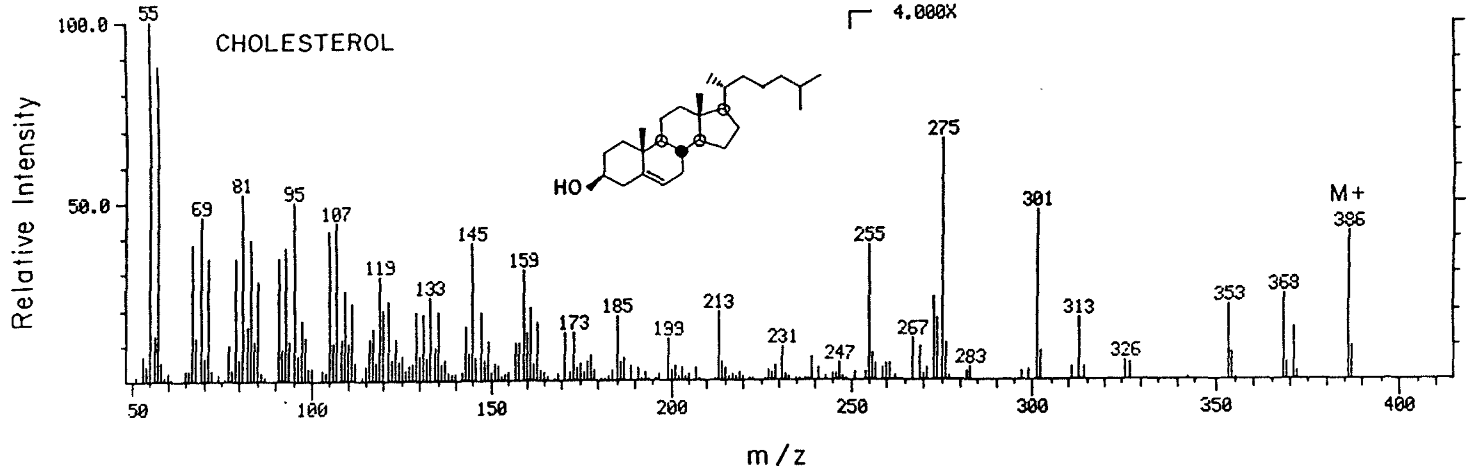

Figure 3.4: An example mass spectrum of underivatized cholesterol present in the smoke aerosol from hamburger cooking.

cyclization creates lanosterol, and after demethylation finally cholesterol (*37*). An example of a summed mass fragmentogram (m/z 213, key ion for steroids, m/z 386, 400, 414, molecular ions of C_{27}–C_{29} steroids) from the GC/MS data is shown in Figure 3.3c. The peak labeled cholesterol has the mass spectrum shown in Figure 3.4 which is identical to that of a cholesterol spectrum provided in the NIST standard library and it also has the same retention time as an authentic cholesterol standard run on the HRGC in our laboratory. Coprosterol and the other C_{28} and C_{29} sterols are not detectable, supporting the absence of vegetable cooking oils and microbial alteration of cholesterol. Thermal alteration products of cholesterol (e.g., dehydration to cholestadiene or aromatization to Diels' hydrocarbon, (*38*)) are not detectable, indicating that the dominant route for injection of cholesterol into the atmosphere is steam–stripping and to a minor degree vaporization. Cholesterol emission rates are lowest for meat frying (7.1 mg kg^{-1} meat), increase by about four–fold when charbroiling extra–lean meat, and increase by 10 fold (to 72.7 mg kg^{-1} meat) when charbroiling regular meat.

Table 3.1 Fine Aerosol Emission Rates for Single Organic Compounds from Charbroiling and Frying Hamburger Meat per kg of Meat Cooked.

Emission Rates^a in mg kg^{-1} of Meat Cooked

PART A

	Frying	Charbroiling		Compound ID^b
	extralean & regular meat	extralean meat	regular meat	
—$\underline{n}$–Alkanes—				
heneicosane	1.2	1.9	1.3	a
docosane	0.9	5.7	5.0	a
tricosane	0.5	0.8	4.1	a
tetracosane	0.5	1.3	20.6	a
pentacosane	0.4	2.2	22.3	a
hexacosane	0.4	0.5	2.5	a
heptacosane	0.6	1.2	3.1	a
octacosane	0.3	1.1	3.4	a
nonacosane	0.7	1.3	3.6	a
Total class emission rate:	5.5	16.0	65.9	
—$\underline{n}$–Alkanoic Acids^c—				
heptanoic acid	4.6	17.5	15.0	a
octanoic acid	4.1	14.8	25.2	a
nonanoic acid	10.2	30.6	47.1	a
decanoic acid	3.5	16.3	25.0	a
undecanoic acid	0.5	3.8	4.3	a
dodecanoic acid	2.1	10.0	33.0	a
tridecanoic acid	3.7	13.3	43.9	a
tetradecanoic acid (myristic acid)	6.2	17.1	87.0	a
pentadecanoic acid	1.1	2.7	24.9	a
hexadecanoic acid (palmitic acid)	14.2	83.5	481.2	a
heptadecanoic acid	3.0	9.2	45.2	a
octadecanoic acid (stearic acid)	8.7	56.3	246.9	a
Total class emission rate:	61.9	275.1	1078.7	
—$\underline{n}$–Alkenoic Acids^c—				
$\underline{\text{cis}}$–9–hexadecenoic acid (palmitoleic acid)	0.8	4.6	52.0	b
$\underline{\text{cis}}$–9–octadecenoic acid (oleic acid)	10.1	82.4	568.0	a
Total class emission rate:	10.9	87.0	620.0	

Table 3.1 (continued)

Emission Rates^a in mg kg^{-1} of Meat Cooked

PART B

	Frying extralean & regular meat	**Charbroiling extralean meat**	**Charbroiling regular meat**	Compound ID^b
—Dicarboxylic Acids^c—				
butanedioic acid (succinic acid)	2.3	7.6	12.0	a
pentanedioic acid (glutaric acid)	0.7	5.2	10.4	a
hexanedioic acid (adipic acid)	1.6	9.1	17.2	a
octanedioic acid (suberic acid)		traces		a
Total class emission rate:	4.6	21.9	39.6	
—n–Alkanals and n–Alkenals—				
nonanal	12.1	44.6	75.7	b
decanal	1.9	8.9	12.4	b
undecanal	2.3	6.7	7.3	b
tridecanal	2.6	4.6	5.2	b
pentadecanal	3.1	6.9	16.5	b
2–octadecenal	n.d.	n.d.	45.4	b
Total class emission rate:	22.0	71.7	162.5	
—n–Alkanones—				
2–nonanone	1.7	3.5	12.1	b
2–decanone	3.9	5.8	17.5	b
2–undecanone	1.7	4.7	6.5	b
2–pentadecanone	4.1	13.5	23.2	b
2–hexadecanone	2.5	7.2	31.6	b
2–heptadecanone	2.9	4.6	9.1	b
2–octadecanone	1.1	6.8	46.5	b
Total class emission rate:	17.9	46.1	146.5	
—Alkanols—				
2,5–hexanediol	0.2	0.6	2.9	b
pentadecanol	1.8	3.5	11.5	b
heptadecanol	traces			b
Total class emission rate:	2.0	4.1	14.4	
—Furans—				
2–pentylfuran^d		identifiable		b
tetrahydro–3–metylfuran	9.0	15.0	16.1	b
Total class emission rate:	9.0	15.0	16.1	

Table 3.1 (continued)

Emission Rates[a] in mg kg^{-1} of Meat Cooked

PART C	Frying extralean & regular meat	Charbroiling extralean meat	Charbroiling regular meat	Compound ID[b]
—Lactones (Furanones)—				
2(3H)–Furanone	0.5	2.1	2.6	b
5–ethyldihydro-2(3H)–furanone	0.7	1.4	1.3	b
5–butyldihydro-2(3H)–furanone	1.5	11.3	17.0	b
5–pentyldihydro-2(3H)–furanone	2.9	11.1	9.4	b
5–hexyldihydro-2(3H)–furanone	1.6	12.9	3.3	b
5–heptyldihydro-2(3H)–furanone	2.0	4.7	10.9	b
5–octyldihydro-2(3H)–furanone	2.6	3.7	18.2	b
5–dodecyldihydro-2(3H)–furanone	1.1	0.9	6.2	b
5–tridecyldihydro-2(3H)–furanone	0.6	1.9	3.7	b
5–tetradecyldihydro-2(3H)–furanone	1.5	2.4	11.0	b
Total class emission rate:	15.0	52.4	83.6	
—Amides—				
hexadecanamide (palmitamide)	0.8	12.3	26.3	b
octadecanamide (stearamide)	0.4	8.6	15.8	b
9–octadecenamide (oleamide)	0.6	8.4	17.2	b
N,N–dibutylformamide	1.0	6.9	10.3	b
Total class emission rate:	2.8	36.2	69.6	
—Nitriles—				
hexadecanenitrile (palmitonitrile)	0.8	2.5	6.8	b
octadecanenitrile (stearonitrile)	0.3	0.7	1.4	b
Total class emission rate:	1.1	3.2	8.2	
—PAHs[e]—				
fluoranthene	0.13	0.12	0.35	a
pyrene	0.09	0.19	0.74	a
benz[a]anthracene	0.02	0.30	0.29	a
chrysene/triphenylene	0.11	0.92	0.95	a
benzo[k]fluoranthene	0.004	0.06	0.27	a
benzo[b]fluoranthene	n.d.	0.04	0.21	a
benzo[e]pyrene	n.d.	0.03	0.19	a
benzo[a]pyrene	n.d.	n.d.	0.19	a
perylene	n.d.	n.d.	0.03	a
benzo[ghi]perylene	n.d.	n.d.	0.24	a
Total class emission rate:	0.354	1.66	3.46	

Table 3.1 (continued)

Emission Rates[a] in mg kg^{-1} of Meat Cooked

PART D	Frying extralean & regular meat	Charbroiling extralean meat	Charbroiling regular meat	Compound ID[b]
	—Pesticides—			
diazinon	0.7	0.8	2.5	b
chlorpyrifos	0.8	3.2	2.8	b
Total class emission rate:	1.5	4.0	5.3	
	—Steroids—			
cholesterol	7.1	26.5	72.7	a
Total class emission rate:	7.1	26.5	72.7	
	—Other Compounds—			
cyclopropaneoctanoic acid, 2–hexyl-[b]	1.0	2.5	18.3	b
2H–pyran–2–one, tetrahydro–6–pentyl-	2.3	4.1	16.8	c

[a] extra-lean/regular = 1:1 with ca. 15.5% fat (extra-lean meat ca. 10.0% fat, regular meat ca. 21% fat);

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

[c] detected as esters; [d] identifiable, but compound is very volatile;

[e] PAHs quantified with GC/MS; [f] for more details see text; n.d. = not detected.

Estimated Emission Rates for Charbroiling and Frying in Los Angeles

To determine whether it is likely that a particular meat smoke aerosol compound should be detectable in the atmosphere, it is useful to estimate the total emission rates of such compounds for all cooking activities combined. In this study, estimates are made for emissions within the greater Los Angeles area. In Table 3.2, meat consumption figures are presented for the two geographic areas shown in Figure 3.5: 1) the heavily populated central area of urban Los Angeles and Orange Counties; and 2) for the entire South Coast Air Basin that surrounds Los Angeles. Bornstein (4) conducted a survey of the amount of meat cooked in restaurants. He found that about 40% of all meat consumed is cooked in restaurants, of which 9% is charbroiled. In the present study, it is assumed that the remainder of the commercially–cooked meat is fried, and that the same cooking practices apply to meat prepared in private homes. (Backyard charcoal grilling is a common practice in Southern California.) Bornstein (4) estimated that ground meat represents over 50% of the meat served. Therefore, the emission data collected from the hamburger meat cooking experiments are used to approximate emissions for meat cooking of all types. In Table 3.3, the organic compound emission rates determined during the present study (Table 3.1) are used along with the meat consumption data of Table 3.2, to estimate the compound class emission rates for the 80×80 km geographic area shown in the center of Figure 3.5. For the charbroiled meat, two alternative cases are considered: 1) charbroiling of equal amounts of extra–lean and regular hamburger meat; and 2) charbroiling of regular hamburger meat only.

From Table 3.3, it is seen that approximately 25.6 to 30.4 kg day^{-1} of fine aerosol cholesterol is emitted from meat cooking operations within the 80×80 km

Table 3.2 Meat Consumption in the Los Angeles Area in 1982

Cooking Method	Estimated Amount of Meat Consumed[a]	
	Metropolitan Los Angeles[bc] (kg day^{-1})	Entire South Coast Basin[b] (kg day^{-1})
Charbroiling	211,000	253,000
Frying	2,129,000	2,561,000

[a] Meat consumption calculated using per capita meat consumption figures (retail weight, excluding meat byproducts) for the U.S. in 1982 (*39*), and 1980 population figures for the area of interest (*1*).

[b] 80 × 80 km heavily urbanized area, see Figure 3.5.

[c] 83% of the South Coast Air Basin's (SoCAB) population.

Table 3.3 **Fine Aerosol Emission Rates for Single Compound Classes from Charbroiling and Frying Meat.**

	—Compound Class Emission Rates[a]—		
	Charbroiled Meat		Fried Meat
	Case 1[b]	Case 2[b]	
	(extralean/reg.)	(only regular)	(extralean/reg.)
Compound Class	(kg day^{-1})	(kg day^{-1})	(kg day^{-1})
Alkanes	8.6	13.9	11.7
Alkanoic Acids	142.8	227.6	131.8
Alkenoic Acids	74.6	130.8	23.2
Dicarboxylic Acids	6.5	8.4	9.8
Alkanals	24.7	34.3	46.8
Alkanones	20.3	30.9	38.1
Alkanols	2.0	3.0	4.3
Furans	3.3	3.4	19.2
Lactones (Furanones)	14.3	17.6	31.9
Amides	11.2	14.7	6.0
Nitriles	1.2	1.7	2.3
PAHs	0.5	0.7	0.8
Pesticides	1.0	1.1	3.2
Cholesterol	10.5	15.3	15.1
Others	4.4	7.4	7.0
Total Identified	325.9	510.8	351.2
Fine Organic Carbon Emissions[c]	2900	4900	1400
Fine Organic Compound Emissions[d]	3500	5900	1700

[a] Estimated emission rates for compound classes calculated by using the meat consumption estimates from Table II for Metropolitan Los Angeles (80x80 km area shown in Figure 3.5), and assuming that hamburger meat is representative of all meat cooked.

[b] For the charbroiled meat, two alternative cases are considered: 1) charbroiling equal amounts of extralean and regular hamburger meat, and 2) charbroiling of regular meat only.

[c] Based on thermal evolution and combustion analysis of source samples to determine the quantity of identified plus unidentified compounds present.

[d] Organic compounds $\approx$ 1.2 x organic carbon.

heavily urbanized area shown in the center of Figure 3.5. The total emissions of primary aerosol organic carbon from all sources combined within that geographic area during 1982 has been estimated to range from 27500 kg day^{-1} (*1*) to 29800 kg day^{-1} (*2*). This corresponds to an emission rate of 33000 to 35800 kg day^{-1} if the organic carbon is restated as the equivalent mass of organic compounds. Thus cholesterol accounts for about 0.07% to 0.08% (calculated using the higher total emission estimate of Hildemann et al. (*2*)) of the fine aerosol organic compound emissions in metropolitan Los Angeles. The data of Gray et al. (*40*) show that fine aerosol organic compound concentrations in the West Los Angeles atmosphere averaged 9.1 μg m^{-3} during October of 1982 (organic compounds $\approx$ 1.2 x organic carbon). If 0.08% of that organic compound mass concentration were present as cholesterol, then ambient fine particle concentrations of cholesterol would reach about 7.3 ng m^{-3}. At those concentrations cholesterol would be detectable in atmospheric samples, and may serve as a useful molecular marker for cooking operations (meat cooking plus cooking of other cholesterol–containing foods).

Comparision of Source and Ambient Data

Atmospheric organic fine aerosol samples ($d_p \leq 2$ μm) taken at West Los Angeles during 1982 by Gray et al. (*40*) have been extracted and analysed by HRGC as reported by Mazurek et al. (*8*). The analysis methods used were essentially identical to those employed to process the source samples discussed here. The West Los Angeles monthly average fine aerosol composite for October 1982 examined by Mazurek et al. (*8*) was subjected to GC/MS analysis as part of the present study, and the atmospheric concentrations of several important compounds that also appear in meat smoke aerosol were determined, as shown

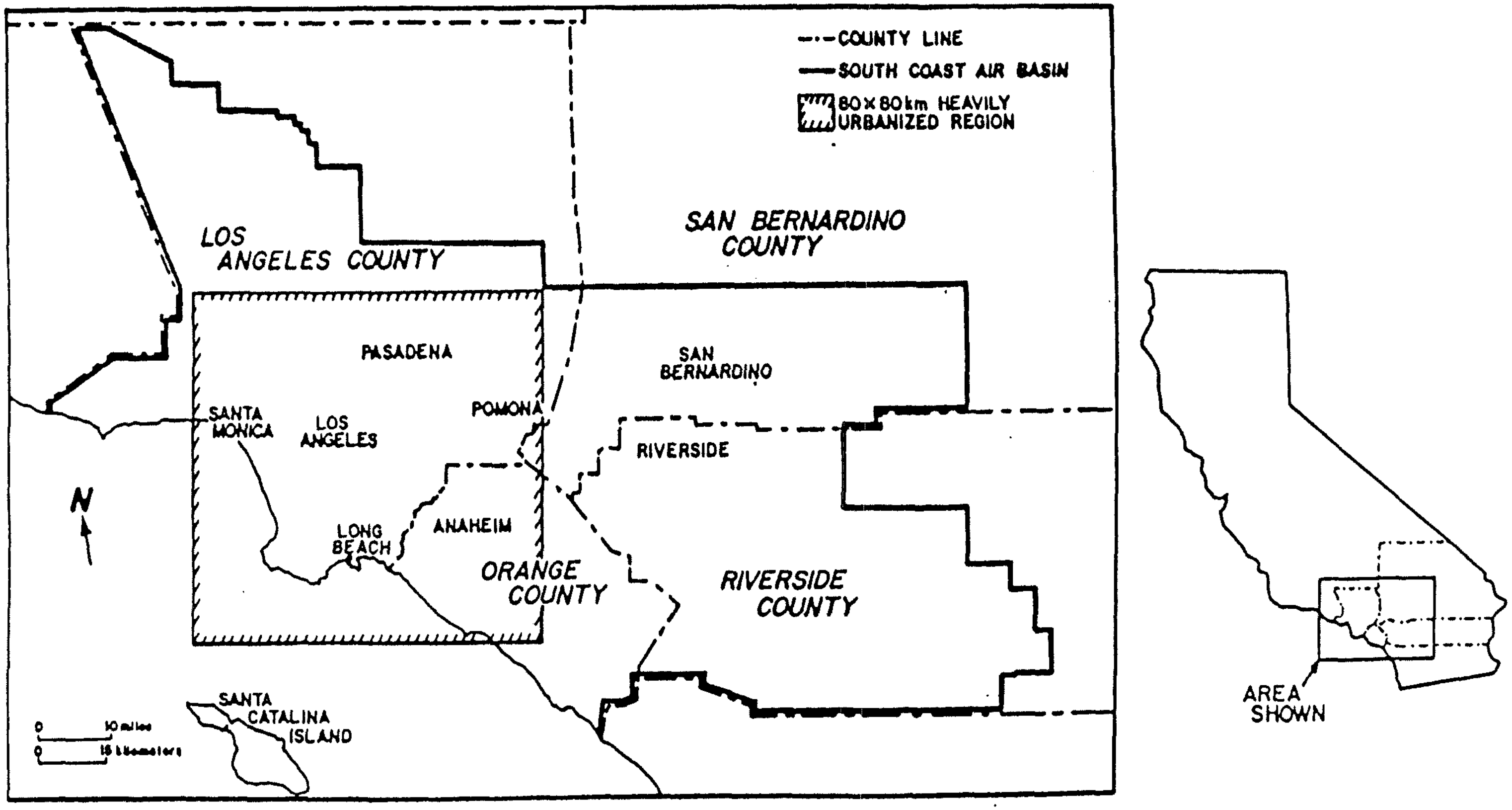

Figure 3.5: Geographic outline of the South Coast Air Basin, showing an 80×80 km square area that contains 83% of the basin's population in 1982.

in Table 3.4. The October 1982 ambient sample analyzed here was chosen for its very clear cholesterol identification. The cholesterol concentration for that month is roughly 5 times higher than the annual mean cholesterol concentration at that site.

Cholesterol is indeed identifiable in the West Los Angeles ambient fine aerosol, as seen in Figure 3.6a and Figure 3.7a. The ambient fine particle concentration of cholesterol in October 1982 when quantified by HRGC is found to be 14.6 ng m^{-3}, within a factor of two of the rough estimate of the meat smoke–derived fine aerosol cholesterol concentration made in the previous section by scaling from emission data. The ambient cholesterol concentration is a little greater than would be expected from meat smoke alone, indicating that there may be other sources of cholesterol. Cholesterol has been reported as a constituent of some plant life (*41–43*) and has been observed as a major constituent of the total sterols in urban and rural aerosols (*41*).

All n–alkanes and n–alkanoic acids (see Figures 3.2a–c and Figure 3.6b) identified in the meat smoke were also identified in the fine ambient organic particulate matter collected. Palmitoleic acid (cis–9–hexadecenoic acid) was below the detection limit in the ambient sample. Stearic acid (cis–9–octadecenoic acid) was present at much higher concentration in the ambient sample than oleic acid, while in the hamburger source emissions this relation was reversed. In addition to succinic acid (butanedioic acid), glutaric acid (pentanedioic acid), and adipic acid (hexanedioic acid) which were present in the meat cooking emissions, malonic acid (propanedioic acid) and azelaic acid (nonanedioic acid) also could be identified in the ambient sample. Suberic acid (octanedioic acid) was only detected in the source aerosol. From the group of normal alkanals, only nonanal

Table 3.4 Fine Aerosol Emission Rates and Ambient Concentrations Normalized to Cholesterol for the 80×80 km Urbanized Los Angeles Area.

	–Meat Cooking Emissions–[a]		Ambient Concentrations West Los Angeles Oct. 1982	
Compound Class	Case1 (Case2)[a] (kg day^{-1})	Normalized to Cholesterol Emissions	(ng m^{-3})	Normalized to Cholesterol Concentrations
	—n-Alkanes—			
Tricosane	1.6 (1.9)	0.06 (0.06)	3.0	0.21
Tetracosane	3.4 (5.4)	0.13 (0.18)	3.7	0.25
Pentacosane	3.4 (5.6)	0.13 (0.18)	6.9	0.47
Hexacosane	1.2 (1.4)	0.05 (0.05)	6.2	0.42
Heptacosane	1.7 (1.9)	0.07 (0.06)	8.1	0.55
Octacosane	1.1 (1.4)	0.04 (0.05)	2.6	0.18
Nonacosane	2.0 (2.3)	0.08 (0.08)	9.4	0.64
	—n-Fatty Acids[b]—			
Palmitic acid	94.5 (141.2)	3.69 (4.63)	106.2	7.27
Stearic acid	50.5 (70.6)	1.97 (2.31)	59.9	4.10
Palmitoleic acid	7.7 (12.7)	0.30 (0.42)	not detected	
Oleic acid	90.1 (141.4)	3.52 (4.64)	29.0	1.99
	—Dicarboxylic Acids[b]—			
Butanedioic acid	5.8 (6.2)	0.23 (0.20)	14.1	0.97
Pentanedioic acid	2.8 (3.2)	0.11 (0.10)	3.1	0.21
Hexanedioic acid	5.5 (6.3)	0.21 (0.21)	7.9	0.54
	—n-Alkanal—			
Nonanal	34.2 (36.4)	1.34 (1.19)	11.8	0.81
	—n-Alkanone—			
2-decanone	9.7 (10.8)	0.38 (0.35)	2.7	0.18
	—Amide—			
Palmitamide	5.8 (7.3)	0.23 (0.24)	0.4	0.03
	—Polycyclic Aromatic Hydrocarbons[c]—			
Fluoranthene	0.33 (0.35)	0.013 (0.011)	0.09	0.006
Pyrene	0.29 (0.35)	0.011 (0.011)	0.13	0.009
Benz[a]anthracene	0.10 (0.10)	0.004 (0.003)	0.16	0.011
Chrysene/Triphenylene	0.43 (0.43)	0.017 (0.014)	0.22	0.015
Benzo[k]fluoranthene	0.04 (0.07)	0.002 (0.002)	1.36	0.093
Benzo[a]pyrene[d]	0.04	0.002	0.29	0.020
	—Steroid—			
Cholesterol	25.6 (30.5)	1.0 (1.0)	14.6	1.0

---

[a] 9% of meat is charbroiled, 91% of meat is fried. In Case 1, the charbroiled and fried meats are taken as a blend of 50% regular meat (21% fat) and 50% extralean meat (10% fat). Numbers in parenthesis refer to (Case 2). In (Case 2), the fried meat is 50% regular and 50% extralean, but the charbroiled meat is all regular hamburger meat with 21% fat.

[b] detected as esters.

[c] PAHs quantified by GC/MS.

[d] only detected for charbroiling meat with 21% fat.

and traces of decanal could be identified in the ambient sample. For normal alkanones, 2–decanone was the only identifiable normal ketone in the ambient sample. None of the alcohols found in the meat cooking emissions could be identified in the airborne fine particulate matter, likewise for the pesticides, furans, lactones, and nitriles. The group of higher lactones could otherwise be used as unique markers. Traces of palmitamide could be found in the airborne fine particulate matter. All PAHs, except perylene, found in the meat smoke were also found as constituents in atmospheric fine particles (see Figure 3.7b and 3.7c).

Many of the organic compounds just discussed in the ambient aerosol come from diverse sources in addition to meat cooking. Fine particle cholesterol appears to be one of the more unusual compounds emitted, and may serve in part as a marker for meat cooking emissions. In Table 3.4, the abundance of the compounds emitted in meat smoke has been normalized relative to the cholesterol emission rates, and the same compounds seen in the West Los Angeles ambient fine aerosol also have been normalized relative to ambient cholesterol concentrations. It is seen that the normal alkanes are enriched in the atmosphere relative to the alkanes content of meat smoke. Normal alkanes have many anthropogenic and biogenic sources (*8, 44, 45*). Therefore, it is not surprising to see increased ambient concentrations of n–alkanes compared to the normalized emissions from meat cooking. The same is true for the two principal n–alkanoic acids considered here: palmitic and stearic acids. These alkanoic acids are major constituents of seed oils that are used as cooking oils and thus may be injected into the atmosphere from cooking operations other than those studied here (*18*). The dicarboxylic acids investigated show a distinct enrichment in the atmosphere beyond that due to meat cooking, consistent with their formation in part due

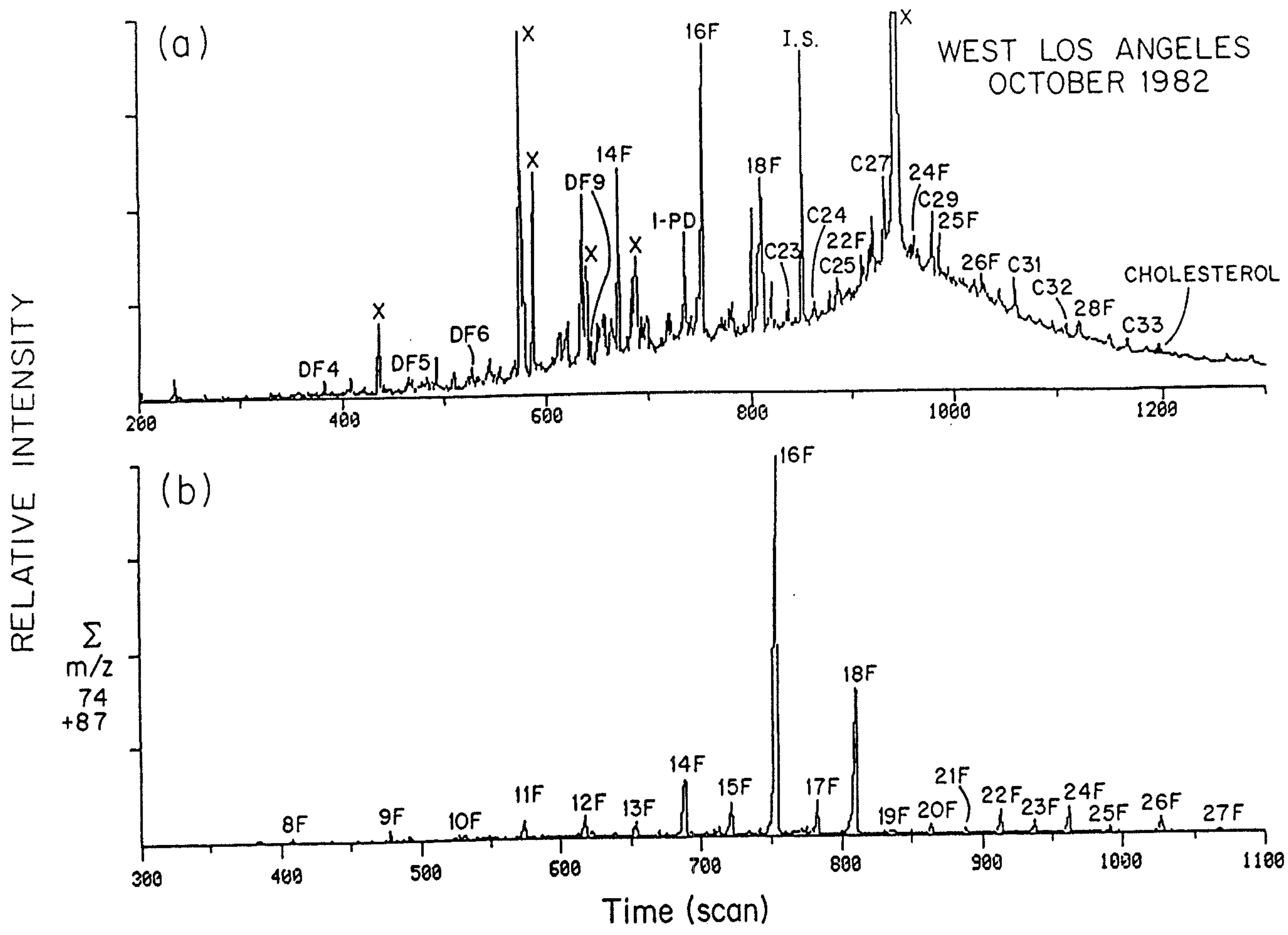

Figure 3.6: Total ion current (a) and summed m/z 74 + 87 traces (b) for the GC/MS data from the acid + neutral fraction of the fine ambient aerosol from West Los Angeles in October 1982 ($d_p \leq 2.0$ μm). Peak labels as in Figure 3.1, and DF = dicarboxylic acid; C_i = n–alkane.

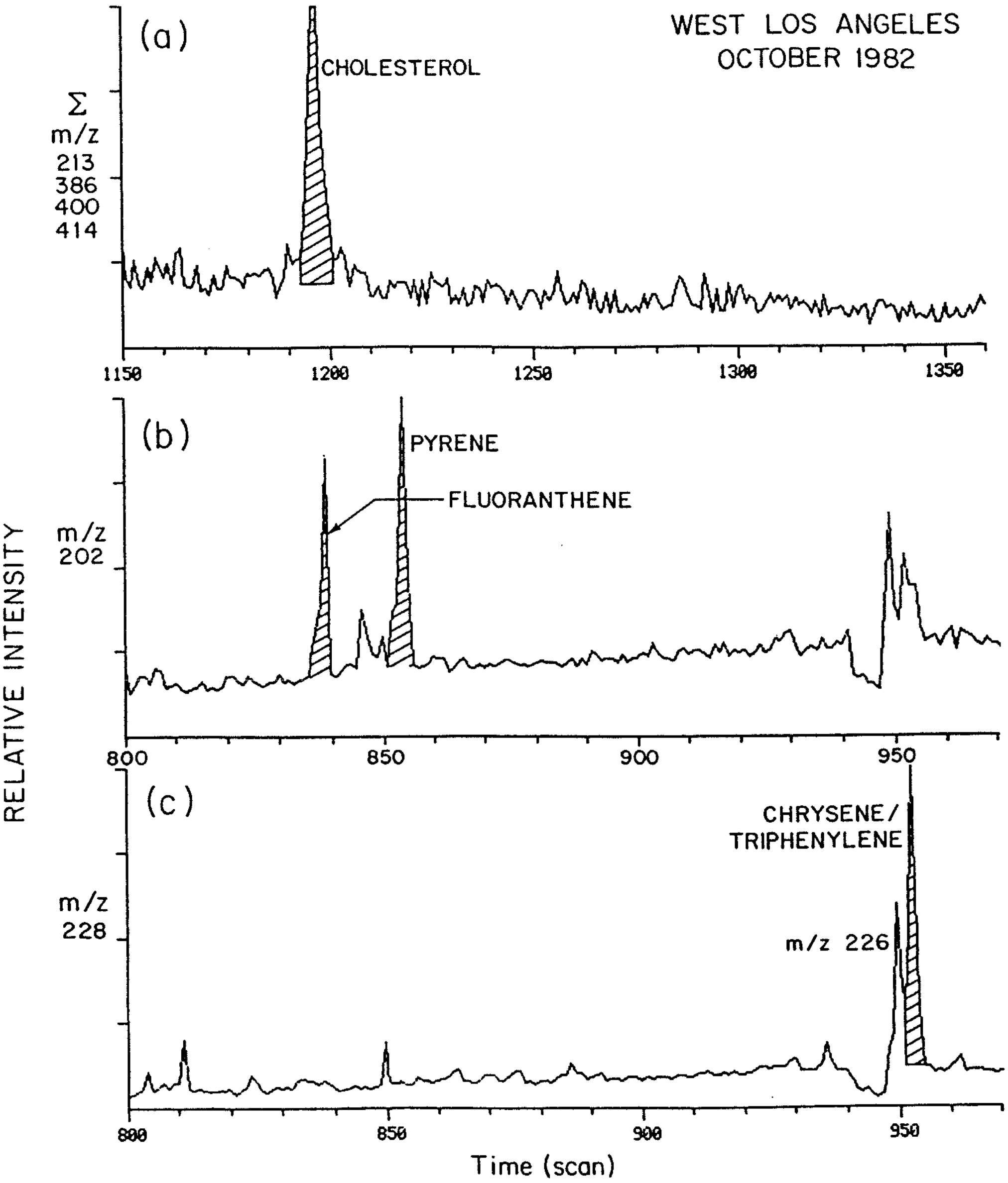

Figure 3.7: Selected mass fragmentograms for sterols (a) and for PAHs (b) + (c) in the acid + neutral fraction of the fine ambient aerosol ($d_p \leq 2.0$ μm) from West Los Angeles in October 1982 (same plot parameters as Figure 3.3).

to gas–to–particle conversion processes in the atmosphere (*25*). Oleic acid, an alkenoic acid, is relatively depleted in the atmospheric fine aerosol compared to cholesterol from meat cooking, in agreement with the suggestion of Mazurek et al. (*8*) that such unsaturated compounds are converted in the atmosphere by heterogeneous chemical reactions. The same is true for the most abundant alkanal present in the meat cooking emissions. Nonanal, a normal aldehyde, may be oxidized in the atmosphere to the more stable n–nonanoic acid. Palmitamide shows the most pronounced depletion in the atmospheric fine particle phase when compared to cholesterol. Polycyclic aromatic hydrocarbons are enriched in the atmosphere relative to meat smoke, consistent with the presence of other anthropogenic combustion sources. The relative depletion of the lower molecular weight PAHs fluoranthene and pyrene could be due to enhanced photodecomposition as suggested by Katz et al. (*46*), or to other atmospheric chemical reactions.

Meat Smoke Tracers in the Atmosphere

In order for a chemical substance to serve as a tracer for source aerosol constituents in the polluted atmosphere, the following conditions must be satisfied: the organic compound must be at least quasi–stable with a half–life in the atmosphere that is longer than the characteristic transport time from source to receptor; the amount released into the atmosphere must be large enough, so that the atmospheric concentration of the compound under consideration is quantifiable by the analytical method used; and finally, either the tracer compound should be unique to the source of interest or alternatively a set of tracer compounds should exist that have a unique emission pattern. Fine aerosol cholesterol can be regarded as a potentially important marker for food cooking operations. A supplemental set of tracer compounds for meat smoke —which as individuals have multiple sources, but as a group reveal a distinct pattern— could consist of : myristic acid (n–tetradecanoic acid); palmitic acid (n–hexadecanoic acid); stearic acid (n–octadecanoic acid); and oleic acid (cis–9–octadecenoic acid) from the fatty acids; the aldehyde nonanal, and the ketone 2-decanone. The lactones, which could constitute an interesting set of tracers, cannot be used in combination with the available atmospheric data, since their ambient concentrations are too low to be quantified in the samples available in the present study.

Conclusion

The chemical composition of the organic fine aerosol released into the atmosphere from charbroiling and frying of hamburger meat has been studied by HRGC and GC/MS techniques. The emission rates for more than 75 individual compounds were quantified, including the series of n–alkanes, n–alkanoic acids, n–alkenoic acids, dicarboxylic acids, n–alkanals, n–alkanols, furans, lactones, amides, nitriles, PAHs, steroids, and pesticide residues. Some of the more abundant compounds isolated in the meat smoke aerosol include palmitic acid (n–hexadecanoic acid), stearic acid (n–octadecanoic acid) and oleic acid (cis–9–octadecenoic acid). Major oxidation products of fatty acids which are found in meat smoke aerosol include nonanal, 2–octadecenal, and 2–octadecanone. In most cases the emission rates for the individual compounds followed the pattern observed for the mass emission rate of total organic carbon. Fine aerosol emissions from charbroiling of regular hamburger meat are higher than from charbroiling extra–lean meat, which in turn are much higher than the emissions from frying the same amount of hamburger meat. Cholesterol was measured in substantial concentrations in the meat smoke aerosol. Fine organic aerosol data from ambient sites and emission rate data for all urban sources combined—

including meat cooking operations— for the greater Los Angeles area suggest that if cholesterol were emitted at the rates measured here, then it should be present in the atmospheric fine aerosol at West Los Angeles in October 1982 at concentrations of about 7.3 ng m^{-3}. Examination of atmospheric fine aerosol samples from that location show ambient cholesterol concentrations of 14.6 ng m^{-3}. While there may be additional sources of cholesterol, this suggests that cholesterol concentrations in the atmospheric fine aerosol are within a factor of two of what one would expect if meat smoke is the dominant source, and suggests that cholesterol may be an important tracer for meat cooking operations. Unsaturated organic acids, such as palmitoleic acid and oleic acid were found to be depleted in the atmospheric aerosol relative to their abundance in meat smoke as traced by cholesterol, suggesting that they undergo atmospheric chemical reactions. Many other compounds, including the n–alkanes, n–alkanoic acids, and PAHs are enriched in the atmosphere relative to the contribution from meat smoke as traced by cholesterol. This confirms that ambient concentrations of these compounds result from the superposition of emissions from other sources in addition to meat smoke.

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Chapter 4

Noncatalyst and Catalyst–Equipped Automobiles and Heavy-Duty Diesel Trucks

Introduction

For more than four decades, exhaust emissions from gasoline and diesel powered vehicles have received attention because of their potential for producing adverse health effects, contribution to visibility deterioration, and their dominant influence on atmospheric smog formation (*1–7*). Because of the complexity of primary particulate vehicular emissions, characterization of the chemical composition of vehicle exhaust aerosol is still under study. Much of the research to date on exhaust emissions from vehicles has been guided by the mutagenic and genotoxic potential of certain compound classes found in the particle-phase, e.g., polycyclic aromatic hydrocarbons (PAH), oxygenated PAH, and nitroarenes (*1, 8–21*). Together, these compounds are considered to be among the most pervasive classes of potential environmental carcinogens (*22*).

Vehicle exhaust aerosols, however, contain a great variety of organic compounds in addition to those that have been studied for their mutagenic or carcinogenic potential. Among these compounds may be relatively stable molecules that could be used to trace and quantify the presence of vehicle exhaust in urban atmospheres. If unique tracer compounds or groups of distinct compound assemblages characteristic of exhaust from gasoline and diesel vehicles could be

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Reference: Rogge, W.F.; Mazurek, M.A.; Hildemann, L.M.; Cass, G.R.; Simoneit, B.R.T. *Environ. Sci. Technol.*, 1993, 27, 636–651.

identified and these compounds could also be measured in ambient air, then the fractions of the ambient aerosol derived from gasoline and diesel vehicles could be accurately determined. In the past, the lead content of gasoline powered vehicle exhaust was used to estimate the contribution of gasoline powered cars to the ambient aerosol (*23-26*). Today, due to the near absence of lead in gasoline and the absence of a unique elemental marker in diesel fuel, it has become very difficult to apply receptor modeling methods to the analysis of vehicle–influenced urban air quality problems. Thus it is quite important to future studies that alternative molecular tracer compounds be identified in both diesel and spark–ignition engine emissions.

In the present study, gasoline and diesel powered vehicle exhaust aerosol samples collected by Hildemann et al. (*27, 28*) are analyzed by gas chromatography/mass spectrometry (GC/MS) to characterize the organic particulate matter in vehicle exhaust at a molecular level.

Experimental Methods

Dilution Sampler

A dilution sampling device was used to measure the fine particulate matter ($d_p \leq 2$ μm) emissions from a fleet of automobiles and diesel trucks, including that portion of the vapor-phase organics that would have condensed onto preexisting particles as the exhaust is cooled by mixing in the atmosphere. The newly developed dilution source sampler was designed and tested by Hildemann et al. (*29*). The motor vehicle source sampling program, including measurement of exhaust aerosol size distributions and bulk chemical characteristics (22 elements, ionic species; elemental carbon (EC) and bulk organic carbon (OC)), has been described in detail elsewhere (*27, 30*). Only a brief description of the test procedures will be provided here.

The dilution source sampler configuration used for motor vehicle tests consisted of a dilution air purification system, predilution tunnel, the main dilution tunnel with its attached residence time chamber, followed by fine aerosol collection downstream of cyclone separators. Hot vehicle exhaust emitted from the tailpipe of the vehicle was introduced directly into the predilution tunnel and diluted (approximately 3-fold for the diesel trucks, and an average of 11- to 23-fold for the automobiles) with a controlled stream of precleaned dilution air (HEPA filtered). By achieving a constant flow rate through the predilution tunnel the exhaust concentration of the vehicle emissions varied according to the vehicle speed. This procedure guaranteed that the exhaust concentration in the predilution tunnel was proportional to the flux of exhaust from the tailpipe at any speed. A constant fraction of the prediluted vehicle exhaust was diverted into a second-stage dilution tunnel and diluted a second time, achieving on average a dilution of 80- to 90-fold for the diesel trucks, and 300- to 600-fold for the automobiles. Aerosol samples were collected on filters located downstream of AIHL-designed cyclone separators (*31*) having a 50% cutoff at 2 μm aerodynamic particle diameter.

Dilution Sampler Preparation

All parts of the sampling system which might come into contact with exhaust emissions were carefully cleaned prior to use to guard against possible contamination. Smaller parts, including the cyclones and filter holders were rinsed with dionized water, and then sequentially sonicated for 5 min each in glass-distilled methanol and glass-distilled hexane. The larger parts, including the predilution tunnel, were vapor-degreased with tetrachloroethylene and then baked out by wrapping electrical heating tape around the stainless steel pieces while drawing purified air through the sampler. For further details, see Hildemann et al. (*27*).

Vehicle Testing Procedures

The vehicle fleet tested during this program consisted of 15 different automobiles and trucks that were in current use in the Los Angeles area, representing a wide range of vehicle ages and accumulated mileage. Six automobiles without catalytic converters, seven catalyst-equipped automobiles, and two heavy-duty diesel trucks listed in Table 4.1 were tested on chassis dynamometers at the California Air Resources Board's Haagen-Smit Laboratory. The thirteen passenger cars were tested following the cold-start Federal Test Procedure (FTP) to simulate urban driving conditions. For the diesel trucks, a heavy-duty chassis dynamometer was used. The heavy-duty driving cycle included idle modes, constant driving speed at ca. 40 km/h and 70 km/h, plus abrupt acceleration and deceleration modes (*27, 30*). Five of the automobiles without catalytic converters were tested with leaded regular gasoline with a lead content of 0.34 g/gal, while the two other noncatalytic cars used premium gasoline with 0.22 g of Pb/gal. The heavy-duty diesel trucks were late model, low mileage trucks provided by the City of Pasadena, and were operated with the diesel fuel normally purchased by the owner. Additional information regarding the vehicles tested can be found in Table 4.1; for a complete description see Hildemann et al. (*27*).

Fine particle exhaust samples were collected downstream of six parallel AIHL cyclone separators, each connected to three 47-mm diameter filter holders which were used to sample particulate matter at a flow rate of 9.0–9.6 L/min per filter, yielding 18 separate fine particle samples. Sixteen filter holders were loaded with

Table 4.1. **Emission Characteristics of the Vehicle Fleet Tested**

Vehicle Fleet	FTP-fuel economy mi gal^{-1}	Fine Particulate Emissions mg/km driven	% Organics (OC x 1.2)	% Elemental Carbon (EC)
6 noncatalyst automobiles[a]	15.7	59.4	78.6	8.0
7 catalyst-equipped automobiles[b]	23.3	18.0	60.1	22.6
2 heavy-duty diesel trucks[c]	7.6[d]	408.0	39.1	40.5

[a] Average of the following vehicles: 1965 Mercury Monterey, 1969 Ford Mustang, 1970 Buick Skylark, 1972 Chevrolet Caprice, 1974 Ford Pinto, and 1976 Volkswagen Beetle.

[b] Average of the following vehicles: 1977 Chevrolet Vega, 1980 Honda Civic 150, 1980 Honda 1500, 1980 Toyota Corolla, 1981 Datsun 200SX, 1983 Chevrolet Malibu CL, 1983 Dodge Omni.

[c] Average of the following diesel trucks: 1987 GMC Truck (2-axle), 1987 Ford Dump Truck (3-axle).

[d] Fuel economy for the truck driving cycle as explained in text.

quartz fiber filters (Pallflex 2500 QAO), and the remaining two filter holders contained Teflon filters (Gelman Teflo, 2.0-μm pore size). All quartz filters were baked at 750°C for 2-4 h before use in order to ensure low organic contamination levels on the blank filter material. After each experiment, three filter samples (2 Teflon and 1 quartz fiber filter sample) were used for the determination of trace metals, ionic species, total organic (OC) and elemental carbon (EC). The remaining quartz fiber filters were reserved for organic compound analysis. All samples were stored at –25°C shortly after completion of each source test.

Sample Extraction

Filter samples from the motor vehicle source tests were grouped to form three composite samples representing, respectively, 7 catalyst-equipped automobiles, 6 automobiles without catalytic converters, and 2 heavy-duty diesel trucks. An extraction protocol was followed which is designed for the quantitative analysis of trace amounts of organic compounds found in particulate matter. The method is described extensively elsewhere (*32–36*). In brief, each filter composite was spiked prior to extraction with known amounts of perdeuterated tetracosane ($\underline{n}$-$C_{24}D_{50}$) which served as a recovery standard. The samples were extracted twice with hexane, followed by successive extraction three times with benzene/2-propanol (2:1). After combining the extracts and reducing the extract volume in a multistep reduction process to 200 - 500 μl, one aliquot of the extract was derivatized by adding freshly produced diazomethane to convert organic acids to their methyl ester analogues and other compounds having active H-atoms (e.g., phenols, enols) to their methoxy analogues.

Compound Identification and Quantification

Compound identification and quantification were conducted using a Finnigan 4000 quadrupole gas chromatograph/mass spectrometer (GC/MS) interfaced with an INCOS data system. The GC/MS-system was operated in the electron impact mode (electron energy of 70 eV). The chromatographic procedure for GC/MS can be described as follows: (1) extract injection at 65°C, (2) isothermal hold at 65°C for 10 min, (3) temperature ramp program of 10°C/min for 21 min, and (4) isothermal hold at 275°C for another 49 min. Additional details are described elsewhere (*32, 33, 35, 36*).

Compound identification was performed with the help of the National Institute of Standards and Technology (NIST) Standard Library (incorporated in the INCOS data system) and, where available, by comparison with the retention times and mass fragmentation patterns of standard reference compounds. Organic compounds that remain undetected include: (a) compounds of molecular weight higher than about 500 (the upper limit of the spectrometer mass scan), e.g., polymeric compounds; (b) organics in very low yields; (c) compounds insoluble in the solvents used; and (d) compounds which do not elute from the chromatographic column used. Within these constraints, compound identification was deemed: (a) positive, when the sample mass spectrum was identical to that of an authentic standard plus the library spectrum and also the retention time data for the sample and standard agreed quite well; (b) probable, same as above except that no authentic standards were available; (c) possible, same as above except that the mass spectrum contained information from other compounds but with minor overlap; or (d) tentative, when the mass spectrum revealed additional fragment ions from several compounds (noise) with overlap.

Quantification was based on the the application of 1-phenyldodecane as coinjection standard and perdeuterated tetracosane ($\underline{n}$-$C_{24}D_{50}$) as the internal surrogate standard. In order to correct for detector response, sets of relative response factors were determined from multiple injections and analyses of standard compounds with the analytical system.

Standard Compounds

Quantification and compound confirmation was achieved using prepared standards. The following standard mixtures were injected onto the GC/MS-systems: (1) normal alkanes ranging from $\underline{n}$–C_{10} to $\underline{n}$–C_{36}; (2) normal alkanoic acids as methyl esters from $\underline{n}$–C_6 to $\underline{n}$–C_{30}; (3) a suite of 40 aromatic and polycyclic aromatic hydrocarbons (PAHs): iso-propylbenzene; indan; neo-pentylbenzene; 1,2,3,4–tetramethyl-benzene; naphthalene; 2–methylnaphthalene; 1–methylnaphthalene; 1,1'–biphenyl; 2,6–dimethylnaphthalene; hexamethylbenzene; 1,3,5–triisopropylbenzene; acenaphthylene; 2,3,4–trimethylnaphthalene; fluorene; 2–methylfluorene; 3–methyl–1,1'–biphenyl; 3,4'–dimethyl–1,1'–biphenyl; dibenzothiophene; phenanthrene; anthracene; fluoranthene; pyrene; 2,3–benzofluorene; 1,1'–binaphthalene; benz[a]anthracene; chrysene; triphenylene; benzo[b]fluoranthene; benzo[k]fluoranthene; benzo[e]pyrene; benzo[a]pyrene; perylene; 9,10–diphenylanthracene; dibenz[a,h]anthracene; benzo[ghi]perylene; anthanthrene; coronene; 1,2,4,5-dibenzopyrene; cyclopenta[cd]pyrene; indeno[1,2,3-cd]pyrene; (4) a set of 10 polycyclic aromatic ketones and quinones: 9H-fluoren-9-one; dibenzofuran; phenyl-p-tolylketone; benzophenone; 9,10-phenanthrenedione; 9,10-anthracenedione; anthrone; xanthone; 7H-benz[de]anthracen-7-one; benz[a]anthracene-7,12-dione; (5) a set of 8 aromatic and polycyclic aromatic N– and S–substituted compounds: 4–hydroxyquinone; phenanthridine; carbazole; 5,6–benzoquinoline; 7,8–benzoquinoline; 1,2,3,4–tetrahydro-9-acridanone; dibenzothiophene; 9–thioxanthenone; (6) a suite of 11 dicarboxylic acids (C_3 – C_{10}) as dimethyl esters; and (7) others: 4–methylbenzaldehyde; 3,4–dimethoxybenzaldehyde; indanone; 20R-5α(H),14α(H),17α(H)-cholestane; 2–methoxypyridine; benzothiazole; 1–methyl-2-pyrrolidinone; N,N–dibutylformamide; 2-(2-butoxyethoxy)-ethanol; 2,3–dihydroxy-1H-indan-1-one.

Results and Discussion

Sources of Particulate Emissions from Combustion Engines

In order to understand how the molecular nature of vehicle exhaust aerosol may be related to vehicle operation, it is useful to consider the mechanisms within the internal combustion engine which contribute to the emissions of particle-phase organic compounds.

The composition and emission rate of particles from internal combustion engines vary with: (a) engine parameters such as engine type and design, size, accumulated operation time, and emission control system; (b) engine operating conditions including length of cold start period, air/fuel ratio, engine load, lubricant oil type, and fuel composition; (c) maintenance schedule for engine adjustment and lubricant oil replacement (*12, 19, 37-39*).

The contribution of fuels and lubricants to the aerosol production process can be further subdivided by tracing the molecular origin of the aerosol back to the following 7 sources and processes: (1) unburned fuel components, (2) unburned lubricant oil components, (3) partially oxidized combustion products from the combustion of fuel, (4) partially oxidized products of the combustion of lubricant oil, (5) pyrolysis products of fuel constituents, (6) pyrolysis products from lubricant oil, and (7) combustion of fuel additives (*13, 37, 38, 40–46*). Gasoline fuels have a final boiling point of less than 220°C, and consist of a complex mixture of hydrocarbons ranging from C_4 to C_{10} in carbon numbers (*47, 48*). Typical diesel fuels on the other hand, show boiling points between 280°C and 360°C and hydrocarbon mixtures that range from roughly C_{10} to C_{25} (*37, 38, 43, 47, 49*). The higher boiling fraction of diesel fuel is largely responsible for the soot formation characteristic of diesel vehicles (*47*). In contrast, lubricating oils usually have final boiling points between 400°C and 550°C and consist of hydrocarbon mixtures from C_{14} to C_{45} (*40, 47, 49, 50*). A number of researchers have investigated the contribution of engine oil to the particulate exhaust emissions from diesel powered vehicles. It was concluded that depending on the operating conditions, 2 – 25% of the particulate mass emitted originated from the lubricating oil. This amounted to 10 – 88% of the solvent-extractable particulate mass emitted (*37–40, 42, 43, 46, 51*). Pedersen et al. (*39*) conducted a number of experiments on a gasoline powered engine. They found that 90% of the engine oil consumed in the combustion chamber had passed the piston and piston rings while 10% passed through the Positive Crankcase Ventilation system (PCV) to reach the combustion chamber. Further, they observed that using a lubricant oil with lower viscosity markedly increased both oil consumption and particulate emissions. The oil consumption and therefore the particulate emissions from high-mileage automobiles are increased as oil mist is passed into the combustion chamber via worn-out intake valve guides (*39*). Since there are distinct differences between the chemical composition of fuels vs. lubricants, it may be possible to identify the relative contribution of each of these sources to the exhaust aerosol during the present source testing program.

Vehicular Mass Emission Rates

Details of the vehicles tested have been published elsewhere, including the fine particle emission rates, the bulk chemical and elemental compositions of the fine particulate matter emitted, and the particle size distributions for the different vehicle types (*27*, *30*). Table 4.1 summarizes the major vehicle fleet emission characteristics including fuel consumption, fine particle emission rates, and bulk content of organics and elemental carbon. Hildemann et al. (*27*) have shown that the fleet-average mass emission rates for these noncatalyst and catalyst-equipped autos compare well with previously published data. The fine particulate emission rates for the two fairly new heavy-duty diesel trucks tested are somewhat lower than have been found by other studies. The organic carbon emission rates from these diesel trucks are similar to earlier studies but the elemental carbon (e.g., black soot) emission rates are lower than for older trucks (*27*).

Mass Balance for Elutable Fine Organic Matter

Material balances that describe the chemical composition of the elutable organic mass as detected by GC/MS were constructed and are shown in Figures 4.1a-c. The elutable organic mass can be subdivided into resolved and unresolved organic mass. The unresolved organic mass often referred to as an unresolved complex mixture (UCM) (*52*), consists mainly of branched and cyclic hydrocarbons and comprises 84.6% (catalyst-equipped autos) to 90.3% (heavy-duty diesel trucks) of the elutable organic mass. From the mass fraction that is resolved as discrete peaks by GC/MS (resolved organic mass), 42.3% (heavy-duty diesel trucks) to 67.9% (noncatalyst autos) could be identified as specific organic compounds. For noncatalyst automobiles, the main portion (61.2%) of the identifiable mass consists of PAH and oxy-PAH such as polycyclic aromatic

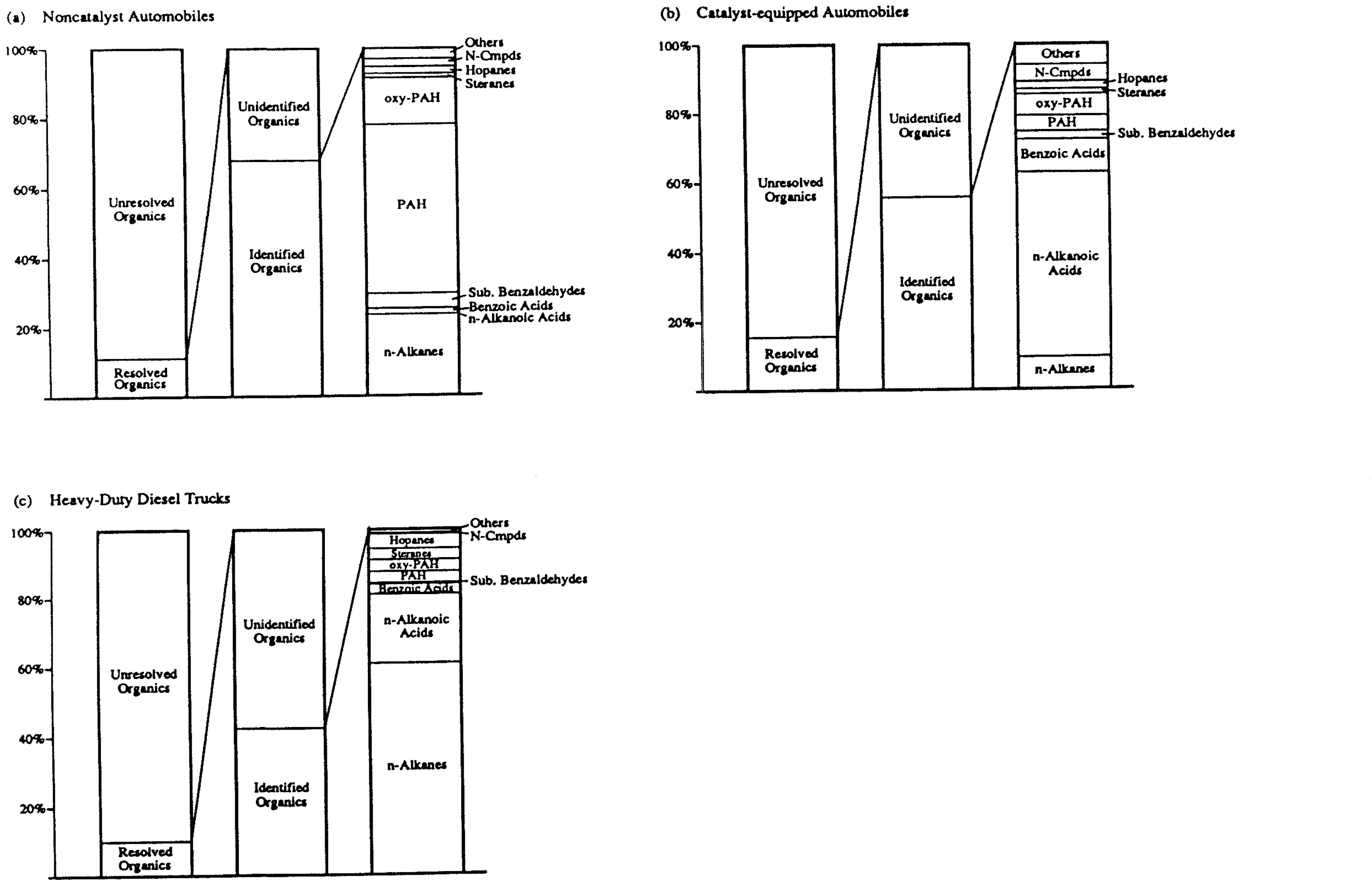

Figure 4.1 Mass balance for elutable organic matter in the fine particle emissions from: (a) automobiles without catalytic converters, (b) catalyst-equipped automobiles, and (c) heavy-duty diesel trucks.

ketones (PAK) and polycyclic aromatic quinones (PAQ). In contrast, 53.4% of all the identifiable resolved organic mass being released from catalyst-equipped autos consists of n-alkanoic acids. For heavy-duty diesel trucks most of the identified resolved organic mass consists of n-alkanes (60.8%). Mechanisms and sources will be discussed below which might explain the compositional differences found in the elutable organic mass emitted as fine aerosols from the vehicle types investigated here.

Exhaust Aerosol Composition

Figures 4.2a-c show the total reconstructed ion current (RIC) plots for (a) autos without catalytic converters, (b) catalyst-equipped autos, and (c) heavy-duty diesel trucks. The variety of compounds identified in vehicular exhaust emissions and their emission rates can be described as follows.

Alkanes

Crude oil, the primary source for gasoline, diesel fuel, and lubricating oil, contains n-alkanes ranging up to about C_{35} with no preference for odd versus even carbon numbers and shows a carbon preference index (CPI_{odd}) of about 1.0 (*52–56*). Because gasoline generally contains only the low boiling crude oil distillates $\leq C_{10}$, virtually no particle-phase n-alkanes ($\geq C_{19}$) should be contributed from unburned gasoline. Diesel fuels contain n-alkanes up to C_{30} with more than 95% of these n-alkanes by mass having carbon numbers less than C_{19} (*54, 57, 58*). Newly refined lubricant oils show only trace amounts of n-alkanes (*55, 59*). To insure trouble-free engine operation at low temperatures a steady supply of lubricant oil is necessary at points of friction in the engine. Because the ability to pump lubricating oil through the engine depends strongly on the wax (n-alkanes)

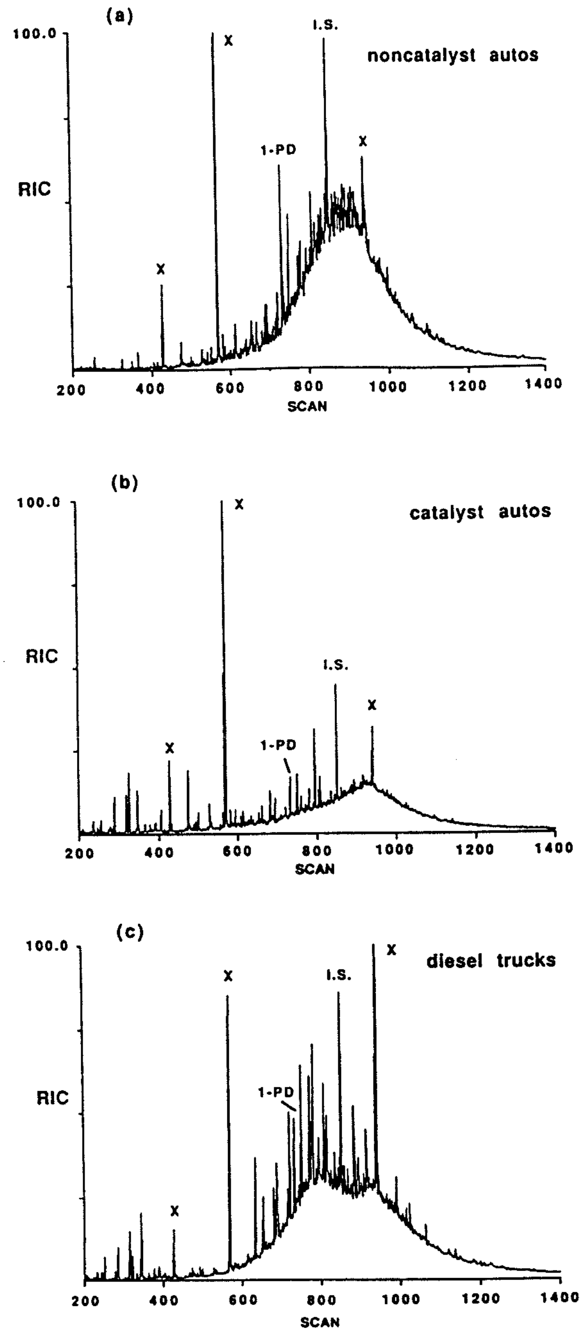

Figure 4.2 Total reconstructed ion current (RIC) for the fine particle organics emitted from the vehicles tested: (a) automobiles without catalytic converters, (b) catalyst-equipped automobiles, and (c) heavy-duty diesel trucks. I.S. is the internal standard ($\underline{n}$-$C_{24}D_{50}$); 1-PD is the coinjection standard (1-phenyldodecane); X denotes a contaminant peak.

content of the oil, crude oil fractions used for lubricant oil production have to be dewaxed (*59–61*). Commercial dewaxing processes remove 92 to 98% of the n-alkane content of oils (*59*). Kissin (*59*) has shown that this dewaxing process does not remove the n-alkyl moieties in the oil such as n-alkyl-substituted naphthenic and naphtheno-aromatic compounds. At elevated temperatures (~ 250 °C) encountered during engine operation, these n-alkyl hydrocarbons undergo mild thermocracking, preferably at the tertiary carbon atoms. This may explain how high molecular weight n-alkanes can appear in the exhaust of vehicles even when the fuels and or lubricants were originally deficient in those compounds.

Using the sampling and analysis techniques described earlier, the emission rates of n-alkanes having carbon numbers ranging from C_{19} to C_{32} have been quantified in fine particulate vehicle exhaust as shown in Table 4.2. Particulate n-alkane emissions for all vehicle classes tested show a more or less bimodal n-alkane carbon number distribution with elevated emission rates between $C_{20} - C_{22}$ and $C_{24} - C_{27}$ (Figures 4.3a,b). Essentially all of the particulate n-alkanes emitted from the gasoline engines come from unburned engine oil. The great relative increase of lower n-alkanes ($\leq C_{22}$) in the diesel exhaust particulate matter reflects the relatively higher lubricant oil consumption of diesel engines and results also from unburned diesel fuel itself. Further, it can be seen from Figure 4.3a that the n-alkanes emission rate for noncatalyst autos is about 4 times higher than that of the catalyst-equipped cars. This difference could be due to one or both of the following factors. First, the noncatalyst autos tested have older, higher mileage engines (on average one and a half times more accumulated mileage than the catalyst-equipped autos tested) with an increased probability that worn engine parts will pass more unburned lubricating oil through the engine. Second, these

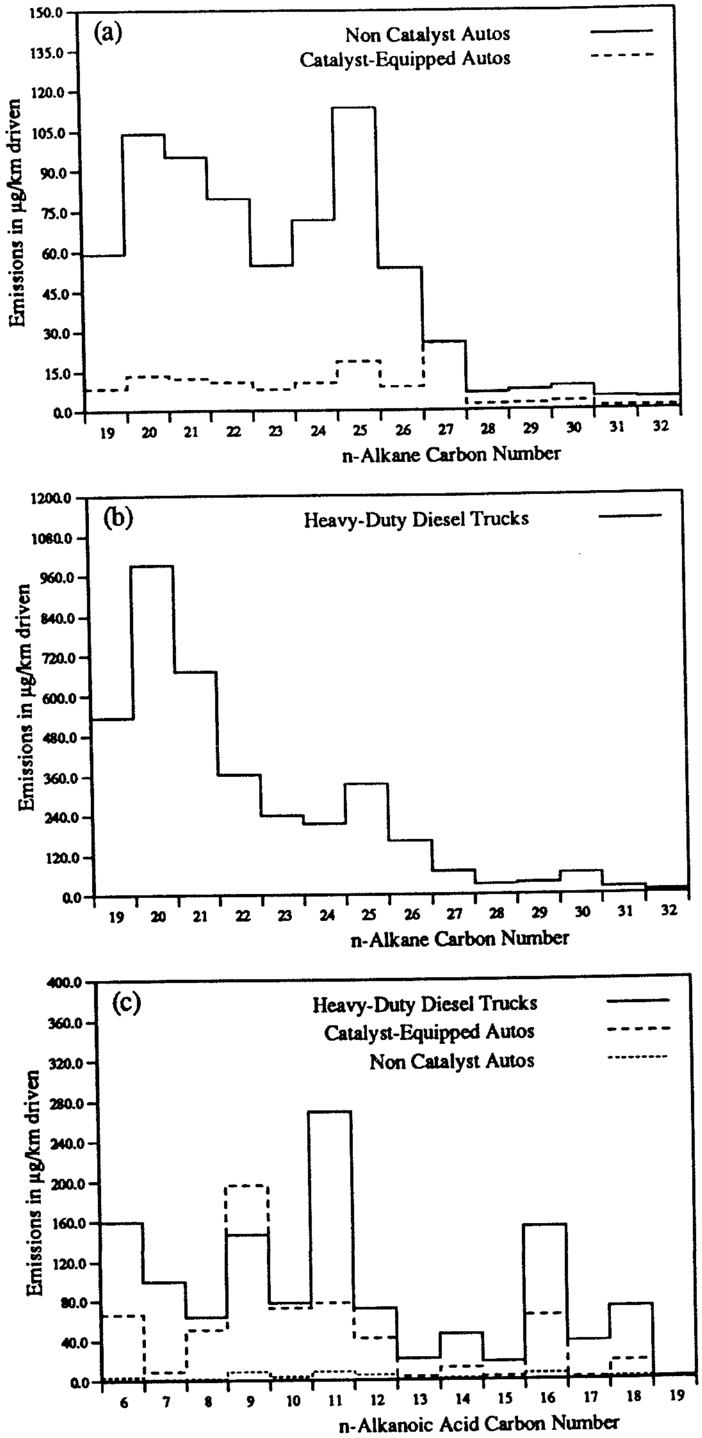

Fig. 4.3: Vehicular emission profiles for fine particle associated n-alkanes and n-alkanoic acids: (a) n-alkanes from automobiles with and without catalytic converters, (b) n-alkanes from heavy-duty diesel trucks, and (c) n-alkanoic acids from the 3 vehicle types tested.

n-alkane emission differences could be due to changes in engine design and post-combustion oxidation in the catalytic converter systems of the newer catalyst-equipped automobiles.

Alkanoic Acids

Particle-bound n-alkanoic acids ranging from C_6 to C_{21} have been identified in the exhaust emissions from the vehicle types tested and are listed in Table 4.2. The catalyst-equipped automobiles emitted more than 600 μg km^{-1} of total n-alkanoic acids, about 13 times the amount emitted by the noncatalyst autos tested. Furthermore, the heavy-duty diesel trucks emitted about twice the quantity of n-alkanoic acids per km driven when compared to the catalyst-equipped automobiles, or 26 times the amount emitted by autos that lack a catalytic converter (Figure 4.3c). Simoneit (*56*) reported a similar relationship when comparing n-alkanoic acid emissions (C_{10} – C_{20}) between a noncatalyst auto and a diesel truck. As a fraction of the total fine particle mass emitted, n-alkanoic acids are found to be highly enriched in catalyst-equipped vehicle exhaust (34,238 μg n-alkanoic acids per g of fine aerosol emitted from catalyst-equipped cars vs. 786 μg/g from noncatalyst gasoline cars and 3033 μg/g from diesel trucks).

Focusing on single compound emission rates, n-hexanoic (C_6), n-nonanoic (C_9), n-undecanoic (C_{11}), and n-hexadecanoic acid (C_{16}) are the most abundant n-fatty acids released from all 3 vehicle types (Figure 4.3c). Kawamura et al. (*62*) examined low molecular weight aliphatic organic acids ranging from C_1 to C_{10} in engine exhaust, new engine oil and used engine oil. To sample the vehicle exhaust, they used a KOH-impregnated filter system to collect directly, without exhaust dilution, from the hot muffler of a gasoline powered automobile. The most abundant n-alkanoic acids identified by Kawamura and co-workers

(*62*) in the vehicle exhaust were the shorter C_1 to C_3 n-alkanoic acids, found exclusively in the gas-phase. Used engine oil contained, compared to new engine oil, enhanced concentrations of formic acid (C_1) and acetic acid (C_2). Because no n-alkanoic acids in the range C_5 to C_{10} were found in engine oil and there is no indication that n-alkanoic acids are part of the fuels used, it is proposed that the higher alkanoic acids (C_6 – C_{22}) quantified in vehicle exhaust (Table 4.2) are formed during the combustion process (*63*) and/or catalytic oxidation process (catalyst auto only) (*64*). Given the relatively high emission rates of organic acids from the catalyst equipped cars when compared to the noncatalyst cars, it is likely that the presence of the catalyst system enhances the formation of organic acids.

Alkenoic Acids

One unsaturated n-fatty acid, oleic acid ($C_{18:1}$), has been identified in all of the vehicular emissions. The emission rates are generally low and increase for catalyst-equipped autos by about 4-times when compared to noncatalyst automobiles. The emission rate for diesel trucks is enhanced by almost 7-fold when compared to the noncatalyst automobiles. Because gasoline fuels do not contain compounds $\geq C_{10}$, the oleic acid would be expected to have come from the combustion system including processing of lubricating oil constituents.

Substituted Benzoic Acids and Benzaldehydes

Benzoic acid and alkylbenzoic acids recently have been identified in vehicular source emissions (*56, 62*). Besides identifying benzoic acid in the exhaust of one noncatalyst auto, Kawamura and coworkers (*62*) also detected benzoic acid in used engine oil. New, unused oil did not show any benzoic acid. In the present study, benzoic acid and 4-methylbenzoic acid together with alkylbenzaldehydes, 4-formylbenzaldehyde, methoxy- and dimethoxybenzaldehydes have been quantified in the vehicular sources tested (Table 4.2). The emission rates for the 2 identified benzoic acids closely follow the emission pattern discussed earlier for n-alkanoic acids. Autos equipped with catalytic converters show a 22-fold higher emission rate than was found for automobiles without catalytic converters. This pronounced emissions increase for the catalyst-equipped automobiles might indicate that post-combustion formation of benzoic acids in the catalytic converter system is an important factor. Substituted benzaldehydes show a reversed emissions pattern, e.g., lower emissions for catalyst autos and diesel trucks than for noncatalytic automobiles.

Dicarboxylic Acids

Kawamura and Kaplan (*65*) have identified dicarboxylic acids in the exhaust emissions from a diesel auto and one gasoline powered automobile. The hot exhaust emissions were collected directly via KOH-impregnated filters from the muffler of each test auto while the engine was running at idle speed. They reported that dicarboxylic acids ranging from oxalic acid (C_2) to sebacic acid (C_{10}) were present in the emissions from both automobiles.

During the source test program conducted by dilution sampling in the present paper, the particulate emissions from all 3 vehicle types were examined for a set of 11 dicarboxylic acids (C_3–C_{10}) that we have previously identified as major compounds present in the Los Angeles atmosphere (*36*). None of the dicarboxylic acids found in ambient fine particulate matter could be detected in the fine particulate vehicular emissions. This suggests that no measurable particle-phase dicarboxylic acids were emitted from the vehicles tested here. Precursor compounds such as cyclic olefins are emitted from vehicle exhaust, which under ambient conditions (as well as under the sampling conditions employed here) are in the gaseous phase. Subsequent atmospheric oxidation (e.g., O_3) leads to some of the dicarboxylic acids observed in the atmosphere (*66*). There may be other gas phase species in the vehicle exhaust (e.g., dialdehydes) that can subsequently form dicarboxylic acids in the atmosphere.

Polycyclic Aromatic Hydrocarbons

The concern that carcinogenic and mutagenic organic compounds could be released from diesel fuel and gasoline powered engines has prompted research efforts on the formation, release, and ambient behavior of PAH and substituted homologues (*8, 11, 12, 15, 16, 18, 67–69*). As a result of this work, it has been shown that fuel aromaticity, engine load, PAH accumulation in lubricant oil, lubricant oil combustion, and cold start behavior influence the emission rates for PAH (*20, 39, 44, 45, 48, 70–72*).

At present, the exact mechanism of PAH formation during combustion is not understood in detail (*73*). Three different pyrolysis mechanisms are currently considered as possible, slow Diels-Alder condensations, rapid radical reactions, and ionic reaction mechanisms (*73*). Because the combustion process within the internal combustion engine has to occur very rapidly, the radical formation mechanism is considered to be favored (*73*). Gaseous hydrocarbon radicals are thought to rearrange quickly, providing the mechanism of PAH formation and growth. The addition of hydrocarbon radicals to lower molecular weight PAH then leads via alkyl-PAH to the formation of higher aromatized PAH (*74*).

During this study, the emission rates for more than 30 individual PAH and alkyl-PAH have been quantified in the vehicular emissions collected (Table 4.2). Noncatalyst automobiles show the highest emission rates for each of the PAH detected. A more than 25-fold higher total PAH emission rate is observed for autos without catalytic converters than for autos equipped with catalytic exhaust emission control devices (1405.5 μg km^{-1} versus 52.5 μg km^{-1}). The two fairly new heavy-duty diesel trucks (avg. 4251 miles) tested showed an average total PAH emission rate per km driven which is only one seventh as large as seen for the noncatalyst automobiles. The emission rates for single PAH emitted from all vehicles are shown in Figure 4.4. While the heavy-duty diesel trucks tested show a preference for low molecular weight PAH (methyl-, dimethylphenanthrenes, anthracenes), the noncatalyst automobiles emit over the whole molecular weight spectrum investigated with greater emission rates for the higher molecular weight PAH such as benzo[ghi]perylene and coronene. Schuetzle and Frazier (*45*) reported that the ratio of pyrene/benzo[a]pyrene in exhaust emissions is approximately 10 times greater for diesel engines than for gasoline powered engines, which is in good agreement with results stated here (ratio close to 13). Emissions of alkyl substituted PAH are particularly high when compared to the emission rates for most individual unsubstituted PAH. This is in agreement with previous studies (*75, 76*). Alkyl homologues of some PAH show similar or even greater mutagenic activities than benzo[a]pyrene (*77–80*). Jensen and Hites (*75*) reported that decreasing the exhaust gas temperature (decreased engine load) increased the total emission rate for alkyl-PAH. In addition they found that the number of alkyl functional groups on the PAH-molecules increases with decreasing combustion temperature. Applying this result to urban traffic situations suggests that an increase in traffic congestion during rush-hour (longer time periods of decreased engine load) could increase the alkyl-PAH emissions relative to unsubstituted

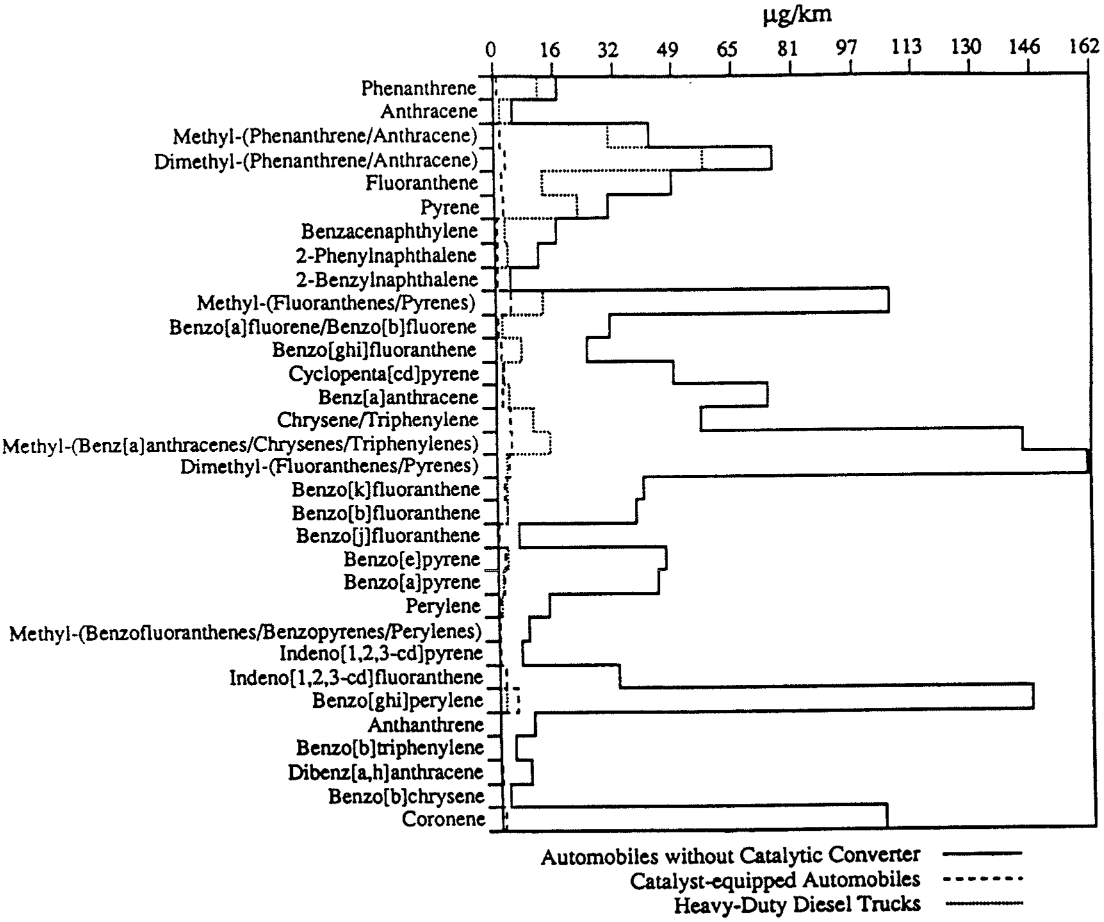

Figure 4.4 Vehicular emission profiles for fine particle polycyclic aromatic hydrocarbons (PAH).

PAH emissions for automobiles without catalytic exhaust control systems.

Polycyclic Aromatic Ketones, Quinones, and Carboxaldehydes

Oxygenated polycyclic aromatic hydrocarbons (oxy-PAH) have been identified previously in particulate emissions from diesel and gasoline engines (*8, 10, 14, 16, 75, 81–85*). Oxy-PAH are believed to be formed during incomplete combustion by addition of oxygen free radicals or molecular oxygen to the PAH with subsequent rearrangement (*85*). To date only relative mass emission rates (μg g^{-1}) for a small number of oxy-PAH emitted from vehicles have been reported (*75*).

During the course of this study, the emission rates for 12 oxy-PAH were measured, including carboxaldehyde, ketone, and quinone derivatives as well as one oxyheterocyclic-PAH (9H-xanthen-9-one); see Figure 4.5. Jensen and Hites (*75*) reported that the diesel engine tested in their experiment showed little evidence for the presence of naphthalenecarboxaldehydes. Fluoren-9-one and alkylfluoren-9-ones, the only ketone-PAH identified in their diesel engine test, instead showed the highest concentrations. This observation is in reasonable agreement with our diesel truck data. The highest emission rate in our tests for a single oxy-PAH released from diesel trucks was found for fluoren-9-one (65.0 ng km^{-1}, followed by 9,10–phenanthrenedione (63.1 ng km^{-1}). In a manner similar to the PAH, the highest oxy-PAH emission rates were measured for automobiles without catalytic emission control systems (oxy-PAH emission ratios—Noncatalyst : Catalyst : Diesel = 5.5 : 1 : 2.9). The emission rate profile for oxy-PAH from heavy-duty diesel trucks shows a trend similar to that observed for PAH; low emission rates for high molecular weight oxy-PAH compared to noncatalyst automobiles (Table 4.2).

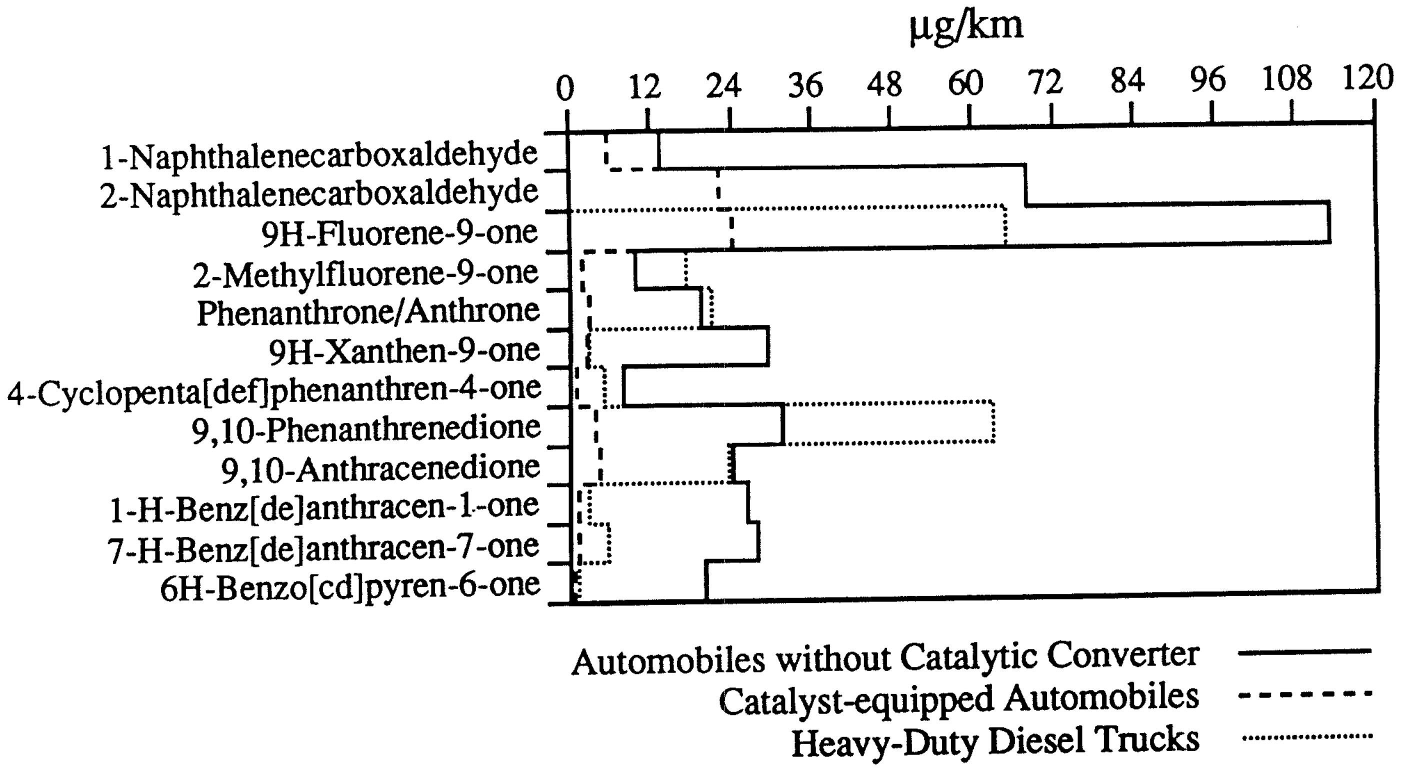

Figure 4.5 Vehicular emission profiles for fine particle oxygenated polycyclic aromatic hydrocarbons (oxy-PAH).

Sterane and Triterpane Hydrocarbons

During the geological maturation processes of source rocks and crude oils, organic material originally contributed by plants and animals is transformed by diagenesis and catagenesis over millions of years (*52, 54, 58, 86–88*). In petroleum geochemistry, steranes and triterpanes, found in petroleum, are used as marker compounds to determine the source rocks from which the crude oil migrated and also to assess the geological maturity of crude oils (*54, 58*). While a large spectrum of steranes and triterpanes are present in petroleum, only the major compounds present in vehicle exhaust were quantified during the course of this study, see Figures 4.6a,b. The triterpanoid hopanes were all identified using information on elution order and the mass spectra of authentic standards (*52, 55, 89*). Among the steranes, 20R-5α(H),14α(H),17α(H)-cholestane is identified and confirmed by injection of the authentic standard on the GC/MS system used in our study. The other steranes are identified according to published mass spectra and ion chromatograms for crude oils, engine oils, and particulate exhaust emissions (*52, 55, 90, 91*). Such ion chromatograms show essentially the same elution order and relative abundance for the steranes and hopanes as those for the vehicle exhausts investigated here. Simoneit (*55*) determined the complete spectrum of pentacyclic triterpanes and steranes in particulate exhaust emissions collected from diesel and gasoline engines, likewise in lubricating oil. The relative abundance of the triterpanes for the vehicular emissions agreed well with the relative abundance found in lubricant oil. Because these fossil petroleum markers belong to the higher boiling fraction of crude oil, they are not found in gasoline or diesel fuel but instead are contributed to the vehicle exhaust from the lubricating oil (*55*). Dividing the vehicular emission rates for these fossil petroleum markers

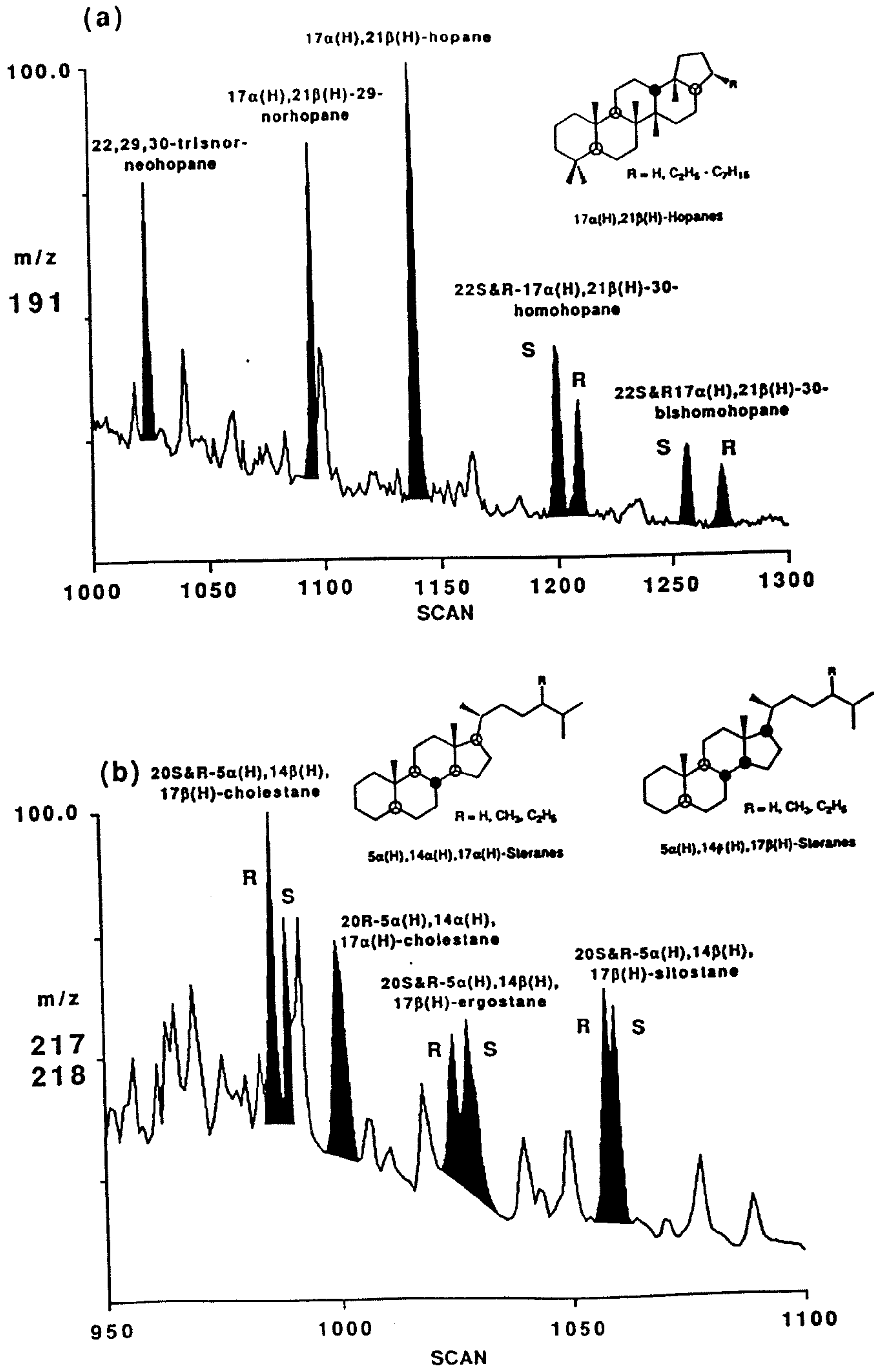

Figure 4.6 Selected mass fragmentograms for fine particle organic aerosol emissions from heavy-duty diesel trucks, (a) m/z 191: indicator for pentacyclic triterpanes, (b) m/z 217 + 218: key fragment ions for steranes.

by the equivalent emission rates found for the catalyst-equipped automobiles, one can estimate that the noncatalyst autos tested emit 2.2 to 2.3 times the amount of unburned lubricating oil per km driven when compared with the catalyst autos. The heavy-duty diesel trucks tested emit in the same manner 10.7 to 11.1 times the amount of unburned lubricant oil per km driven as the catalyst autos (steranes—Noncatalyst : Catalyst : Diesel = 2.2 : 1.0 : 11.1 and triterpanes—Noncatalyst : Catalyst : Diesel = 2.3 : 1.0 : 10.7). Applying the same technique to the higher molecular weight n-alkanes (C_{28} – C_{32}) which also are contributed by uncombusted engine oil, the relative lubricating oil contribution to the exhaust aerosol shows a similar pattern (Noncatalyst : Catalyst : Diesel = 3.0 : 1.0 : 15.3).

N–Containing Compounds

Among the identified nitrogen-containing compounds found in vehicular exhaust emissions (Table 4.2) are two azanaphthalenes: quinoline and iso-quinoline. Recently, quinolines have also been identified in urban ambient fine particle samples (*36*). They also are known to occur in crude oils and shale oil (*92, 93*). Therefore, it is possible that the two quinolines found in the vehicular exhaust emissions may be derived from unburned fuel or lubricant oil constituents. The other two N-containing compounds (1–methyl-2-pyrrolidinone and N,N–dibutylformamide) have not yet been reported in the vehicle exhaust literature.

Other Compounds

In addition to the compound classes discussed above, three other organic compounds (2-(2-butoxyethoxy)-ethanol, 5-methylphthalide, and indanone) present in the exhaust emissions have been quantified (Table 4.2).

Table 4.2. Fine Aerosol Emission Rates for Single Organic Compounds from Noncatalyst and Catalyst Automobiles and from Heavy-Duty Diesel Trucks.

	Emission Rates[a] in μg km^{-1}			
PART A	**Automobiles**		**Heavy-Duty Diesel Trucks**	Compound ID[b]
	Noncatalyst	**Catalyst**		
	—n–Alkanes—			
n–nonadecane	59.0	8.5	532.7	a
n–eicosane	103.9	13.3	991.3	a
n–heneicosane	95.2	12.1	673.0	a
n–docosane	79.8	10.9	363.6	a
n–tricosane	54.7	8.1	241.4	a
n–tetracosane	71.6	10.6	216.1	a
n–pentacosane	113.5	18.4	334.2	a
n–hexacosane	53.4	9.0	163.0	a
n–heptacosane	25.5	7.0	72.3	a
n–octacosane	6.8	2.4	32.1	a
n–nonacosane	7.6	2.7	37.2	a
n–triacontane	9.0	3.1	63.8	a
n–hentriacontane	4.8	1.4	21.9	a
n–dotriacontane	4.6	1.3	12.0	a
Total class emission rate:	689.4	108.8	3754.6	
	—n–Alkanoic Acids[c]—			
n–hexanoic acid	3.6	65.8	159.2	a
n–heptanoic acid	0.8	8.4	99.4	a
n–octanoic acid	2.1	51.1	63.3	a
n–nonanoic acid	8.6	196.2	146.9	a
n–decanoic acid	3.2	72.7	77.4	a
n–undecanoic acid	8.8	77.3	269.9	a
n–dodecanoic acid	5.5	41.4	71.5	a
n–tridecanoic acid	0.56	3.3	21.2	a
n–tetradecanoic acid (myristic acid)	1.7	11.9	45.7	a
n–pentadecanoic acid	0.40	3.4	17.5	a
n–hexadecanoic acid (palmitic acid)	6.0	63.9	153.1	a
n–heptadecanoic acid	0.45	2.4	38.0	a
n–octadecanoic acid (stearic acid)	3.0	18.0	72.5	a
n–nonadecanoic acid	0.59	0.48	1.8	a
n–eicosanoic acid	0.27	n.d.	n.d.	a
n–heneicosanoic acid	0.11	n.d.	n.d.	a
Total class emission rate:	46.68	616.28	1237.4	

Table 4.2 (continued)

PART B	Emission Rates[a] in μg km^{-1}			Compound ID[b]
	Automobiles		Heavy-Duty Diesel Trucks	
	Noncatalyst	Catalyst		
—n–Alkenoic Acid[c]—				
cis–9–octadecenoic acid (oleic acid)	1.2	5.0	8.0	a
Total class emission rate:	1.2	5.0	8.0	
— Benzoic Acids[c]—				
benzoic acid	4.2	99.9	170.7	b
4-methylbenzoic acid	0.62	7.7	14.4	a
Total class emission rate:	5.22	107.6	185.1	
—Substituted Benzaldehydes—				
2–methylbenzaldehyde	15.2	2.8	5.0	b
3–methylbenzaldehyde	3.5	0.53	1.6	b
4–methylbenzaldehyde	7.7	1.7	2.3	a
dimethylbenzaldehydes	56.4	10.9	8.6	b
trimethylbenzaldehydes	16.7	4.1	n.d.	b
1,4–benzenedicarboxaldehyde (4–formylbenzaldehyde)	19.2	5.2	1.5	b
3–methoxybenzaldehyde	5.4	1.7	n.d.	b
3,4–dimethoxybenzaldehyde	0.87	0.72	n.d.	a
Total class emission rate:	124.97	27.65	19.0	
—Polycyclic Aromatic Hydrocarbons—				
phenanthrene	17.3	0.88	12.2	a
anthracene	5.1	0.11	1.6	a
methyl–(phenanthrenes, anthracenes)	42.2	1.9	31.3	b
dimethyl–(phenanthrenes, anthracenes)	75.5	3.0	56.9	b
fluoranthene	48.3	2.0	13.0	a
pyrene	31.0	2.5	22.6	a
benzacenaphthylene	16.5	0.77	2.9	b
2–phenylnaphthalene	11.9	0.57	3.5	b
2–benzylnaphthalene	4.3	0.72	n.d.	b
methyl–(fluoranthenes, pyrenes)	106.9	4.2	12.8	b
benzo[a]fluorene/benzo[b]fluorene	31.0	0.72	1.9	a
benzo[ghi]flouranthene	24.7	1.3	6.9	b
cyclopenta[cd]pyrene	49.3	1.7	1.4	a
benz[a]anthracene	73.8	1.9	3.6	a
chrysene/triphenylene	55.8	3.8	9.9	a
methyl–(benz[a]anthracenes, chrysenes, triphenylenes)	143.5	3.4	2.7	b

Table 4.2 (continued)

Emission Rates^a in μg km^{-1}

PART C	**Automobiles**		**Heavy-Duty Diesel Trucks**	Compound ID^b
	Noncatalyst	**Catalyst**		
dimethyl–(fluoranthenes, pyrenes)	161.1	4.1	14.6	b
benzo[k]fluoranthene	40.7	2.0	2.7	a
benzo[b]fluoranthene	37.9	2.9	2.9	a
benzo[j]fluoranthene	6.0	0.54	n.d.	b
benzo[e]pyrene	45.8	2.0	2.6	a
benzo[a]pyrene	43.5	1.9	1.3	a
perylene	14.0	0.60	1.0	a
methyl–(benzofluoranthenes, benzopyrenes, perylenes)	6.4	0.47	n.d.	b
indeno[1,2,3-cd]pyrene	6.4	0.47	n.d.	a
indeno[1,2,3-cd]fluoranthene	32.6	1.7	n.d.	b
benzo[ghi]perylene	145.4	4.7	1.6	a
anthanthrene	9.4	0.08	n.d.	a
benzo[b]triphenylene	4.0	0.09	n.d.	b
dibenz[a,h]anthracene	8.3	0.33	n.d.	a
benzo[b]chrysene	2.3	0.02	n.d.	b
coronene	104.6	1.1	n.d.	a
Total class emission rate:	1405.5	52.47	209.9	
—Polycyclic Aromatic Carboxaldehydes—				
1–naphthalenecarboxaldehyde (1–formylnaphthalene)	13.5	5.5	n.d.	b
2–naphthalenecarboxaldehyde (2–formylnaphthalene)	68.0	22.2	n.d.	b
Total class emission rate:	81.5	27.7		
—Polycyclic Aromatic Ketones (PAKs) and Quinones (PAQs)—				
9H–fluoren-9-one (fluorenone)	113.4	24.3	65.0	a
2–methylfluoren-9-one	9.7	1.9	17.2	b
9,10–phenanthrenedione (phenanthrenequinone)	31.6	3.8	63.1	a
9,10–anthracenedione (anthraquinone)	24.3	4.4	23.5	a
phenanthrone/anthrone	19.4	2.8	20.9	a
9H–xanthen-9-one (xanthone)	29.4	2.6	2.7	a
4–cyclopenta[def]phenanthren-4-one	7.9	1.0	5.1	b
1–H–benz[de]anthracen-1-one	26.3	1.2	2.7	b
7–H–benz[de]anthracen-7-one	27.9	1.3	5.6	a
6H–benzo[cd]pyren-6-one (benzo[cd]pyrenone)	20.0	0.78	1.2	b
Total class emission rate:	309.9	44.08	207.0	

Table 4.2 (continued)

PART D	Emission Rates[a] in μg km^{-1}			
	Automobiles			
	Noncatalyst	Catalyst	Heavy-Duty Diesel Trucks	Compound ID[b]
—Regular Steranes—				
20S&R-5α(H),14β(H),17β(H)-cholestanes	8.4	3.6	39.6	b
20R-5α(H),14α(H),17α(H)-cholestane	9.3	4.0	43.0	a
20S&R-5α(H),14β(H),17β(H)-ergostanes	7.9	4.1	43.4	b
20S&R-5α(H),14β(H),17β(H)-sitostanes	11.4	5.4	63.4	b
Total class emission rate:	37.0	17.1	189.4	
—Pentacyclic Triterpanes—				
22,29,30-trisnorneohopane	6.8	3.0	23.1	b
17α(H),21β(H)-29-norhopane	10.7	5.9	39.6	b
17α(H),21β(H)-hopane	18.2	9.0	94.2	b
22S-17α(H),21β(H)-30-homohopane	8.3	3.1	38.0	b
22R-17α(H),21β(H)-30-homohopane	5.5	1.9	38.3	b
22S-17α(H),21β(H)-30-bishomohopane	4.7	1.5	22.7	b
22R-17α(H),21β(H)-30-bishomohopane	3.5	1.1	16.0	b
Total class emission rate:	57.7	25.5	271.9	
—N-Containing Compounds—				
quinoline	5.3	0.57	0.46	b
iso-quinoline	4.9	3.4	4.1	b
1-methyl-2-pyrrolidinone (m-pyrol)	54.4	33.0	16.4	a
N,N-dibutylformamide	4.7	20.7	7.6	a
Total class emission rate:	69.3	57.67	28.56	
—Other Compounds—				
2-(2-butoxyethoxy)-ethanol	42.6	53.6	55.0	a
5-methyl-1(3H)-iso-benzofuranone (5-methylphthalide)	39.7	9.1	n.d.	b
2,3-dihydroxy-1H-indan-1-one (indanone)	4.9	2.5	10.8	a
Total class emission rate:	87.2	65.2	65.8	

[a] n.d. = not detected; accuracy determinations were performed for both polar and nonpolar standard compounds, showing that the relative standard deviations were between 4 to 8% depending on the amount of the standard compounds injected.

[b] for more details see text: a, positive; b, probable; c, possible; d, tentative.

[c] detected as methyl ester.

Comparison to Prior Source Emission Data

In Tables 4.3 and 4.4, the organic emission rates for the gasoline and diesel powered vehicles measured in the present work are compared to those few past studies where the cold start Federal Test Procedure was used in conjunction with dilution sampling (*8, 94*). The organic compound emission rates measured in the present study for noncatalyst cars are higher than in previous studies shown in Table 4.3. The automobiles tested by the other researchers were usually preadjusted to meet their respective emission standards, and contaminated lubricating oils were replaced with new oil to guarantee intercomparison between consecutive experiments. Replacing the lubricating oil reduces emissions from accumulated combustion products present in used engine oils. In the present study, in order to determine emission rates for particle phase organics that are as relevant as possible to air quality at an actual urban site, the automobiles were tested in as–received condition without tuning the engines or changing the lubricant oils. This approach was intended to ensure that the exhaust emission rates of the vehicle fleets tested were representative of the actual emission rates of the vehicles used within the greater Los Angeles area. Table 4.4 compares organic compound emissions rates for heavy-duty diesel trucks from this study with previous results (*21, 72, 95*). The data from this table show that the fairly new heavy-duty diesel trucks tested here show organic compound emissions per km driven comparable to the heavy-duty diesel trucks tested by other researchers with much higher accumulated miles driven.

Table 4.3 Comparison of the Present Study with Results from Previous Studies (using cold start-FTP only): Organic Particulate Emissions from Noncatalyst and Catalyst-Equipped Automobiles.

	Emission Rates in μg km⁻¹				
	Noncatalyst Automobiles			Catalyst-Equipped Automobiles	
Compound Name[a]	Present Study[b]	Alsberg et al.[c,e] (*8*)	Lang et al.[d,e] (*94*)	Present Study[b]	Lang et al.[d,e] (*94*)
phenanthrene	17.3	2.8	-	0.9	-
anthracene	5.1	0.7	-	0.1	-
methyl-phenanthrenes/anthracenes	42.2	14.0	-	1.9	-
dimethyl-phenanthrenes/anthracenes	75.5	23.5	-	3.0	-
2-phenylnaphthalene	11.9	2.5	-	0.57	-
fluoranthene	48.3	17.0	-	2.0	-
pyrene	31.0	29.5	11.7	2.5	6.2
benzo[ghi]flouranthene	24.7	8.8	-	1.3	-
cyclopenta[cd]pyrene	45.9	7.5	-	1.6	-
benzo[a]anthracene	73.8	5.8	-	1.9	-
chrysene/triphenylene	55.8	7.7	-	3.8	-
benzo[b]- & benzo[k]fluoranthene	78.6	5.5	-	4.9	-
benzo[j]fluoranthene	6.0	1.0	-	0.54	-
benzo[e]pyrene	45.8	4.4	-	2.0	-
benzo[a]pyrene	43.5	3.2	9.1	1.9	2.0
perylene	14.0	0.4	-	0.60	-
indeno[1,2,3-cd]pyrene	6.4	2.7	-	0.47	-
indeno[1,2,3-cd]fluoranthene	32.6	0.6	-	1.7	-
benzo[ghi]perylene	145.4	9.5	-	4.7	-
anthanthrene	9.4	0.75	-	0.08	-
coronene	104.6	9.3	-	1.1	-

Table 4.3 (continued)

[a] Only those compounds measured in both the present study and at least one previous study are listed.

[b] Six noncatalyst (avg. odometer reading: 117,504 miles) and seven catalyst (avg. odometer reading: 76,623 miles) automobiles were tested, for more detail see Hildemann et al. (*27*). Half the miles driven by noncatalyst vehicles in 1982 were driven by cars older than 10 years and a typical 10 year old car has an accumulated mileage of 117,300 miles (*97*). Emission rates are for compounds present in the fine particle fraction only.

[c] Saab 900 Gl (noncatalyst) with a four-cylinder carbureted engine (odometer reading: 2769 miles), commercial leaded fuel (0.15 g of Pb/l, 96 octane) was used. The vehicle was preadjusted by the manufacturer prior testing and samples were collected on Teflon-coated glass fiber filters (*8*).

[d] Four noncatalyst (avg. odometer reading: 44848 miles) and sixteen catalyst (avg. odometer reading: 27,186 miles); model years from 1970 to 1981 (*94*).

[e] lubricant oils were drained and replaced before FTP-testing.

Table 4.4. Comparison of the Present Study with Results from Previous Studies: Organic Particulate Emissions from Heavy Duty Diesel Trucks.

Compound Name[a]	Emission Rates in $\mu g\ km^{-1}$			
	Present Study[b]	Westerholm et al.[c] (*72*)	Westerholm et al.[d] (*21*)	Dietzmann et al.[e] (*95*)
phenanthrene	12.2	11.0	29.0	-
anthracene	1.6	2.7	3.3	-
methyl-phenanthrenes/anthracenes	31.3	-	159.0	-
fluoranthene	13.0	22.0	17.0	-
pyrene	22.6	22.0	11.0	-
benzo[ghi]flouranthene	6.9	6.2	1.5	-
cyclopenta[cd]pyrene	1.3	2.2	0.18	-
benzo[a]anthracene	3.6	2.7	0.47	-
chrysene/triphenylene	9.9	8.8	2.8	-
benzo[b]- & benzo[k]fluoranthene	5.7	4.1	0.29	-
benzo[e]pyrene	2.6	1.3	0.15	-
benzo[a]pyrene	1.3	0.57	< 0.06	1.5

[a] Only those compounds measured in both the present study and at least one previous study are listed.

[b] 1987 GMC truck (2-axle), odometer: 2920 miles, engine displac.: 636 cu in.; 1987 Ford dump truck (3-axle), odometer: 5581 miles, engine displac.: 636 cu in.; chassis dynamometer test, emission rates are for compounds present in the fine particulate fraction only, for more details and the driving cycle used see Hildemann et al. (*27*).

[c] Heavy-duty diesel truck (Volvo) with 157kW, engine displac.: 403 cu in.; truck was operated according to New York City Cycle on chassis dynamometer, see Westerholm et al. (*72*).

[d] Heavy-duty diesel truck (Scania 14311) with 331 kW, odometer: 125,000 miles, engine displac.: 866 cu in.; truck was operated according to German city bus cycle, see Westerholm et al. (*21*).

[e] Four heavy-duty diesel trucks (Caterpiller 3208 (1979), Mack ENDT 676 (1979), Cummins Formula 290 (1979), Detroit Diesel 8V-71 (1977)) were tested on the chassis version of the 1983 transient procedure (Federal Register (*96*)), odometer: 7000 to 69000 (avg. 40500) miles, see Dietzmann et al. (*95*).

Molecular Tracers of Vehicular Exhaust

In order to use the steranes and pentacyclic triterpanes as molecular tracers in the atmosphere for the presence of particulate emissions from internal combustion engines, the ambient concentrations of such compounds must be dominated by emissions from the source types of interest. Using the emission inventory by Gray (*97*) and updated by Hildemann et al. (*27*) for all sources contributing fossil petroleum markers to the Los Angeles urban atmosphere, it is possible to estimate the mass of steranes and pentacyclic triterpanes emitted from internal combustion engines on a daily basis. Likewise, the emission strengths of these compounds from tire wear, resuspension of road dust, oil burning industrial and residential boilers, roofing tar pots, and asphalt roof manufacturing also can be determined by measuring their content in the source samples taken by Hildemann et al. (*27*). For those minor sources that have not yet been tested including surface coatings, organic chemical processes, and miscellaneous petroleum industry emissions, the fractional sterane and pentacyclic triterpane content of the organic aerosol emissions will be assumed to be the same as was found for roofing tar pot emissions (*27*). Then by totaling all of the known sources for fossil petroleum marker emissions, it can be shown that roughly 85% of all particle associated steranes and triterpanes emitted to the Los Angeles area atmosphere are contributed by internal combustion engines. Hence, it may be possible to use these compounds as markers for the contribution of vehicle-derived aerosols if it can be shown that they are sufficiently stable in the atmosphere. If organic compounds are to be used as tracers, their rate of reaction in the atmosphere must be slow relative to transport times from source to receptor (*98, 99*). Moderately reactive organic gases such as the alkanes, benzene, and certain chlorinated organics can be used as tracers in Los Angeles as their half-life with respect to chemical degradation here is of the order of 20 hours or more (*100*). In the present paper we use fossil petroleum markers such as hopanes and steranes as tracers that have been stable over geological time scales and that are extensively used in geochemistry as marker compounds (*54, 58*). It is unlikely that these compounds will react in the atmosphere at rates fast enough to harm their use as an atmospheric tracer over the spatial scale of an urban area (i.e., time scales of a few hours).

Estimated Mobile Source Contributions to the Los Angeles Atmosphere

The compilation of vehicular source profiles from a fleet of vehicles actually driven in the greater Los Angeles area provides the opportunity to estimate source contributions from different types of combustion engines to the southern California atmosphere. Gray (*97*) compiled an extensive inventory for primary fine particulate organic carbon (OC) and elemental carbon (EC) emissions for the year 1982 within: (a) the heavily populated central area of urban Los Angeles (an 80 × 80 km square area) and (b) for the larger South Coast Air Basin comprising the populated portions of the four counties that surround Los Angeles. That same emission inventory was updated recently by using new data gained from a source testing campaign (27) that included the vehicles tested here plus source samples taken from other important urban sources of organic aerosol (Table 4.5). Using this updated emission inventory for the 80 × 80 km urban Los Angeles area in conjunction with the emission rates from Table 4.2 for single organic compounds, it is possible to estimate the total mass emission rates of key compound classes representing all vehicle traffic within that urban area, as shown in Table 4.6 (for more details see the footnotes). From Table 4.6, it is seen that more than

Table 4.5. **Estimate of the Mobile Source Emissions of Fine Aerosol Organic Carbon (OC) and Fine Aerosol Organics within an 80×80 km Urbanized Area Centered over Los Angeles (for 1982).**

	Fine Particulate Emissions[a] in kg day^{-1}	
Mobile Sources	Organic Carbon (OC)	Organic Compounds[b]
Gasoline Powered Vehicles		
noncatalyst automobiles	2088	2506
other noncatalyst vehicles[c]	1372	1646
catalyst-equipped automobiles	780	936
other catalyst-equipped vehicles[d]	79	95
Diesel Powered Vehicles		
heavy-duty trucks	1242	1490
other diesel vehicles[e]	870	1044
Total Mobile Source Emissions	6431	7717
Total Primary Emissions[a]	29822	35786

[a] originally from Gray (*97*) as updated by Hildemann et al. (*27*); for a map of the geographic area see Rogge et al. (*35*).

[b] organic compounds estimated as 1.2 x organic carbon (OC).

[c] other noncatalyst vehicle types: light trucks, medium trucks, heavy trucks, motorcycles, off-highway vehicles, and stationary gasoline engines.

[d] other catalyst equipped vehicles: light trucks, medium trucks.

[e] other diesel vehicles: diesel autos, light trucks, and off-highway vehicles as given by ref (*27*) plus diesel ships and railroad engines.

Table 4.6. **Fine Aerosol Emission Rates for Single Compound Classes Released from Noncatalyst and Catalyst-Equipped Automobiles and from Heavy-Duty Diesel Trucks within the Urbanized (80 x 80 km) Los Angeles Study Area for 1982.**

Compound Class	Emission Rates in kg day^{-1}		
	Gasoline Vehicles[a]		Diesel
	Noncatalyst[b,e]	Catalyst[c,e]	Vehicles[d,e]
n-Alkanes	61.7	15.4	60.2
n-Alkanoic Acids	4.2	87.0	19.8
n-Alkenoic Acids	0.11	0.71	0.13
Benzoic Acids	0.47	15.2	3.0
Substituted Benzaldehydes	11.2	6.4	0.3
Polycyclic Aromatic Hydrocarbons (PAH)	125.8	7.4	3.4
Polycyclic Aromatic Carboxaldehydes	7.3	3.9	
Polycyclic Aromatic Ketones (PAK) and Quinones (PAQ)	27.7	6.2	3.3
Steranes	3.3	2.6	3.0
Pentacyclic Triterpanes	5.2	3.9	4.4
N-Containing Compounds	6.2	5.2	2.6
Other Identified Compounds	7.8	5.8	5.9
Total Identified	260.98	159.71	106.03

[a] collective distance traveled daily within the 80 x 80 km area in 1982: noncatalyst autos 53.7 x 10^6 km; catalyst autos 140.0 x 10^6 km, and heavy-duty diesel trucks 9.4 x 10^6 km.

[b] includes the other noncatalyst vehicles as described in Table V.

[c] includes the other catalyst vehicles as described in Table V.

[d] includes the other diesel vehicles as described in Table V.

[e] to include the emissions from the other noncatalyst, catalyst, and diesel vehicles these other vehicles were assigned mass emission rates based on source tests present in the literature and reported in Table V; then the chemical composition of those emissions was assumed to be like that of the closest analogous vehicle tested in the present study (i.e. "other" diesel engines were assumed to have the chemical nature of the diesel trucks tested here; noncatalyst trucks were assumed to have the exhaust composition of noncatalyst autos, etc.).

85% of the fine particle bound PAH, PAK, and PAQ vehicular emissions to the urban Los Angeles atmosphere in 1982 were contributed by automobiles without catalytic exhaust emission control systems. In contrast, the n-alkanoic acids in vehicle exhaust were emitted mainly from autos equipped with catalytic converters ($> 80\%$).

Vehicular particle phase tracer compounds comprised of the steranes and triterpanes quantified in Table 4.2 are emitted within that 80 × 80 km urban area at a estimated rate of 22.4 kg day^{-1}. Figure 4.7a shows the emission rates for each of these fossil petroleum marker compounds within the 80 × 80 km Los Angeles study area. The highest emission rate for a single marker compound was found for 17α(H), 21β(H)-hopane (1.75 kg day^{-1}). The emissions of primary particulate organic carbon (OC) from all sources combined for the area discussed was estimated to total 29820 kg day^{-1} (Table 4.5). Restated, this amounts to 35800 kg day^{-1} of equivalent organic compound mass (organic compounds $\simeq 1.2 \times$ organic carbon). Thus, the fossil petroleum markers studied here, when combined, account for 0.063% of the fine particulate organic compound emissions. From the OC data of Gray et al. (*101*), the ambient annual mean fine particulate total organic compound concentrations ($d_p \leq 2\ \mu$m) can be calculated to be: West Los Angeles 6.94 μg m^{-3}, downtown Los Angeles 8.63 μg m^{-3}, and Pasadena 8.06 μg m^{-3} during 1982 (organic compound concentrations $\simeq 1.2 \times$ organic carbon). If 0.063% of the fine total organic compound concentrations at the three sampling sites were present as the steranes and triterpanes, then ambient fine particle concentrations of these compounds totaling approximately 4.37 ng m^{-3} at West Los Angeles, 5.43 ng m^{-3} in downtown Los Angeles, and 5.08 ng m^{-3} at Pasadena should be measured.

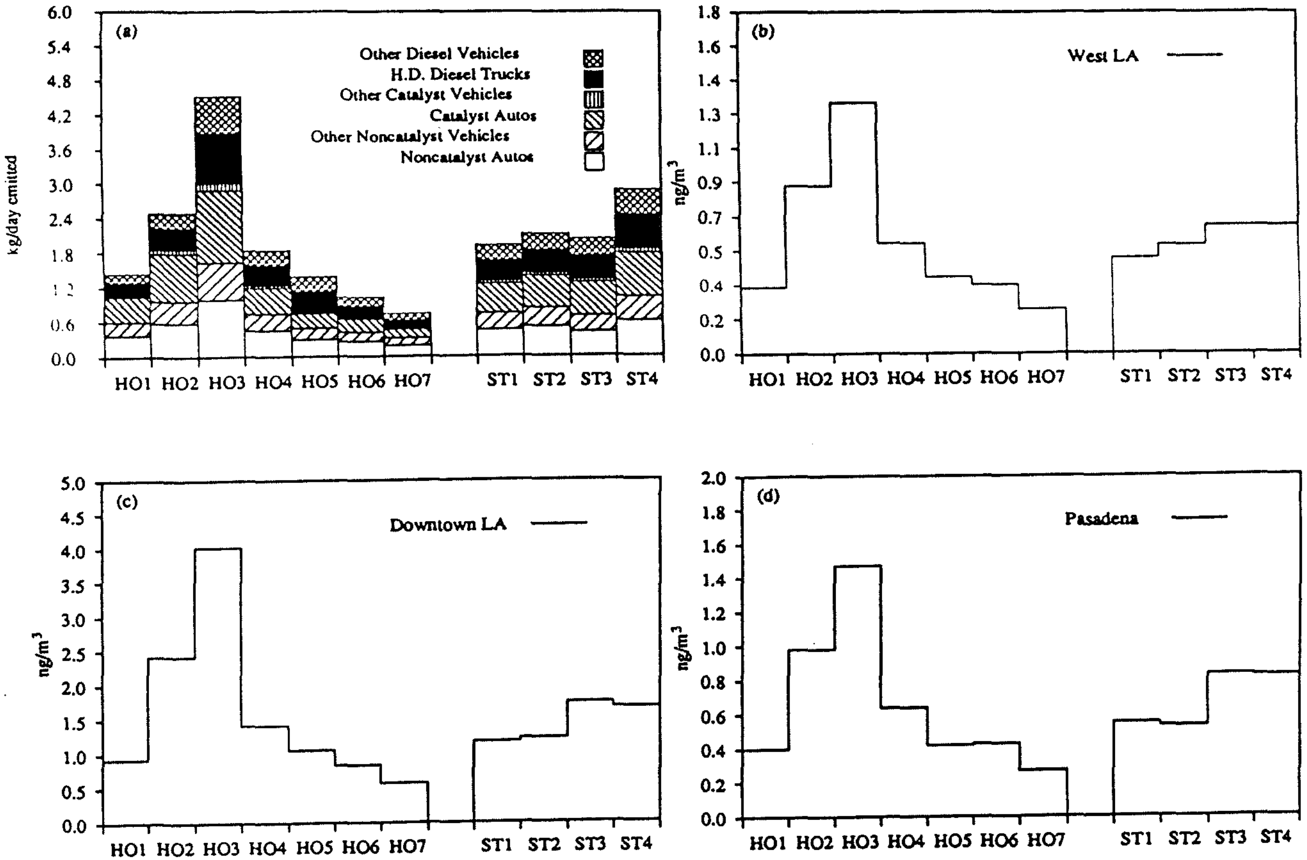

Figure 4.7 Vehicular emission profiles and ambient concentration profiles of fine particle fossil fuel markers: (a) 1982 emission rates for the 80 × 80 km greater Los Angeles area; measured 1982 annual average concentrations at (b) West Los Angeles, (c) downtown Los Angeles, and (d) Pasadena. HO1: 22,29,30–trisnorneohopane; HO2: 17α(H),21β(H)-29-norhopane; HO3: 17α(H),21β(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.

Comparison of Source and Ambient Data

Recently, Rogge et al. (*36*, *102*) compiled an extensive data set on fine aerosol organic compound concentrations for the year 1982 for the 80 × 80 km greater Los Angeles study area discussed here. The aerosol sampling strategy and the analytical procedures used in that study were nearly identical to those used for vehicle testing. Hence, the results from both studies allow direct comparison. Most of the compounds identified in the particulate automobile exhaust emissions have also been quantified in the ambient aerosol. Indeed, hopanes and steranes have been quantified in the ambient fine aerosol collected at the three sampling sites mentioned above within the Los Angeles air basin. In Figures 4.7b-d, the ambient annual average concentration profiles for the sterane and hopane fossil petroleum markers are plotted for the three urban sites within the target area. Although absolute concentration levels of the fossil petroleum markers vary from sampling site to sampling site, the relative abundance of these markers is very similar at each site. Further, when comparing the relative abundance of these fossil petroleum markers in vehicle emissions (Figure 4.7a) to the ambient concentration profiles for the same fine particle compounds (Figures 4.7b-d) remarkably good agreement is seen. This indicates that the relative distribution between these fossil petroleum hydrocarbons is preserved from the source to the receptor sites.

Average annual ambient concentrations of the steranes and triterpanes of interest here were measured and found to be 6.53 ng m^{-3} at West Los Angeles, 17.10 ng m^{-3} at downtown Los Angeles, and 7.84 ng m^{-3} at Pasadena for the year 1982. At West Los Angeles and Pasadena, the measured ambient concentrations compare rather well with the concentrations estimated above by scaling from the areawide emissions of these marker substances from vehicles. At downtown Los Angeles, the measured fossil petroleum marker concentrations are higher roughly by a factor of three compared to the concentrations predicted by assuming that the air column over that area could be represented by an air basin-wide mixture of equally spaced source emissions. This local enrichment near downtown Los Angeles may be explained by the unusually high vehicle traffic densities near that site. In wintertime, the wind often stagnates and the ambient concentrations for many particle bound organic compound classes peak over downtown Los Angeles (*36*). Indeed, as seen in Figures 4.8a,b, the ambient concentrations of the fossil petroleum markers studied here are markedly elevated in wintertime at downtown Los Angeles.

In Figure 4.9, the scaling technique described above was applied to single fossil petroleum markers released from internal combustion engines to estimate ambient concentrations at West Los Angeles. The ambient concentrations of fossil petroleum markers estimated due to vehicle exhaust emissions follow the relative ordering of those marker concentrations measured in ambient air. These concentrations estimated from basin-wide emission data for vehicles fall short of matching the ambient concentrations in part because only about 85% of the mass emissions of these compounds to the Los Angeles atmosphere are from gasoline and diesel engines. Therefore, it is promising that ambient fossil petroleum marker concentrations can be used directly to estimate the contributions from vehicular source types to the ambient fine aerosol complex.

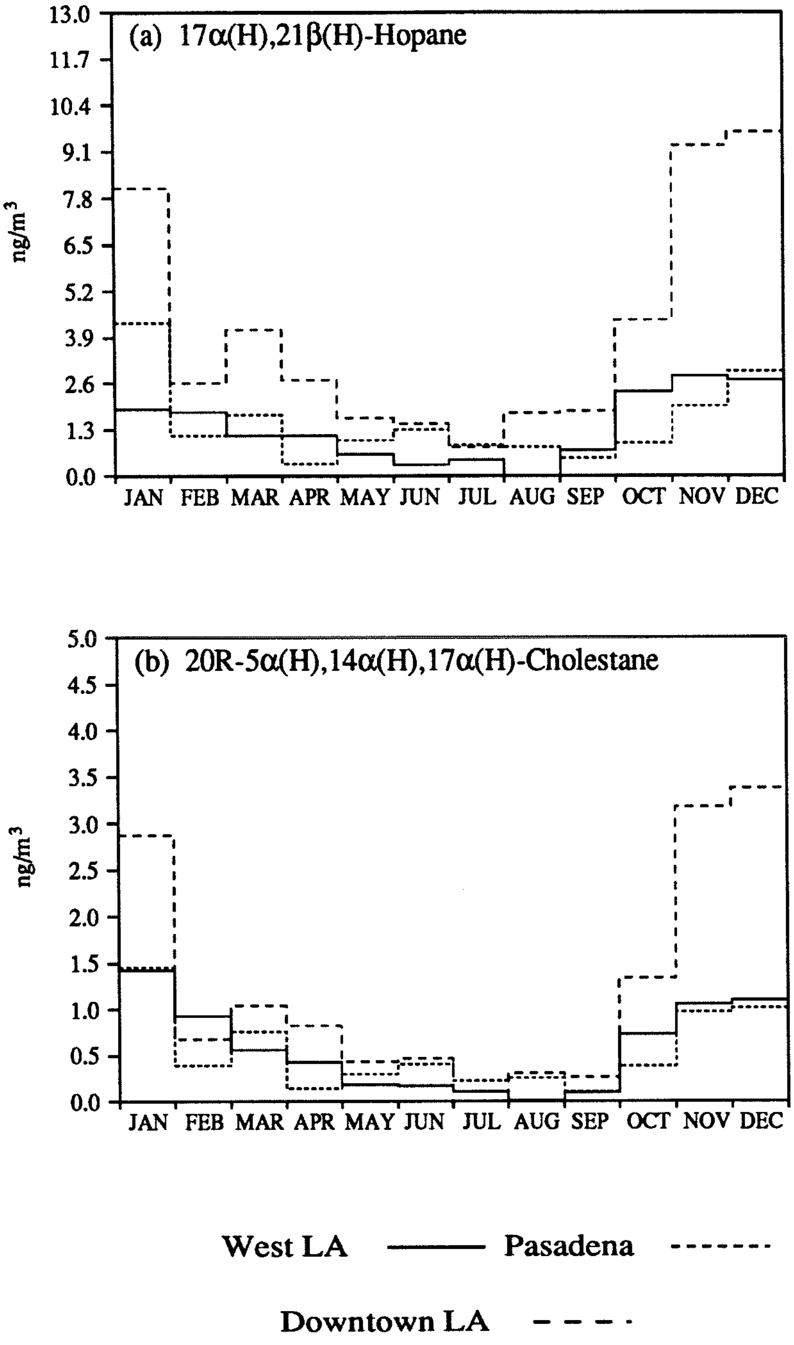

Fig. 4.8: Measured monthly average ambient fine particle concentrations for two fossil fuel markers during 1982. (a) 17α(H),21β(H)-hopane; (b) 20R-5α(H),14α(H),17α(H)-cholestane.

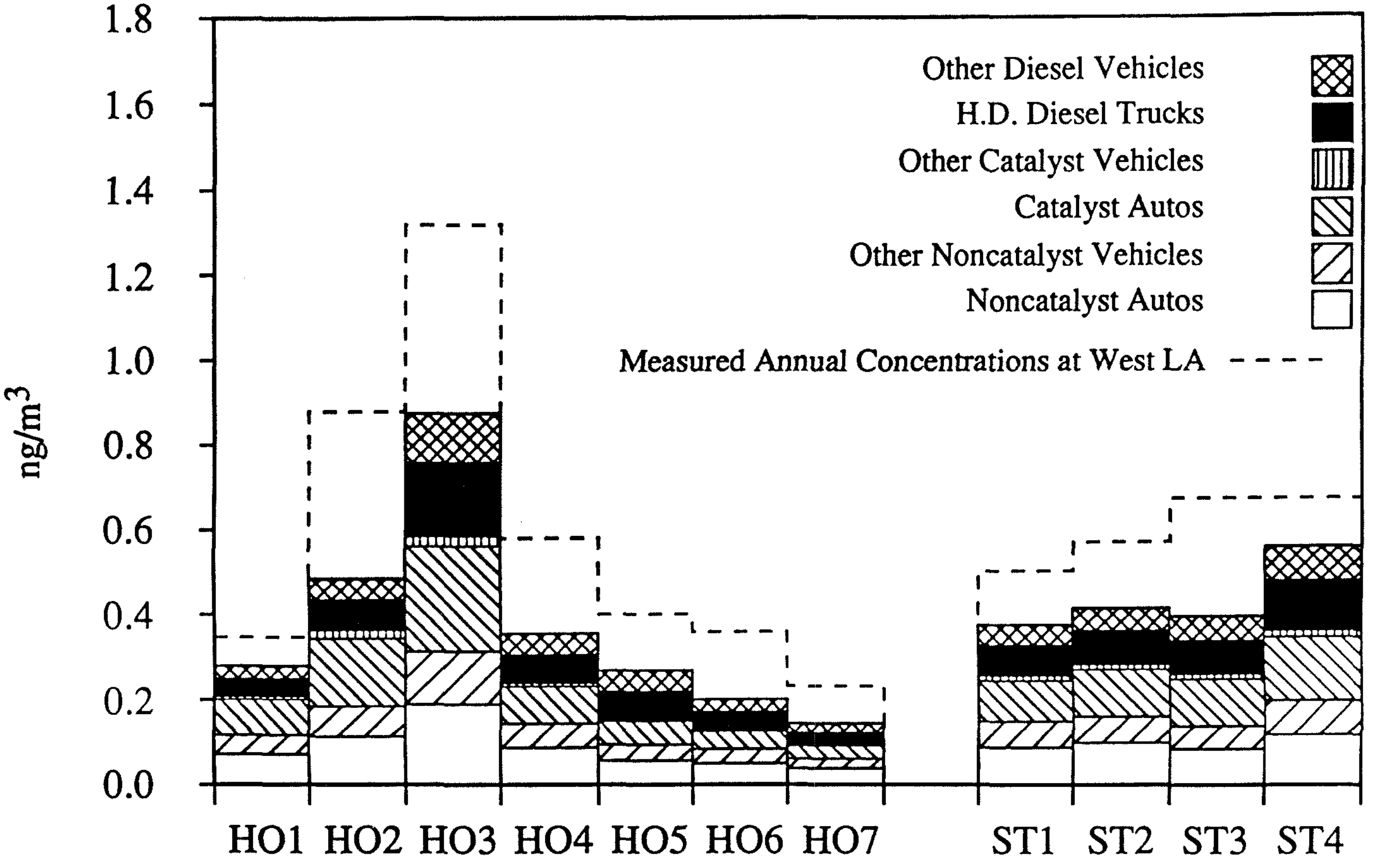

Figure 4.9 Estimated and measured ambient annual averaged concentrations of fine particle fossil fuel markers at West Los Angeles. HO1–HO7 and ST1–ST4 as in Fig. 4.7.

Conclusion

The chemical composition of organic fine particulate matter ($d_p \leq 2\ \mu m$) emitted from noncatalyst and catalyst-equipped automobiles and from heavy-duty diesel trucks has been studied by GC/MS techniques. In the current study, more than 100 organic compounds were quantified including the series of n-alkanes, n-alkanoic acids, one n-alkenoic acid, benzoic acids, substituted benzaldehydes, PAH, oxy-PAH, steranes, pentacyclic triterpanes, azanaphthalenes, and others. It has been shown that PAH and oxy-PAH emission rates are highest for automobiles without catalytic converter systems. The PAH emission rate measured for noncatalyst autos exceeds that for catalyst-equipped autos by more than 26-fold. In contrast, most of the n-alkanoic acids released from automobiles are released from catalyst-equipped autos. Heavy-duty diesel trucks show high emission rates for n-alkanes and n-alkanoic acids. PAH emission rates per km driven are about four times higher from diesel trucks than from catalyst-equipped automobiles, but nearly seven times lower than from noncatalyst autos. Fossil petroleum markers such as steranes and pentacyclic triterpanes (hopanes) are readily identified in the exhaust emissions. Because they are not constituents of gasoline or diesel fuels, they are introduced into the exhaust via engine oil. For the greater Los Angeles area it has been found that these fossil petroleum markers are released mainly from internal combustion engines. Furthermore, the relative abundance of these marker compounds as seen in vehicular source emissions is preserved in the Los Angeles urban atmosphere. Thus, these fossil petroleum markers can be used as suitable tracer compounds to estimate the contributions from vehicular sources to the southern California atmosphere.

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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

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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 ($d_p \leq 2$ μm) 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 μm 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 μm 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 μl. 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 $\underline{n}$-$C_{24}D_{50}$ 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

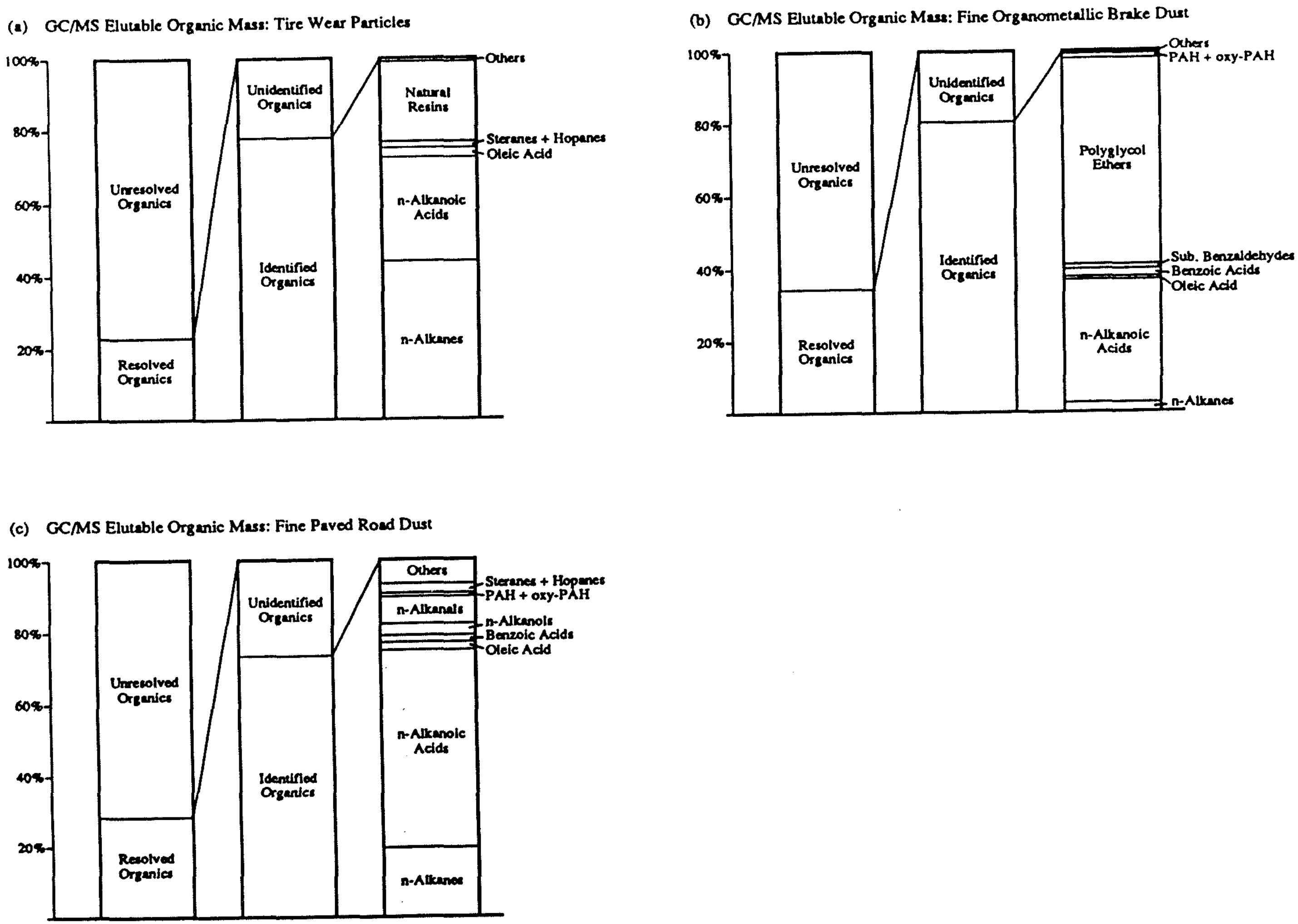


Fig. 5.1: Mass balance for elutable organic matter from (a) tire wear particles, (b) fine brake lining wear particles, and (c) fine paved road dust.

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 μm 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*).

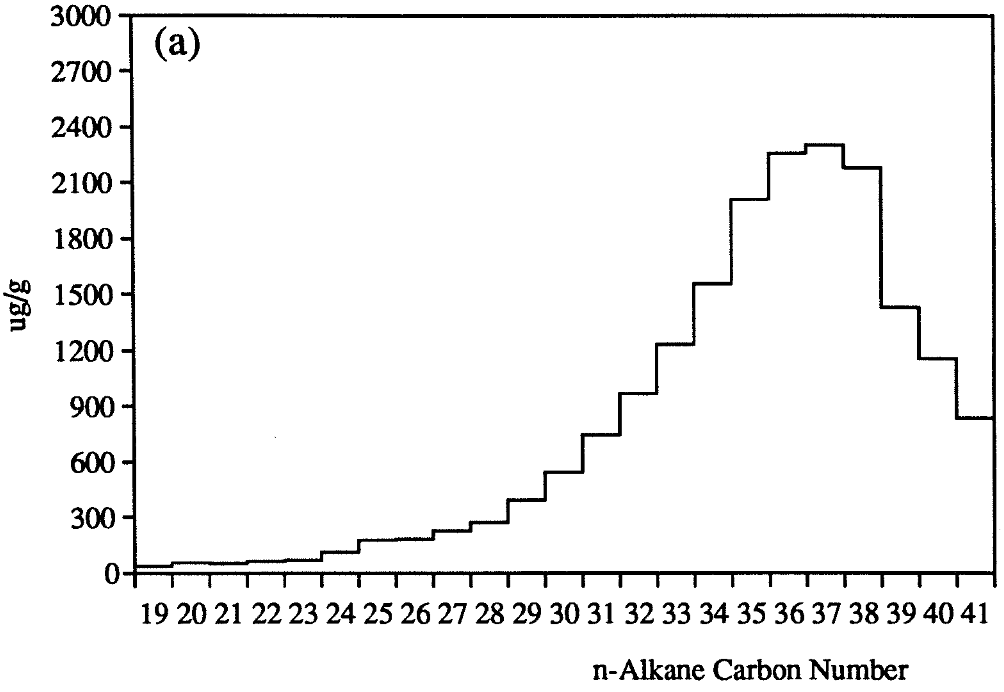
Particulate tire tread in urban air has been evaluated by previous investigators, who have used characteristic tire pyrolysis products such as benzothiazole to trace tire wear debris in the urban atmosphere (*12, 24, 25*). Pierson and Brachaczek (*22*) traced the presence of tire rubber particles in 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



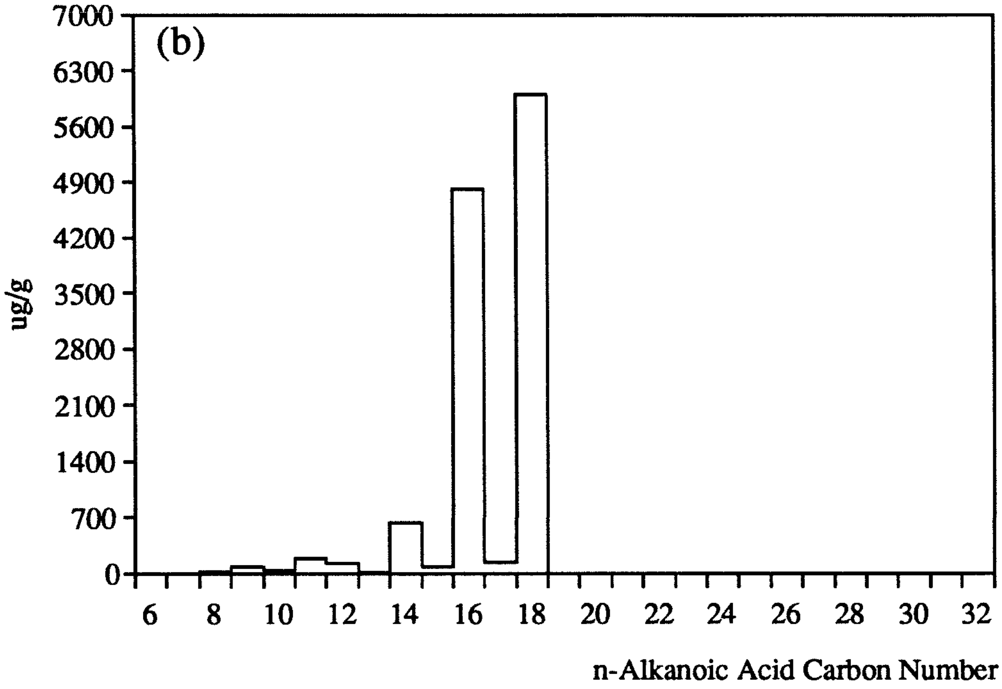


Fig. 5.2.: Mass concentration distributions for tire wear organic constituents in $\mu g\ g^{-1}$ of total (fine plus coarse) tire wear debris for (a) n-alkanes and (b) n-alkanoic acids.

'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 μg 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 μg/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 μg/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

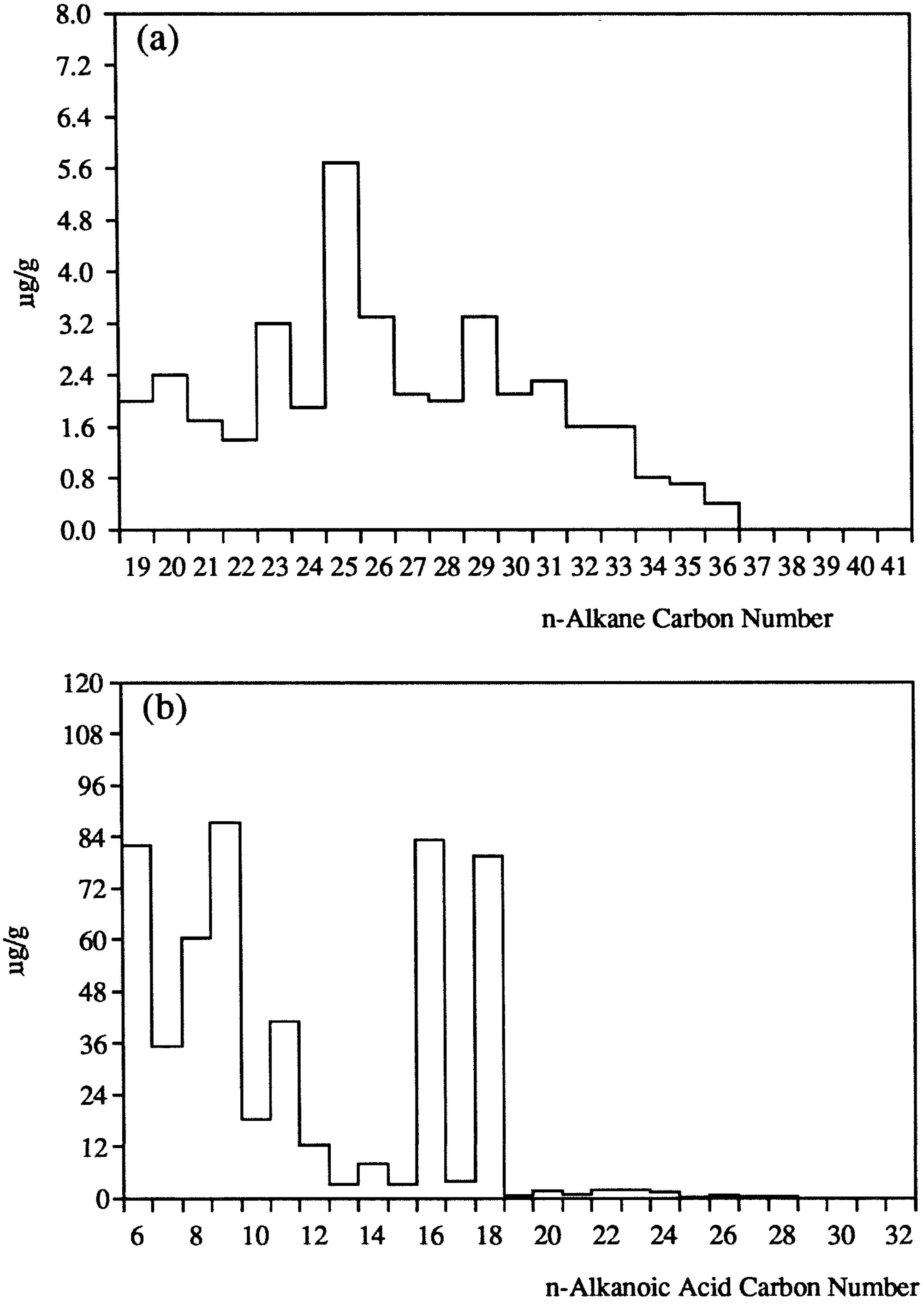


Fig. 5.3.: Mass concentration distributions for brake lining wear organic constituents in μg g^{-1} of fine brake lining particles for (a) n-alkanes and (b) n-alkanoic acids.

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 μg/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

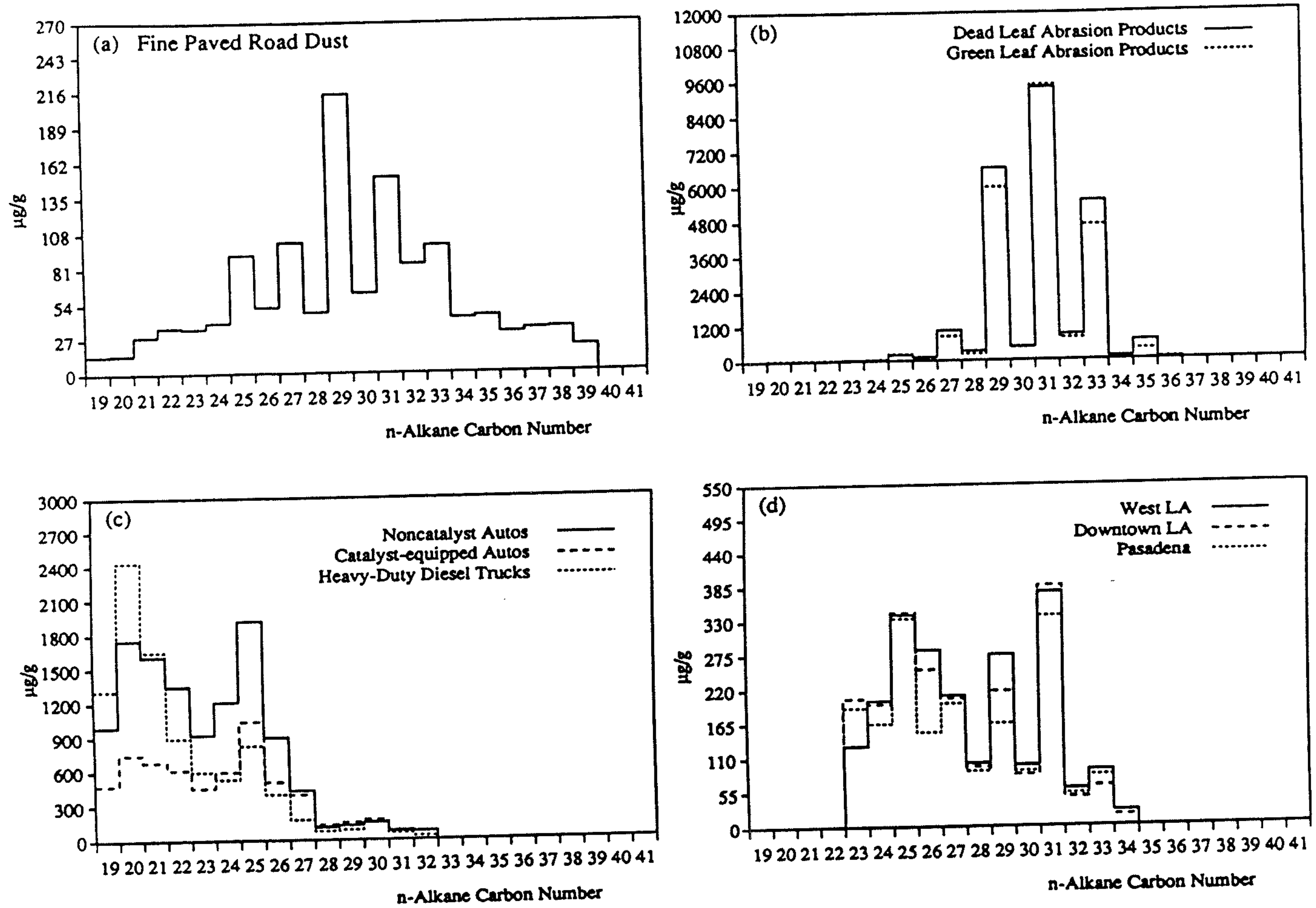


Fig. 5.4: n-Alkanes mass concentration distributions (in μg g^{-1} of particulate matter) for (a) fine paved road dust, (b) fine particulate dead and green leaf surface abrasion products, (c) fine particulate exhaust emissions from noncatalyst and catalyst-equipped autos and heavy-duty diesel trucks, 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, α-terpineol, β-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.

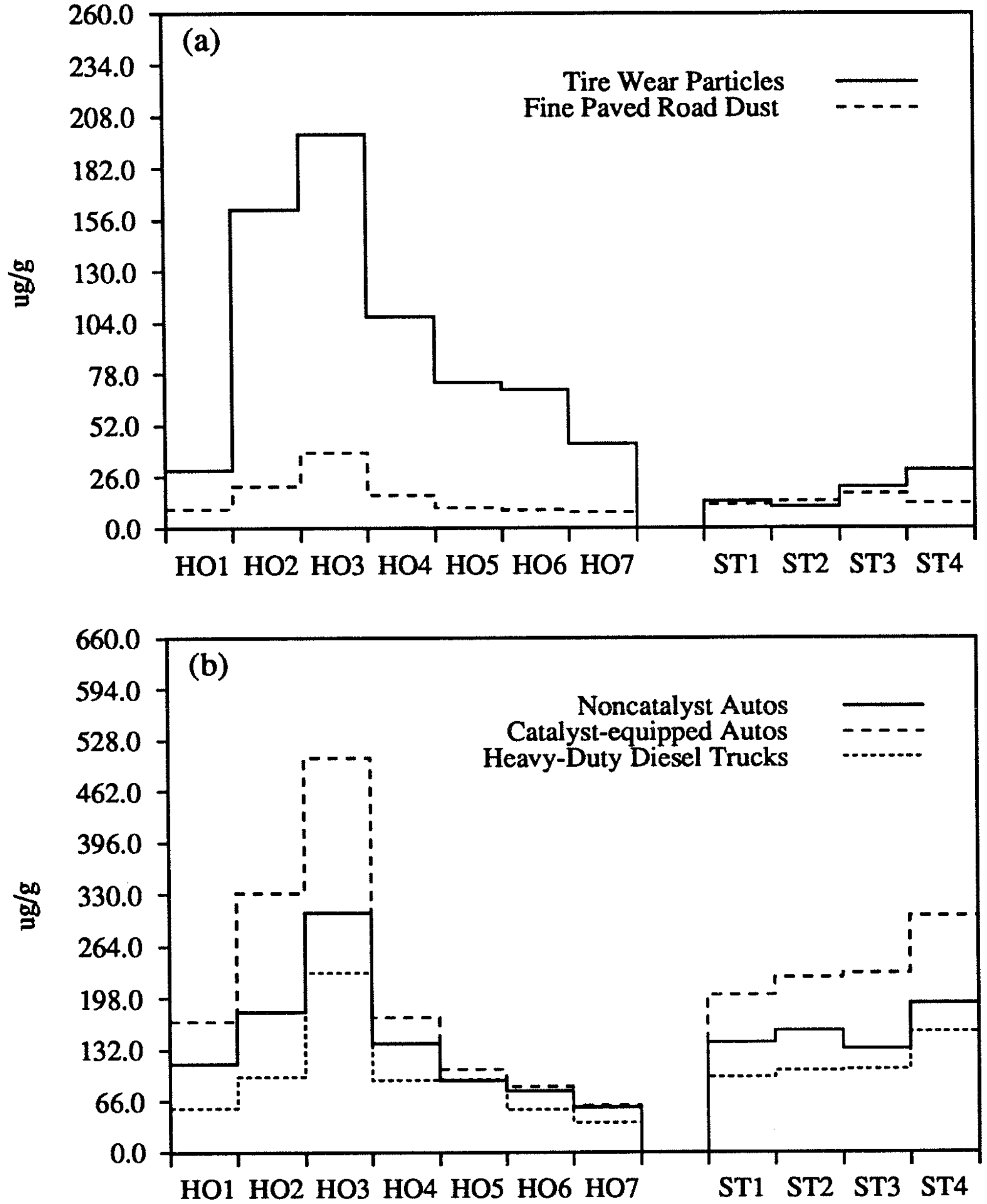


Fig. 5.5.: Fossil fuel marker mass concentrations for (a) tire wear particles and fine paved road dust and (b) noncatalyst and catalyst-equipped autos and heavy-duty diesel trucks. HO1: 22,29,30-trisnorneohopane; HO2: 17α(H),21β(H)-29-norhopane; HO3: 17α(H),21-β(H)-hopane; HO4: 22S-17α(H),21β(H)-30-homohopane; 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 ($d_p \leq 2.0$ μm) 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 17α(H),21β(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.**

	Concentrations[‡] in μg g^{-1} of Particle Sample			
PART A	**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)

	Concentrations[‡] in μg g^{-1} of Particle Sample			
PART B	**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)

	Concentrations[‡] in μg g^{-1} of Particle Sample			
PART D	**Tire Wear Particles**	**Brake Lining Particles**	**Road Dust Particles**	Compound ID[§]
— 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-5α(H),14β(H),17β(H)-cholestanes	13.5	0.30	12.1	b
20R-5α(H),14α(H),17α(H)-cholestane	10.7	0.26	13.8	a
20S&R-5α(H),14β(H),17β(H)-ergostanes	20.7	0.99	17.3	b
20S&R-5α(H),14β(H),17β(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 $\mu g\ g^{-1}$ 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	Tire Wear Particles	Brake Lining Particles	Road Dust Particles	Compound ID[§]
	Concentrations[‡] in $\mu g\ g^{-1}$ of Particle Sample			
	—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 μm 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.

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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

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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 μm aerodynamic particle diameter) and collected on quartz fiber filters (Pallflex 2500 QAO) and Teflon filters (Gelman Teflo, 2.0 μm 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 μl 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

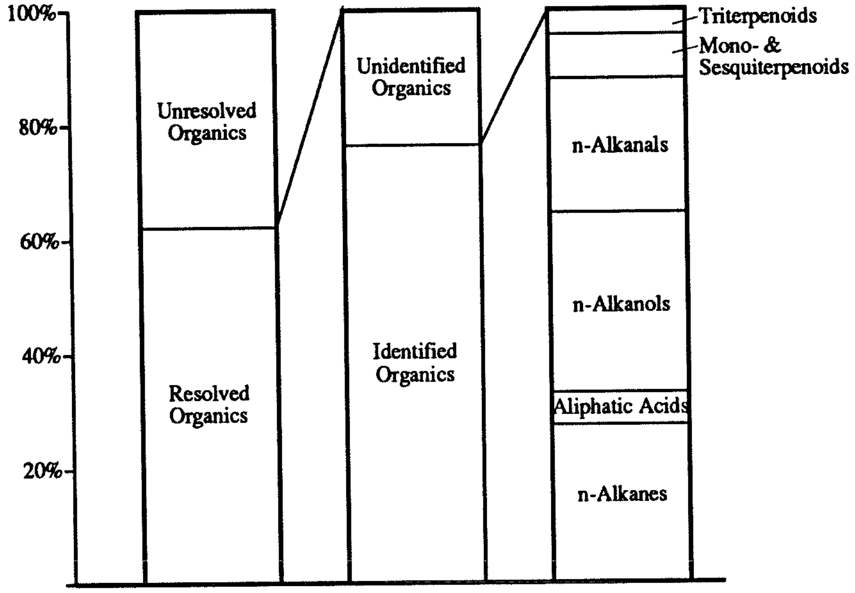
The leaf surfaces of vascular plants generally consist of a lipophilic polymer membrane (cuticle) whose monomers are mostly hydroxy fatty acids (*24, 30-32*). Embedded and growing from the cuticular membrane are waxlike lipids forming crystalline structures of micron to submicron dimensions and intercrystalline 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*).

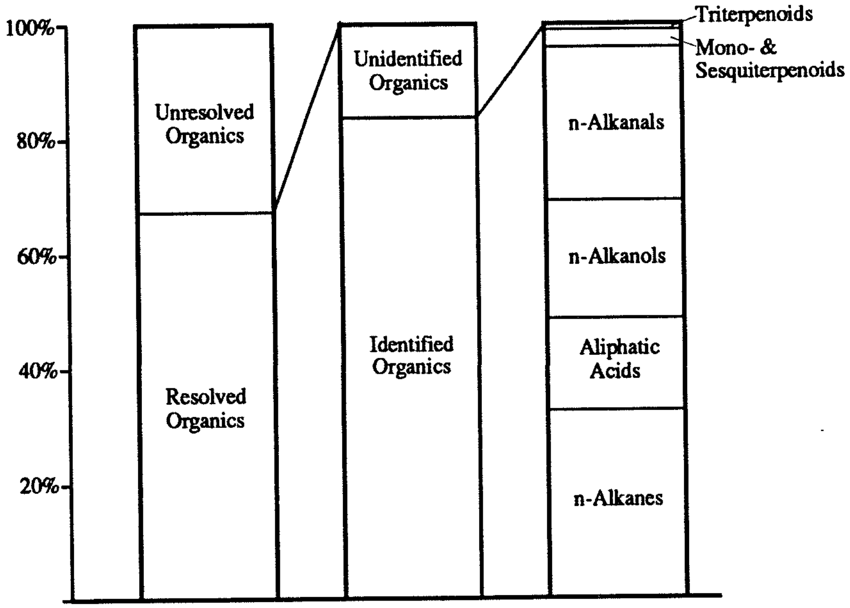
In the following sections, the organic composition of fine particulate matter collected from the agitation of green and dead leaf composites characteristic of the Los Angeles basin will be discussed. Then these leaf surface emissions will be related to other sources that emit biogenic particulate matter.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

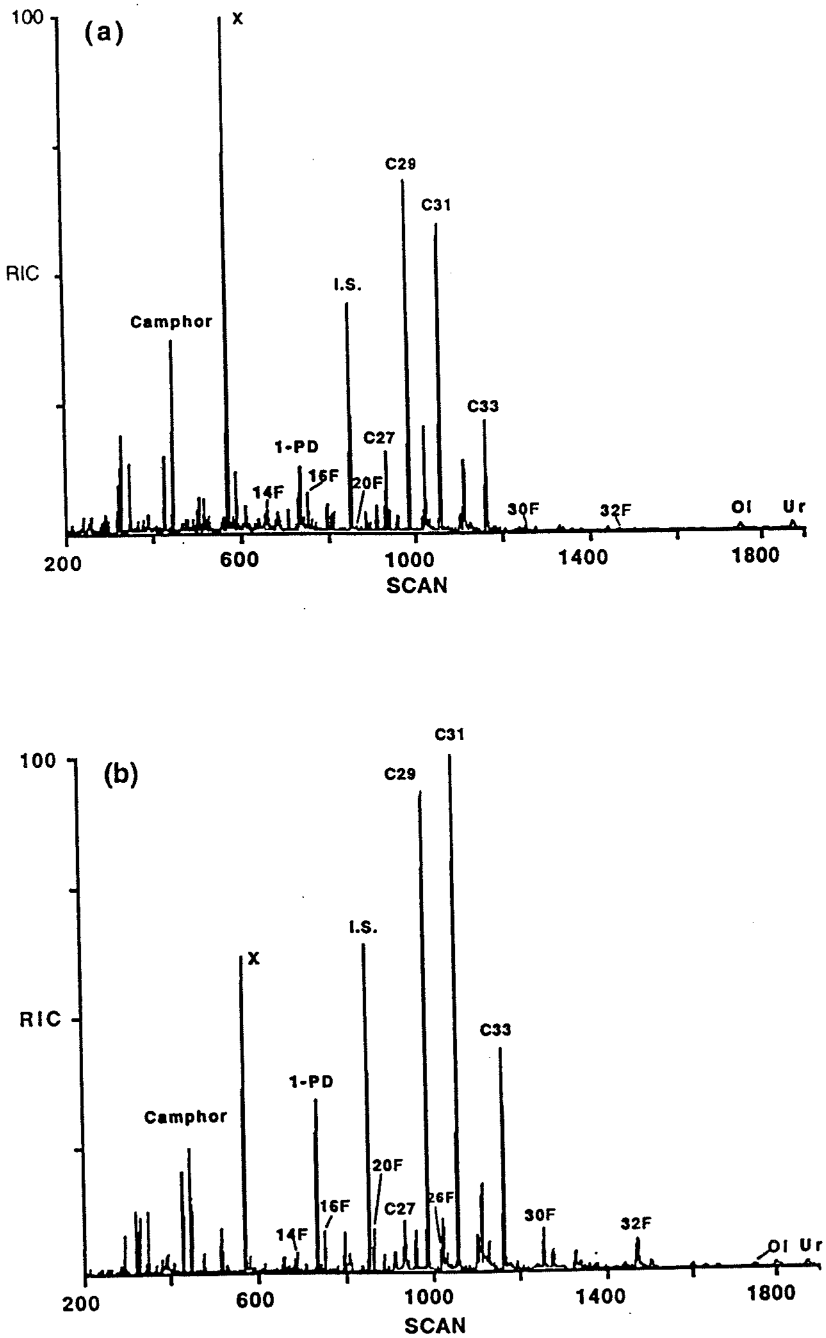


Fig. 6.2: Total reconstructed ion current (RIC) chromatogram (GC/MS) for fine leaf surface particulate matter shed from: (a) green leaf and (b) dead leaf composites. Numbers refer to carbon chain length of compounds: C, *n*-alkanes; F, *n*-alkanoic acids (detected as methyl esters); Ol, oleanolic acid 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.

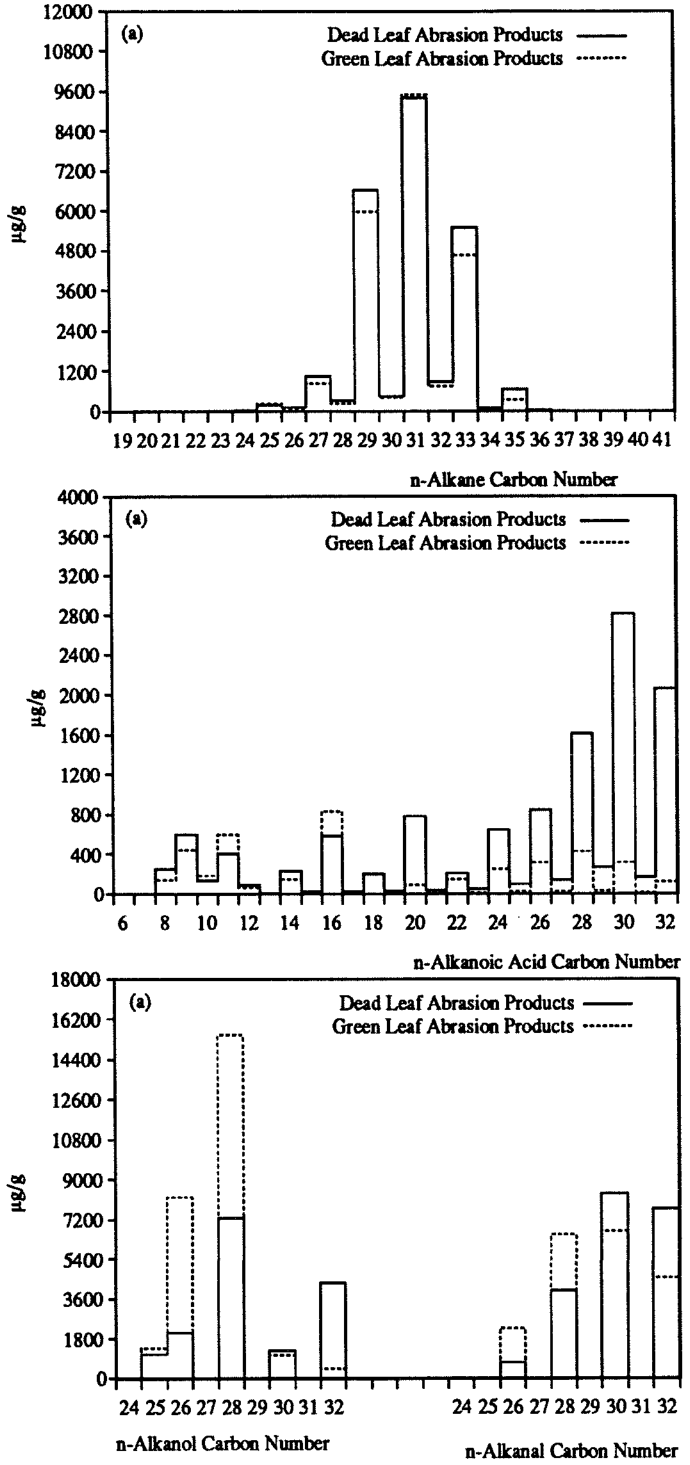


Fig. 6.3: Compound concentrations per gram of fine particulate matter shed from leaf surfaces: (a) n-alkanes, (b) n-alkanoic acids, and (c) n-alkanols and n-alkanals.

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 (μg 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 μm. Only 10% of the bacteria show diameters ≤ 2 μm. Molds and their spores show exclusively diameters > 2 μm (*86*). Consequently bacteria and bacterial spores which might be found in the particle size range $d_p \leq 2$ μm 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

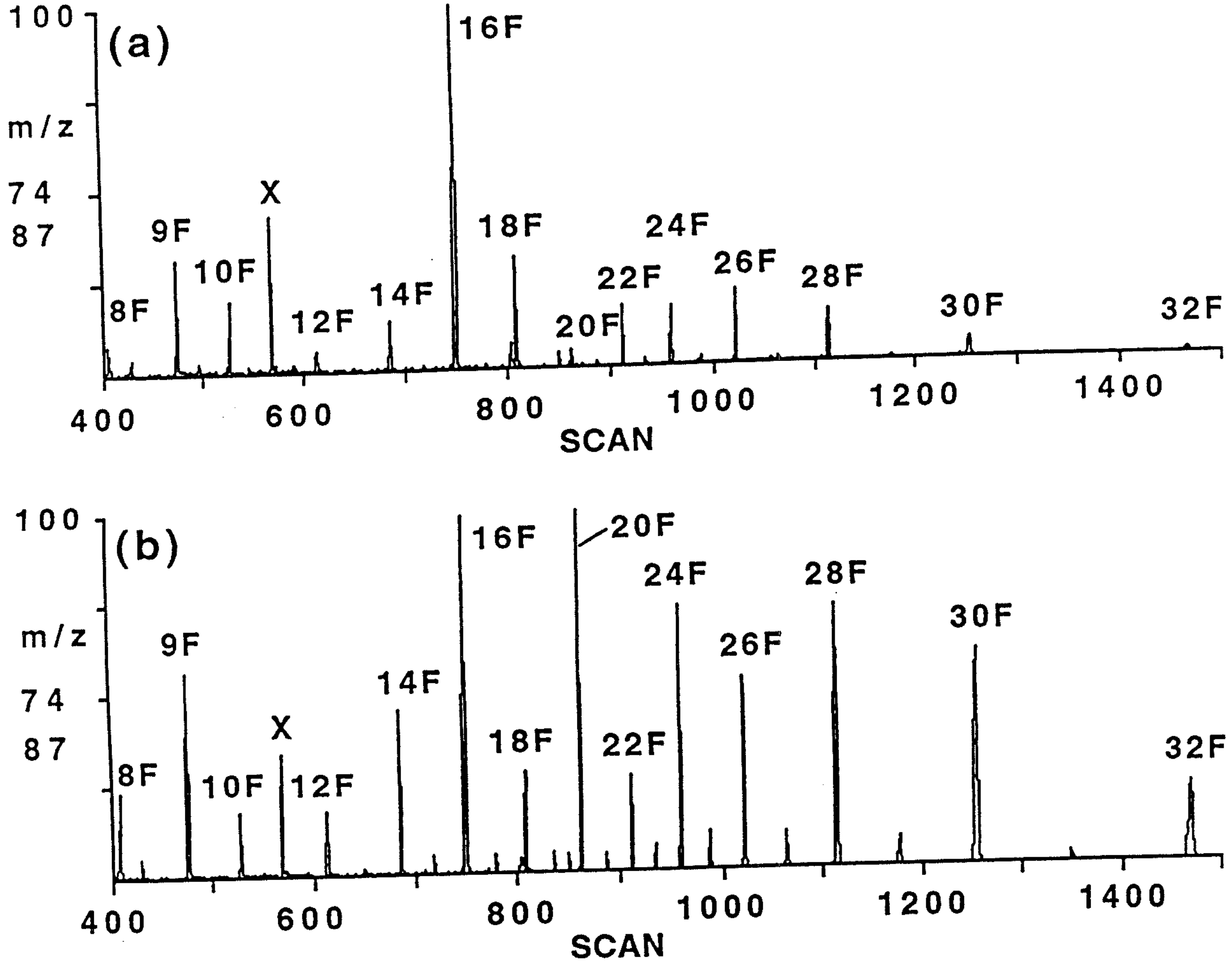


Fig. 6.4: Selected mass fragmentograms for *n*-alkanoic acids as methyl esters (sum: m/z 74 + 87) found in fine particulate leaf abrasion products: (a) green leaf and (b) dead leaf composites. Numbers refer to the carbon chain length of the n-alkanoic acids (detected as methyl esters).

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

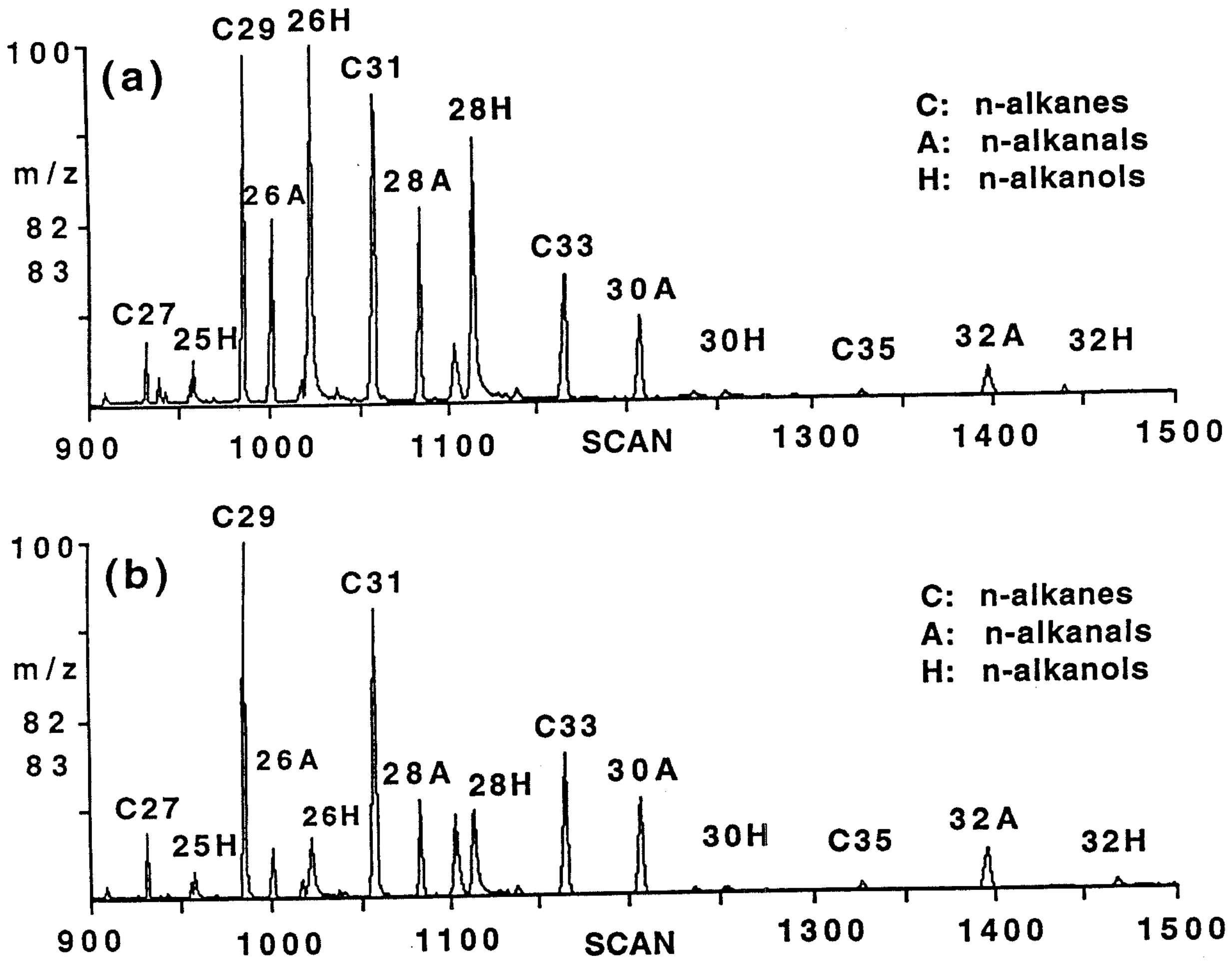


Fig. 6.5: Selected mass fragmentograms typical for *n*-alkanols and *n*-alkanals (sum: m/z 82 + 83) found in fine particulate leaf abrasion products: (a) green leaf and (b) dead leaf composites. Numbers refer to the carbon chain length of the molecules: A, *n*-alkanals; C, *n*-alkanes; H, *n*-alkanols.

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 μg g^{-1}) and dead ($\sim$ 1600 μg g^{-1}) fine particulate leaf abrasion product samples studied here.

One triterpenol (β-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].**

Concentrations in μg g^{-1} of Leaf Abrasion Products[b]

PART A

	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 μg 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 μg 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

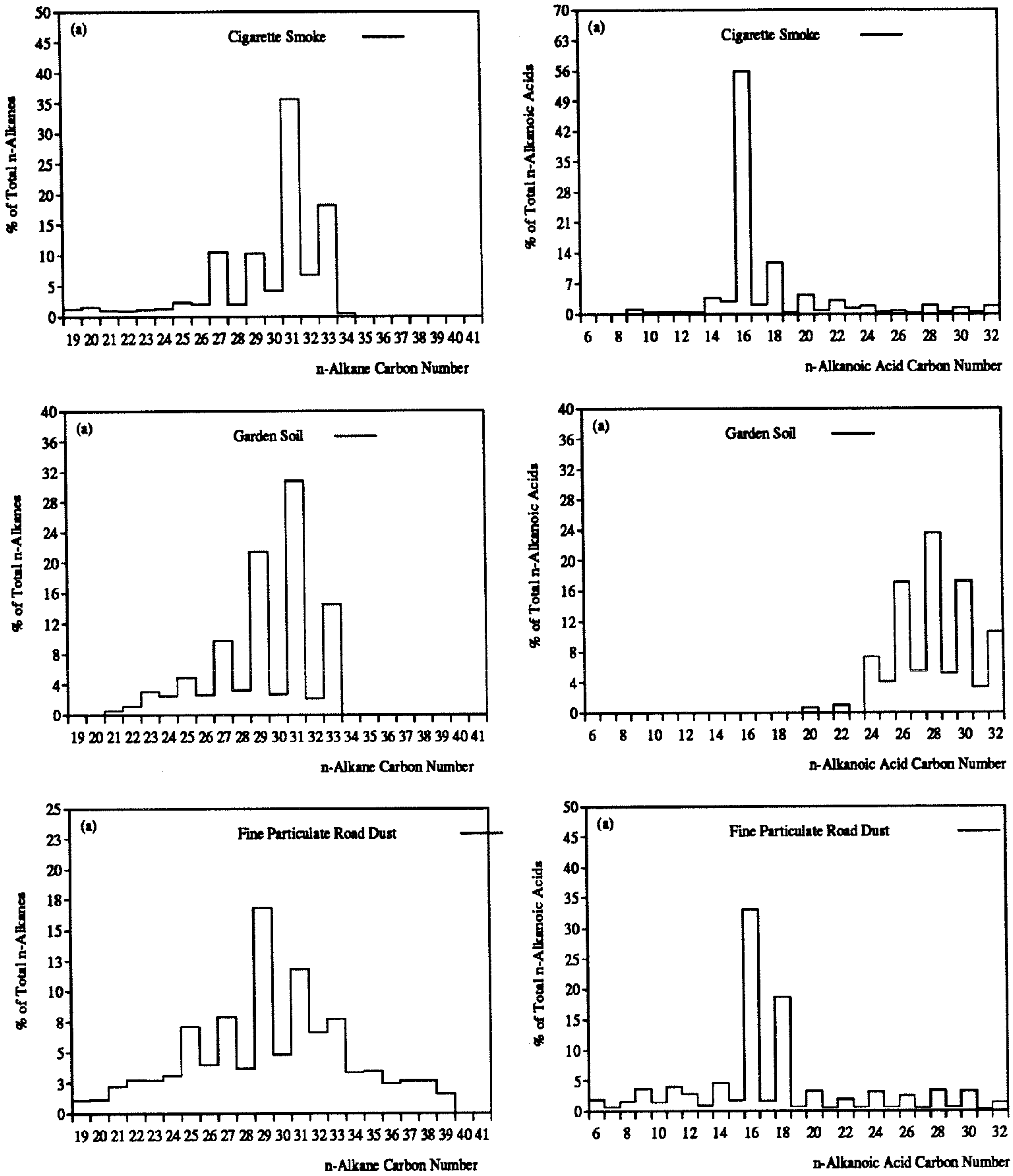


Fig. 6.6: Relative mass concentration expressed as % of that compound class present in fine particles: (a) *n*-alkanes from cigarette smoke; (b) *n*-alkanoic acids from cigarette smoke; (c) *n*-alkanes from garden soil (from Morrison and Blick, 1967); (d) *n*-alkanoic acids from garden soil (from Morrison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

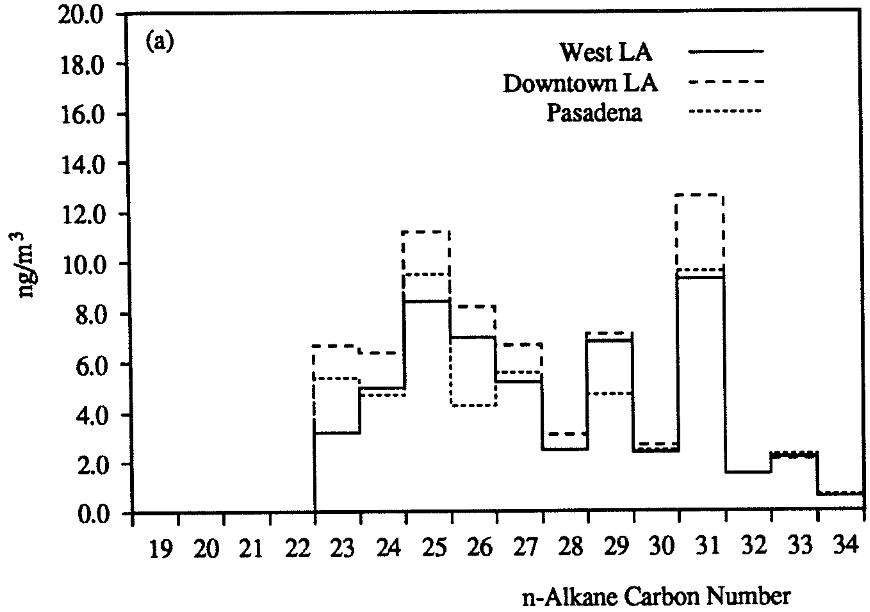
Morrison and Blick (*75*) analyzed garden soil for several compound classes including *n*-alkanes (C_{21} – C_{33}) and *n*-alkanoic acids (C_{20} – C_{34}). Their results for both compound classes are shown in Figures 6.6c,d and compare well with the green and dead leaf abrasion product samples studied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



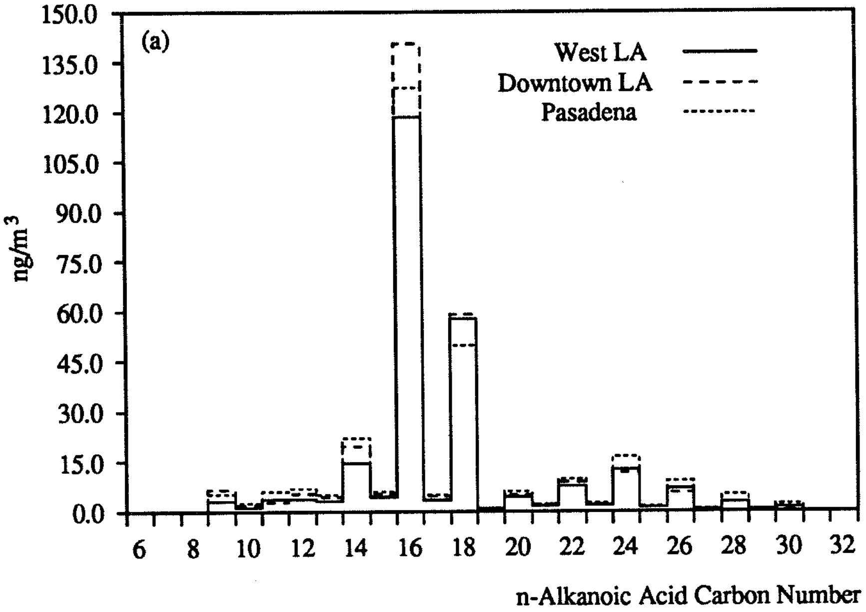


Fig. 6.7: Annual average concentration profiles for fine airborne particulate matter in 1982: (a) n-alkanes and (b) n-alkanoic acids.

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, α-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 (μg 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.

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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 ($\underline{n}$-$C_{24}D_{50}$) used as an internal standard was spiked onto the filter composites. To ensure that the amount of $\underline{n}$-$C_{24}D_{50}$ 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 μl 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 non-polar 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.

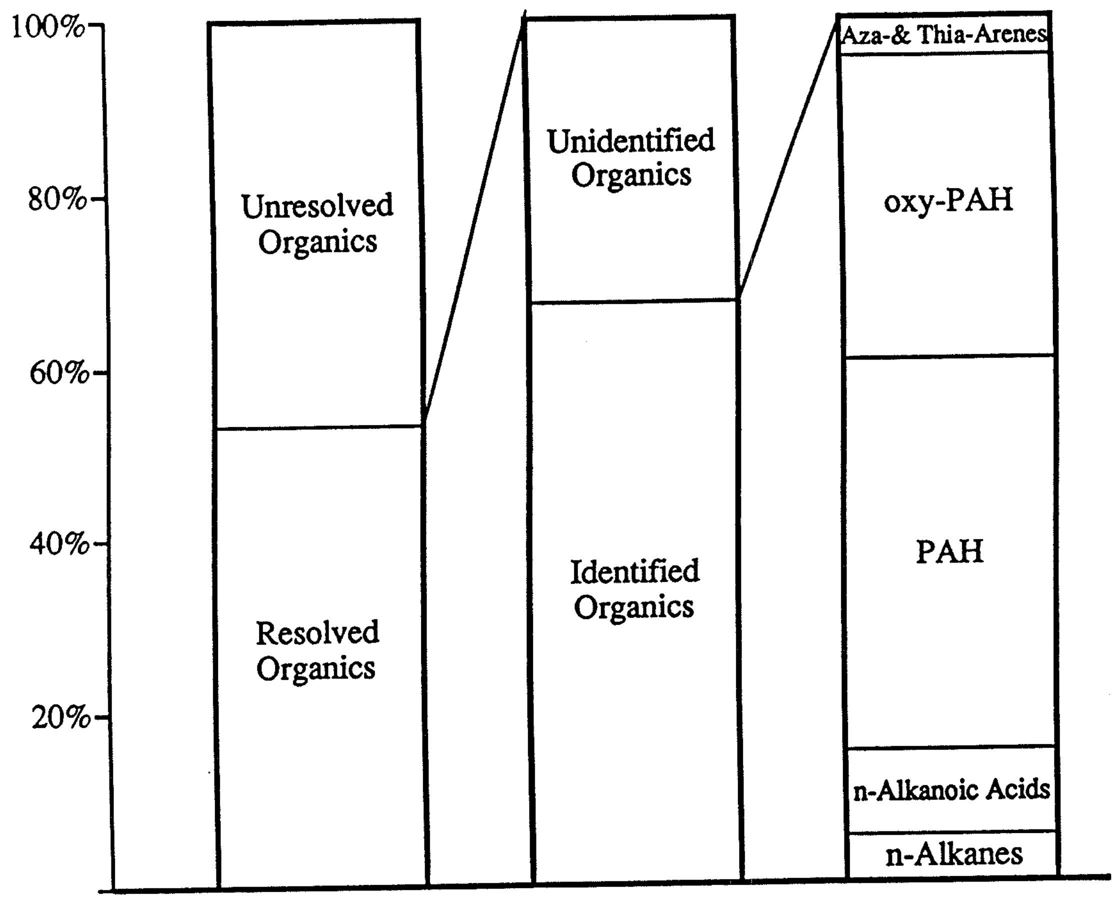


Fig. 7.1: Mass balance for elutable organic matter in the fine particle emissions (front filters only) of natural gas-fired home appliances.

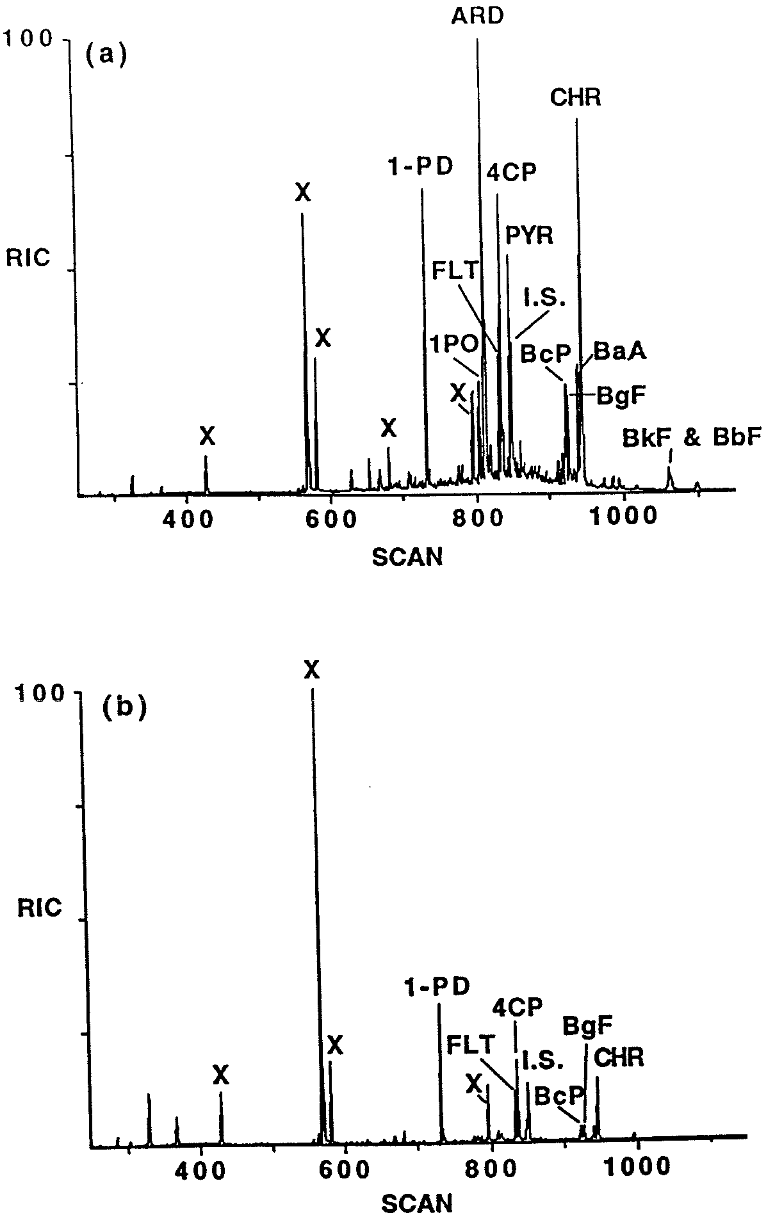


Fig. 7.2: Total reconstructed ion current (RIC) for exhaust emissions from natural gas-fired home appliances: (a) fine particle front filter samples, (b) backup filter samples. I.S.: internal standard ($\underline{n}$-$C_{24}D_{50}$); 1-PD: coinjection standard; 1PO: 1H-phenalen-1-one; FLT: fluoranthene; 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

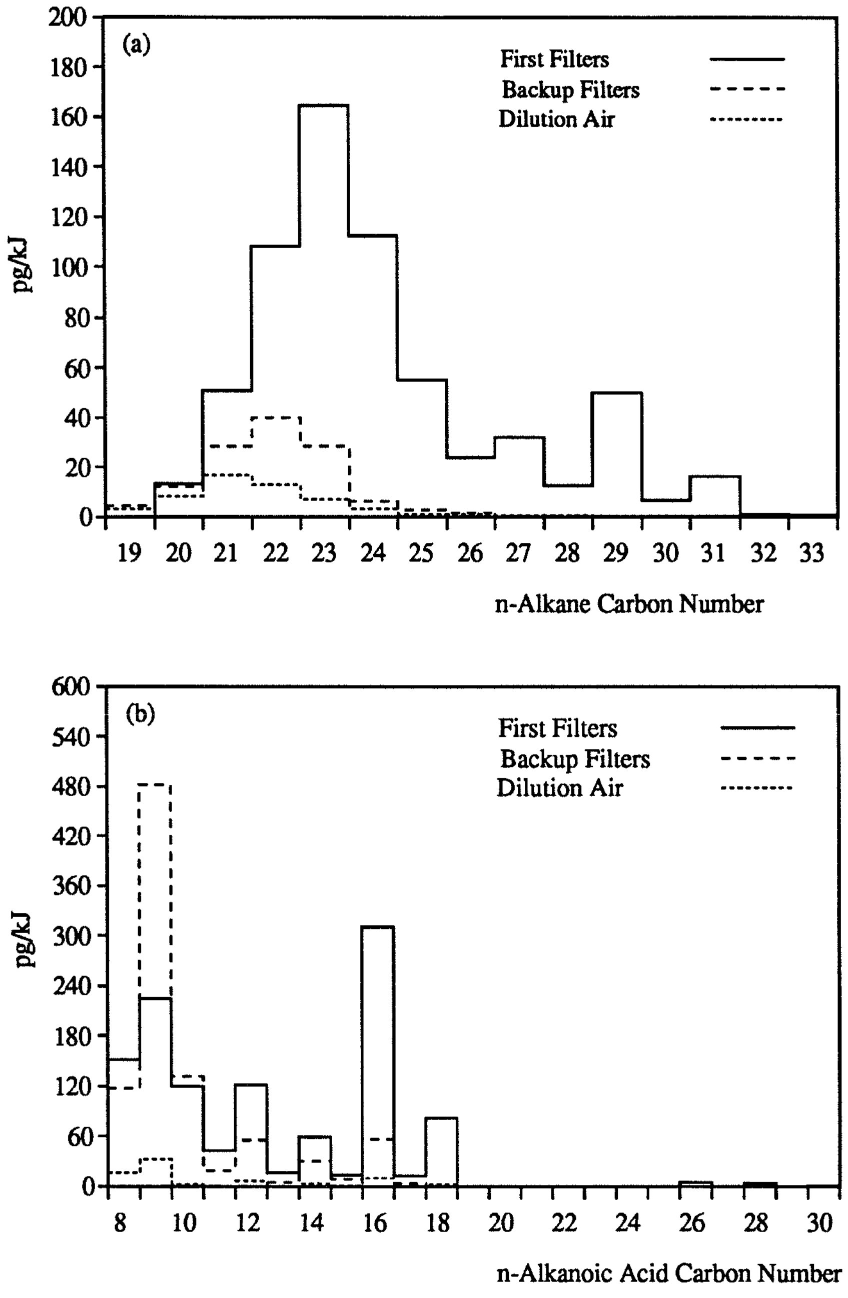


Fig. 7.3: Emission profiles for natural gas-fired home appliances: (a) n-alkanes and (b) n-alkanoic acids.

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).

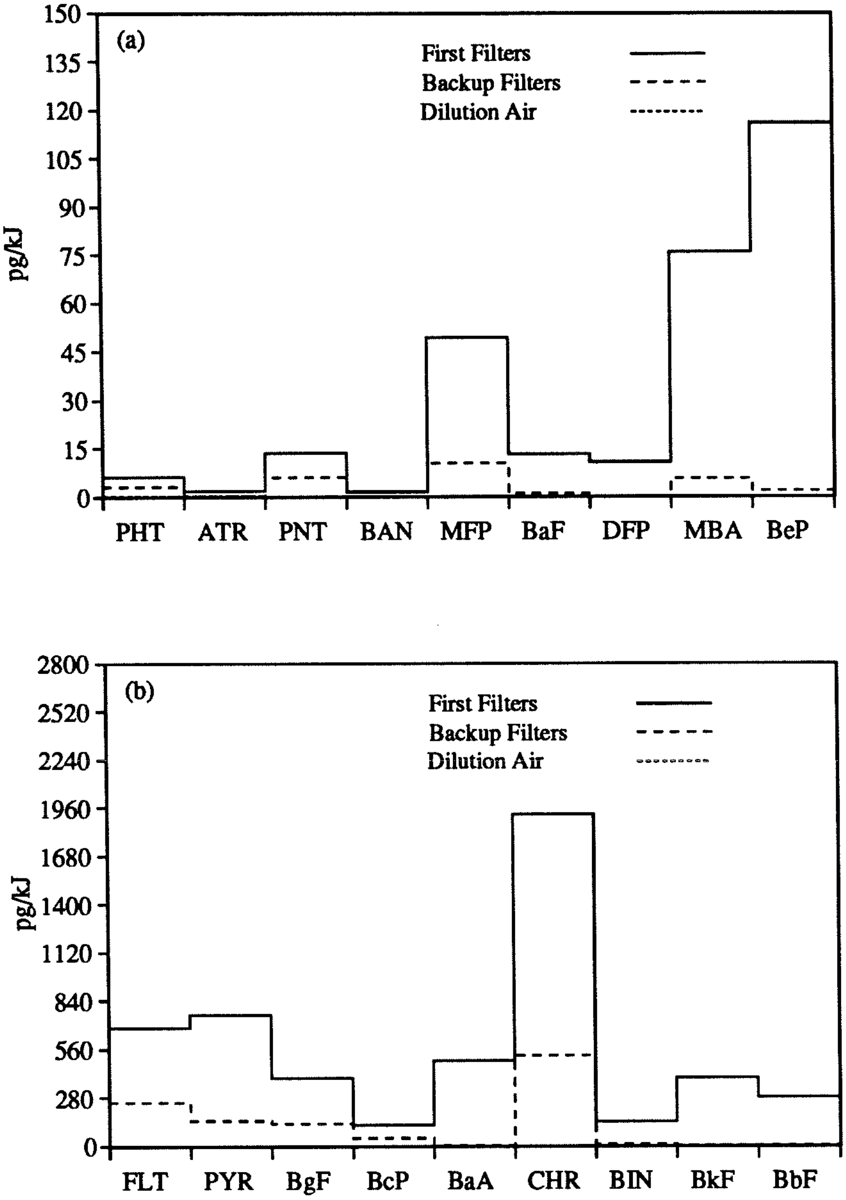


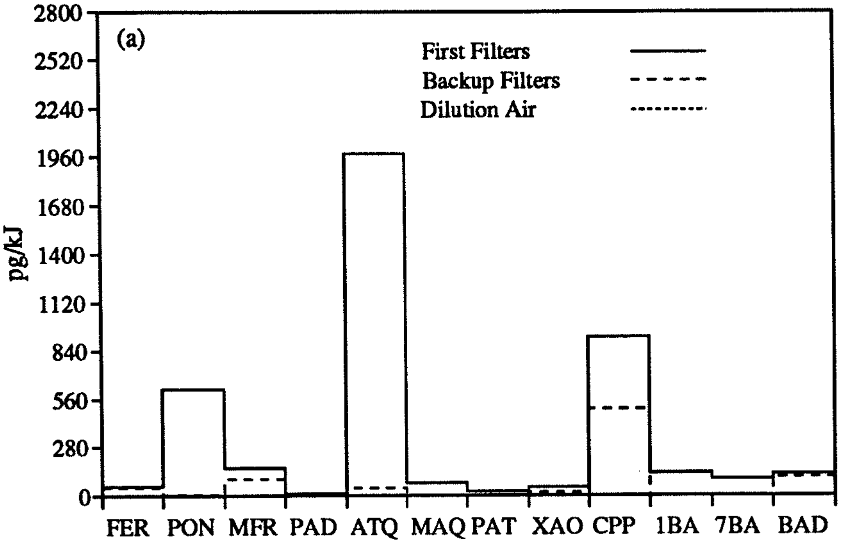
Fig. 7.4: Emission profiles for natural gas-fired home appliances: (a) low concentration PAH and (b) high concentration PAH. PHT: phenanthrene; ATR: anthracene; PNT: 2-phenylnaphthalene; BAN: benzacenaphthylene; MFP: methyl-(fluoranthenes, pyrenes); BaF: benzo[a]fluorene; DFP: dimethyl-(fluoranthenes, 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



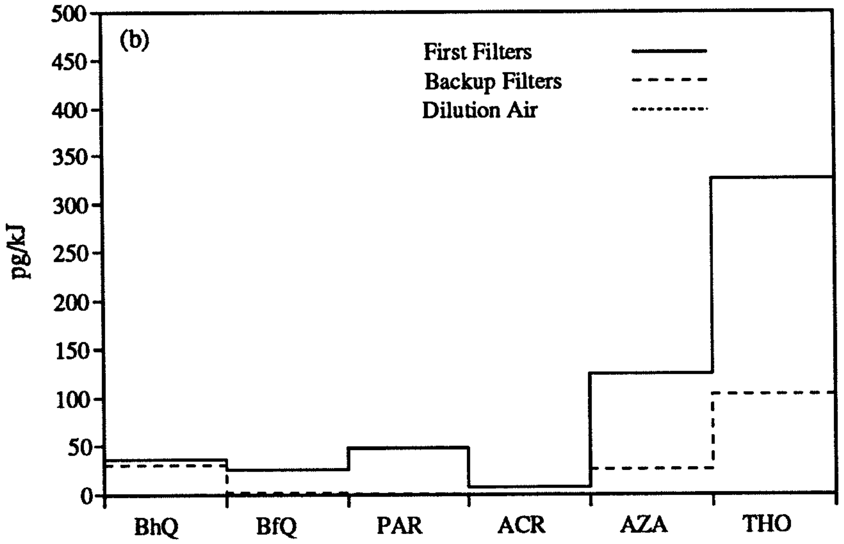


Fig. 7.5: Emission profiles for natural gas-fired home appliances: (a) oxy-PAH and (b) aza- and thia-arenes. FER: 9H–fluoren-9-one; PON: 1H-phenalen-1-one; MFR: methylfluorenones; PAD: phenanthrenequinone; ATQ: anthraquinone; MAQ: 2-methylanthraquinone; PAT: phenanthrone/anthrone; XAO: xanthone; CCP: 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].

	Emission Rates in pg/kJoule			
PART A	HEPA-filtered Dilution Air	Space & Water Heater		Compound ID[b]
		First Filter	Backup Filter	
	—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 HEPA-filtered Dilution Air	Space & Water Heater First Filter	 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)

PART C	Emission Rates in pg/kJoule			
	HEPA-filtered Dilution Air	Space & Water Heater		Compound ID[b]
		First Filter	Backup Filter	
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

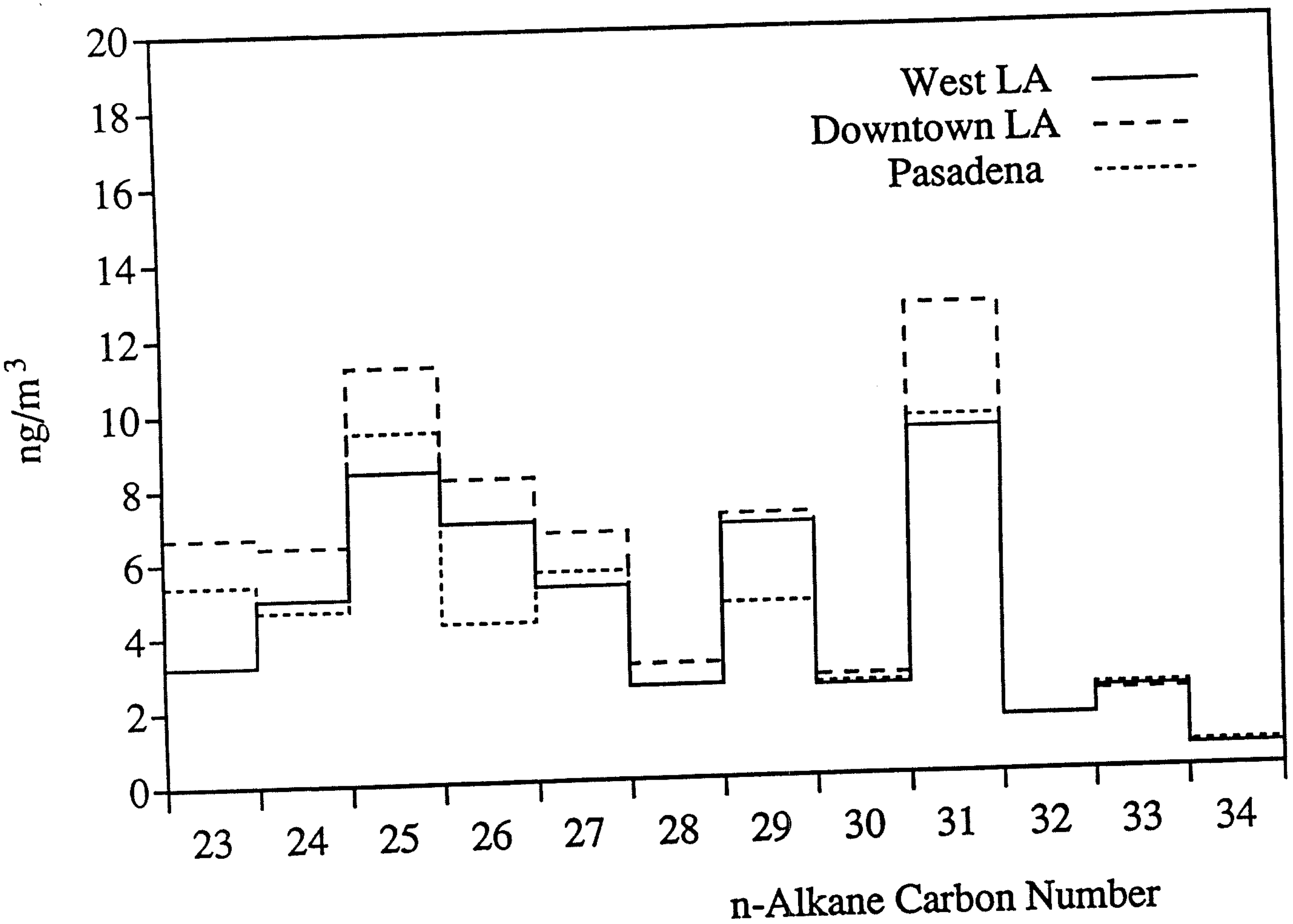


Fig. 7.6: Ambient n̲-alkane fine particle concentrations; annual averages for West Los Angeles, downtown Los Angeles, and Pasadena in 1982 (from reference *22*).

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.

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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 μm from the air stream. Fine particulate matter ($d_p \leq 2.0$ μm) 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-μm 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 μl. 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.

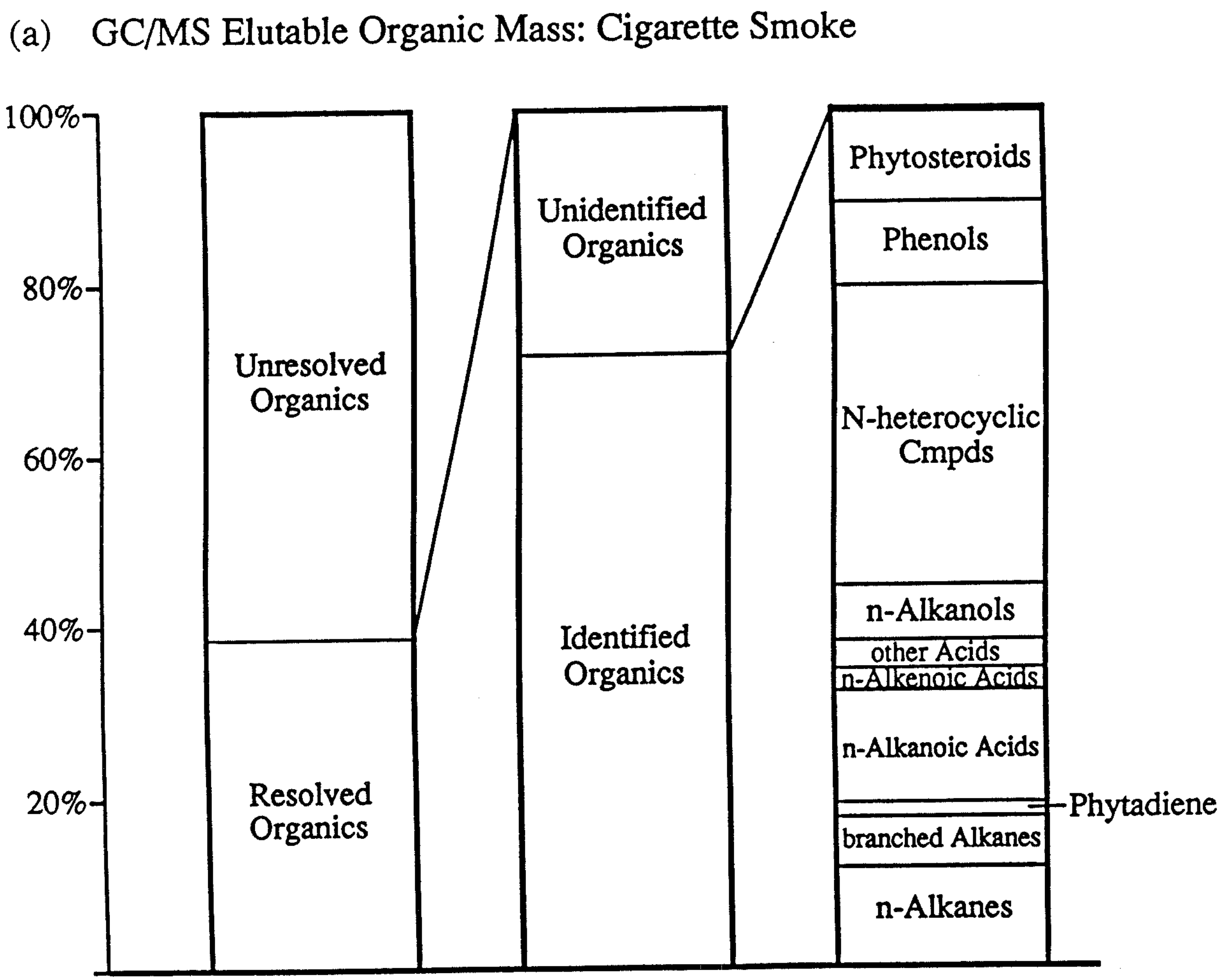


Fig. 8.1: Mass balance for elutable organic matter contained in fine cigarette smoke particles.

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 (μg/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;

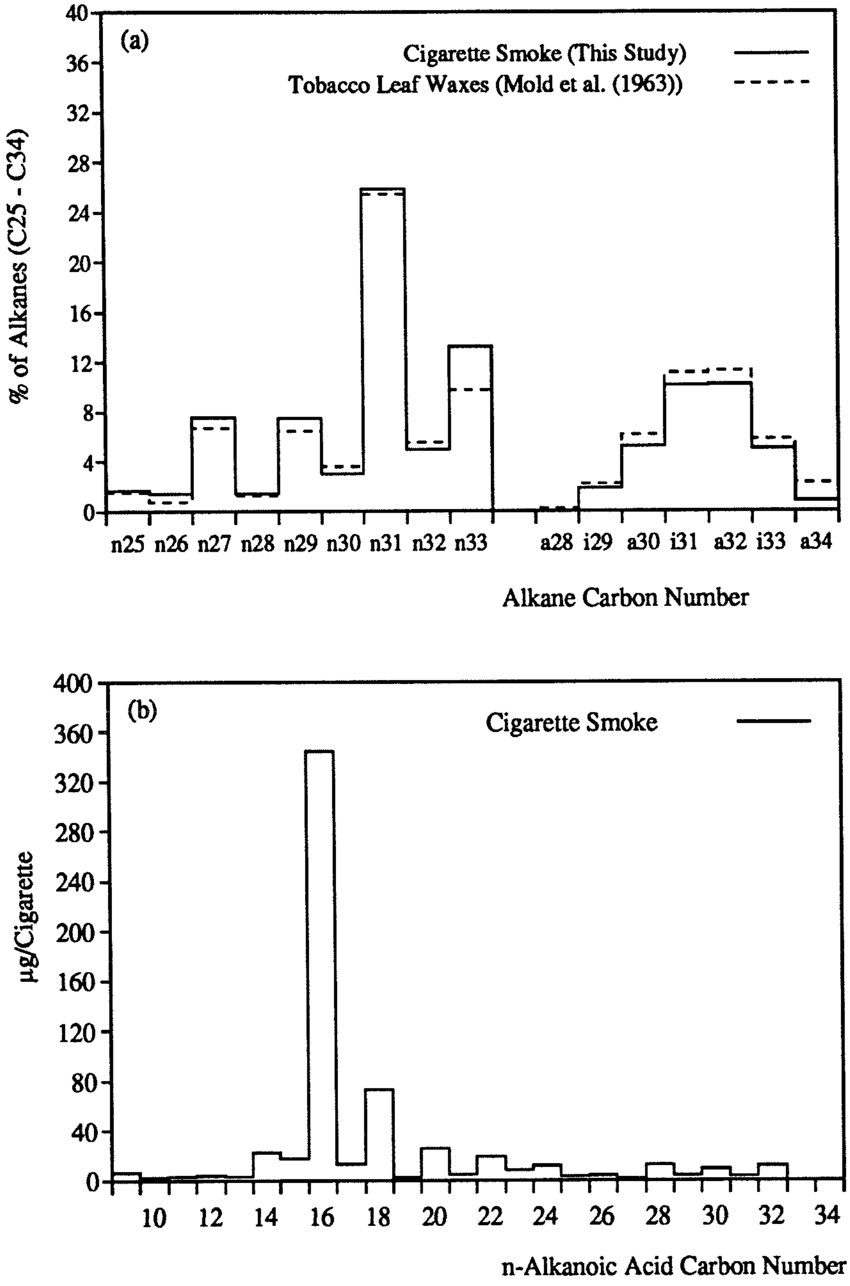


Fig. 8.2: Concentration distributions for cigarette smoke constituents: (a) *n*-alkanes in cigarette smoke (this study) compared to the tobacco leaf wax data of Mold et al. (1963) (in mass % relative to total alkanes in the range from C_{25} to C_{36}), and (b) *n*-alkanoic acids in cigarette smoke (this 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 μg/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 13.5μg/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			Compound ID[c] for this Study
	This Study[a] exhaled MS + SS	Other Studies[b]		
		SS	MS	
	—*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 MS + SS**	**Other Studies[b]**		Compound ID[c] for this Study
		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			Compound ID[c] for this Study
	This Study[a] exhaled MS + SS	Other Studies[b]		
		SS	MS	
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			
	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 μg/g of tobacco).

[k] Elmenhorst (1972), mainstream condensate of nonfilter cigarettes (conc. in μg/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 μg/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 (μg/g of fine particulate abraded leaf surface material) and fine tobacco smoke particles (μg/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.

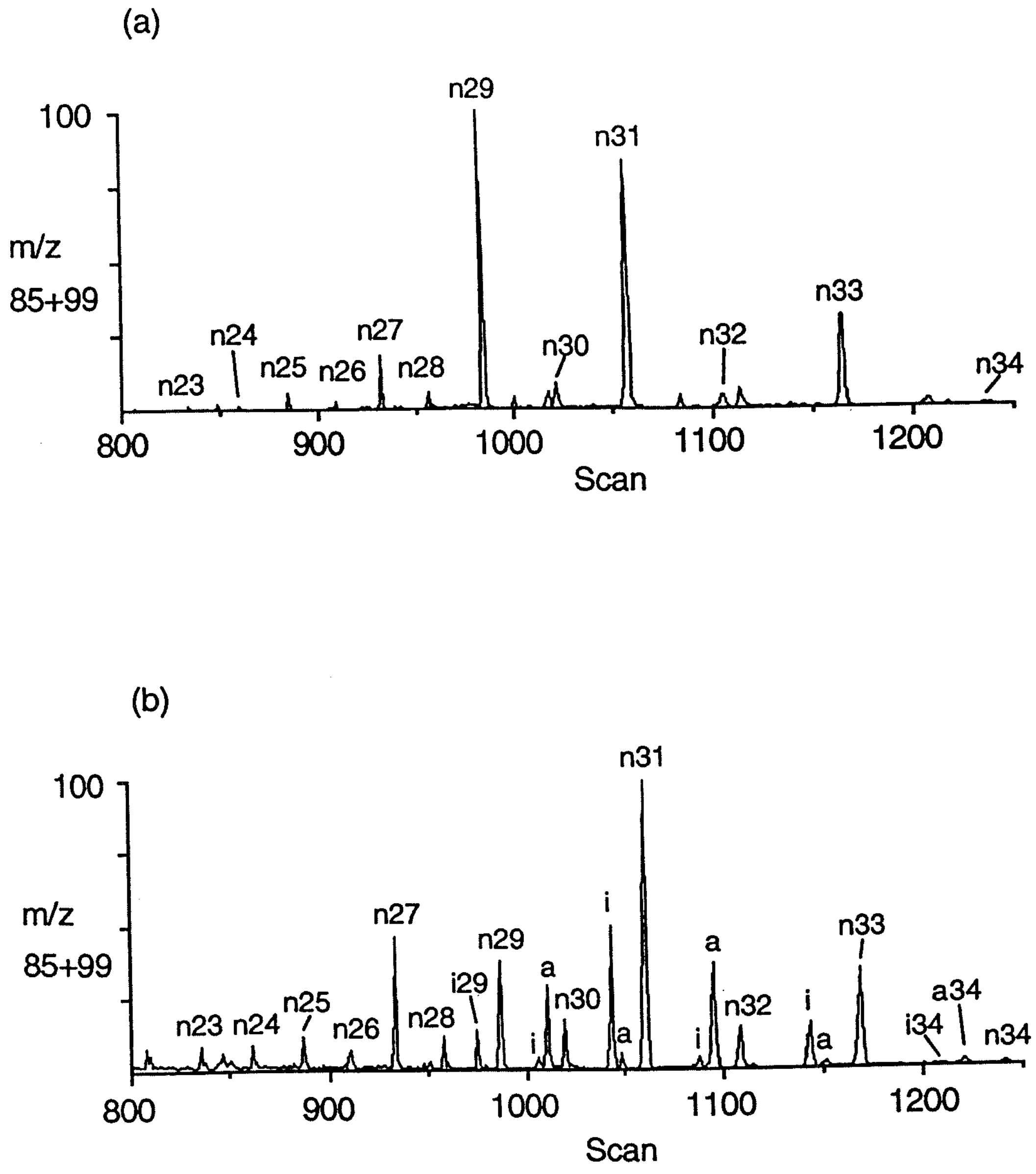
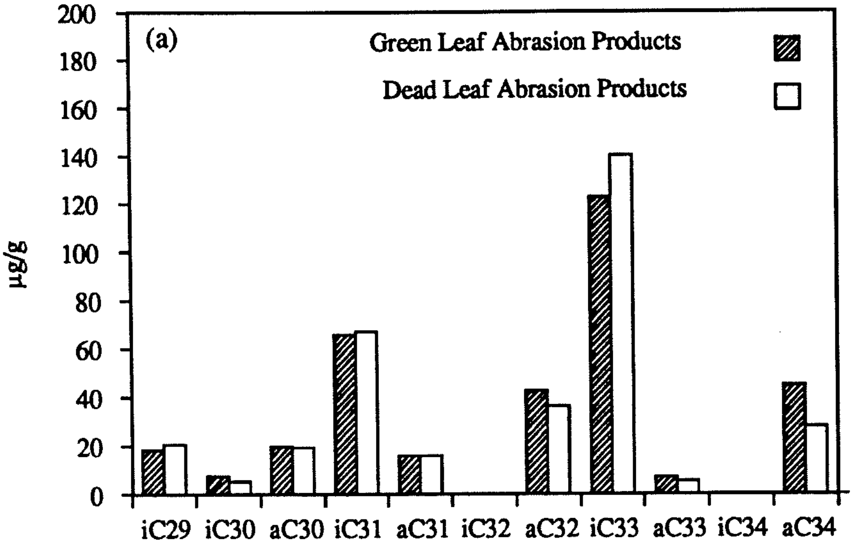


Fig 8.3: Selected mass fragmentograms for *n*-, *iso*-, and *anteiso*-alkanes (sum: m/z 85 + 99) found in: (a) leaf abrasion products from green leaf composites typical of the Los Angeles area, and (b) cigarette smoke aerosol. Numbers refer to the carbon chain length of the molecules: n: *n*-alkanes;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



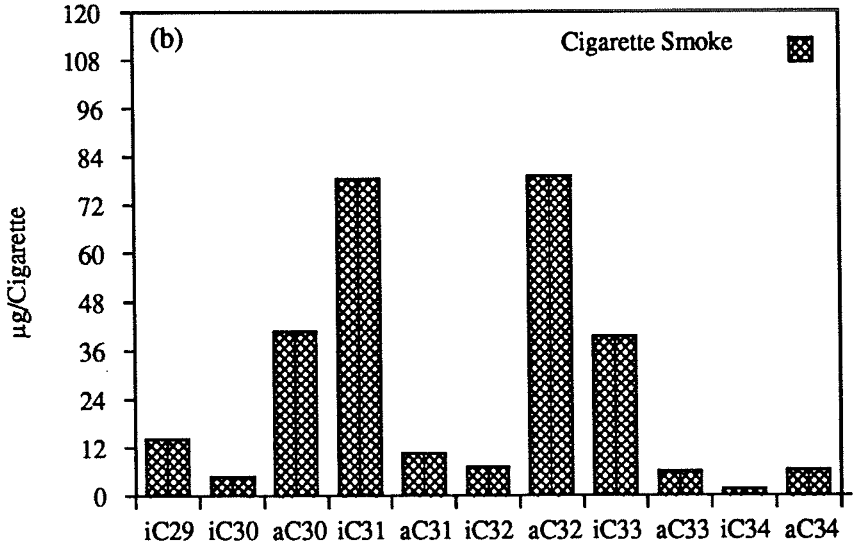


Fig. 8.4: *iso-* and *anteiso-*Alkane concentrations measured in (a) leaf surface abrasion products from green and dead leaf composites typical of the Los Angeles area, and (b) cigarette smoke aerosol collected in this study.

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 μm 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 μm 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 × 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 x 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 x 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 x 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 x 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 x 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 μg 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

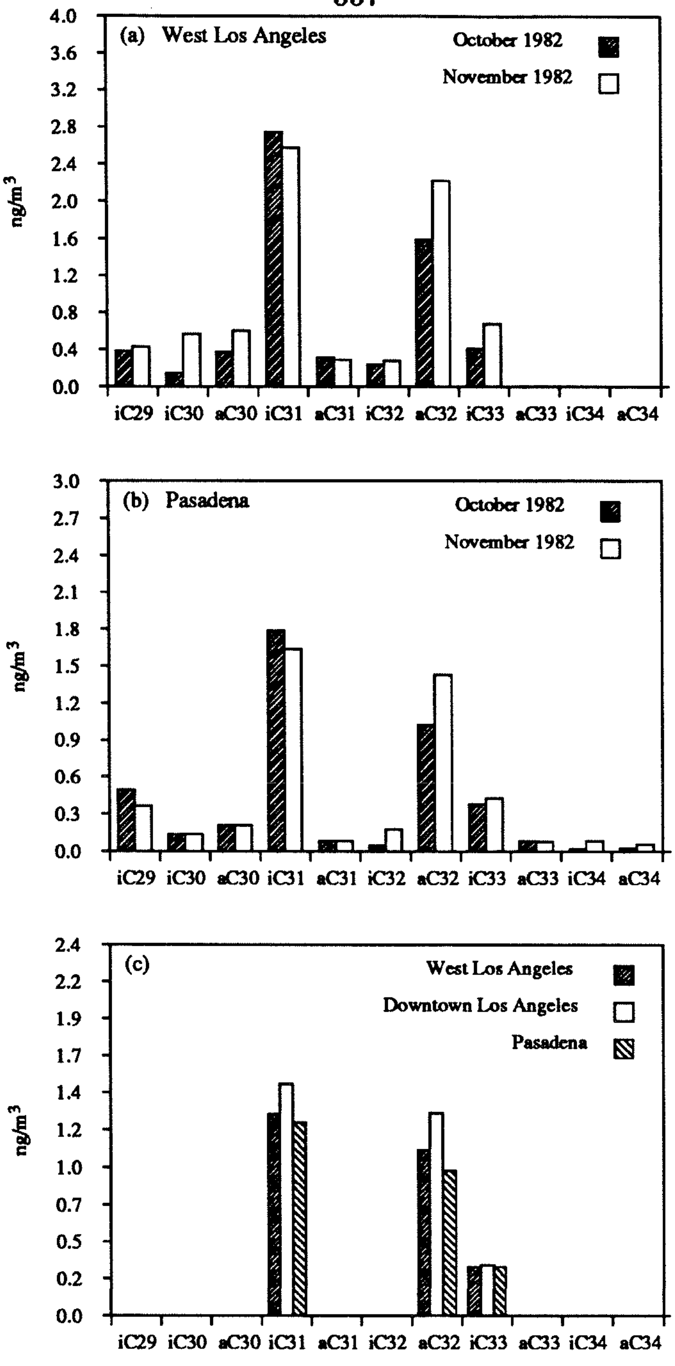


Fig. 8.5: Ambient *iso-* and *anteiso-*alkane concentrations measured at (a) West Los Angeles and (b) Pasadena, both in October and November 1982, and (c) annual average concentrations measured at West Los Angeles, downtown Los Angeles, and Pasadena during 1982.

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 μg m^{-3}.

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Chapter 9

Hot Asphalt Roofing Tar Pot Fumes

Introduction

Bituminous materials such as asphalt and coal tar are commonly used for road construction and roof sealing purposes. The bituminous products used in the United States are manufactured principally from crude oils ($> 99\%$) and to a minor extent from coal. Nearly 30 million tons of asphalts were consumed in the United States during 1988, roughly one third of the world production (Tyler et al., 1990). About 15% of the bituminous type material produced is consumed by the building industry for roofing purposes (Kirk-Othmer, 1985) including asphalt roll and asphalt shingle roofing. During the construction of hot-process built-up roofs, hot asphalt tar or coal tar pitch is used as an adhesive. In order to fluidize the asphalt adhesives and sealant at construction sites, small portable heater units are used. These heaters, called roofing tar pots, produce a visible plume of particulate matter derived from the hot asphalt batch. Gray (1986) estimated that particulate emissions from roofing tar pots contributed roughly 920 kg/day of fine particulate matter ($d_p \leq 2.0$ μm) to an 80 km × 80 km heavily urbanized area centered over Los Angeles during the year 1982.

Roofing tar fumes that are released during roof construction work, might be mutagenic and carcinogenic. For that reason, prior studies of roofing tar fumes have been concerned exclusively with the determination of the risk to roofing workers from exposure to such fumes (e.g., Bingham et al., 1980; Niemeier et al., 1988; Malaiyandi et al., 1982; Reed and Liss, 1984; Williams and Lewtas, 1985).

The purpose of the present study is different. A more complete characterization of the organic chemical composition of roofing tar pot aerosol is sought. These data on aerosol emissions from roofing tar pots will be combined with parallel studies on the other major urban organic aerosol sources (Rogge et al.,1991, 1993b-i). The complete set of data on all major organic aerosol sources can be used to support a comprehensive air quality modeling study of emissions and air quality relationships for urban organic aerosols.

Experimental Methods

Sampling

Petroleum-based build-up roofing asphalt (GAF brand) was heated in a typical roofing tar kettle to workable plasticity. The temperature of the tar pot was maintained between 250 – 300°C. Sample collection was performed using a specially designed dilution source sampling system (Hildemann et al., 1991a). Hot tar fumes (2 lpm) were sampled from above a vent opening at the top of the asphalt kettle and diluted 18-fold with precleaned air (activated carbon-filtered and HEPA-filtered). The cooled and diluted asphalt fumes were subsequently drawn through an AIHL-design cyclone separator that removed particles with an aerodynamic diameter > 2.0 μm. The cyclone separator was operated at a flow rate of 27.9±0.3L/min. Sampling time was 10 - 15 min for each test. Fine particulate matter was collected downstream of the cyclone separators on three parallel quartz fiber filters (Pallflex 2500QAO), and one Teflon filter (Gelman Teflo, 2.0 μm pore size). All quartz fiber filters were annealed at 750°C for 2-4h before use to ensure low contamination levels for organic substances.

Bulk Chemical Analysis

Trace elements, ionic species, organic carbon (OC), and elemental carbon (EC) have been previously quantified in the roofing tar pot samples. These data on the bulk chemical properties of roofing tar pot emissions are published elsewhere (Hildemann et al., 1991a).

Sample Extraction

An extraction scheme has been followed that originally was developed for ambient fine particulate matter by Mazurek et al. (1987) and subsequently has been used in several studies and companion papers (Mazurek et al., 1989, 1991; Hildemann et al., 1991b; Rogge et al., 1991, 1993a-d). The extraction protocol can be described as follows: Prior to sample extraction, perdeuterated tetracosane (n-$C_{24}D_{50}$) which served as an internal standard was spiked onto the filter composites. The internal standard should be in a concentration range comparable to the expected organic compound concentrations in the actual sample. To ensure that n-$C_{24}D_{50}$ is in a suitable concentration range, the amount to be added as internal standard was estimated using the OC-data acquired from EC/OC-combustion analysis of a sample taken in parallel with the samples that were to be extracted.

The quartz fiber filter samples were extracted together in a sequential procedure that included extraction with hexane (2 x 30 ml) followed by extraction with benzene/2-propanol (2:1 mixture, 3 x 30 ml). Each extraction sequence was conducted for 10-min and supported by mild ultrasonic agitation. Following each extraction step, the filter extracts were filtered and combined. 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 μl. 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 in the dark at -21°C prior to GC/MS analysis.

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 supported 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 spectral 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 that was operated with the same physical column and temperature program as used during GC/MS-analysis (Hildemann et al., 1991b). Additional information describing the analytical procedure can be found elsewhere (Mazurek et al., 1987, 1989; 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 for a large set of polar and nonpolar standard compounds, dilution air testing and more. For a more detailed discussion, the reader is refered to accompanying source and ambient fine organic particle studies published earlier (Mazurek et al., 1989; Rogge et al., 1991, 1993a,b).

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 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 refered 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. (1992b). 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}); and (14) one suite made up of 7 aromatic di- and tri- carboxylic acids all as their methyl ester analogues; and (15) other compounds.

Results and Discussion

For hot-process built-up roofs, coal tar pitch and asphalt tar products are typically used as an adhesive (Niemeier et al., 1988; Malaiyandi et al., 1982). Coal tar pitches are a byproducts resulting from the pyrolysis of coal, often termed carbonization. Typically the carbonization process is conducted in the high temperature range of 900 - 1200°C (Kirk-Othmer, 1985). At those temperatures coal tars are distillated off of the bituminous coal leaving solid coke as a residue.

Asphalt, although also naturally occurring, is mainly obtained as byproduct from crude oil refining. Depending on the application and crude oil quality, asphalt is manufactured by straight reduction, air-blowing, propane deasphalting, and thermal cracking (Kirk-Othmer, 1985). During the refining process crude oil is injected into a fractionation column at temperatures ranging from 340 to 400°C. After removing the lighter crude oil fractions by distillation, the residuum is commonly termed straight-reduced asphalt. Straight-reduced asphalt is mainly used for road pavements. For roof surface coatings, an asphalt is desired that is more viscous and less resilient. To remove the more volatile organic fraction and to improve the quality of the asphalt by partial oxidation, straight-reduced asphalt is heat-treated by continously bubbling hot air through the asphalt at temperatures from 200 to 275°C. "Air-blown" asphalt is then used to produce asphalt impregnated paper rolls and asphalt shingles. For hot-process built-up roofs, asphalt tar is the adhesive of choice in oil producing countries.

Before application, asphalt tar (or alternatively coal tar pitch) is reheated to reach the desired workability. The recommended kettle temperature is 200 - 270°C (Niemeier et al., 1988). Commonly, the kettle temperature is poorly controlled and kettle temperatures above 600°C have been measured (Thomas and Mukai, 1975). At such high temperatures and in the absence of oxygen, pyrolysis of asphalt-containing precursor constituents leads to PAH-type compound synthesis resulting in increased mutagenic and carcinogenic activity of the hot tar fumes (Penalva et al., 1983; Niemeier et al., 1988).

Here, fine particulate roofing asphalt tar fumes are examined on a molecular level to provide a fine particulate source profile that can be used to estimate the contribution of organic matter released from hot-process built-up roofing to the urban atmosphere.

Mass Balance for Fine Particulate Organic Tar Pot Fumes

A material balance has been constructed for the extractable organic portion of fine particulate matter released from roofing tar pot operations and is shown schematically in Figure 9.1. Of the extractable and chromatographically elutable organic matter close to 16% is chromatographically resolved as single compound peaks. More than 50% of the chromatographically resolved compound mass could subsequently be identified. The overwhelming majority of the elutable organic mass that could be identified consists of *n*-alkanes (73%) and carboxylic acids such as *n*-alkanoic acids (17%) and to a minor extent benzoic acids. Of the identifiable mass 7.9% was made-up of polycyclic aromatic hydrocarbons (PAH) and thia-arenes (S-PAH). A quantitative assessment of individual compounds and compound classes is given in Table 9.1.

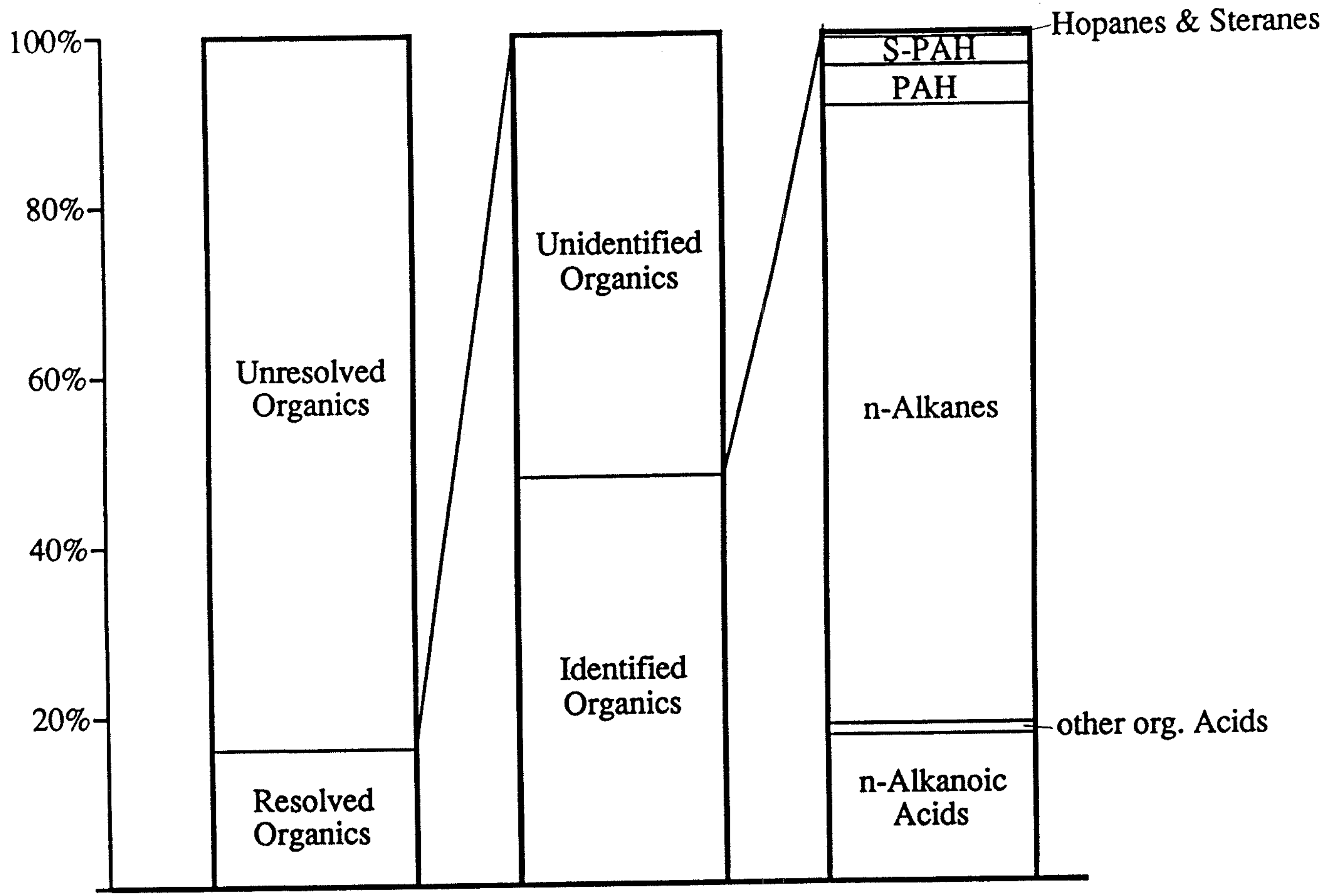

Fig. 9.1: Mass balance for elutable organic matter in the fine particle emissions of roofing tar pot fumes.

Alkanes

Figure 9.2a depicts the *n*-alkane concentration pattern found in the roofing asphalt fume particulate matter. *n*-Alkanes have been identified ranging from C_{14} to C_{32} with C_{17} as the most prominent member. At typical ambient concentrations and temperature, in the urban atmosphere, *n*-alkanes up to C_{18} are mainly found in the gas-phase (Cautreels and Van Cauwenberghe, 1978), while higher molecular weight *n*-alkanes are preferably found in the particle-phase (Cautreels and Van Cauwenberghe, 1978; Rogge et al., 1993a).

Adsorption of gas-phase organics onto the filter material is a known cause for the presence of some lower molecular weight organic compounds in aerosol samples. The increased low molecular weight particle-phase *n*-alkane concentrations ($< C_{18}$) found here is also caused in part by high *n*-alkane asphalt fume concentrations which favor formation of particle-phase material during the partitioning between the gas- and particle-phase that occurs as the tar pot vapors are cooled. Niemeier and coworkers (1988) pointed out that the carcinogenic activity of asphalt fumes cannot be explained solely on the basis of their PAH-content and hypothesized that co-carcinogenic effects of aliphatic hydrocarbons could be responsible for part of the carcinogenic activity, as was emphasized earlier by other researchers (Bingham and Nord, 1977; Horten et al., 1957; Bingham and Falk, 1969).

Carboxylic Acids

n-Alkanoic acids (C_8 - C_{24}) have been found in concentrations that are typically several times lower than for the *n*-alkanes. The *n*-alkanoic acids concentration profile in Figure 9.2b shows highest concentrations for hexadecanoic acid,

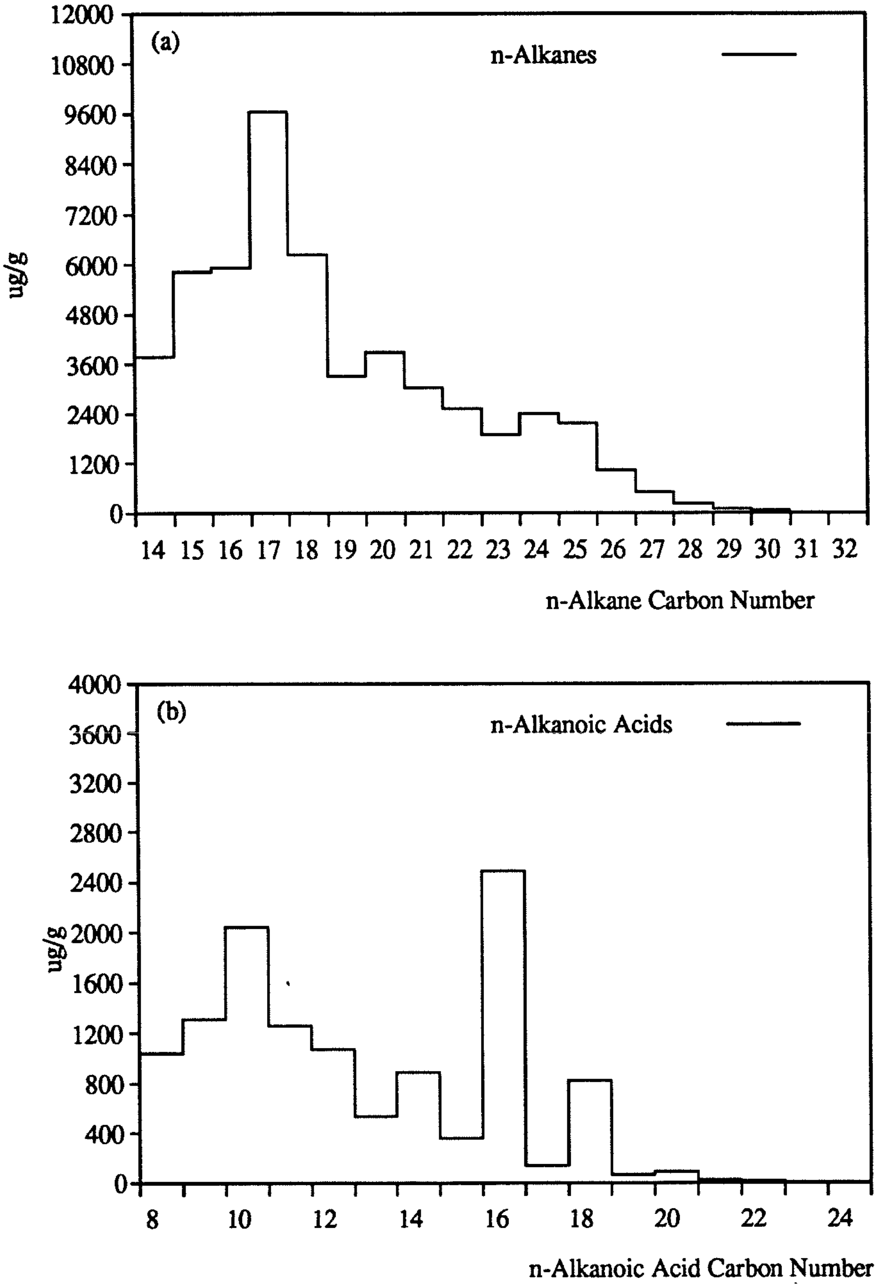

Fig. 9.2: Emission profiles for roofing tar pot fumes: (a) *n*-alkanes and (b) *n*-alkanoic acids.

which is commonly found in the emissions of fossil fuel burning sources (Rogge et al., 1993b). In addition, several methyl substituted benzoic acids and benzeneacetic acid have been identified. Of the benzoic acid-type compounds, 4-methylbenzoic acid is most abundant (see Table 9.1).

Polycyclic Aromatic Hydrocarbons

Because of their mutagenic and carcinogenic potential and the resulting health risk to roofing workers, the PAH content of asphalt and coal tar pitch fumes has been extensively investigated in the past. PAH concentrations have been measured in the raw material itself, in fume condensates, and as ambient samples in the breathing zone of roofing workers (Lijinsky et al., 1963; Niemeier et al., 1988; Malaiyandi et al., 1982; Wallcave et al., 1971). Roofing coal tar pitches have been found to contain PAH-levels several orders of magnitude higher than that of roofing asphalt tar. For example, benzo[a]pyrene concentrations have been determined in roofing asphalt ranging from 1 to 8 ppm, whereas roofing coal tar pitches revealed benzo[a]pyrene concentrations from 2,000 to 11,000 ppm (Lijinsky et al., 1963; Malaiyandi et al., 1981; Wallcave et al., 1971). Accordingly, ambient PAH-levels in the work environment of roofers differ drastically depending on the type of hot adhesive used (Malaiyandi et al., 1982).

During the course of the present study 17 individual PAH and alkyl-PAH have been identified in the roofing asphalt fumes. Phenanthrene and anthracene and their methyl- and dimethyl- alkylated analogues accounted for about 65% of the PAH-mass concentration identified. In contrast benzo[a]pyrene, a PAH typically monitored in roofing tar fumes (Niemeier et al., 1988; Malaiyandi et al., 1982; Williams et al., 1986), is found to contribute only 0.2% of the PAH-mass identified. Similar distribution patterns have been found in condensed asphalt tar fumes and in ambient air at roofing sites (Niemeier et al., 1988; Malaiyandi et al., 1981). In addition, heterocyclic aromatic hydrocarbons containing sulfur (S-PAH) such as dibenzothiophene and its methyl-substituted analogues have been identified at concentration levels similar to that of phenanthrene and its alkylated analogues. S-PAH show mutagenic potentials similar to other PAH, but due to their slightly increased polarity they are more soluble in water and more prone to aquatic bioaccumulation (Vassilaros et al., 1982; Willey et al., 1982).

Sterane and Triterpane Hydrocarbons

Fossil fuels such as coal and crude oil are the products of biogenic matter transformed by diagenesis and catagenesis over millions of years (Simoneit, 1984; Hunt, 1979; Tissot and Welte, 1984; Mackenzie et al., 1982). In geochemistry, steranes and triterpanes are commonly used as marker compounds to assess the maturity of crude oil and to trace its migration from the source rocks to the crude oil pockets (Hunt, 1979; Tissot and Welte, 1984). Steranes and triterpanoid hopanes have been identified in lubricating oils, vehicular exhaust, road dust, tire wear, and subsequently in airborne suspended particles (Simoneit, 1984, 1985; Simoneit et al., 1991; Rogge et al., 1993a-c). Among the spectrum of steranes and triterpanes present in petroleum, only those previously reported by Rogge et al. (1993b,c) have been quantified in the fine particulate asphalt tar fume samples. The results are summarized in Table 9.1. As shown by Rogge et al. (1993b) steranes and triterpanes can be used to trace the presence of motor vehicle exhaust in the urban atmosphere. The importance of the data on hopane and sterane emissions from roofing tar pots given in Table 9.1 is that these data help to quantify the magnitude of any possible interferences from roofing tar pot

Table 9.1 Mass Concentration of Organic Compounds in the Fine Aerosol Emissions from Hot Asphalt Roofing Tar Pot Fumes.

PART A	Emission Rates in $\mu g\ g^{-1}$	Compound[a] ID
	—*n*–Alkanes—	
n–tetradecane	3788.0	a
n–pentadecane	5827.0	a
n–hexadecane	5936.0	a
n–heptadecane	9659.0	a
n–octadecane	6231.0	a
n–nonadecane	3319.0	a
n–eicosane	3890.0	a
n–heneicosane	3042.0	a
n–docosane	2536.0	a
n–tricosane	1888.0	a
n–tetracosane	2396.0	a
n–pentacosane	2171.0	a
n–hexacosane	1040.0	a
n–heptacosane	496.5	a
n–octacosane	228.4	a
n–nonacosane	100.6	a
n–triacontane	64.6	a
n–hentriacontane	35.8	a
n–dotriacontane	17.9	a
Total class emission rate:	52666.8	
	—*n*–Alkanoic Acids[b]—	
n–heptanoic acid	87.1	a
n–octanoic acid	1043.0	a
n–nonanoic acid	1312.0	a
n–decanoic acid	2043.0	a
n–undecanoic acid	1263.0	a
n–dodecanoic acid	1081.0	a
n–tridecanoic acid	537.1	a
n–tetradecanoic acid (myristic acid)	894.9	a
n–pentadecanoic acid	362.4	a
n–hexadecanoic acid (palmitic acid)	2492.0	a
n–heptadecanoic acid	139.6	a
n–octadecanoic acid (stearic acid)	823.4	a
n–nonadecanoic acid	64.2	a
n–eicosanoic acid	89.8	a
n–heneicosanoic acid	28.5	a

Table 9.1 (continued)

PART B	Emission Rates in $\mu g\ g^{-1}$	Compound[a] ID
n–docosanoic acid	17.0	a
n–tricosanoic acid	7.3	a
n–tetracosanoic acid	8.3	a
Total class emission rate:	12293.6	
—*n*–Alkenoic Acid[b]—		
cis–9–octadecenoic acid (oleic acid)	338.8	a
Total class emission rate:	338.8	
— other Organic Acids[b]—		
3,5-dimethylbenzoic acid	97.2	b
2-methylbenzoic acid	38.9	b
3-methylbenzoic acid	124.6	b
4-methylbenzoic acid	477.7	a
benzeneactic acid	62.6	a
Total class emission rate:	801.0	
—Polycyclic Aromatic Hydrocarbons—		
dimethylnaphthalenes	604.6	a
phenanthrene	462.3	a
anthracene	130.3	a
methyl–(phenanthrenes, anthracenes)	844.5	b
dimethyl–(phenanthrenes, anthracenes)	751.8	b
fluoranthene	71.6	a
pyrene	136.9	a
benzacenaphthylene	11.4	b
2–phenylnaphthalene	46.2	b
methyl–(fluoranthenes, pyrenes)	124.9	b
benzo[a]fluorene/benzo[b]fluorene	61.2	a
benzo[ghi]flouranthene	4.3	b
benz[a]anthracene	24.8	a
chrysene/triphenylene	64.9	a
benzo[k]fluoranthene	11.7	a
benzo[b]fluoranthene	6.7	a
benzo[e]pyrene	6.0	a
benzo[a]pyrene	5.8	a
Total class emission rate:	3369.9	

Table 9.1 (continued)

PART C	**Emission Rates in $\mu g\ g^{-1}$**	Compound[a] ID
—Thia-Arenes—		
dimethylbenzo[b]thiophenes	244.6	a
dibenzothiophene	257.8	a
methyldibenzothiophene	629.9	b
dimethyldibenzothiophenes	1170.3	b
Total class emission rate:	2302.6	
—Regular Steranes—		
20S&R-5α(H),14β(H),17β(H)-cholestanes	113.9	b
20R-5α(H),14α(H),17α(H)-cholestane	101.4	a
20S&R-5α(H),14β(H),17β(H)-ergostanes	96.1	b
20S&R-5α(H),14β(H),17β(H)-sitostanes	34.0	b
Total class emission rate:	345.4	
—Pentacyclic Triterpanes—		
22,29,30-trisnorneohopane	34.1	b
17α(H),21β(H)-29-norhopane	54.8	b
17α(H),21β(H)-hopane	47.2	b
22S-17α(H),21β(H)-30-homohopane	21.7	b
22R-17α(H),21β(H)-30-homohopane	9.5	b
Total class emission rate:	167.3	

[a] for more details see text: a, positive; b, probable; c, possible; d, tentative.

[b] detected as methyl ester.

emissions when conducting a vehicular tracer analysis. For more details about fossil steranes and triterpanes the interested reader is refered to the literature cited above.

Estimated Roofing Tar Pot Emissions to the Los Angeles Atmosphere

Gray (1986) compiled an inventory for fine particulate organic carbon emissions within an 80 km × 80 km area centered over Los Angeles for the year 1982. A map of this study area is shown elsewhere; see Rogge et al. (1991). Roofing tar pot emissions are estimated to contribute on average 920 kg of fine particulate matter per day to the urban atmosphere within that study area. Because crude oil is the major fossil fuel processed and used in the Los Angeles area, it is a good assumption that asphalt-type roofing tars rather than coal tar pitches are used in Southern California.

Using Gray's overall emission estimate for roofing tar pot fumes along with the data of Table 9.1 of the present study and assuming that only asphalt-type roofing tars are used in the Los Angeles area, then the emissions of particular compound classes from roofing tar applications can be estimated for an average day during 1982; see Table 9.2. *n*-Alkanes constitute the dominant compound class released from roofing tar pot operations with daily emissions of 48.6 kg. In contrast PAH amount to 3.1 kg emitted daily. The daily PAH-emissions from built-up roofing would be appreciably higher if coal tar pitch instead of asphalt tar were used.

Recently, Rogge et al. (1993b) determined fine particle-associated vehicular PAH emissions within the 80 km × 80 km Los Angeles study area for 1982. Compared to the emissions from roofing tar use, the PAH emissions from catalyst-equipped vehicles (7.4 kg/day) are about threefold larger.

Table 9.2 Estimated Fine Aerosol Emission Rates for Single Compound Classes Released from Hot Asphalt Roofing Tar Pot use within the Urbanized (80 km × 80 km) Los Angeles Study Area for 1982[a].

Compound Class	Emission Rate (kg day^{-1})
n-Alkanes	48.6
n-Alkanoic Acids	11.3
n-Alkenoic Acids	0.031
Other Organic Acids	0.074
Polycyclic Aromatic Hydrocarbons (PAH)	3.1
Thia-Arenes (S-PAH)	2.1
Steranes	0.032
Pentacyclic Triterpanes	0.015
Total Identified	65.25

[a] Gray (1986) estimated that 920 kg/day of fine particulate matter is released within the study area from roofing tar pots where asphalt tar or coal tar pitch is used. Here, it is assumed that asphalt tar is used exclusively for construction of built-up roofs in the Los Angeles area, given that petroleum refineries provide a large local source of asphalt and coal is not used locally.

Instead, PAH-emissions from diesel automobiles plus heavy-duty diesel trucks (3.4 kg/day) are comparable to that from asphalt tar used to construct built-up roofs.

Conclusions

Fine organic aerosols are released with the hot fumes from asphalt tar that is commonly used as an adhesive for hot-process built-up roofs. The particulate organic compound emission rates from roofing tarpot use have been measured in the present study. Roughly 73% of the identifiable organic fine particulate mass consists of *n*-alkanes, which constitute the dominant compound class identified. Of the roofing asphalt tar fume aerosols collected 0.57% of the aerosol mass emitted consisted of PAH and S-PAH. When compared to the PAH content determined in fine particulate exhaust emitted from catalyst-equipped automobiles ($\sim$ 0.5%) and heavy-duty diesel trucks ($\sim$ 0.1%) (Rogge et al., 1993b), roofing tar pot aerosols show a PAH-content similar to that of vehicular exhaust.

If it is assumed that only asphalt tar is used for constructing built-up roofs in Southern California, then the daily PAH-emissions to the atmosphere of an 80 km × 80 km study area centered over Los Angeles area due to hot-process built-up roofing activities can be estimated at 3.1 kg/day. That is the same magnitude as the PAH emissions from all diesel vehicles in the same study area (3.4 kg/day). Because coal tar pitches are used as well for built-up roofs and show markedly increased PAH-contents, the daily PAH emission estimate provided here for asphalt use places a lower limit on PAH emitted from roofing operations to the Los Angeles atmosphere.

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Chapter 10

Boilers Burning No.2 Distillate Fuel Oil

Introduction

No.2 distillate fuel oil is commonly used for residential and commercial heating purposes and for steam and power generation in industrial utility boilers. The quality and composition of No.2 distillate fuel oil depends to a large degree on the type of crude oil refined. Although sulfur contents are typically kept low in No.2 fuel oil (0.1–0.4%) as a result of the desulfuration process, the content of aromatic compounds in the No.2 oil is typically directly proportional to the aromaticity found in the parent crude oils. Lee (1992) has shown that the particulate emission rate, when burning No.2 fuel oil, increases with the aromatics content and viscosity of the fuel oil. Goldstein and Siegmund (1976) as well as Hildemann et al. (1991a) have shown that there exists an optimal level of excess oxygen (as measured in the stack gas emissions) at which the particulate emission rate is at its minimum. In addition, it has been found that organic chlorine in the fuel burned promotes enhanced soot and PAH formation (e.g., Frenklach, 1990; Marr et al., 1992; McKinnon and Howard, 1990; Mulholland et al., 1993; Tsang, 1990). In contrast, organometallic additives, such as e.g., ferrocene derivatives, suppress soot formation (Mitchell, 1991; Somasundaram and Sunavala, 1989). Consequently, the chemical composition and particulate matter emission rate depends both on operating conditions and on the fuel batch burned.

In the present paper, an industrial-scale boiler burning No.2 fuel oil has been tested by dilution sampling, and the fine particulate matter collected from 2 out of 5 experiments has been analyzed to determine the organic compounds that are emitted. The purpose of this study is to provide detailed insight into the chemical nature of fine particulate organic matter emitted from oil-fired boilers that can be used along with the other studies in this series to provide quantitative input data needed by source-oriented models that relate organic aerosol emissions to ambient air quality.

Experimental Methods

Sampling

Fine particulate emissions were collected from an industrial boiler burning No.2 distillate fuel oil. The boiler was a Babcock & Wilcox Dual Fuel FM-type industrial-scale water tube boiler (steam production capacity of 53×10^6 kJ/hr) equipped with a steam atomizer burner.

The oil-fired boiler tested was operated in steady state mode at about 60% of its capacity using a second boiler to adsorb the demand fluctuations. Sample collection was conducted using a dilution tunnel sampling system that was set up on the roof of the steam plant, as previously described in detail by Hildemann et al. (1989; 1991a). The stack was accessed from the roof via built-in sampling ports. The 1.1-m diameter stack was traversed twice during each experiment and samples taken from five equidistant points. The stack velocity was measured at each sampling point to allow isokinetic particle collection.

Five experiments were conducted with test durations ranging from 185 min to 375 min. The source testing program was executed over a period of three weeks with different batches of No.2 fuel oil. For more details see Hildemann et al. (1991a).

Hot emissions were withdrawn from the stack via a cyclone separator that removed particulate matter with an aerodynamic diameter of > 10 μm. The remaining source effluent was drawn, using a heated inlet-line, into the sampling device dilution tunnel where the hot exhaust emissions were cooled and diluted with precleaned air (activated carbon filtered and HEPA-filtered). A portion of the diluted and cooled stack emissions were then diverted into a residence time chamber to allow gaseous organic compounds that would have condensed onto preexisting particulate matter in the atmospheric plume downwind of the source to equilibrate between gas- and particle-phase before sampling. Fine particulate matter was subsequently collected downstream of 8 AIHL-design cyclone separators operated in parallel, each connected to three 47-mm diameter filter holders which were used to sample particulate matter at a flow rate of 9.0 – 9.6 L/min per filter. Up to 18 filter holders were loaded with quartz fiber filters (Pallflex 2500 QAO) and the remaining filter holders contained Teflon filters (Gelman Teflo, 2.0-μm pore size). All quartz fiber filters were annealed at 750°C for 2-4h before use to ensure low organic contamination levels on the blank filter material.

Bulk Chemical Analysis

The emission rates of trace elements, ionic species, organic carbon (OC), and elemental carbon (EC) have been previously quantified are published elsewhere (Hildemann et al., 1991a).

Sample Extraction

An extraction scheme has been followed that originally was developed for the analysis of ambient fine organic particulate matter by Mazurek et al. (1987) and subsequently has been used in several studies (Mazurek et al., 1989, 1991;

Hildemann et al., 1991b; Rogge et al., 1991, 1993a-d). Briefly, the extraction protocol can be described as follows: Prior to sample extraction, perdeuterated tetracosane (n-$C_{24}D_{50}$) which served as an internal standard was spiked onto the filter composites. This internal standard should be applied in a quantity comparable to the organic compounds that are expected to be measured. In the present study, the amount of n-$C_{24}D_{50}$ added as an internal standard was estimated using the OC-data acquired from an EC/OC-combustion analysis of samples taken in parallel with those chosen for detailed organic chemical analysis.

The quartz fiber filter samples taken during each test were extracted together in a sequential procedure that included extraction twice with hexane (2 × 30 ml) followed by extraction three times with benzene/2-propanol (2:1 mixture, 3 × 30 ml). Each extraction sequence was conducted for 10-min and supported by mild ultrasonic agitation. Following each extraction step, the filter extracts were filtered and combined. 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 μl. 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 in the dark at -21°C prior to GC/MS analysis.

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 supported 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 spectral 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 that was operated with the same physical column and temperature program as used during GC/MS-analysis (Hildemann et al., 1991b). Additional information describing the analytical procedure can be found elsewhere (Mazurek et al., 1987, 1989; Rogge et al., 1991, 1993a,b).

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 for possible contaminants, recovery experiments for a large set of polar and nonpolar standard compounds, dilution air testing and more. For a detailed discussion, the reader is referred to accompanying source and ambient fine organic particle measurement studies published earlier (Mazurek et al., 1989; Rogge et al., 1991, 1993a,b).

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 labeled accordingly: (a) *positive* — the sample mass spectrum, library 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-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}); and (14) one suite made up of 7 aromatic di- and tri- carboxylic acids all as their methyl ester analogues; and (15) other compounds.

Results and Discussion

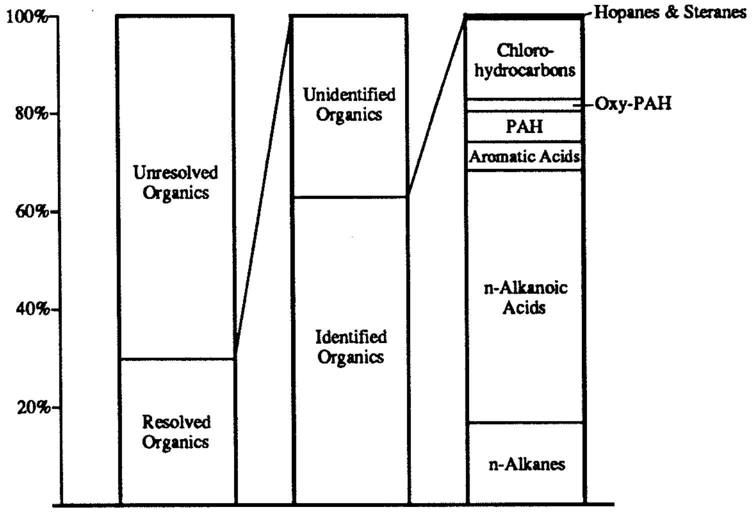
The industrial-scale boiler was tested burning different batches of No.2 fuel oil. To evaluate emission variations as a function of fuel batch, five consecutive tests were conducted over a 3 week time period. The fine particulate mass emission rates varied between the tests from 5 to 13 μg/kJ of fuel burned with an average fine particle emission rate of 9 (±3) μg/kJ. The fine particulate matter collected consisted on average of 32% sulfates, 29% elemental carbon (EC), 6% NH_4^+, 6% organic matter, and other materials (Hildemann et al., 1991). From prior studies it is known that the particulate emission rate and the composition of the fine particle organic matter depends on the excess oxygen in the stack gases, fuel batch used, and boiler operating conditions (Lee, 1992; Costa et al., 1991; Goldstein and Siegmund, 1976; Bennett et al., 1979; Barrett et al., 1973; Cato et al., 1976; Cato, 1976). In order to evaluate the range of fine particle organic compound mass emitted during typical boiler operation, 2 of the 5 test sample sets that revealed markedly different GC-traces were further subjected to a detailed investigation using GC/MS-techniques.

Mass Balance for Elutable Fine Particulate Organic Matter

For experiments No.2 and No.5 of this series, material balances have been constructed (Figure 10.1a,b) for the solvent extractable organic portion of the fine particulate matter collected during the boiler testing program. The organic matter that is both extractable and that will elute from the GC column used is comprised of resolved compounds (single chromatographically separated peaks) plus an unresolved complex mixture (UCM) that appears as a hump in the total reconstructed ion chromatogram (RIC). For both experiments, the portion of the organic matter that consists of resolved compounds is in the range 29.8 – 31.8%. For experiment No.2 (Figure 10.1a) the identifiable portion of the resolved organic matter is 62.8%, about twice as high as for experiment No.5 (Figure 10.1b).

The mass identified as particular organic compounds in both experiments is dominated by carboxylic acids (47.8–74.1%) of which *n*-alkanoic acids make up the biggest portion. Polycyclic aromatic hydrocarbons (PAH) and oxygenated polycyclic aromatic hydrocarbons (oxy-PAH) are more prominent in the particulate matter collected during experiment No.2 than during experiment No.5 (3.1 vs 8.6% of the identified compound mass), indicating that changes in fuel batch and operating conditions influence appreciably the amount of PAH and oxy-PAH formed (see also Table 10.1). Aside from typical hydrocarbons, fine particle associated chlorinated organic compounds have been identified in both experiments amounting to 5.8–16.4% of the identified organic compound mass emitted. In the following sections, the organic compound emission rates for both tests will be discussed and differences in concentrations between tests will be interpreted.

(a) GC/MS Elutable Organic Mass: Oil Boiler Experiment No. 2



(b) GC/MS Elutable Organic Mass: Oil Boiler Experiment No. 5

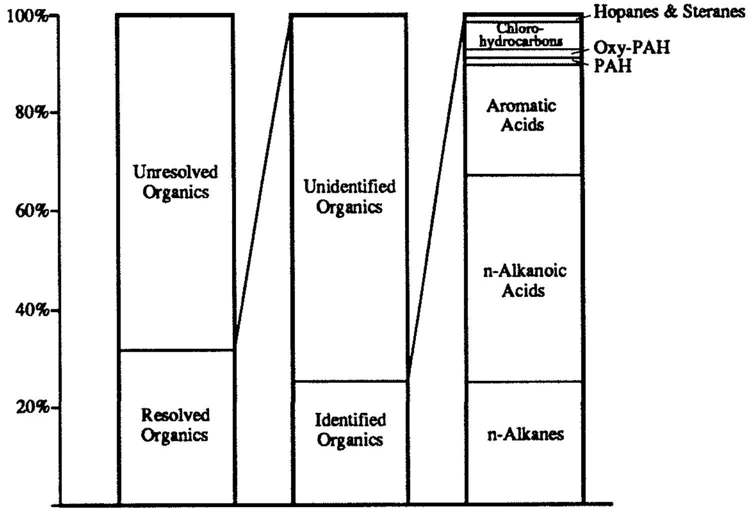


Fig. 10.1: Mass balance for elutable organic matter in the fine particle emissions from an industrial-scale boiler burning No.2 fuel oil: (a) experiment No.2, (b) experiment No.5.

Alkanes

Aliphatic hydrocarbons such as *n*-alkanes are common constituents in crude oils and are usually found up to C_{40+} with typically C_{22}–C_{25} as the most abundant homologues, followed by decreasing concentrations with further increases in weight (e.g., Bray and Evans, 1961; Kissin, 1987; Kvenvolden and Weiser, 1967; Simoneit, 1978; Tissot and Welte, 1984). The fine particulate organic matter emitted from the combustion of No.2 distillate oil contains *n*-alkanes ranging from C_{19}–C_{33} with C_{21} (experiment No.2) and C_{23} (experiment No.5) as the dominant *n*-alkanes. These *n*-alkanes either originated directly from fuel *n*-alkanes or indirectly from *n*-alkyl-substituted naphthenic and naphtho-aromatic fuel compounds that underwent mild thermo-cracking during oil combustion (Kissin, 1990). The total *n*-alkane emission rate during oil-fired boiler test No.2 was roughly 80% higher than was found for experiment No.5 (see Table 10.1) emphasizing the diversity in fuel oil composition.

Carboxylic Acids

Organic acids such as aliphatic *n*-alkanoic acids, aromatic acids and chlorine-substituted aromatic acids were identified in fine particulate matter emitted from the oil-fired boiler tested. *n*-Alkanoic acids, the most abundant compound class identified, showed a typical sawtooth pattern with even carbon numbered homologues predominating (see Table 10.1). The highest emission rates were for palmitic acid (C_{16}) and stearic acid (C_{18}). Only 2.2% of the *n*-alkanoic acids emitted showed carbon numbers $> C_{18}$; the main portion of the *n*-alkanoic acids mass identified has a molecular weight less than or equal to that of stearic acid. A similar *n*-alkanoic acid concentration pattern was found in emissions from other petroleum-based sources such as gasoline and diesel powered vehicles (Rogge et al., 1993b) and asphalt roofing tar pot fumes (Rogge et al., 1993f). Tire wear debris and road dust show a similar enrichment in lower molecular weight *n*-alkanoic acids (Rogge et al., 1993c). Consequently, ambient organic aerosol samples collected throughout Los Angeles reveal a similar concentration pattern (Rogge et al., 1993a).

Although the *n*-alkanoic acid concentration distributions for both oil-fired boiler experiments resemble each other, the emission rates for test No.2 were about three times higher than was found for test run No.5 (see Table 10.1). In contrast, aromatic acids such as benzoic acid and benzenedicarboxylic acids are more abundant in the emissions collected during experiment No.5. A different batch of No.2 distillate fuel oil and therefore modified combustion chemistry might provide a possible explanation for the observed differences in emissions.

Chlorinated Hydrocarbons

Chlorine-substituted aromatic compounds such as mono-, and dichlorohydroxybenzes, mono-, and dichlorobenzoic acids have been identified in the oil-fired boiler emissions (see Table 10.1). At this point, it is not clear if these chloro-organics are products from chlorinated organic precursor compounds or if they were simply synthesized from inorganic chlorine during combustion, or both. Oil desalting processes typically remove > 90% of the salts inherent in crude oils (Kirk-Othmer, 1988), so one expects that the chloride content of fuel oil will be quite low.

The inorganic chloride ion content of the oil-fired boiler aerosol was measured by ion chromatography (Hildemann et al., 1991a) and indicated that on average over all 5 experiments only 0.056% of the fine particulate mass emitted consisted of Cl$^-$ (experiment No.2: 0.040% Cl$^-$; experiment No.5: 0.027% Cl$^-$). The total chloro-organic mass quantified in experiment No.5 amounted to only 12.7% of that found in experiment No.2; see Table 10.1.

Recently, Mulholland et al. (1993) pointed out that the pyrolysis of chlorinated organics during oil combustion leads to increased soot production and PAH formation. The PAH synthesis is promoted by initial chlorine-catalyzed organic compound degradation resulting in enhanced aryl radical formation that leads to increased aromatic condensation and subsequently PAH formation (Frenklach, 1990). PAH formation increases with a greater Cl/H-ratio in the fuel combusted. It was found that at low fuel Cl/H-ratios organic chlorine is mainly removed from the combustion process by HCl formation, at intermediate Cl/H-ratios of 0.3–0.6 mono- and dichlorinated aromatics are formed, and at high fuel Cl/H-ratios of 3 perchloroaromatics were synthesized (Mulholland et al., 1993). Consequently, with increased fuel chlorine content, not only are higher PAH emission levels observed but also possibly hazardous chlorinated compounds are generated.

Polycyclic Aromatic Hydrocarbons

Because No.2 distillate fuel oil (sulfur $< 0.4\%$) is commonly used for residential and commercial heating as well as commercial steam and power generation, one would like to know the emission rates of potentially mutagenic and carcinogenic compounds.

In the present study, individual PAH and alkyl-PAH have been identified in the exhaust emissions from both boiler experiments and are summarized in Table 10.1. The highest single PAH emission rate for experiment No.2 was found for chrysene and or triphenylene. Because the two PAH show a very similar mass fragmentation pattern and elute together from the column used, they can not be distinguished and therefore are mentioned together. Experiment No.5 in contrast to experiment No.2 revealed much lower PAH emission rates. Bennett et al. (1979) reported similar inter-experimental variations in PAH emissions from an oil-fired power plant burning different batches of residual fuel oil with a sulfur content of 2.5%. Further, comparing the emission ratio of PAH to that of chloro-organics between the two boiler tests conducted shows that changes in PAH and chloro-organics emissions track each other more closely than is the case for all other compound classes (PAH-test5/test2 = 1:12.7; chloro-organics–test5/test2: = 1:7.9).

Several factors could be responsible for the different PAH emission rates encountered between tests in the present study: (1) differences in fuel oil composition (e.g., aromaticity) and fuel oil properties (e.g., ***API***-Gravity) (Bennett et al., 1979; Lee, 1992); (2) boiler operating conditions (e.g., combustion air temperature, degree of flue gas recirculation, excess oxygen) (Cato, 1976; Goldstein and Siegmund, 1976; Hildemann et al., 1991a); and (3) the content of chlorinated compounds as discussed above (e.g., Frenklach, 1990; Marr et al., 1992; McKinnon and Howard, 1990; Mulholland et al., 1993; Tsang, 1990).

Polycyclic Aromatic Ketones and Quinones

Oxygenated polycyclic aromatic hydrocarbons (oxy-PAH) have been quantified in the oil-fired boiler aerosol. Emission rates are comparable to single PAH; see Table 10.1. Anthraquinone and 2-methylfluoren-9-one are predominant and roughly 2 to 5 times more abundant in the fine particulate matter collected during experiment No.2 than was found during experiment No.5. The relative change in oxy-PAH emissions from one test to the other is less pronounced than that of the normal PAH.

Hopanes and Steranes

Fossil fuels such as coal and crude oil are the products of biogenic matter transformed by diagenesis and catagenesis over millions of years (Simoneit, 1984; Hunt, 1979; Tissot and Welte, 1984; Mackenzie et al., 1982). In geochemistry, steranes and triterpanes are commonly used as marker compounds to assess the maturity of crude oil and to trace its migration from the source rocks to the crude oil pockets (Hunt, 1979; Tissot and Welte, 1984). Sterane and triterpanoid hopanes have been identified in lubricating oils, vehicular exhaust, road dust, tire wear, roofing tar pot fumes, and subsequently in airborne suspended particles (Simoneit, 1984, 1985; Rogge et al., 1993a-c,f). Among the large spectrum of steranes and triterpanes present in petroleum, only the major compounds previously reported by Rogge et al. (1993b) have been quantified in the fine particulate samples. The results are summarized in Table 10.1. For more details about fossil steranes and triterpanes the interested reader is referred to the literature cited above.

Table 10.1 Fine Aerosol Emission Rates for Single Organic Compounds from an Industrial-Scale Boiler Burning No.2 Distillate Fuel Oil.

PART A	Emission Rates[a] in pg kJ^{-1}		
	Experiment		Compound
	No. 2	No. 5	ID[b]
	— *n*–Alkanes —		
n–nonadecane	416.8	62.5	a
n–eicosane	654.6	112.3	a
n–heneicosane	718.6	170.6	a
n–docosane	567.7	266.8	a
n–tricosane	428.2	358.0	a
n–tetracosane	318.4	322.0	a
n–pentacosane	226.0	234.2	a
n–hexacosane	114.8	119.0	a
n–heptacosane	86.9	98.2	a
n–octacosane	49.9	45.1	a
n–nonacosane	65.1	92.2	a
n–triacontane	50.8	78.3	a
n–hentriacontane	19.3	47.0	a
n–dotriacontane	9.7	13.3	a
n–tritriacontane	7.1	4.0	a
Total class emission rate:	3733.9	2023.5	
	— *n*–Alkanoic Acids[c] —		
n–nonanoic acid	184.8	n.d.	a
n–decanoic acid	337.3	58.4	a
n–undecanoic acid	195.5	n.d.	a
n–dodecanoic acid	1349.4	157.2	a
n–tridecanoic acid	83.4	n.d.	a
n–tetradecanoic acid (myristic acid)	879.8	283.8	a
n–pentadecanoic acid	264.9	78.2	a
n–hexadecanoic acid (palmitic acid)	5717.3	1956.2	a
n–heptadecanoic acid	146.6	75.7	a
n–octadecanoic acid (stearic acid)	2104.4	715.3	a
n–nonadecanoic acid	71.2	n.d.	a
n–eicosanoic acid	66.3	41.0	a
n–heneicosanoic acid	16.0	n.d.	a
n–docosanoic acid	33.4	15.1	a
n–tricosanoic acid	9.0	n.d.	a
n–tetracosanoic acid	35.2	18.1	a
n–pentacosanoic acid	6.8	n.d.	a
n–hexacosanoic acid	10.8	n.d.	a
Total class emission rate:	11512.1	3399.0	

Table 10.1 (continued)

PART B	Emission Rates[a] in pg kJ^{-1}		
	Experiment		Compound
	No. 2	No. 5	ID[b]
— Aromatic Acids[c] —			
benzoic acid	898.7	1443.7	b
1,3-benzenedicarboxylic acid	217.4	243.4	a
1,4-benzenedicarboxylic acid	180.4	143.7	a
Total class emission rate:	1296.5	1830.8	
— Chloro–Hydrocarbons —			
1-chloro-4-hydroxybenzene	1035.7	58.1	b
1,3-dichloro-2-hydroxybenzene	163.2	179.4	b
3-chlorobenzoic acid[c]	2124.7	172.2	b
2,5-dichlorobenzoic acid[c]	349.8	55.9	b
Total class emission rate:	3673.4	465.6	
— Polycyclic Aromatic Hydrocarbons (PAH) —			
phenanthrene	75.9	19.1	a
anthracene	4.9	1.2	a
methyl–(phenanthrenes, anthracenes)	105.0	26.7	b
dimethyl–(phenanthrenes, anthracenes)	84.3	29.6	b
fluoranthene	119.4	9.0	a
pyrene	133.2	7.3	a
benzo[ghi]flouranthene	88.4	5.0	b
benz[a]anthracene	118.7	1.5	a
chrysene/triphenylene	414.6	11.0	a
benzo[k]fluoranthene	105.3	n.d.	a
benzo[b]fluoranthene	99.4	n.d.	a
benzo[e]pyrene	47.8	n.d.	a
benzo[a]pyrene	3.3	n.d.	a
Total class emission rate:	1400.2	110.4	

Table 10.1 (continued)

PART C	Emission Rates[a] in pg kJ^{-1}		
	Experiment		Compound
	No. 2	**No. 5**	ID[b]
— Polycyclic Aromatic Ketones (PAK) and Quinones (PAQ) —			
9H-fluoren-9-one (fluorenone)	32.3	25.0	a
2-methylfluoren-9-one	174.7	59.8	b
9,10-anthracenedione (anthraquinone)	297.9	48.5	a
1-H-benz[de]anthracen-1-one	8.8	3.5	b
7-H-benz[de]anthracen-7-one	24.1	4.0	b
Total class emission rate:	537.8	140.8	
— Regular Steranes —			
20R-5α(H),14α(H),17α(H)-cholestane	22.1	16.1	a
20S&R-5α(H),14β(H),17β(H)-ergostanes	50.4	34.8	b
20S&R-5α(H),14β(H),17β(H)-sitostanes	23.1	13.6	b
Total class emission rate:	95.6	64.5	
— Pentacyclic Triterpanes —			
22,29,30-trisnorneohopane	20.7	9.5	b
17α(H),21β(H)-29-norhopane	28.8	12.9	b
17α(H),21β(H)-hopane	42.1	24.2	b
22S-17α(H),21β(H)-30-homohopane	13.5	5.7	b
22R-17α(H),21β(H)-30-homohopane	7.2	4.8	b
22S-17α(H),21β(H)-30-bishomohopane	5.5	n.d.	b
22R-17α(H),21β(H)-30-bishomohopane	3.8	n.d.	b
Total class emission rate:	121.6	57.1	

[a] n.d. = not detected; accuracy determinations were performed for both polar and nonpolar standard compounds, showing that the relative standard deviations were between 4 to 8% depending on the amount of the standard compounds injected.

[b] for more details see text: a, positive; b, probable; c, possible; d, tentative.

[c] detected as methyl ester.

Conclusions

Organic compounds present in the fine particulate emissions from an industrial oil-fired boiler burning different batches of No.2 distillate fuel oil have been quantified by GC/MS techniques. Organic compounds including *n*-alkanes, *n*-alkanoic acids, aromatic acids, chlorinated hydrocarbons, PAH, oxy-PAH, and fossil petroleum compounds such as hopanes and steranes have been identified. Although the compound emission rates varies appreciably between the two boiler tests discussed here, the relative magnitude of the identified compound classes vary less dramatically. Carboxylic acids constitute the largest part (47.8–74.1%) of the total compound mass identified. PAH and oxy-PAH (3.1–8.6%) together with chlorinated hydrocarbons (5.8–16.4%) show the largest variations in emission rates between the two experiments reported here. The relative increase in chlorinated hydrocarbon emissions between tests is similar to the increase observed for PAH which may follow the results of laboratory experiments that suggest that the presence of chlorinated compounds can enhance PAH formation.

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Chapter 11

Pine, Oak, and Synthetic Log Combustion in Residential Fireplaces

Introduction

Wood combustion has been identified in earlier studies as a non-fossil fuel source (biofuel) that can contribute appreciably to the deterioration of ambient air-quality (Core et al., 1984; Hawthorne et al., 1992; Ramdahl et al., 1984; Sexton et al., 1984; Standley and Simoneit, 1987). Due to their mutagenic and carcinogenic potential, previous studies characterizing wood smoke emissions have focused on the identification of PAH-type compounds in wood smoke. (Claessens and Lammerts van Bueren, 1987; Freeman and Cattell, 1990; Guenther et al., 1988; Kleindienst et al, 1986; Kamens et al., 1984, 1985; Ramdahl, 1983; Ramdahl and Becher, 1982). In the present work, we seek a more complete description of the organic compounds found in wood smoke emissions, with particular emphasis on the detection of compounds that may serve as nearly unique tracers for the presence of woodsmoke in ambient aerosol samples.

To identify the contribution of wood smoke aerosols to ambient particle concentrations several different organic tracer compounds have been proposed including resin acids, retene, and methoxylated phenols (Edye and Richards, 1991; Ramdahl, 1983; Hawthorne et al., 1988, 1989; Standley and Simoneit, 1990; Simoneit et al., 1993; Simoneit and Mazurek, 1982). In addition to the potential wood smoke tracer compounds already mentioned, lignans (dimers of substituted phenols) recently have been suggested as wood smoke tracers that aid in distinguishing between coniferous versus deciduous wood fires (Simoneit et al., 1993).

In this study, combustion aerosols from pine and oak wood, as well as from synthetic logs have been characterized on a molecular level. That analysis provides source profiles that can be used to test whether or not certain organic compounds can be used to trace wood smoke aerosols in the urban atmosphere.

Experimental Methods

The wood combustion experiments were conducted in a single-family house using a traditional undampered brick fireplace that is typical of those found in Southern California. Each wood type (seasoned pine and oak wood) or synthetic log (Pine Mountain brand, 5lb) was burned in separate combustion experiments, typically over the course of about 3h for each experiment. To start the fire, a few pieces of newspaper were used. Kindling was exclusively made of the type of wood tested.

For the pine and oak wood fires, wood logs having weights from 1 kg to 6 kg were used. To mimic traditional undampered fires in residential fireplaces, wood logs were added to the fire at intervals and the fire was periodically stirred (wood burned per test: 12.5 kg to 20 kg). In contrast, the synthetic log was left burning undisturbed during testing according to the manufacturer's guidelines. For more details on the sampling procedure see Hildemann et al., 1991.

Smoke aerosols were withdrawn from the chimney at four different horizontal sampling points along the axis of the chimney and collected using the dilution sampling system described in the previous chapters. Fine particulate emission rates averaged over the course of each experiment ranged from 6.2 ± 0.3 g/kg of oak wood, 13.0 ± 4.1 g/kg of pine wood, and 12.0 g/kg of synthetic log burned.

Fine organic particulate emissions from the fireplace combustion of pine, oak, and synthetic logs have been analyzed on a compound by compound basis using GC/MS-techniques identical to those described in the previous chapters. Compounds either have been identified by comparison to authentic standards or by comparison to library mass spectra. Lignans have been identified by comparison to published mass spectra (Duffield, 1967; Pelter, 1967, 1968; Pelter et al., 1966). In general, lignans show strong molecular ions, facilitating the identification process (Simoneit et al., 1993).

Results and Discussion

Emissions from the combustion of any type of fuel depends directly on the chemical composition of the fuel and the combustion conditions. Upon their genesis, different species of trees show markedly different lignin constitutions. In temperate regions conifers are prolific resin acid producers, while deciduous trees, for example oak, are not. Synthetic logs are typically proprietary products manufactured using sawdust and petroleum waxes. Such differences in fuel composition will be seen to be directly reflected in the compounds emitted during the different source tests.

The results of the organic analyses of this study are summarized in Table 11.1. The total compound mass identified and quantified in this study resembles closely the trend observed for the fine particulate emission rates. Fireplace combustion of oak wood produces the lowest emission rates with 620 mg of total identified compound mass released per kg of oak wood burned. In comparison, pine wood combustion shows for the same compound classes an emission rate roughly 40% higher (912 mg/kg). Synthetic logs release identifiable organic matter at emission rates higher (1300 mg/kg) than was found for pine or oak.

On a detailed molecular level, the emissions of *n*-alkanes, *n*-alkenes, cyclohexylalkyls, *n*-alkanals, PAH, and oxy-PAH are highest for the synthetic log combustion. Per kg of material burned, synthetic logs produce PAH emission rates that are somewhat higher than was found for pine wood and roughly two times higher than for oak wood. Even though synthetic logs show the highest PAH emission rates per kg of wood burned, it is possible that the emission rate per unit time that such fires burn is lower than for oak or pine. That is because one synthetic log of 2.3 kg is burned typically over a 3-hour period. In contrast, a natural wood fire could easily consume 12 to 20 kg of wood over the same 3-hour period.

Carboxylic acids such as *n*-alkanoic acids, and *n*-alkenoic acids show emission rates per kg of fuel burned that are comparable for all three fireplace fuels. Unaltered natural resin acids (e.g., abietic, pimaric, and *iso*-pimaric acids) and their partially altered combustion products (e.g., dehydroabietic acid) instead show highest concentrations when burning pine wood. Small amounts of dehydroabietic acid also have been found during the oak wood burning experiments conducted here. Because oak wood typically does not contain resinous compounds, there might have been some carry over of compounds evolved from soot deposits on the chimney walls due to previous fires burning pine wood in the same fireplace.

The synthetic logs burned during the present experiments show no traces of resin acids. On the contrary retene (1-methyl-7-isopropylphenanthrene), a pyrolysis product of resin diterpenoids that have an abietane skeleton (including resin acids such as abietic, dehydroabietic, pimaric acid, and others; Ramdahl, 1983; Simoneit and Mazurek, 1982), is substantially more abundant in the synthetic log smoke than in pine or oak smoke aerosol emissions. This indicates that the slow combustion process inherent with synthetic logs produces an enhanced tendency to pyrolyze log constituents, which is also expressed in the form of the increased PAH-emissions from such logs.

Lignin, a biopolymer and major part of woody tissue is typically made up of aromatic phenol/alcohols such as *p*-coumaryl, coniferyl, and sinapyl alcohols (e.g., Simoneit et al., 1993). The lignin of gymnosperms (e.g., pine) is primarily derived from coniferyl-alcohol type compounds, whereas the lignin of angiosperms (e.g., oak) is enriched in products from sinapyl alcohols. Upon combustion of wood, lignin breakdown products include hydroxylated and methoxylated phenols that often preserve the original substituents on the phenyl ring. From Table 11.1 it can be seen that phenolic compounds with two substituents are typically favored in pine smoke (coniferyl type), whereas phenolic compounds with three substituents are mainly found in oak wood smoke (sinapyl type).

In addition to combustion products derived from lignins, lignans that are a part of woody plants also were identified. Lignans are basically dimers of coniferyl and sinapyl alcohols and are found mainly in pine wood smoke including compounds such as divanillyl, tetrahydro-3,4-divanillylfuran, matairesinol, and others, see Table 11.1. Dimers related to sinapyl type compounds are bisguaiacylsyringyl and disyringyl and are exclusively found in the smoke from oak wood.

Likely Woodsmoke Markers

Of the wood smoke compounds identified in the present study, all resin acids, except abietic acid, have been identified in the ambient aerosol samples characterized in Chapter 2. Atmospheric fine particulate resin acid concentrations are dominated by dehydroabietic acid, and show a sesonal pattern that follows closely the seasonal use of wood for space heating. Such diterpenoid acids, especially dehydroabietic acid, *iso*-pimaric acid, and pimaric acid have been used in the past to evaluate the impact on ambient air quality of wood use for heating purposes (Hawthorne et al., 1988; Standley and Simoneit, 1987, 1990; Ramdahl, 1983).

Although retene is expected to be an endproduct of the aromatization and decarboxylation process ongoing during combustion, it has been detected only in trace amounts in the Los Angeles atmosphere. This is in good agreement with the low retene emission rates found in this study for the fireplace combustion of pine and oak wood.

Conclusions

The fine particulate emissions from combustion of wood fuels typically used in the Los Angeles area have been examined on a molecular level. Together, more than 100 organic compounds have been identified ranging from aliphatic compounds (e.g., *n*-alkanes) to aromatic compounds (e.g., PAH). The data set provided can be used to determine the compound by compound contributions of wood combustion to the urban atmosphere, provided that it is known how much wood is burned in a given time in the area of interest. Ambient fine aerosol data have been presented in Chapter 2 that include wood smoke related compounds such as resin acids. Those data can be used to calculate the contribution of wood smoked to the urban atmosphere via molecular tracer techniques.

Table 11.1 Emission Rates for Organic Compounds released from Burning Pine Wood, Oak Wood, and Synthetic Logs in Residential Fireplaces.

	Emission Rates[a] in mg kg^{-1} of Logs Burned			
PART A	**Pine Wood**	**Oak Wood**	**Synthetic Logs**	Compound ID[b]
	— *n*-Alkanes—			
nonadecane	n.d.	n.d.	8.80	a
eicosane	n.d.	n.d.	21.74	a
heneicosane	0.44	0.32	15.98	a
docosane	0.45	0.28	16.41	a
tricosane	0.41	0.41	19.94	a
tetracosane	0.29	0.26	20.24	a
pentacosane	0.28	0.25	18.03	a
hexacosane	0.36	0.20	17.74	a
heptacosane	0.47	0.094	18.18	a
octacosane	0.41	0.13	17.58	a
nonacosane	0.61	0.15	17.62	a
triacontane	0.42	0.089	17.19	a
hentriacontane	0.48	0.077	18.84	a
dotriacontane	0.19	n.d.	18.97	a
tritriacontane	0.13	0.027	23.63	a
tetratriacontane	0.12	0.023	29.45	a
pentatriacontane	n.d.	n.d.	37.53	a
hexatriacontane	n.d.	n.d.	39.22	a
heptatriacontane	n.d.	n.d.	44.15	b
octatriacontane	n.d.	n.d.	45.36	b
nonatriacontane	n.d.	n.d.	42.87	b
tetracontane	n.d.	n.d.	38.01	b
Total class emission rate:	5.06	2.31	547.48	
	— *n*-Alkenes—			
nonadecene	n.d.	n.d.	12.48	b
eicosene	n.d.	n.d.	18.11	b
heneicosene	n.d.	n.d.	24.40	b
docosene	n.d.	n.d.	19.98	b
tricosene	n.d.	n.d.	20.67	b
tetracosene	n.d.	n.d.	22.96	b
pentacosene	n.d.	n.d.	23.99	b
hexacosene	n.d.	n.d.	21.92	b
heptacosene	n.d.	n.d.	19.13	b
octacosene	n.d.	n.d.	14.81	b
nonacosene	n.d.	n.d.	10.88	b
triacontene	n.d.	n.d.	14.55	b
hentriacontene	n.d.	n.d.	10.32	b

Table 11.1 (continued)

PART B	Emission Rates^a in mg kg^{-1} of Logs Burned			
	Pine Wood	**Oak Wood**	**Synthetic Logs**	Compound ID^b
dotriacontene	n.d.	n.d.	8.29	b
tritriacontene	n.d.	n.d.	5.70	b
tetratriacontene	n.d.	n.d.	5.34	b
pentatriacontene	n.d.	n.d.	5.19	b
hexatriacontene	n.d.	n.d.	5.97	b
heptatriacontene	n.d.	n.d.	4.40	b
octatriacontene	n.d.	n.d.	4.38	b
nonatriacontene	n.d.	n.d.	4.31	b
tetracontene	n.d.	n.d.	3.82	b
Total class emission rate:			281.60	
— Cyclohexylalkanes —				
cyclohexylpentacosane	n.d.	n.d.	0.77	b
cyclohexylhexacosane	n.d.	n.d.	0.71	b
cyclohexylheptacosane	n.d.	n.d.	0.75	b
cyclohexyloctacosane	n.d.	n.d.	1.77	b
cyclohexylnonacosane	n.d.	n.d.	3.13	b
cyclohexyltriacontane	n.d.	n.d.	4.17	b
cyclohexylhentriacontane	n.d.	n.d.	3.99	b
cyclohexyldotriacontane	n.d.	n.d.	2.59	b
cyclohexyltritriacontane	n.d.	n.d.	2.18	b
cyclohexyltetratriacontane	n.d.	n.d.	1.17	b
Total class emission rate:			21.23	
—*n*-Alkanals —				
nonanal	n.d.	n.d.	2.97	a
decanal	n.d.	n.d.	1.13	b
undecanal	n.d.	n.d.	0.94	b
dodecanal	n.d.	n.d.	2.25	b
tridecanal	n.d.	n.d.	n.d.	b
tetradecanal	n.d.	n.d.	4.12	b
pentadecanal	n.d.	n.d.	8.02	b
hexadecanal	n.d.	n.d.	6.15	b
heptadecanal	n.d.	n.d.	9.19	b
octadecanal	n.d.	n.d.	13.48	b
nonadecanal	n.d.	n.d.	8.82	b
eicosanal	n.d.	n.d.	12.54	b
heneicosanal	n.d.	n.d.	14.64	b
docosanal	n.d.	n.d.	20.21	b
tricosanal	n.d.	n.d.	17.21	b

Table 11.1 (continued)

Emission Rates[a] in mg kg^{-1} of Logs Burned

PART C	**Pine Wood**	**Oak Wood**	**Synthetic Logs**	Compound ID[b]
tetracosanal	n.d.	n.d.	16.27	b
pentacosanal	n.d.	n.d.	14.56	b
hexacosanal	n.d.	n.d.	13.89	b
heptacosanal	n.d.	n.d.	16.28	b
octacosanal	n.d.	n.d.	20.59	b
nonacosanal	n.d.	n.d.	31.95	b
triacontanal	n.d.	n.d.	41.17	b
hentriacontanal	n.d.	n.d.	39.76	b
dotriacontanal	n.d.	n.d.	31.60	b
Total class emission rate:			347.74	
		—*n*-Alkanoic Acids[c]—		
nonanoic acid	n.d.	0.24	0.97	a
decanoic acid	0.095	0.39	0.70	a
undecanoic acid	n.d.	n.d.	0.82	a
dodecanoic acid	1.85	1.65	1.41	a
tridecanoic acid	n.d.	n.d.	1.26	a
tetradecanoic acid	1.74	4.89	2.27	a
pentadecanoic acid	0.85	1.55	2.64	a
hexadecanoic acid	13.91	21.46	10.11	a
heptadecanoic acid	1.62	2.55	1.79	a
octadecanoic acid	4.31	3.33	2.33	a
nonadecanoic acid	0.51	0.41	0.93	a
eicosanoic acid	6.46	2.59	1.46	a
heneicosanoic acid	5.15	1.50	0.92	a
docosanoic acid	7.98	4.65	0.99	a
tricosanoic acid	1.63	2.16	0.55	a
tetracosanoic acid	9.87	13.89	1.70	a
pentacosanoic acid	0.85	1.29	0.80	a
hexacosanoic acid	1.55	6.76	0.67	a
heptacosanoic acid	0.096	0.33	0.49	a
octacosanoic acid	0.15	0.64	0.49	a
nonacosanoic acid	n.d.	0.098	0.38	a
triacontanoic acid	n.d.	0.079	0.29	a
Total class emission rate:	58.621	70.457	33.97	

Table 11.1 (continued)

Emission Rates[a] in mg kg^{-1} of Logs Burned

PART D	**Pine Wood**	**Oak Wood**	**Synthetic Logs**	Compound ID[b]
—*n*-Alkenoic Acids[c]—				
cis-9–octadecenoic acid (oleic acid)	7.62	1.15	0.93	a
9,12-octadecadienoic acid (linoleic acid)	8.35	1.45	n.d.	a
Total class emission rate:	15.97	2.60	0.93	
— Dicarboxylic Acids[c]—				
propanedioic acid	38.35	n.d.	n.d.	a
butanedioic acid	0.89	11.68	n.d.	a
methylbutanedioic acid	n.d.	3.35	n.d.	a
pentanedioic acid	6.65	5.44	n.d.	a
hexanedioic acid	0.63	1.75	n.d.	a
Total class emission rate:	46.52	22.22		
— Resin Acids[c]—				
abietic acid	1.06	n.d.	n.d.	b
dehydroabietic acid	37.23	5.60	n.d.	a
13-isopropyl-5α-podocarpa-6,8,11,13--tetraen-16-oic acid	2.02	n.d.	n.d.	b
8,15-pimaradien-18-oic acid	4.02	n.d.	n.d.	b
pimaric acid	24.17	n.d.	n.d.	a
iso-pimaric acid	6.55	n.d.	n.d.	b
7-oxodehydroabietic acid	3.31	n.d.	n.d.	a
sandaracopimaric acid	47.03	n.d.	n.d.	b
Total class emission rate:	125.39	5.60		
—Other Acids[c] —				
2-furancarboxylic acid	3.02	1.77	n.d.	b
2-hydroxybenzoic acid[d]	4.28	7.53	n.d.	b
3,4-dimethoxybenzoic acid (veratric acid)[e]	65.04	18.68	0.69	a
3,4-dimethoxyphenylacetic acid (homoveratric acid)	5.72	n.d.	n.d.	a
4-hydroxy-3-methoxyphenylacetic acid (homovanillic acid)	82.82	15.02	n.d.	a
3,4,5-trimethoxybenzoic acid[f]	n.d.	22.57	n.d.	a
Total class emission rate:	160.88	66.57	0.69	

Table 11.1 (continued)

PART E	Emission Rates[a] in mg kg^{-1} of Logs Burned			
	Pine Wood	Oak Wood	Synthetic Logs	Compound ID[b]
—Hydroxylated/Methoxylated Phenols —				
1,4-benzenediol (hydroquinone)[g]	61.78	22.52	n.d.	b
1,3-benzenediol (resorcinol)[h]	3.33	3.54	n.d.	b
3-methyl-1,2-benzenediol (3-methylcatechol)[i]	34.94	13.27	n.d.	b
4-methyl-1,2-benzenediol (4-methylcatechol)[j]	19.53	3.33	n.d.	a
4-propyl-benzenediol[k]	18.75	n.d.	n.d.	b
2-methyl-5-(1-methylethyl)-2,5-cyclohexadien--1,4-dione (thymoquinone)	0.58	n.d.	n.d.	b
2-methoxy-4-(2-propenyl)phenol (eugenol)	1.54	n.d.	n.d.	b
2-methoxyphenol (guaiacol)	0.21	0.067	n.d.	b
2-methoxy-3-methylphenol (3-methylguaiacol)	0.78	0.042	n.d.	b
2-methoxy-4-propylphenol (1-guaiacylpropane)	19.53	3.37	n.d.	b
2-methoxy-5-(1-propenyl)phenol	8.04	0.16	n.d.	b
2,6-dimethoxyphenol (syringol)	1.13	10.81	n.d.	a
1-(4-methoxyphenyl)ethanone	5.19	3.78	n.d.	b
3,4-dimethoxyphenylacetone (veratrylacetone)	10.41	6.34	n.d.	b
1-(2,4-dimethoxyphenyl)propan-2-one	8.98	2.37	n.d.	b
1-(4-hydroxy-3-methoxyphenyl)ethan-2-one (guaiacylacetone)	36.27	3.63	0.78	b
1-(4-hydroxy-3-methoxyphenyl)propan-2-one	39.32	10.73	0.79	b
1-(3,5-dimethoxy-4-hydroxyphenyl)ethan-2-one	n.d.	55.52	15.79	a
1-(3,5-dimethoxy-4-hydroxyphenyl)propan-2-one (1-syringylpropanone)	n.d.	20.82	5.93	b
2,6-dimethoxy-4-(2-propenyl)phenol	n.d.	1.98	n.d.	b
1-(3,4,5-trimethoxyphenyl)ethan-2-one	n.d.	35.61	5.55	b
1-(3,4,5-trimethoxyphenyl)propan-2-one	n.d.	80.27	n.d.	b
dimers				
bis(3,4-dimethoxyphenyl)methane	6.34	0.81	n.d.	b
divanillyl	22.25	2.38	n.d.	b
tetrahydro-3,4-divanillylfuran	22.87	0.60	n.d.	b
tetrahydro-3-vanillyl-4-veratrylfuran	8.93	0.35	n.d.	b
matairesinol	2.78	n.d.	n.d.	b
dihydro-3,4-diveratryl-2(3H)-furanone	2.24	n.d.	n.d.	b
tetrahydro-3,4-diveratrylfuran	3.84	0.13	n.d.	b
dihydrovanillylsyringol-2(3H)-furanone	4.93	n.d.	n.d.	b
bisguaiacylsyringyl	n.d.	3.08	n.d.	b
disyringyl	n.d.	7.10	n.d.	b
bis(3,4,5-trimethoxyphenyl)ethane	n.d.	0.77	n.d.	b
Total class emission rate:	344.49	293.379	28.84	

Table 11.1 (continued)

PART F	Emission Rates[a] in mg kg^{-1} of Logs Burned			
	Pine Wood	Oak Wood	Synthetic Logs	Compound ID[b]
— Substituted Benzenes/Benzaldehydes —				
1,2-dimethoxybenzene (veratrole)	2.96	1.89	n.d.	a
1,3-dimethoxybenzene	1.02	1.84	n.d.	b
1,4-dimethoxybenzene	n.d.	1.52	n.d.	b
1,4-dimethoxy-2-methylbenzene	28.12	n.d.	n.d.	b
3-methoxy-4-hydroxybenzaldehyde (vanillin)	29.27	2.05	n.d.	a
3-methoxybenzaldehyde	0.74	n.d.	n.d.	b
3,4-dimethoxybenzaldehyde (veratraldehyde)	22.62	4.60	n.d.	a
4-hydroxy-3,5-dimethoxybenzaldehyde (syringaldehyde)	n.d.	66.61	15.86	a
3,4,5-trimethoxybenzaldehyde	n.d.	62.42	5.28	a
Total class emission rate:	84.73	140.93	21.14	
— Phytosterols —				
β-sitosterol	45.50	9.94	n.d.	a
stigmast-4-en-3-one	2.87	1.29	n.d.	b
Total class emission rate:	48.37	11.23		
—Polycyclic Aromatic Hydrocarbons (PAH)—				
phenanthrene	0.47	0.30	0.46	a
anthracene	0.051	0.057	0.07	a
methyl–(phenanthrenes, anthracenes)	n.d.	n.d.	0.75	b
dimethyl–(phenanthrenes, anthracenes)	n.d.	n.d.	0.79	b
1-methyl-7-isopropylphenanthrene (retene)	0.68	0.11	2.72	a
fluoranthene	1.24	0.40	0.70	a
pyrene	1.59	0.53	0.94	a
benzacenaphthylene	0.57	0.16	0.24	b
2–phenylnaphthalene	n.d.	n.d.	0.21	b
methyl–(fluoranthenes, pyrenes)	1.19	0.33	0.99	b
benzo[a]fluorene/benzo[b]fluorene	0.056	0.11	0.56	a
benzo[ghi]fluoranthene	0.27	0.11	0.24	a
cyclopenta[cd]pyrene	0.72	0.23	n.d.	a
benzo[c]phenanthrene	0.15	0.033	n.d.	a
benz[a]anthracene	0.63	0.21	0.38	a
chrysene/triphenylene	0.98	2.83	0.75	a
methyl–(benz[a]anthracenes, chrysenes, triphenylenes)	n.d.	n.d.	0.56	b
dimethyl–(fluoranthenes, pyrenes)	n.d.	n.d.	0.78	b
benzo[k]fluoranthene	0.51	0.26	0.51	a
benzo[b]fluoranthene	0.53	0.21	0.42	a

Table 11.1 (continued)

Emission Rates[a] in mg kg^{-1} of Logs Burned

PART G	Pine Wood	Oak Wood	Synthetic Logs	Compound ID[b]
benzo[j]fluoranthene	0.28	0.11	0.14	a
benzo[e]pyrene	0.30	0.13	0.44	a
benzo[a]pyrene	0.62	0.23	0.40	a
perylene	0.12	0.038	0.043	a
indeno[1,2,3-cd]pyrene	0.087	0.047	0.10	a
indeno[1,2,3-cd]fluoranthene	0.35	0.15	0.26	a
benzo[ghi]perylene	0.32	0.13	0.52	a
anthanthrene	0.12	0.039	n.d.	a
dibenz[a,h]anthracene	0.079	0.012	0.045	a
benzo[b]triphenylene	n.d.	n.d.	0.19	b
coronene	n.d.	n.d.	0.10	a
Total class emission rate:	11.913	6.766	14.318	
—Polycyclic Aromatic Ketones (PAK) and Quinones (PAQ)—				
1H-phenalen-1-one	1.87	0.81	0.75	b
9,10–phenanthrenedione (phenanthrenequinone)	n.d.	n.d.	0.38	a
1H–benz[de]anthracen-1-one	0.13	0.076	n.d.	a
7H–benz[de]anthracen-7-one	0.50	0.19	0.30	a
6H–benzo[cd]pyren-6-one (benzo[cd]pyrenone)	n.d.	n.d.	0.11	b
Total class emission rate:	2.50	1.076	1.54	

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[a] n.d. = not detected.

[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.

[d] determined as 2-methoxybenzoic acid (o-Anisic acid).

[e] could also have been originally 4-hydroxy-3-methoxybenzoic acid (vanillic acid) or both due to the methylation step.

[f] could also have been originally 4-hydroxy-3,5-dimethoxybenzoic acid (syringic acid) or both due to the methylation step.

[g] determined as 2-methoxyphenol in the methylated fraction only.

[h] determined as 3-methoxyphenol in the methylated fraction only.

[i] determined as 2-methoxy-3-methylphenol in the methylated fraction only.

[j] determined as 2-methoxy-4-methylphenol in the methylated fraction only.

[k] determined as 2-methoxy-4-propylphenol in the methylated fraction only.

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Chapter 12

Modeling the Contributions of Fine Particulate Organic Compound Emissions to the Los Angeles Atmosphere

Introduction

Determination of the partial contributions of the emissions from particular source types to ambient pollutant concentrations is an important prerequisite to the design of air pollution control programs. Methods for assigning aerosol carbon concentrations to their sources are less well developed than for most other air pollution problems. That occurs because so many different source types release carbon particles to the atmosphere and because many of these source effluents appear to be similar in composition if only a total carbon analysis is used to characterize the source emissions and ambient aerosol samples. The problem of source attribution is further complicated by the production in the atmosphere of secondary organic aerosols that result from condensation of the low vapor pressure products of gas phase chemical reactions. The additional possibility that directly emitted particle-phase organic compounds may be destroyed by atmospheric chemical reactions also must be considered.

In the present research, unique data sets on the organic chemical composition of both source effluents and atmospheric fine particulate matter have been developed. These data sets provide new opportunities to test our current understanding of the relationships between emissions and air quality for organic aerosols.

In the present chapter, a comprehensive emission inventory for more than 400 organic compounds that are present in primary organic aerosol emissions first will be assembled for an 80 km × 80 km study area centered over Los Angeles, CA. That study area is mapped in Figure 3.5 of Chapter 3 of this thesis. The combined emissions from the major primary organic aerosol sources acting together first will be compared to measured pollutant concentrations. It will be seen that there is an obvious and close correspondence between these two data sets for the case of the least chemically reactive compounds studied.

Next, the emission inventory data will be matched to an existing mathematical model for atmospheric transport and dilution. The time series of the concentrations of single particle-phase organic compounds and major compound classes that would be expected in the absence of any further atmospheric chemical reactions will be computed in the Los Angeles area for each month of the year 1982. Comparisons will be drawn between the predicted source contributions to ambient organic concentrations versus the concentrations measured at West Los Angeles, downtown Los Angeles, and Pasadena reported in Chapter 2 of this work. Evidence for the production of secondary organic aerosols and for the degradation of primary organic species by volatilization and/or chemical reaction will be sought through examination of the source and ambient data sets.

Model Description

Atmospheric pollutant transport through the Los Angeles basin is driven by differential solar heating of the land and sea, leading to a daily cyclic land and sea breeze. During morning and early evening hours, the winds are often stagnant with no prevailing direction over short observation times of one hour or less. From midday until late afternoon the wind typically flows from the ocean toward the land. At night, slow drainage winds proceed from the land towards the sea. In addition to the daily land/sea wind reversal, there is a strong diurnal variation in the height of the base of the atmospheric temperature inversion over the Los Angeles basin. In the early morning, with the onset of solar heating of the land, the inversion base rises progressively until the afternoon. In the evening cooling by re-radiation from the ground or continued subsidence caused by the Pacific Anticyclone causes the inversion base to descend again.

An air quality model that predicts long-term average nonreactive pollutant concentrations for the unsteady meteorological conditions just described was originally developed by Cass (1977, 1981) and later modified by Gray (1986) to predict elemental and total organic fine particulate carbon concentrations in the greater Los Angeles area atmosphere. Because of the unsteady flow field that is typically encountered in the Los Angeles area, a Lagrangian particle-in-cell modeling technique was chosen that simulates advection, dispersion, and deposition of pollutants, in response to the hourly time sequence of the measured winds and the daily fluctuating height of the temperature inversion aloft.

Hypothetical mass points marked with the mass emission rate of organic carbon aerosols are released successively at short time intervals from each source type separately at the effective stack height of the source of interest. Each source is located within an 80 km × 80 km area centered over Los Angeles that has been further subdivided into 625 computational cells of size 3.2 km × 3.2 km each. Depending on the effective stack height (actual stack height, h, plus plume rise, Δh) the source emissions can be injected either below or above the base of the atmospheric temperature inversion. Fluid parcels that are either above or below the inversion base can be exchanged depending on the ascent or decent of the base of the temperature inversion with time. For fine particulate source emissions inserted below the inversion base, three vertical transport regimes are considered: (1) when the inversion base height is substantially heigher than the effective stack height of the pollutant source, the inversion base has no effect on the vertical dispersion of the plume and the pollutant concentration assumes a Gaussian distribution in the vertical domain; (2) as the air parcel moves away from its source, the vertical dispersion increases until the inversion layer begins to trap the air parcel below; (3) far from the source, the plume becomes completely mixed between the ground and the inversion base.

Trajectories of single fluid parcels starting from each source form streaklines that are computed from the hourly time series of ground level wind speed and direction. Horizontal diffusion is then simulated by adding small displacements to each air parcel location at each hour that are drawn from a Gaussian distribution that expands with downwind travel time in accordance with experimental observations on atmospheric dispersion rates.

The ambient pollutant concentration within the ground level layer of each computational cell is obtained by integrating over the magnitude and location of all pollutant parcels that fall within the ground level layer of that cell. Computationally, the monthly average pollutant concentration increments, $\overline{< c(\mathbf{x};T,t_s) >}$, at each receptor site are obtained by evaluating the Lagrangian formulation of the atmospheric dispersion equation, as follows:

$$\overline{< c(\mathbf{x};T,t_s) >} = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\left[\frac{1}{T}\int_{t_s}^{t_s+T}\int_{0}^{+\infty}\mathbf{Q}(\mathbf{x},t|\mathbf{x}',t-\tau)\omega(t-\tau)d\tau dt\right]\overline{S}(\mathbf{x}')d\mathbf{x}' \qquad (12.1)$$

where

$\mathbf{Q}(\mathbf{x}, t \mid \mathbf{x}', t - \tau)$	is the transition probability density function that describes the probability that a fluid particle will be found at location **x** at present time t given that it was located previously at **x'** at time $t-\tau$; these probabilities are computed by tracking the fluid particles through the simulation of horizontal and vertical transport described earlier.
$\omega(t-\tau)$	is the normalized diurnal variation in the emission rate for the source type of interest;
$\overline{S}(\mathbf{x}')$	is the time-averaged source strength at location **x'** of the source class of interest;
T	is the length of the averaging time, in our case T equals one month;
t_s	is the starting time.

Finally, by adding all incremental concentration contributions from all source classes and superimpossing these monthly average concentrations onto an estimate of organic aerosol background air quality, estimates of the ambient organic aerosol concentrations due to primary emissions of particulate matter from all sources acting together are obtained.

Prior Model Application

The air quality model discussed above has been applied by Gray (1986) to predict monthly average concentration levels for fine particulate elemental carbon (EC) and total carbon (TC) at seven urban monitoring sites within the Los

Angeles study area for the year 1982.

As part of the input data prepared for that model simulation, an inventory of fine carbon particle emissions was compiled for mobile as well as stationary sources that are located within the modeling domain. The spatial and temporal distribution of emissions was estimated for over 70 different source types. Emissions from major point sources were assigned to the actual locations of those sources. Residential source emissions were distributed throughout the grid system in proportion to population density. Vehicular exhaust emissions were allocated to the grid system in proportion to traffic densities observed on surface streets and freeways. For all other source classes the source locations and emissions strengths were extracted from a spatially distributed emission inventory forecast provided by the California Air Resources Board (see Gray, 1986). Seasonal changes in fuel consumption, e.g., fireplace combustion of wood, were estimated for fuel combustion sources. Other source classes were assumed to operate without any seasonal trend. Emissions from sources that have a pronounced diurnal operation pattern were represented in the model through estimation of the function $\omega(t-\tau)$ that appears in equation (12.1) for each source type.

Paved road surfaces act as a repository for dirt and dust that has settled out of the atmosphere. Under suitable conditions, these road dust deposits are reintrained into the atmosphere as a function of traffic density, wind speed, and other meteorological conditions. It is difficult to assess the daily emission rate of fine particulate road dust. Therefore, Gray (1986) specified a receptor modeling approach in which Al and Si tracer concentrations in airborne fine particulate matter and in fine paved road dust are used to derive from actual ambient measurements an upper limit on the road dust contributions to the ambient aerosol complex. That approach will be used to model road dust contributions to ambient air quality in the present study as well. For a detailed discussion see Gray (1986).

In addition to source emission data, other model input data include hourly wind fields that were computed from observed data over central Los Angeles and paired with hourly mixing depth data that were obtained by impressing a diurnal pattern onto the morning and afternoon mixing depth measurements reported daily by the South Coast Air Quality Management District.

To evaluate the performance of the model, ambient fine particulate matter samples were collected at ten urban sampling sites and one remote off-shore sampling site at six day intervals throughout the entire year 1982. The duration of each sampling period was 24h. Typically good agreement was found between modeled and measured ambient elemental carbon (EC) and total carbon (TC) concentrations (see Gray, 1986).

Recently, Hildemann et al. (1990) used the same model and meteorological data to predict primary organic aerosol characteristics from measured source emissions. To complement the ambient sampling program conducted by Gray in 1982, the major urban source types were tested that together represent close to 80% of the primary organic carbon emissions to the Los Angeles atmosphere. These source test results were used to modify the OC-emission inventory complied originally by Gray (1986). That revised emission inventory is shown in Table 12.1. The organic aerosol characteristics of both source samples and ambient samples were defined through measurements of elutable organic matter as detected by a high resolution gas chromatograph (GC) equipped with a flame ionization detector system (Hildemann et al., 1990). A 52–parameter "fingerprint" was

Table 12.1 Estimate of Fine Aerosol Organic Carbon (OC) Emissions within the 80 × 80 km Study Area Centered over Los Angeles for 1982.

Source Type	OC emitted kg/day	Profile No. of Source tested in this study	Source Profile used for Modeling[a]
(1) Meat-cooking operations			
Charbroiling	4938	1,2[b]	1
Frying	1393	3	3
(2) Paved road dust	4728	4	4
(3) Fireplaces			
Pine wood	3332	5	5
Oak wood	840	6	6
Synthetic logs	n.k.	7	7
(4) Noncatalyst gasoline vehicles			
Automobiles	2088	8	8
Other vehicles[c]	1372		8
(5) Diesel vehicles			
Heavy-duty trucks	1242	9	9
Other vehicles[d]	617		9
(6) Surface Coating	1433		
(7) Forest Fires	877		
(8) Cigarettes	802	10	10
(9) Catalyst-equipped gasoline vehicles			
Automobiles	780	11	11
Other vehicles[e]	79		11
(10) Organic chemical processes	692		
(11) Brake lining	690	12	12
(12) Roofing tar pots	556	13	13
(13) Tire wear	414	14	14
(14) Misc industrial point sources	393		
(15) Natural gas combustion			
Residential/commercial	30	15	15
Other sources[f]	262		15
(16) Misc petroleum industry processes	278		
(17) Primary metallurgical processes	228		
(18) Railroad (diesel oil)	211		9
(19) Residual oil stationary sources[g]	206		16
(20) Refinery gas combustion	195		15
(21) Secondary metallurgical processes	167		
(22) Mineral industrial processes	158		
(23) Other organic solvent use	106		
(24) Jet aircraft	92		
(25) Asphalt roofing manufacturing	81		13
(26) Coal burning	76		
(27) Wood processing	74		

Table 12.1 continued **Source Type**	OC emitted kg/day	Profile No. of Source tested in this study	Source Profile used for Modeling[a]
(28) Residual oil-fired ships	66		
(29) Structural fires[h]	63		5
(30) Distillate oil stationary sources			
Industrial[i]	13	16	16
Other[j]	23		16
(31) Vegetative detritus			
Green leaf abrasion products[k]	n.k.	17	17
Dead leaf abrasion products	n.k.	18	
(32) Other sources[l]	226		8,9,15,16
Total	29822		

n.k. = not known

[a] source profiles of sources tested also are used to characterize emissions from similar source types.

[b] profile No. 1: charbroiling regular hamburger meat with a fat content of 21%; profile No. 2: charbroiling extra-lean meat with a fat content of 10%.

[c] noncatalyst light trucks, medium trucks, heavy-duty trucks, off-road gasoline vehicles, and motorcycles (for more details see Gray, 1986).

[d] diesel autos, diesel light trucks, and off-road diesel vehicles (for more details see Gray, 1986).

[e] catalyst-equipped light and medium trucks (for more details see Gray, 1986).

[f] electric utilities boilers NG, electric utilities turbines NG, refineries NG, industrial boilers NG; NG = natural gas used (for more details see Gray, 1986).

[g] electric utility boilers burning residual oil, refineries burning residual oil, industrial boilers burning residual oil, residential/commercial combustion of residual oil (for more details see Gray, 1986).

[h] structural fires are assumed to show a similar organic compound profile as found for pine wood combustion in residential fireplaces.

[i] the average compound emission rates from two single source tests are used (see Rogge et al, 1993).

[j] residential/commercial distillate oil combustion (for more details see Gray, 1986).

[k] for model calculations only the source profile derived from green leaf abrasion products is used (see Rogge et al., 1993).

[l] other sources include: Diesel powered ships, electric utilities burning distillate oil, refineries burning ref. gas, industrial boilers burning LPG, industrial boilers burning distillate oil, industrial internal combustion engines using gasoline (for more details see Gray, 1986).

constructed to characterize the emissions from each source type by measuring the quantity of the organic compounds in both the non-polar and polar fractions of each source sample that elutes from the GC column between the successive elution points of the C_{12} to C_{36} *n*-alkanes. The data on the mass emissions from each source type within each GC elution zone defined above were entered into the air quality model. The model then was used to predict the characteristic distribution of organic aerosol mass as a function of polarity and elution time that would be found in ambient air if these source effluents were transported without chemical reaction. Model results were compared against high resolution GC measurements of ambient samples taken at West Los Angeles, downtown Los Angeles, and Pasadena. More details regarding the source "fingerprinting" technique and modeling results can be found in the work by Hildemann (1990).

It is useful to the present study to note the general degree of agreement between total organic carbon concentrations (as measured by combustion techniques) versus ambient organics levels achieved in the modeling studies by Gray (1986) and by Hildemann (1990). The time series of monthly mean predicted and observed OC concentrations at West Los Angeles, downtown Los Angeles, and Pasadena during 1982 are shown in Figures 12.1a-c. The model predictions are indicated by the horizontal lines in each graph while the small circles give the mean of the measured values. The error bars represent the standard deviation of the 5 to 6 ambient samples collected during each month. The uncertainties in the winter months are quite large. That uncertainty arises not because of laboratory analytical errors but because of the great variations from day to day in the ambient aerosol concentrations in the winter. Since ambient samples were taken at six day intervals, and not all days were sampled, the monthly mean

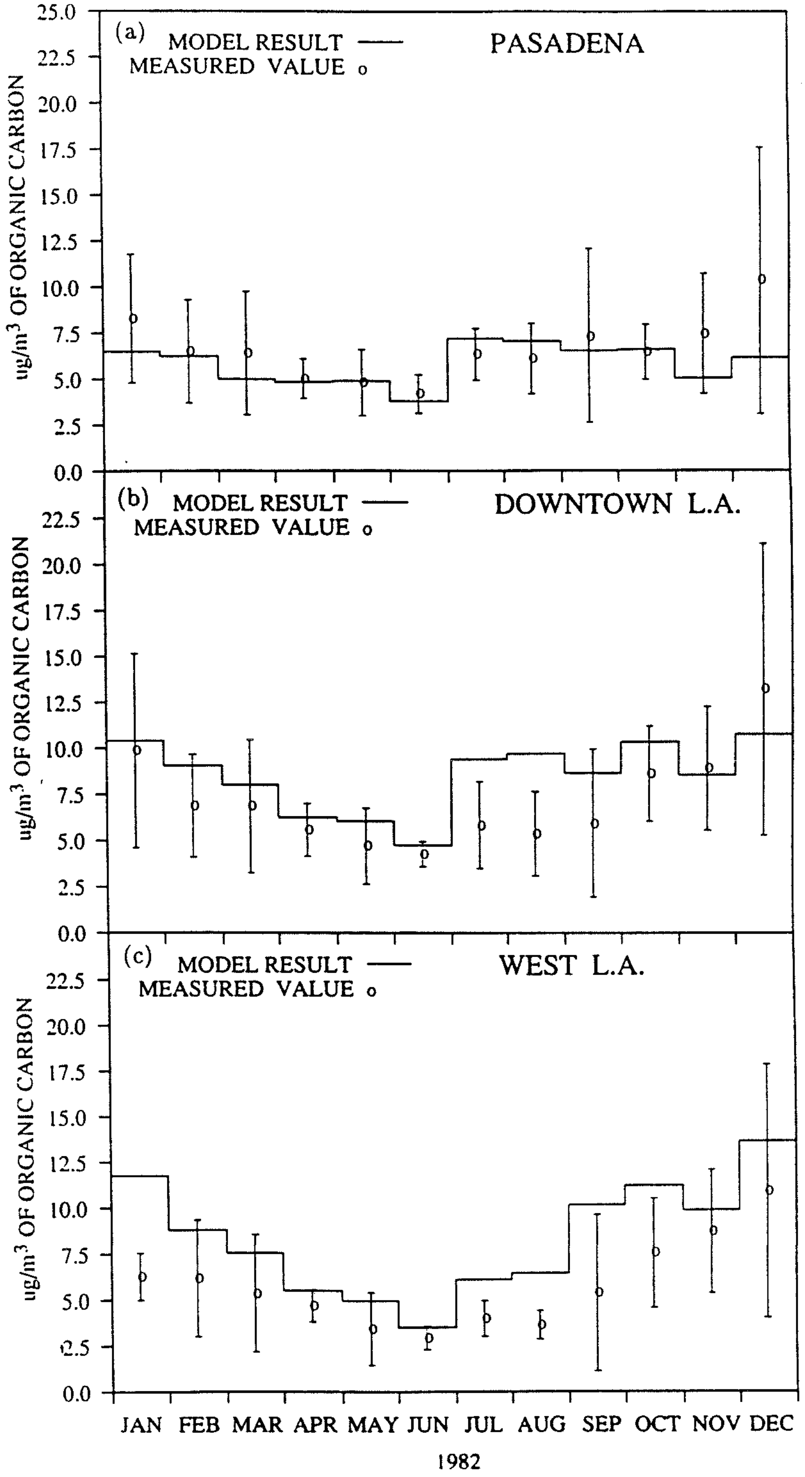


Fig. 12.1: Ambient fine organic carbon (OC) concentrations: Model predictions versus measurements at (a) Pasadena, (b) downtown Los Angeles, and (c) West Los Angeles for 1982 (from Hildemann, 1990).

is not known precisely.

It is important to keep this fact in mind when considering the comparison of single compound concentration predictions and observations that follows. Note from Figure 12.1 that winter concentrations at Pasadena that seem to be underestimated by the model still fall within the error bounds on the ambient observations. It is not possible to perform such a detailed uncertainty analysis at the single compound level because all ambient filter samples for each month had to be pooled prior to extraction in order to enhance detection limits. Nevertheless, it is likely that the same variability from day to day that contributes to uncertainty in the monthly mean OC concentrations also appears at the single compound level.

Present Model Application

In the present study, ambient concentrations of individual organic compounds that are associated with the fine particulate source emissions are predicted. The OC-emission inventory originally compiled by Gray (1986) and updated by Hildemann (1991) is combined with the chemical characterization of the emissions from each source that was presented in Chapters 3 – 11 of this thesis. These emissions data are supplied to the air quality model developed by Gray (1986) and are used to predict monthly average organic compound concentrations over the year 1982. Predicted ambient concentrations are compared to the measured ambient organic compound concentrations reported in Chapter 2 of this thesis.

Organic Compound Aerosol Source Profiles

The fine particle samples collected during the source testing campaign by Hildemann et al. (1991) were analyzed using GC/MS-techniques (Rogge et al., 1991, 1993b-i). Organic chemical composition profiles for eighteen source types were generated that together include roughly 400 different organic compounds.

Ambient samples used in this study were collected by Gray et al. (1986) at West Los Angeles, downtown Los Angeles, Pasadena, and Rubidoux (outside the modeling region to the east) during the year 1982. The filter samples were composited month by month prior analysis. All fine particle samples, including the source and ambient samples were collected using comparable equipment and materials and were processed by the same analytical extraction technique that was originally developed by Mazurek et al. (1987, 1989). All source and ambient samples were characterized and quantified by the same GC/MS-techniques as described in full detail by Rogge et al. (1991, 1993a-i).

Of the 18 organic compound source profiles generated (see Table 12.1), 15 profiles were used as input data for the model simulations. The other three profiles were bypassed for the following reasons. The organic aerosol released as meat is charbroiled was assumed to be best characterized by charbroiling regular meat (21% fat content; profile 1) and not by charbroiling extra-lean meat (10% fat content; profile 2). Combustion of synthetic logs in fireplaces has not been included in the model calculations due to a lack of data on synthetic log consumption. The relative magnitude of the emissions of particles shed from the surfaces of green vegetation, as distinct from dead vegetation, is not yet known. Because the waxy leaf surface abrasion products from green and dead leaves do not differ significantly, only the source profile for green vegetative detritus will be used in this study.

Individual Emission Sources Considered

A multitude of different urban sources contribute fine particulate matter to the urban atmosphere. Of the more than 70 source types included in the inventory compiled by Gray (1986), 43 sources were chosen that are either directly represented by the authentic source profiles available (Rogge et al., 1991, 1993b-i) or that are closely related to the sources tested. For example, the source profile obtained for the noncatalyst gasoline-powered vehicles tested is also applied to noncatalyst light-duty trucks, medium-duty gasoline-powered trucks, heavy-duty gasoline-powered trucks, off-road gasoline-powered vehicles, and motorcycles. Table 12.1 lists the source profiles that are used for each of the 43 sources considered. That table also shows that the sources included in the model account for 83.4% of the primary OC emissions within the Los Angeles area. In order to organize the discussion of the modeling results, the 43 sources studied are further grouped into 12 source categories that are described in Table 12.2.

Before using the organic compound source data sets to model respective ambient concentrations, the overall daily emission rates of organic compound mass based on the OC-emission inventory first will be discussed. Next, the total daily single compound emission rates (kg/day) summed over all source categories will be compared to the measured monthly ambient organic compound concentrations, determined as the mean of the monthly concentrations measured at West Los Angeles, downtown Los Angeles, and Pasadena. Finally, ambient organic compound concentrations will be estimated using the air quality model.

Table 12.2 Source Categories used to Group the Individual Emission Sources that are used in the Air Quality Model Calculations.

Source Categories

(I) Catalyst-equipped Vehicles

1 Catalyst-equipped autos
2 Catalyst-equipped light trucks
3 Catalyst-equipped medium trucks

(II) Noncatalyst Vehicles

4 Noncatalyst autos
5 Noncatalyst light trucks
6 Noncatalyst medium trucks
7 Noncatalyst heavy-duty trucks
8 Motorcycles
9 Noncatalyst off-road vehicles

(III) Diesel Vehicles

10 Diesel autos
11 Diesel light trucks
12 Diesel heavy-duty trucks
13 Diesel off-road vehicles
14 Railroad diesel locomotives
15 Diesel Ships

(IV) Brake and Tire Dust

16 Tire wear dust
17 Brake lining attrition

(V) Paved Road Dust

18 Paved Road Dust

(VI) Natural Gas Combustion

19 Natural gas–residential/commercial
20 Natural gas–electric utility boilers
21 Natural gas–electric utility turbines
22 Natural gas–refineries
23 Refinery gas–refineries
24 Natural gas–industrial boilers
25 LPG–industrial boilers
26 LPG–residential/commercial

Table 12.2 continued

Source Categories
(VII) Stationary Source Fuel Oil Combustion
27 Residual oil–electrical utilities
28 Distillate oil–electric utilities
29 Residual oil–refineries
30 Residual oil–industrial boilers
31 Distillate oil–industrial boilers
32 Industrial internal combustion gasoline engines
33 Residual oil–residential/commercial
34 Distillate oil–residential/commercial
(VIII) Wood Combustion
35 Pine wood burning fireplaces
36 Oak wood burning fireplaces
37 Structural fires
(IX) Meat Cooking
38 Charbroiling meat
39 Frying meat
(X) Cigarette Smoking
40 Cigarettes
(XI) Roofing Tar Pots
41 Roofing tar pots
42 Asphalt roofing manufacturing
(XII) Vegetation
43 Green leaf abrasion products

Daily Mean Organic Compound Class Emissions

Using the organic compound source profiles (see Rogge et al., 1991, 1993b-i) together with the OC-emission inventory (Table 12.1), the mean daily emission rates of identified organic compounds from each source type can be estimated. Because the source strength for leaf surface abrasion products is not known a priori, emissions from that source category cannot be included in these calculations.

In Figure 12.2, the identified organic compounds associated with each of eleven major source profiles are grouped into 16 compound classes based on organic chemical structural similarities. The amount of identified compound mass associated with each source profile that is emitted to the 80 km × 80 km study area on average throughout 1982 also is listed in kg/day in Table 12.2. The emissions of identified compounds from these sources total 2836 kg/day, or 9.5% of the total fine primary organic aerosol emitted in the study area as shown in Table 12.2. The remaining primary organic aerosol emissions consist largely of compounds that are not solvent-extractable or are not elutable under the analytical conditions used here or are present as part of the large hump of unresolved compounds present in many source samples that cannot be identified as single compound peaks.

From Figure 12.2 it can be concluded that no two source categories possess a similar organic compound emissions profile. While the identified portion of the exhaust emissions from catalyst-equipped vehicles mainly consists of *n*-alkanoic acids, the identified fraction of the organic fine particulate emissions from non-catalyst vehicles is dominated by polycyclic aromatic hydrocarbons (PAH). In contrast diesel exhaust emissions show a strong preference for *n*-alkanes. The identified compounds present in particles from products such as brake linings

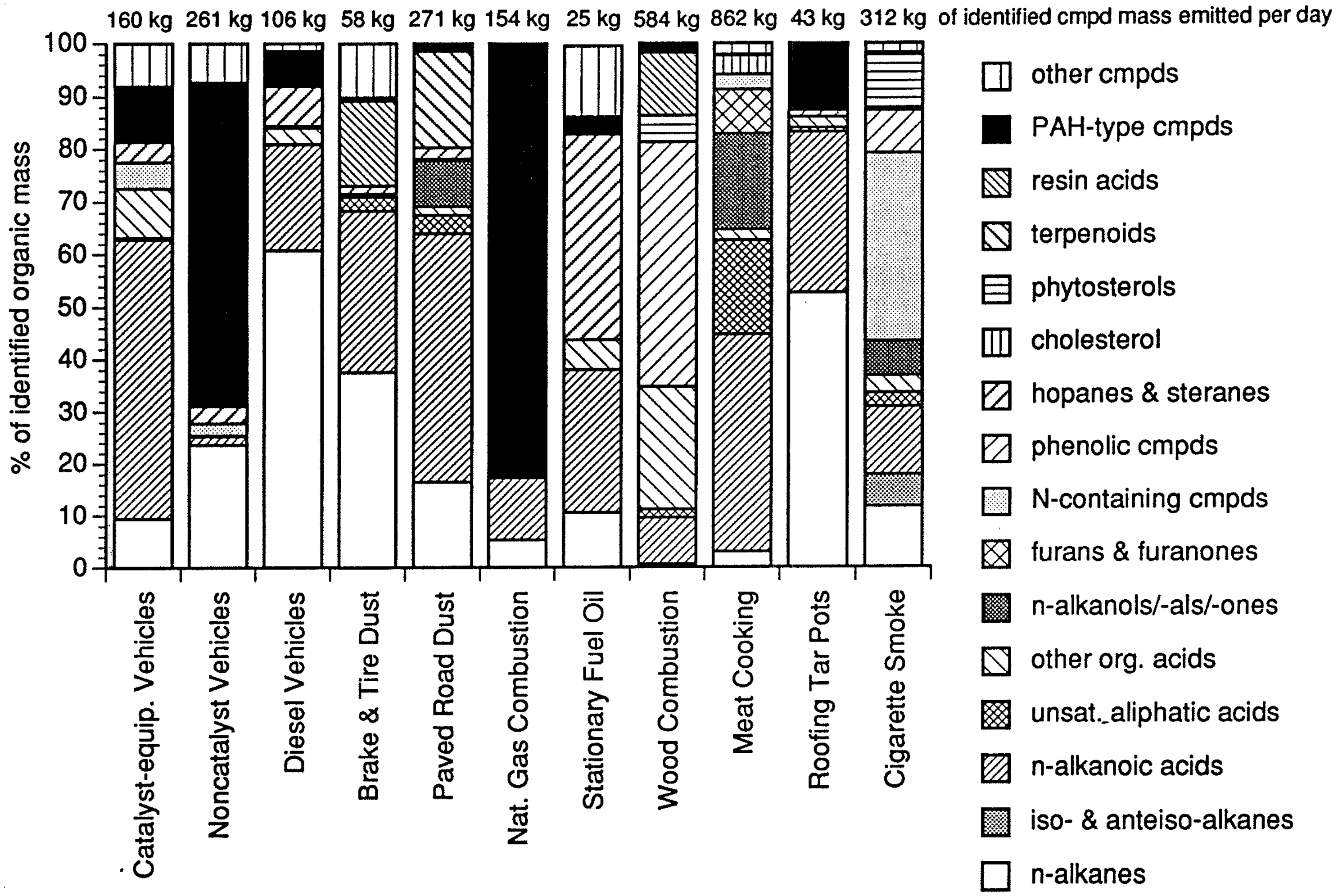


Figure 12.2: Compound class distributions of the organics that can be identifed as single compounds emitted from the 11 source categories

and car tires, together as a source category, are dominated by *n*-alkanes, *n*-alkanoic acids, and resin acids. Fine particulate paved road dust reveals an organic composition similar to ambient fine particle samples with *n*-alkanoic acids as the major identified compound class (Rogge et al., 1993c). Although very low in fine particulate emission rates, natural gas combustion aerosols consist to an appreciable fraction (22.5% of total fine particle mass; more than 80% of identified compound mass) of PAH, oxy-PAH, aza-arenes, and thia-arenes (Rogge et al., 1993e). Stationary sources burning fuel oil, such as electric utility boilers, industrial boilers, and others, show relatively low total OC-emissions (154.9 kg of fine particulate OC per day), and the identified compound mass emitted is low as well (25 kg/day). Most of the identified compound mass emitted from boilers consists of *n*-alkanoic acids and fossil petroleum markers such as hopanes and steranes. More than 85% of the hopanes and steranes emitted to the study area are released from vehicular exhaust emissions. The rest comes mainly from paved road dust and to a small extent from tire wear debris and asphalt roofing tar pots.

Burning wood in domestic fireplaces is the third largest source of fine particulate OC (see Table 12.1), and is the second largest source in terms of identified compound mass emitted per day (584 kg/day). The identified compounds consist mainly of phenolic type compounds that are breakdown products derived from wood lignin (see Rogge et al., 1993i). Resin acids are the next most prominent compound class in wood smoke emissions (Rogge et al., 1993i; Simoneit et al., 1993).

Meat cooking, the source category with the highest daily fine particulate OC-emission rates, also shows the largest amount of identifiable compound mass

(862 kg/day). *n*-Alkanoic acids and their unsaturated homologues such as oleic ($C_{18:1}$) and palmitoleic ($C_{16:1}$) acids are by far the dominant compound classes emitted, responsible for more than 60% of the identified compound mass.

The last two source categories in Figure 12.2 are asphalt roofing tar pots and cigarette smoke. Roofing tar pot emissions (Rogge et al., 1993g) are dominated by *n*-alkanes, *n*-alkanoic acids, and PAH-type compounds. N-containing heterocyclic compounds such as pyridine alkaloids (e.g., nicotine) make up the largest portion of the identified compounds in cigarette smoke, followed by several other compound classes including source specific *iso*- and *anteiso*-alkanes (Rogge et al., 1993f).

Ambient Concentrations vs. Daily Emission Rates for Single Aerosol Organic Compounds

In the study by Gray (1986), a known stable tracer, elemental carbon (EC), was used to confirm transport calculations. In the current study, single organic compounds are tracked that may be partitioned between the gas-phase and the aerosol-phase and whose chemical stability in the urban atmosphere often is unknown. Therefore, it is useful at the outset of the present work to examine the source and ambient data sets for evidence that the two data sets are or are not clearly related to one another.

One possible method to deduce qualitative information regarding single organic compound stability is to graphically compare the daily organic compound emission rates with ambient concentration data on a compound by compound basis. Discrepancies between these two data sets can occur due to the following reasons: (1) not all emissions sources are yet considered; (2) the most volatile compounds might partition to the gas-phase in the presence of diurnal temperature variations; (3) semi-volatile compounds might react preferentially in the gas-phase causing a net flux from the particle-phase to the gas-phase as concentrations re-equilibrate; and (4) heterogeneous chemical reactions might occur on the particle surface itself causing a loss of certain reactive compounds. Very limited knowledge presently exists concerning the atmospheric stability of semi-volatile and reactive non-volatile organic compounds. The current study will provide at least a qualitative examination of the likely stability of such compounds.

Figures 12.3a and 12.3b show the primary emissions of single organic compounds in kg/day released to the atmosphere of the Los Angeles study area. The annual mean ambient compound concentrations averaged over all measurements made at West Los Angeles, downtown Los Angeles, and Pasadena throughout the entire year 1982 are shown on the same graph. The alignment of the emissions and ambient concentration axes is arbitrary; no air quality modeling calculations are involved here. Included in these figures are most of the organic compounds identified in the year long study of ambient air quality detailed in Chapter 2 along with the respective compounds released from the source types investigated (Rogge et al.,1991, 1993a-i).

Figure 12.3a shows that organic compounds such as the *n*-alkanes, *iso*- and *anteiso*-alkanes, higher molecular weight *n*-alkanoic acids, and fossil petroleum compounds including hopanes and steranes, display changes in relative emission rates between compounds that are quite similar to the measured relative abundance of such compounds in ambient air. This indicates that such particle-bound compounds are relatively stable chemically at least for the time that it takes for

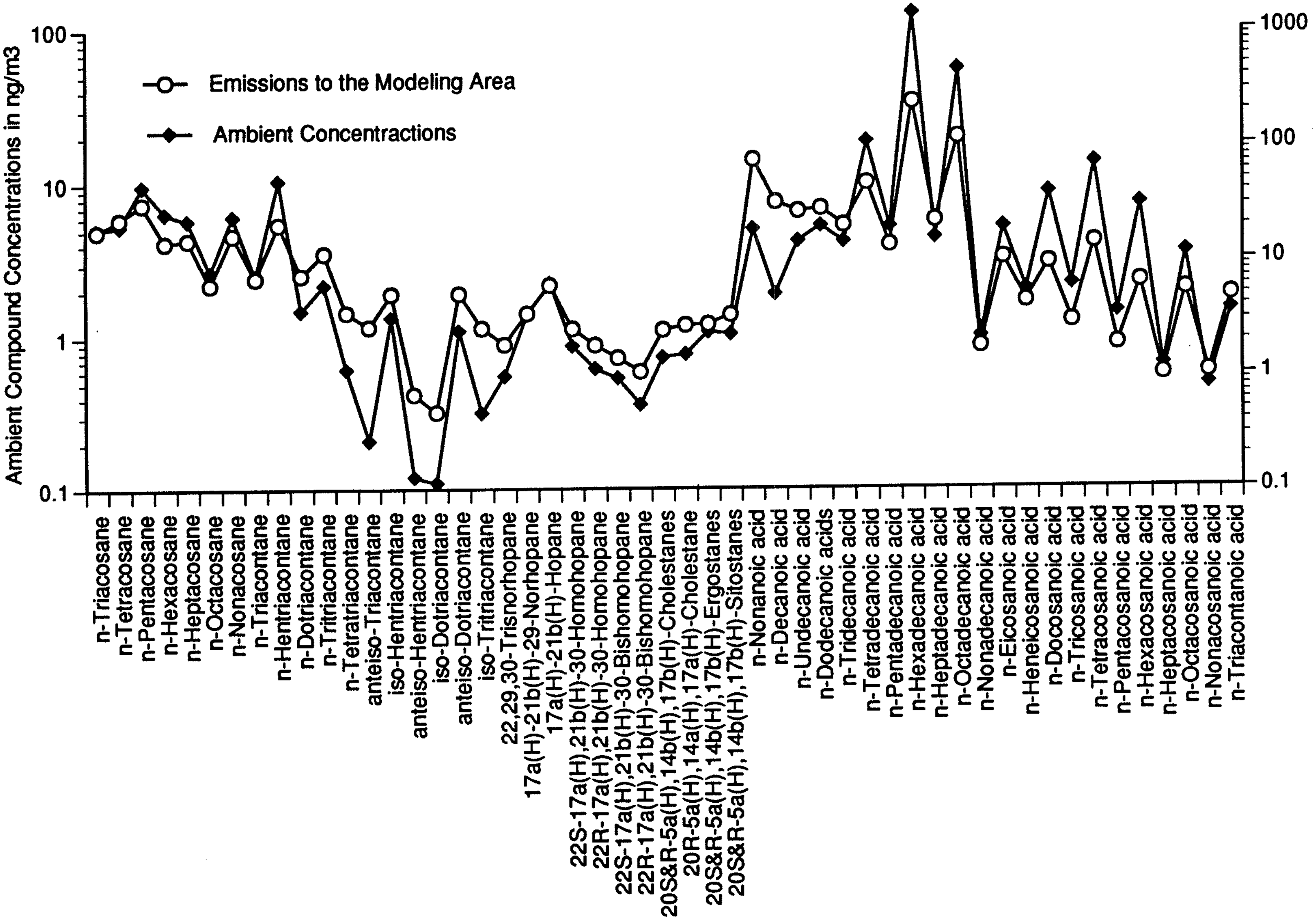


Figure 12.3a: Comparison between compound emission rates and ambient concentrations

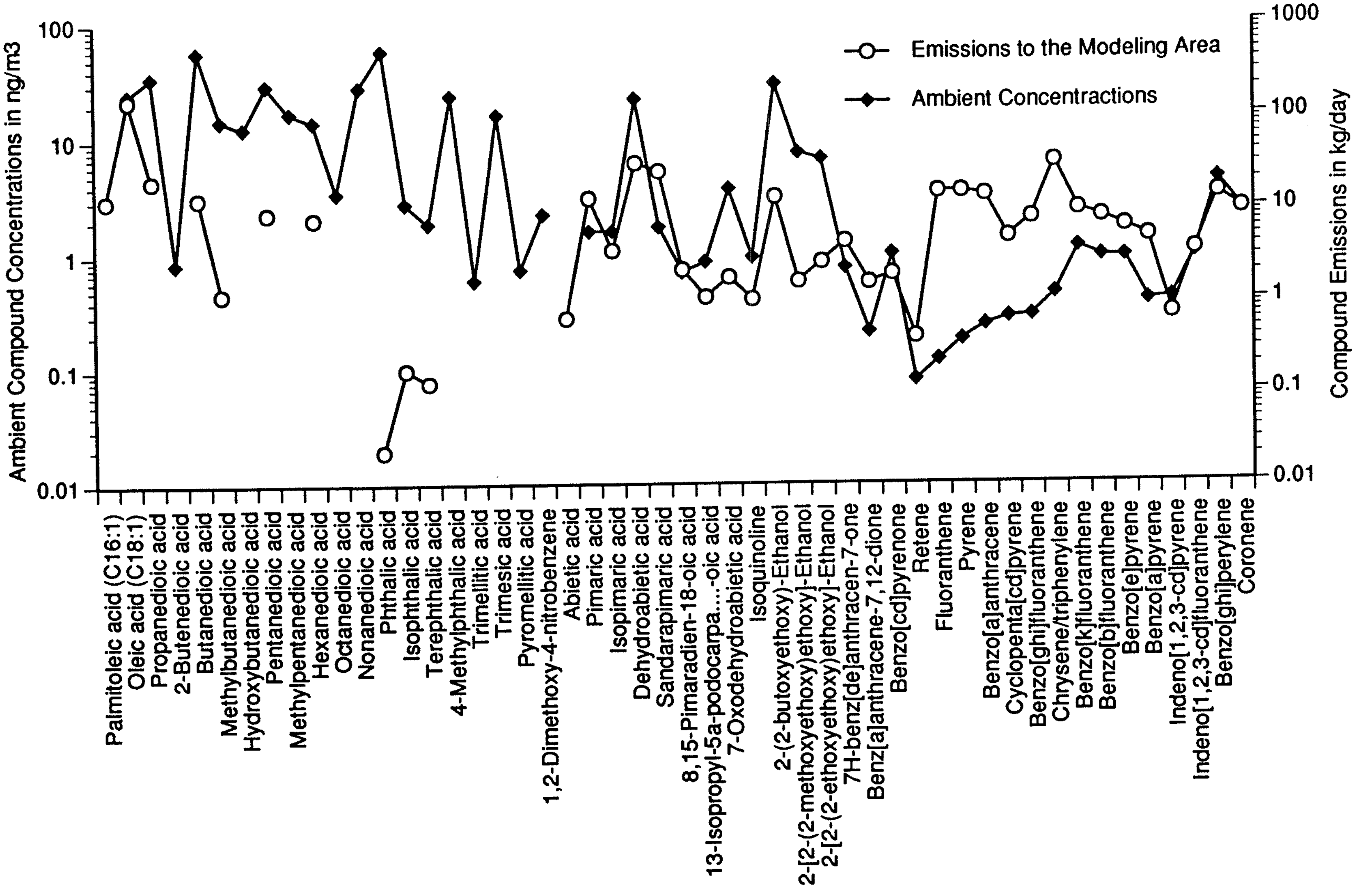


Figure 12.3b: Comparison between compound emission rates and ambient concentrations

the transport from the sources to the ambient monitoring sites. For lower molecular weight *n*-alkanoic acids ($C_9 - C_{14}$), the emission profile is somewhat elevated compared to the ambient concentration profile. Possibly, such low molecular weight *n*-alkanoic acids are lost from the fine aerosol-phase via volatilization or chemical reaction.

Palmitoleic acid ($C_{16:1}$) and oleic acid ($C_{18:1}$), are two unsaturated fatty acids that are mainly released from meat cooking operations within the current emission inventory. While oleic acid was identified in the atmospheric aerosol samples, palmitoleic acid was not found (see Figure 12.3b). This difficulty in measuring palmitoleic acid in the atmosphere could either be due to its low emission rate compared to oleic acid, or due to its higher volatility and possible degradation in the gas-phase, or due to heterogeneous attack on the double-bond by ozone or other radicals yielding in part aliphatic dicarboxylic acids as suggested by several researchers (e.g., Kawamura and Kaplan, 1987; Killops, 1986).

Aliphatic dicarboxylic acids and aromatic polycarboxylic acids have been quantified in the ambient aerosol characterization study conducted by Rogge et al. (1993a). Both compound classes are important due to their possible formation by chemical reactions in the atmosphere (Grosjean, 1977; Grosjean and Friedlander, 1980; Grosjean and Seinfeld, 1989; Hatakeyama et al., 1985, 1987; Rogge et al., 1993a; Tao and McMurry, 1989). During the source emission characterization campaign, aliphatic dicarboxylic and aromatic polycarboxylic acids have been found only in trace amounts in the emissions of some of the sources tested. Accordingly, the ambient compound concentration profile is not matched at all by the source emission profile as indicated in Figure 12.3b. This in turn suggests that such aliphatic and aromatic polycarboxylic acids are indeed of secondary origin, formed by atmospheric chemical processes.

Moving to the right in Figure 12.3b, the next group of compounds, resin acids, are mainly released during the combustion of pine wood in fireplaces in Southern California. Abietic acid is released only in small amounts and therefore is below detection in the ambient samples. Polyalkylene glycol ethers (e.g., 2-(2-butoxyethoxy)-ethanol), that are typically used as hydraulic fluids (e.g., in vehicle braking systems; Rogge et al., 1993c), show a pattern of relative concentrations that is similar between the sources and ambient data but the absolute magnitude of the ambient concentrations seems to exceed the known emission rates. This suggests that there are sources of these compounds other than brake dust.

While higher molecular weight PAH such as indeno[1,2,3-cd]pyrene, indeno-[1,2,3-cd]fluoranthene, benzo[ghi]perylene, and coronene show close agreement between ambient concentration and emission rate data, lower molecular weight PAH (e.g., fluoranthene, pyrene and others) show concentrations significantly lower than emission data would suggest. This suggests that such low moleculer weight PAH may preferably degrade in the gas-phase by photochemical processes and radical attack (Kamens et al., 1990; Pitts et al., 1969, 1978, 1980, 1985; Lane and Katz, 1977; Van Cauwenberghe, 1983) which leads in turn to further volatilization of such particle-phase associated PAH in the attempt to restore the gas-/particle-phase equilibrium. Alternatively, the low molecular weight PAH may be degraded by heterogeneous chemical reactions between gas-phase oxidants and particle-phase PAH.

Observed vs. Predicted Organic Compound Concentrations

Ambient concentrations of fine particle-associated organic compounds that are emitted from 41 urban sources are predicted using a mathematical model that simulates release to and transport in the urban atmosphere. Fine particulate road dust contributions are estimated separately using a source/receptor modeling approach based on Al and Si as tracers for the soil content of road dust as outlined earlier. The ambient fine organic aerosol source contributions from each of these 42 urban sources are superimposed onto background organic aerosol concentrations measured upwind of Los Angeles at San Nicolas Island. Model predictions for West Los Angeles, downtown Los Angeles, and Pasadena are singled out and compared against actual measured data. To simplify the visual presentation of these results, the 42 source types modeled have been collected into the 12 groups of similar sources outlined in Table 12.2.

The air quality model treats all organic compound emissions as if they were chemically stable in the atmosphere. Hence, (1) the "perfect model" would predict ambient concentration levels of "stable" organic compounds that match perfectly the measured ambient concentrations. In contrast, (2) if chemically reactive organic compounds are emitted that degrade rapidly in the atmosphere then the present model which tracks dispersion alone will produce higher predicted ambient concentrations than are actually observed. Further, (3) organic compounds that are found in only trace amounts in primary source emissions, but that are measured in substantial quantities in the urban atmosphere must be the result of atmospheric chemical formation from gas-phase precursor compounds (secondary aerosol).

In the discussion that follows, model performance will be judged by comparison of predicted to observed concentrations of the most stable organic compounds considered. Compounds that decay by reaction in the atmosphere and compounds that are formed from gas phase precursors will be discussed as two separate categories, where the degree of atmospheric transformation can be judged by comparison to the model result that would have been obtained in the absence of any atmospheric chemical reactions.

Including Vegetative Detritus as an Additional Source

Leaves of plants and trees show a waxy surface layer that when magnified consists of waxy protrusions of micron and submicron dimensions. When entrained into the atmosphere due to the action of wind and weather, such fine particulate leaf surface abrasion products show a characteristic predominance of odd over even carbon numbered *n*-alkanes, typically with highest concentrations for the C_{29}, C_{31}, and C_{33} *n*-alkanes. This concentration pattern is more or less preserved in ambient fine particulate matter. Similarly, such leaf abrasion products reveal a characteristic predominance of even over odd carbon numbered *n*-alkanoic acids (Rogge et al., 1993d).

While the emission rate of vegetative detritus to the atmosphere is not yet known, the magnitude of the concentration increment present due to this source can be estimated based on the presence in the atmosphere of high molecular weight *n*-alkanes that show the odd carbon number predominance characteristic of plant waxes. In this study, model predictions for *n*-alkanes are first calculated by including within the transport model all sources except vegetative detritus emissions. Figures 12.4a,b and Figures 12.5a,b show the observed versus predicted annual mean ambient *n*-alkane concentrations at West Los Angeles and

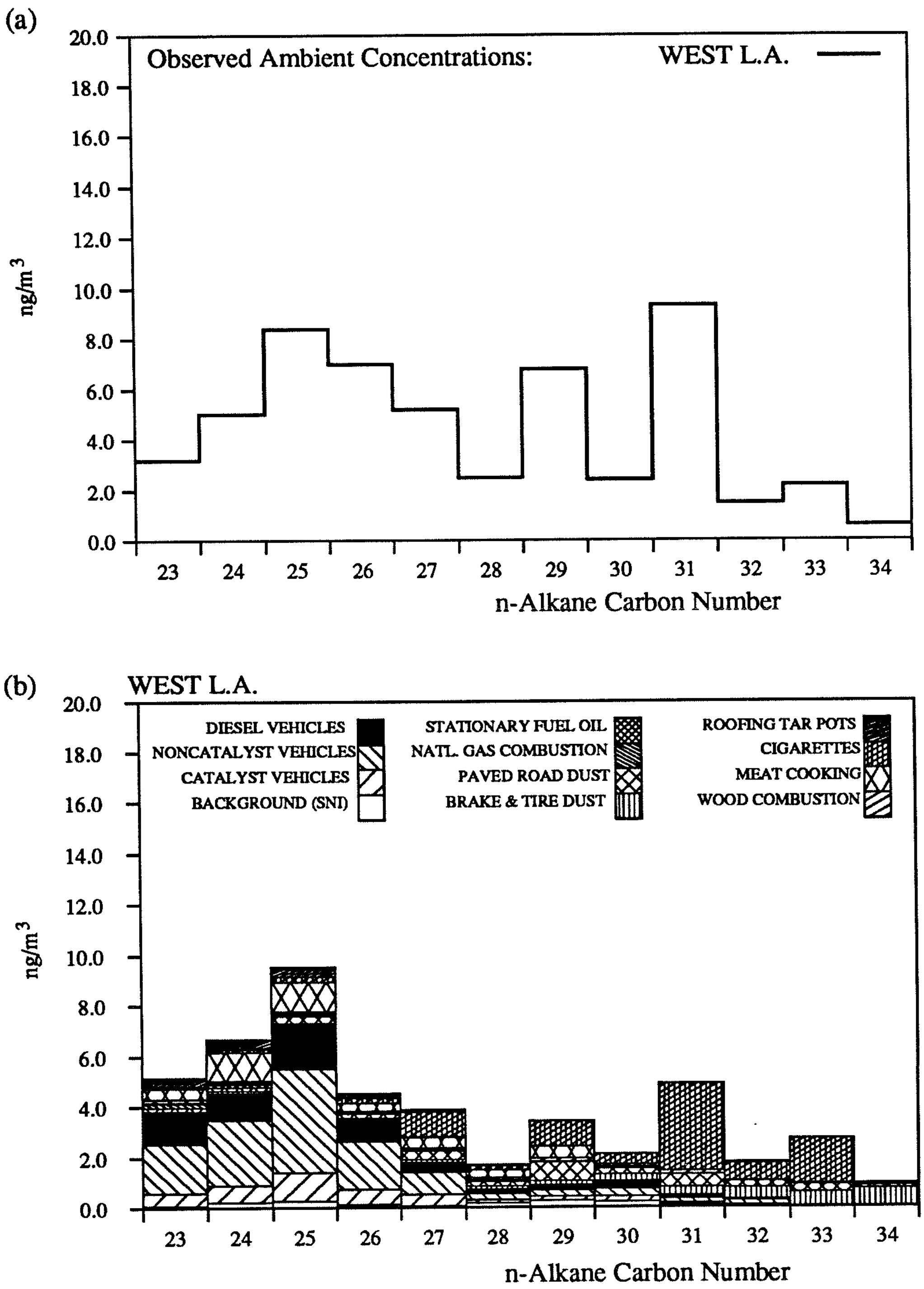


Fig. 12.4: Annual mean n-alkane concentrations at West Los Angeles (1982): (a) observed, (b) source contributions predicted in the absence of the input from vegetative detritus.

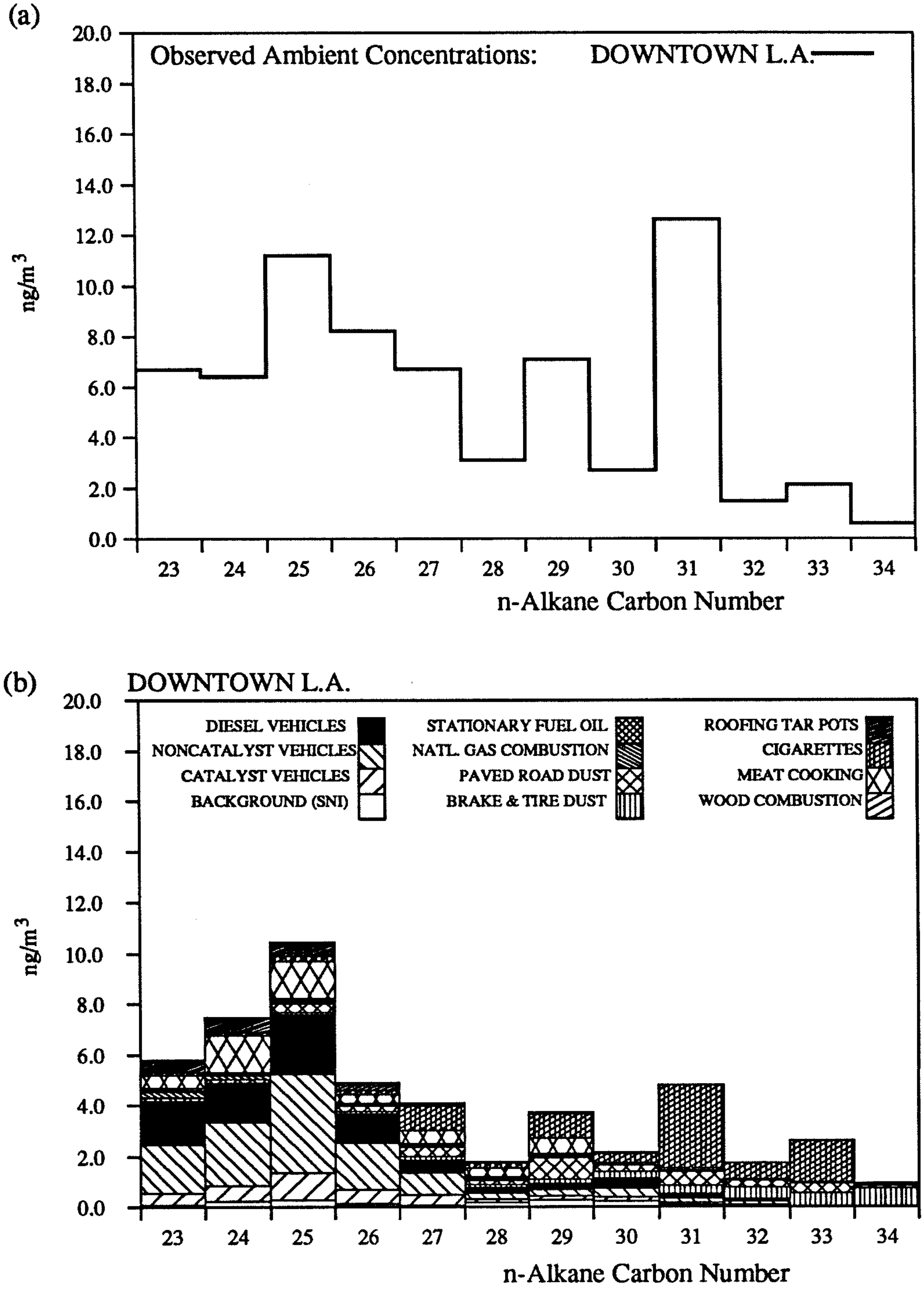


Fig. 12.5: Annual mean n-alkane concentrations at downtown Los Angeles (1982): (a) observed, (b) source contributions predicted in the absence of the input from vegetative detritus.

downtown Los Angeles that would prevail without vegetative detritus contributions. Comparing the measured and estimated ambient *n*-alkane concentrations, it can be seen that the predicted concentrations of lower molecular weight *n*-alkanes (up to C_{27}) compare well with measurements from the three sampling sites (Pasadena not shown). In contrast, the measured concentrations of the C_{29} and C_{31} *n*-alkanes are appreciably higher than those predicted by the model, indicating, as expected, that an important contribution from vegetative detritus is missing.

To derive an estimate of the fine particulate leaf surface abrasion products contributions to the ambient aerosol complex, the following approach has been chosen: the distribution of C_{28} to C_{34} *n*-alkanes present in the emissions of green leaf abrasion products is matched against the difference between measured minus predicted ambient *n*-alkane concentrations. The fitting process was conducted by least squares regression analysis for each month at each site. The ambient concentrations of all other organic compounds that are emitted as part of the leaf abrasion products are determined in proportion to the C_{28} – C_{34} *n*-alkane content attributed to leaf abrasion products, and these concentration increments are then added to the respective predicted ambient compound concentrations.

Alkanes

Figures 12.6a and 12.6b show air quality model predictions of the annual mean source contributions to *n*-alkane concentrations including the estimated contributions from vegetative detritus (12 source categories). The *n*-alkanes considered here fall into two groups according to their origin. *n*-Alkanes $< C_{27}$ mainly originate from sources burning fossil fuels, while *n*-alkanes $> C_{27}$ come to an appreciable extent from cigarette smoke and leaf surface abrasion products.

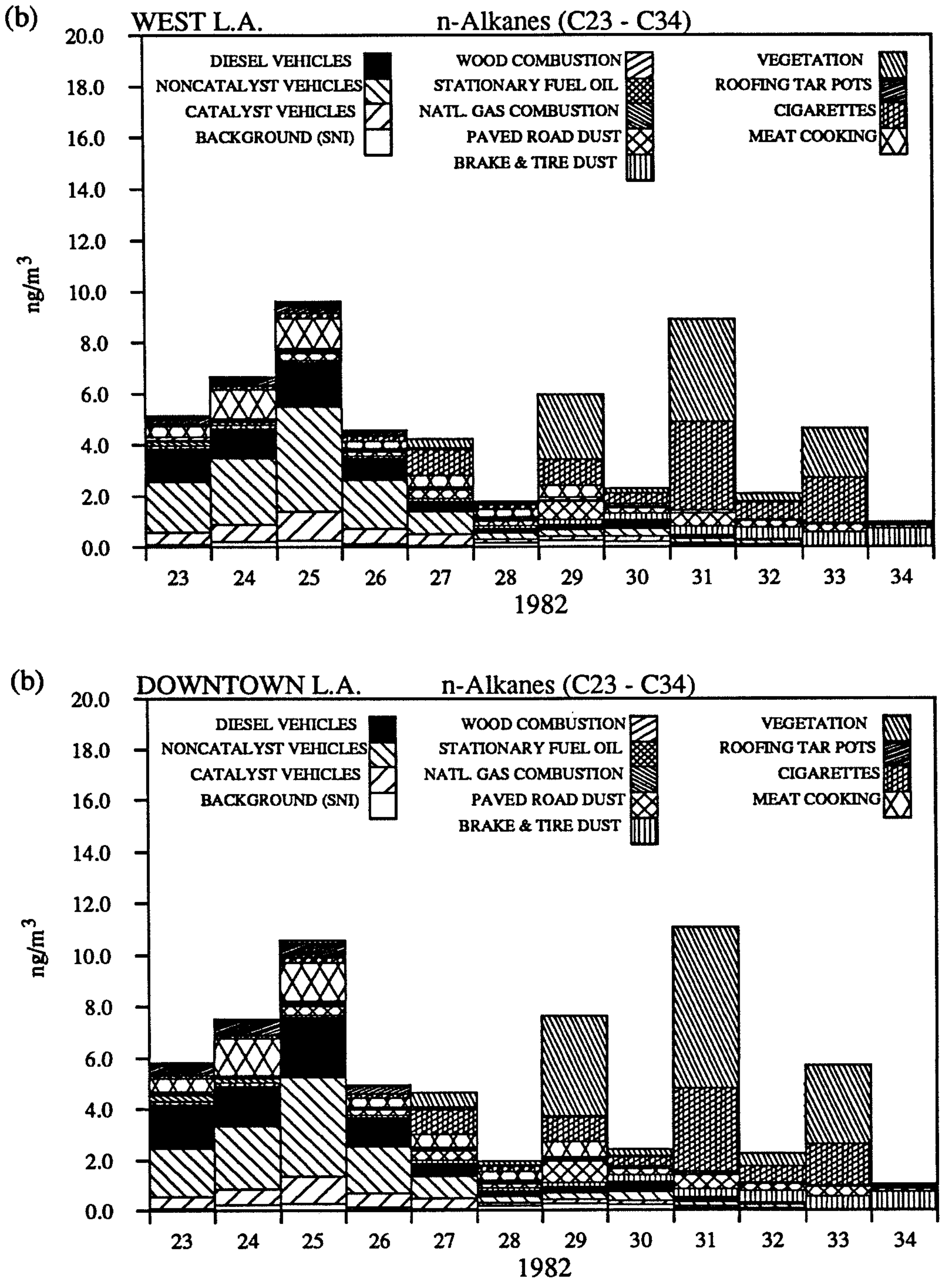


Fig. 12.6: Annual mean *n*-alkane concentration predictions including contributions from vegetative detritus (1982): (a) West Los Angeles, (b) downtown Los Angeles.

While the C_{29} and C_{31} n-alkane concentration predictions fit well with the respective measured ambient concentrations, the concentration of the C_{33} n-alkane is overpredicted by roughly a factor of two. This discrepancy results from the fact that the leaf composites from which the vegetative detritus source sample was generated (made up of 62 plant species typically found in the Los Angeles area; Rogge et al., 1993d) show a relatively higher C_{33} n-alkane concentration than is observed in the Los Angeles urban atmosphere.

The time series of predicted monthly averaged total n-alkane (C_{23} – C_{34}) concentration predictions are compared to the measured concentrations for the entire year 1982 at West Los Angeles (Figure 12.7a,b), downtown Los Angeles (Figure 12.8a,b), and Pasadena (Figure 12.9a,b). At West Los Angeles (Figures 12.7a,b), the predicted total n-alkane concentrations agree very well with the observations, with little overprediction in late summer and small underprediction in November and December. The major source categories contributing include all three vehicle types tested, cigarette smoke, and leaf abrasion products from urban vegetation. At downtown Los Angeles (Figures 12.8a,b), the measured total n-alkane concentrations are appreciably higher during January, November, and December than predicted. At Pasadena, both predicted and measured total n-alkane concentration profiles show, except during January, a rather flat ambient concentration pattern. Note by reference to Figure 12.1 and to the prior discussion that the uncertainty of the monthly means of the measured concentrations in the winter months is quite high and that the differences between predicted and observed concentrations may not be statistically significant.

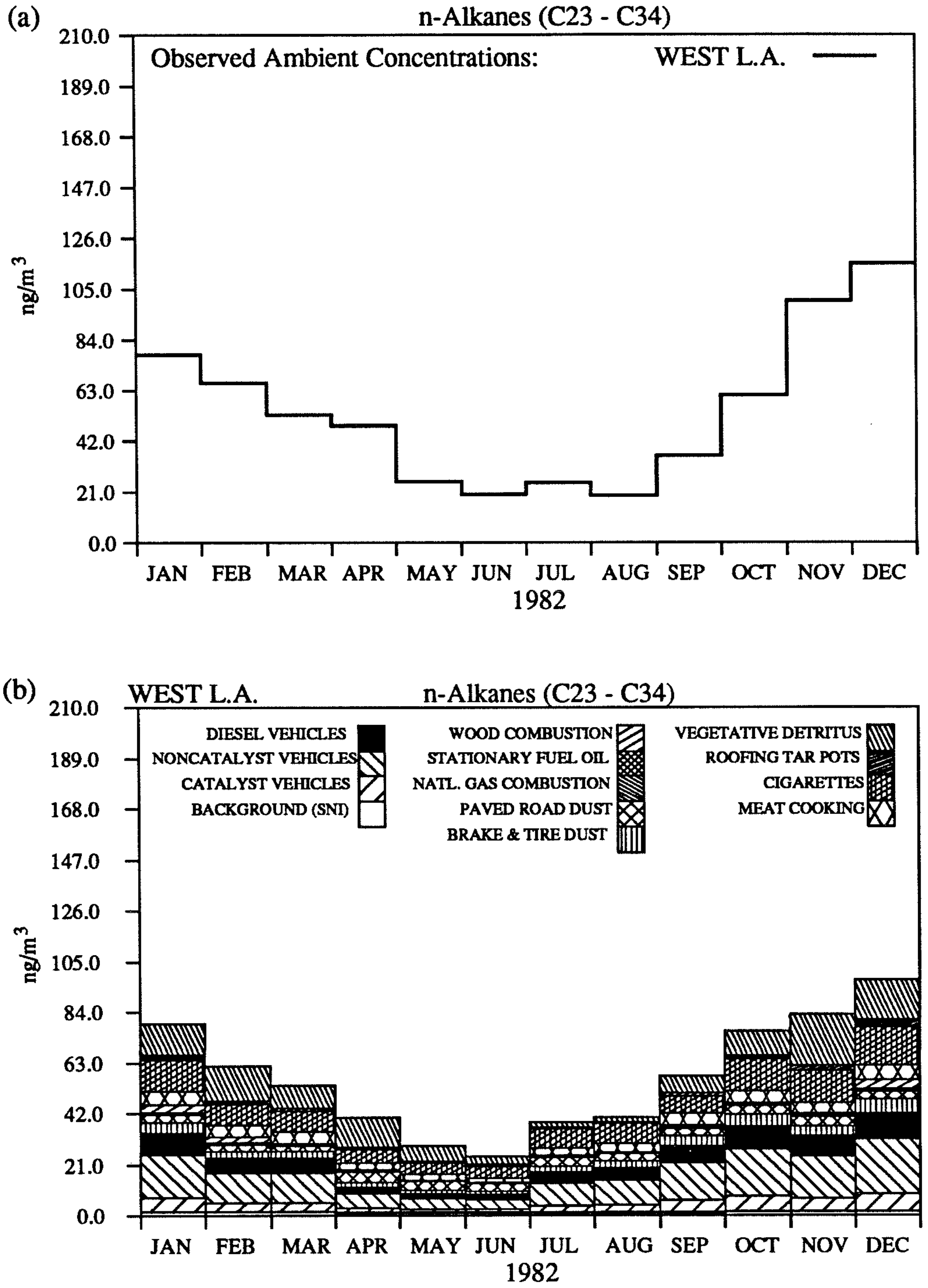


Fig. 12.7: Monthly mean n-alkane concentrations at West Los Angeles (1982): (a) observed, (b) predicted source contributions.

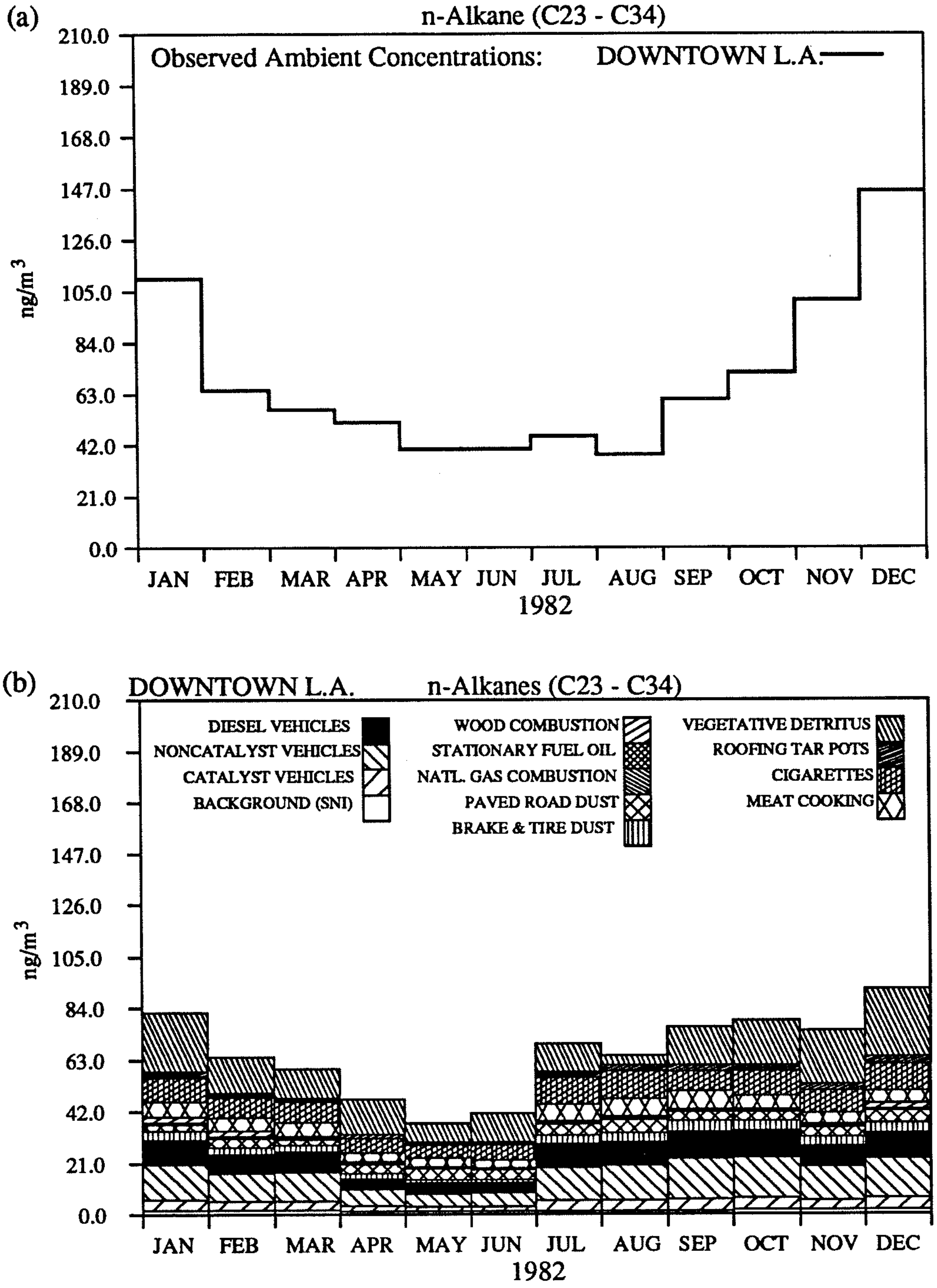


Fig. 12.8: Monthly mean n-alkane (C_{23} - C_{34}) concentrations at Downtown Los Angeles (1982): (a) observed, (b) predicted source contributions.

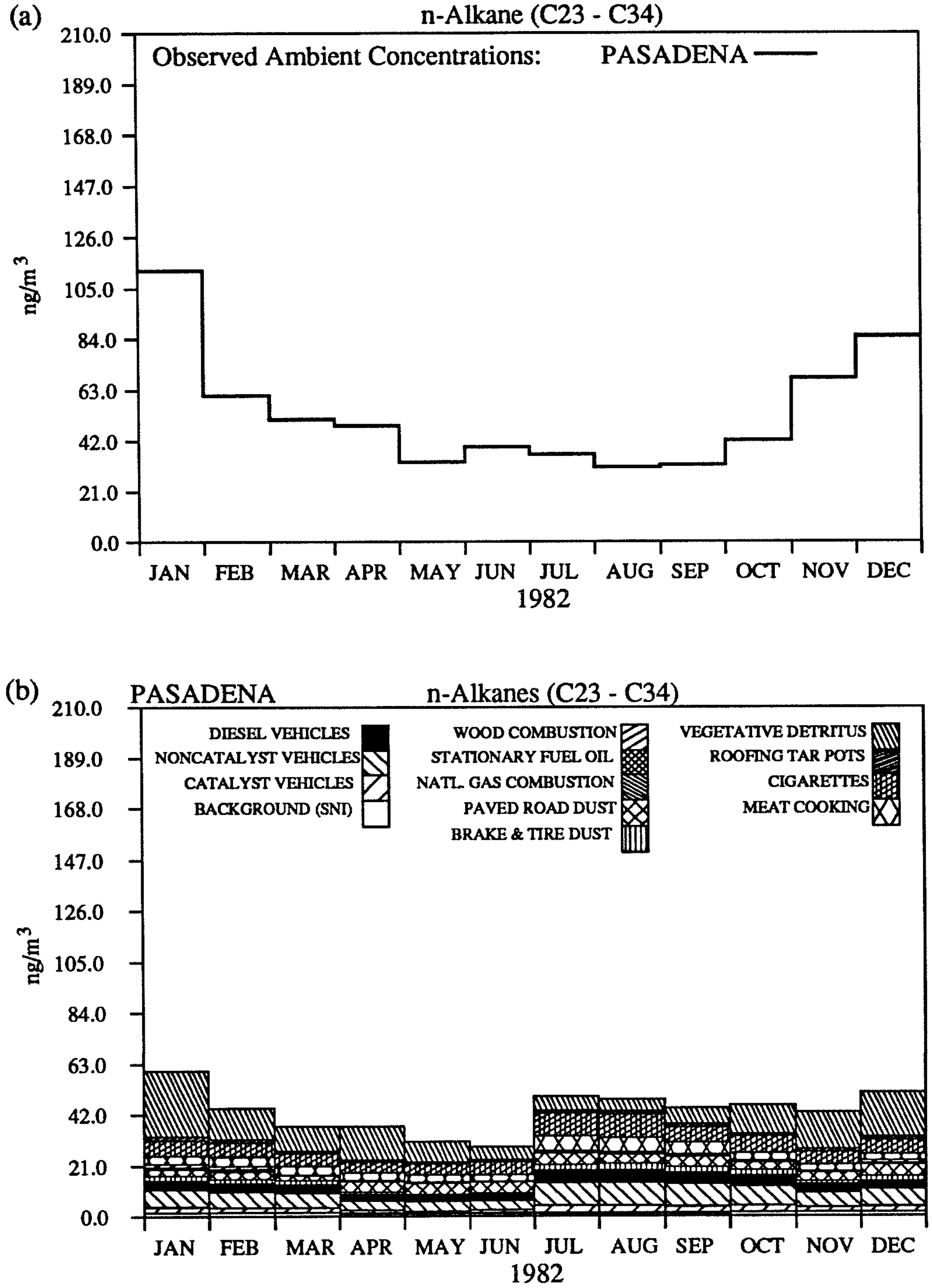


Fig. 12.9: Monthly mean *n*-alkane (C_{23} - C_{34}) concentrations at Pasadena (1982): (a) observed, (b) predicted source contributions.

Single *n*-alkane emissions fall into two source groups (fossil fuel combustion $< C_{27}$; cigarette smoke and vegetative detritus $> C_{27}$). Within each group the *n*-alkanes show very similar concentration patterns.

Figures 12.10a,b – 12.12a,b show the observed and predicted concentrations of *n*-pentacosane (C_{25}), the major fossil fuel combustion derived *n*-alkane. Comparing the observed with predicted *n*-pentacosane concentrations at each of the sites, typically reasonably good agreement exists except during January, November, and December at downtown Los Angeles and Pasadena, where the nominal measured concentrations are higher than predicted. Again, it is important to recall that the uncertainty of the measured ambient values in these winter months is unusually high.

n-Hentriacontane, the most prominent member of the second source group (cigarette smoke and release of leaf surface abrasion products) shows a seasonal concentration pattern with less pronounced summer/winter differences than was observed for *n*-pentacosane (compare Figures 12.13a,b to 12.15a,b). Surprisingly, cigarette smoke adds amounts of higher molecular weight *n*-alkanes to the urban atmosphere that are comparable to the contributions from vegetative detritus. Despite different release mechanisms, these compounds originate from the leaf surface waxes in both cases.

Recently, Rogge et al. (1993f) isolated higher molecular weight branched alkanes in cigarette smoke that reveal a unique concentration pattern not matched by any other known sources in Los Angeles. Hence, these higher molecular weight branched alkanes with *iso*-hentriacontane and *anteiso*-dotriacontane as the most prominent members were proposed as possible markers that can be used to trace cigarette smoke in the urban atmosphere. The model predictions shown in Figures 12.16a,b – 12.18a,b reveal good agreement between observed and predicted *iso*-hentriacontane and *anteiso*-dotriacontane concentrations, supporting previous source attribution calculations for ambient outdoor cigarette smoke (Rogge et al., 1993f).

Polycyclic Aromatic Hydrocarbons

Synthesized during incomplete combustion of fossil and contemporary renewable fuels (e.g., wood), particle-bound polycyclic aromatic hydrocarbons (PAH) are released to the atmosphere with fine particulate matter of micron and submicron dimensions (e.g., Katz and Chan, 1980; Miguel and Friedlander, 1978; Leuenberger et al., 1988; Albagli et al., 1974; Van Vaeck et al., 1979). PAH have received appreciable attention due to their mutagenic and carcinogenic potential and their ubiquitous distribution within the biosphere (e.g., Bingham et al., 1980; IARC, 1989; La Voie et al., 1979, 1985). To determine the stability of such compounds in the urban atmosphere, PAH have been exposed to OH, O_3, NO, NO_2, N_2O_5 and other oxidants and likewise to UV solar radiation (Brorström et al., 1983; Kamens et al., 1990; Nielson, 1988; Pitts et al., 1969, 1978, 1980, 1985; Khan et al., 1967; Kummler et al., 1969; Lane and Katz, 1977; Van Cauwenberghe, 1983; Grosjean, 1983; Fox and Olive, 1979; Inscoe, 1964). These studies were conducted either with the test PAH deposited on glass, on alumina, on silica gel, or on filter materials made of glass, quartz or Teflon. Several other researchers have examined the decomposition of PAH contained in coal fly ash, diesel smoke, or wood smoke particles using outdoor smog chambers, fluidized bed photoreactors and other devices that keep the particulate matter suspended in air while exposing it to oxidants and UV radiation. (e.g., Daisey et al., 1982; Kamens et al., 1984, 1986, 1990; Korfmacher et al., 1980, 1981).

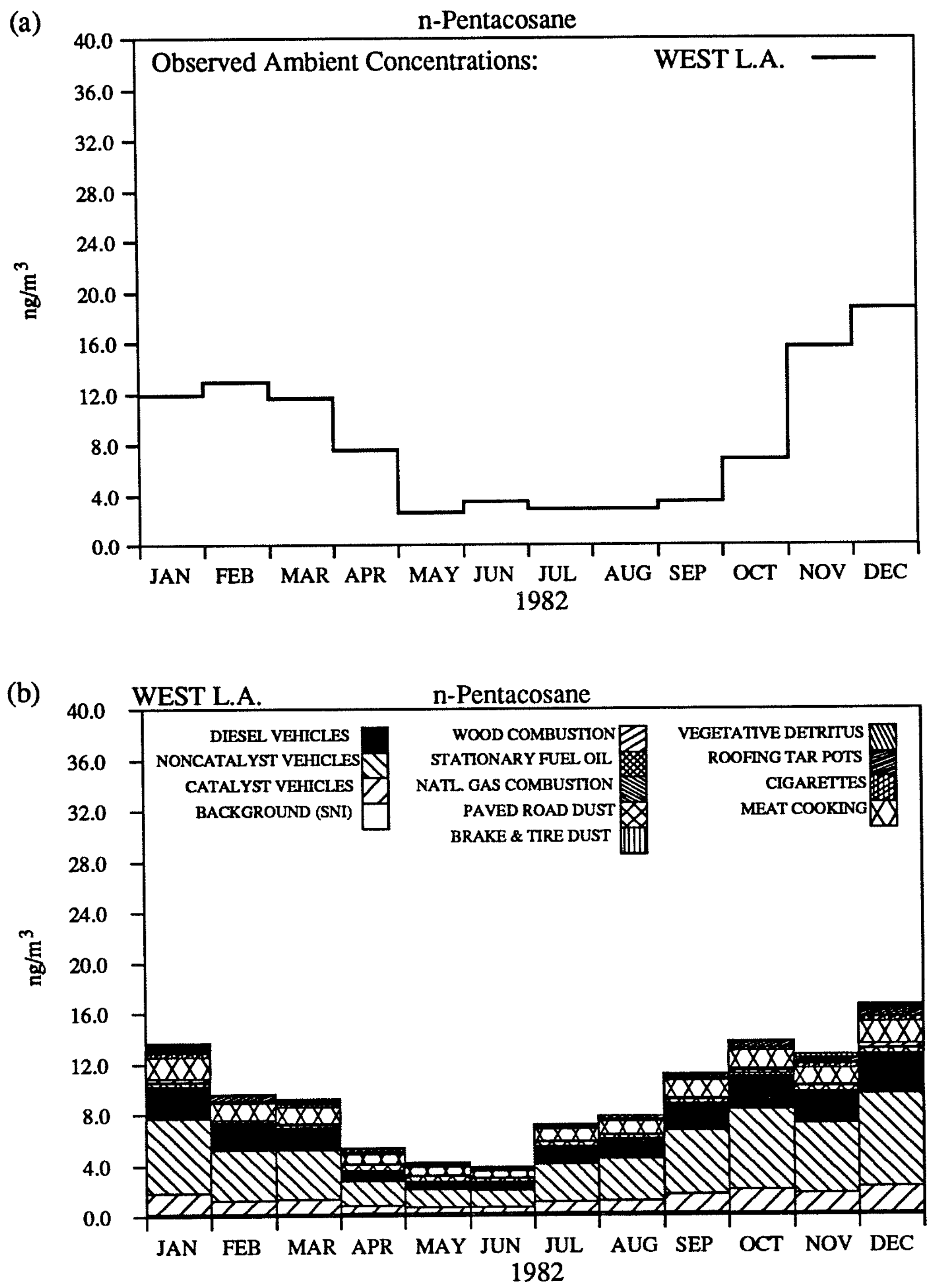


Fig. 12.10: Monthly mean n-pentacosane (C_{25}) concentrations at West Los Angeles (1982): (a) observed, (b) predicted source contributions.

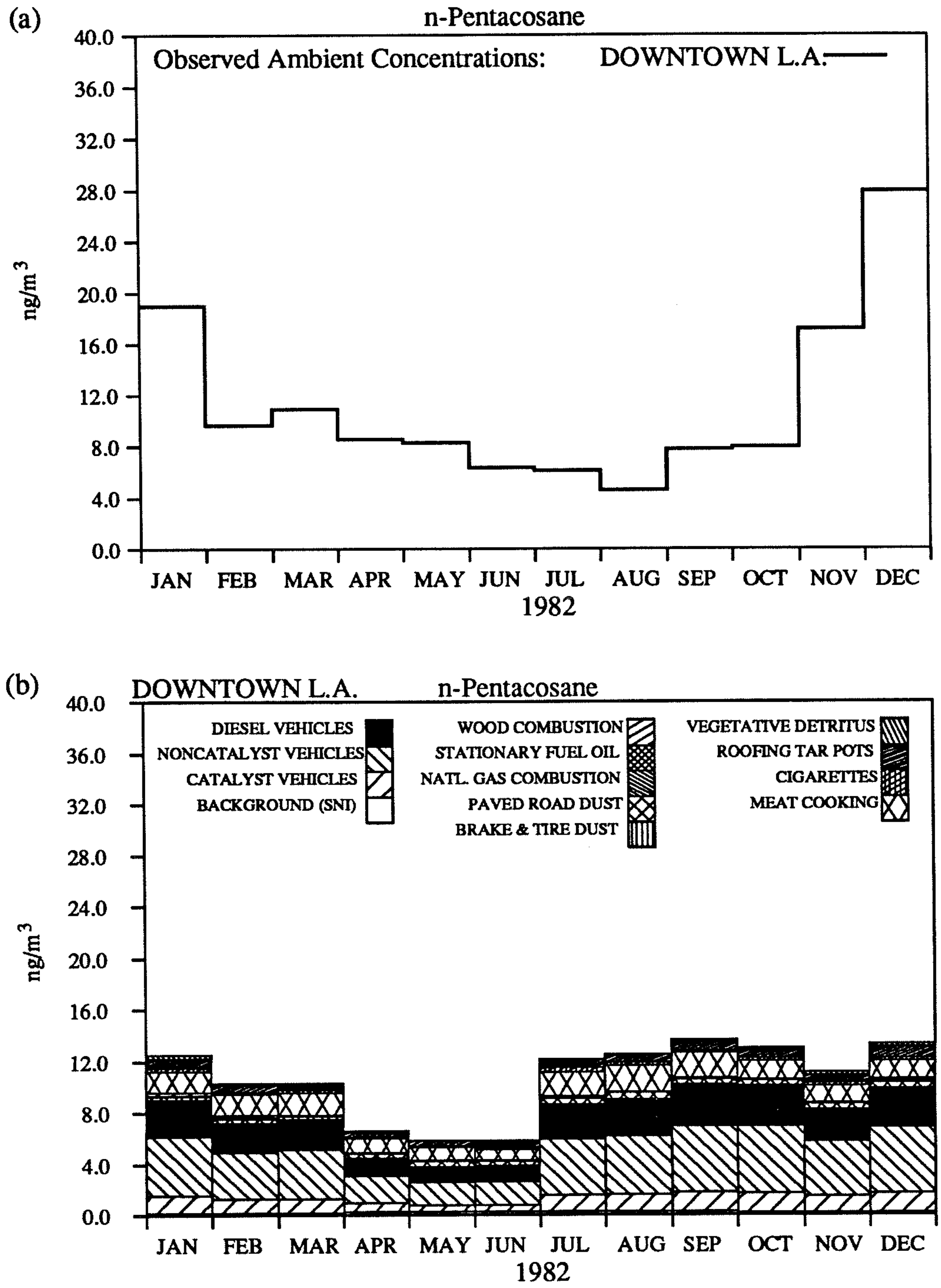


Fig. 12.11: Monthly mean *n*-pentacosane (C_{25}) concentrations at Downtown Los Angeles (1982): (a) observed, (b) predicted source contributions.

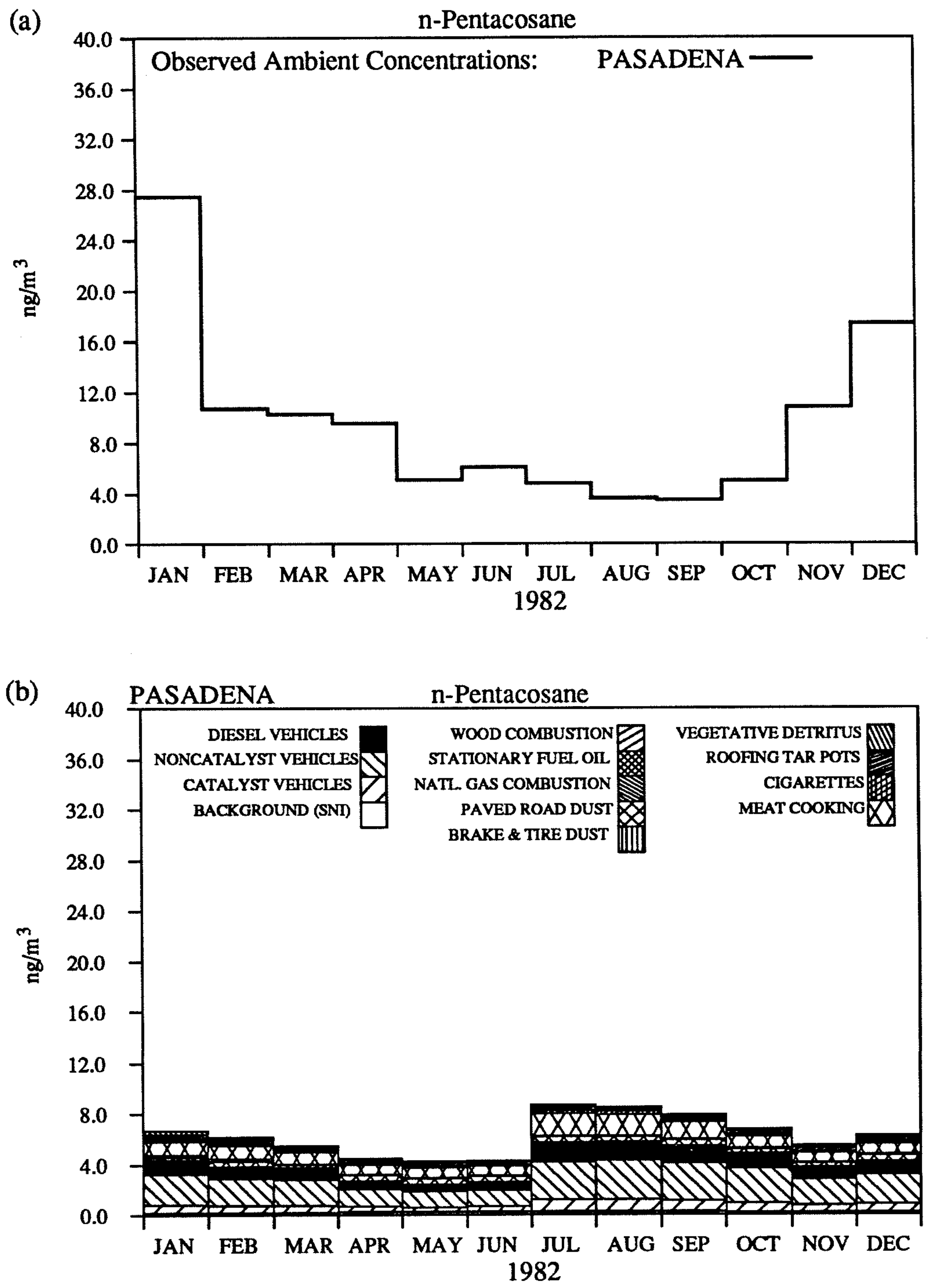


Fig. 12.12: Monthly mean *n*-pentacosane (C_{25}) concentrations at Pasadena (1982): (a) observed, (b) predicted source contributions.

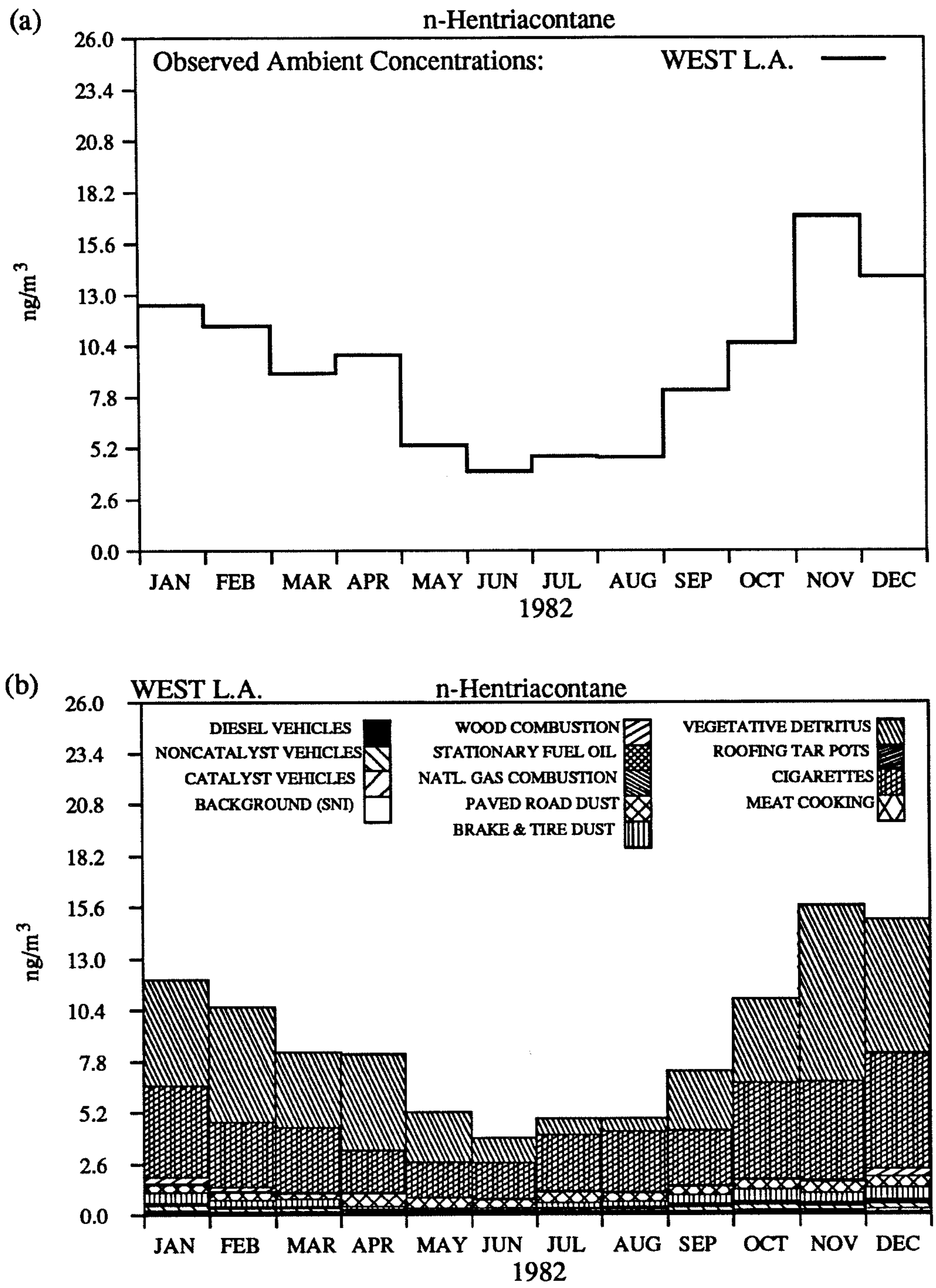
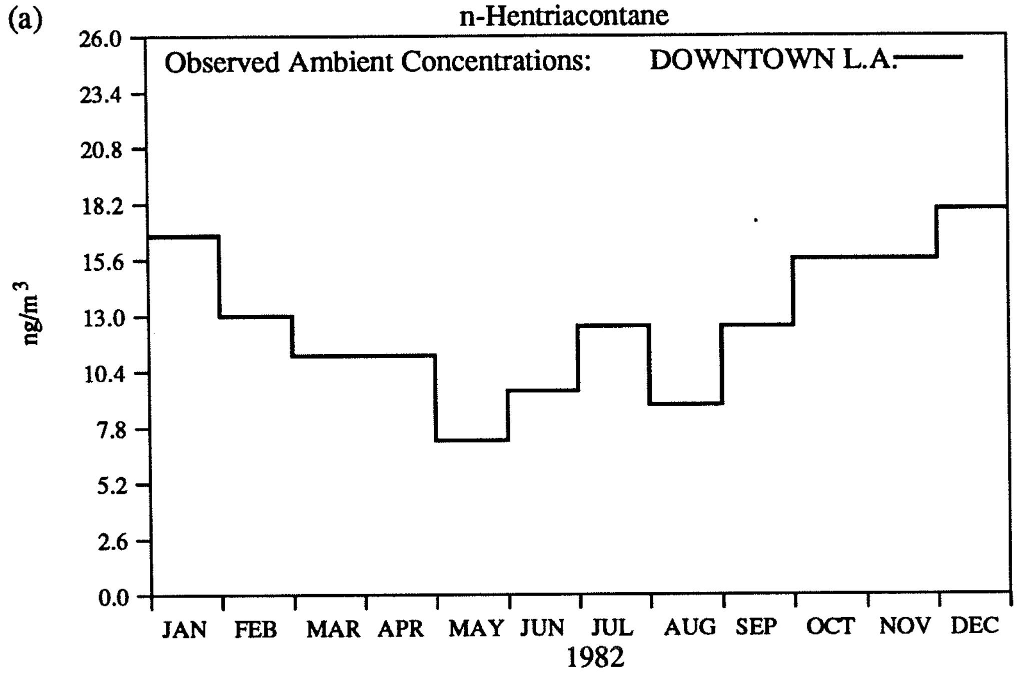


Fig. 12.13: Monthly mean n-hentriacontane (C_{31}) concentrations at West Los Angeles (1982): (a) observed, (b) predicted source contributions.



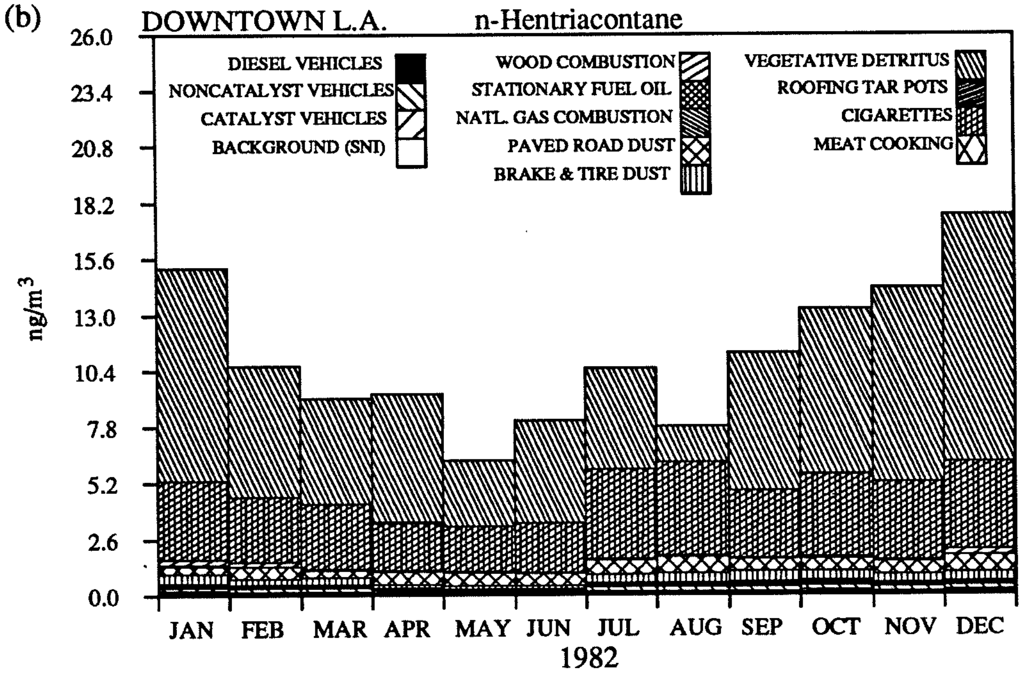


Fig. 12.14: Monthly mean *n*-hentriacontane (C_{31}) concentrations at Downtown Los Angeles (1982): (a) observed, (b) predicted source contributions.

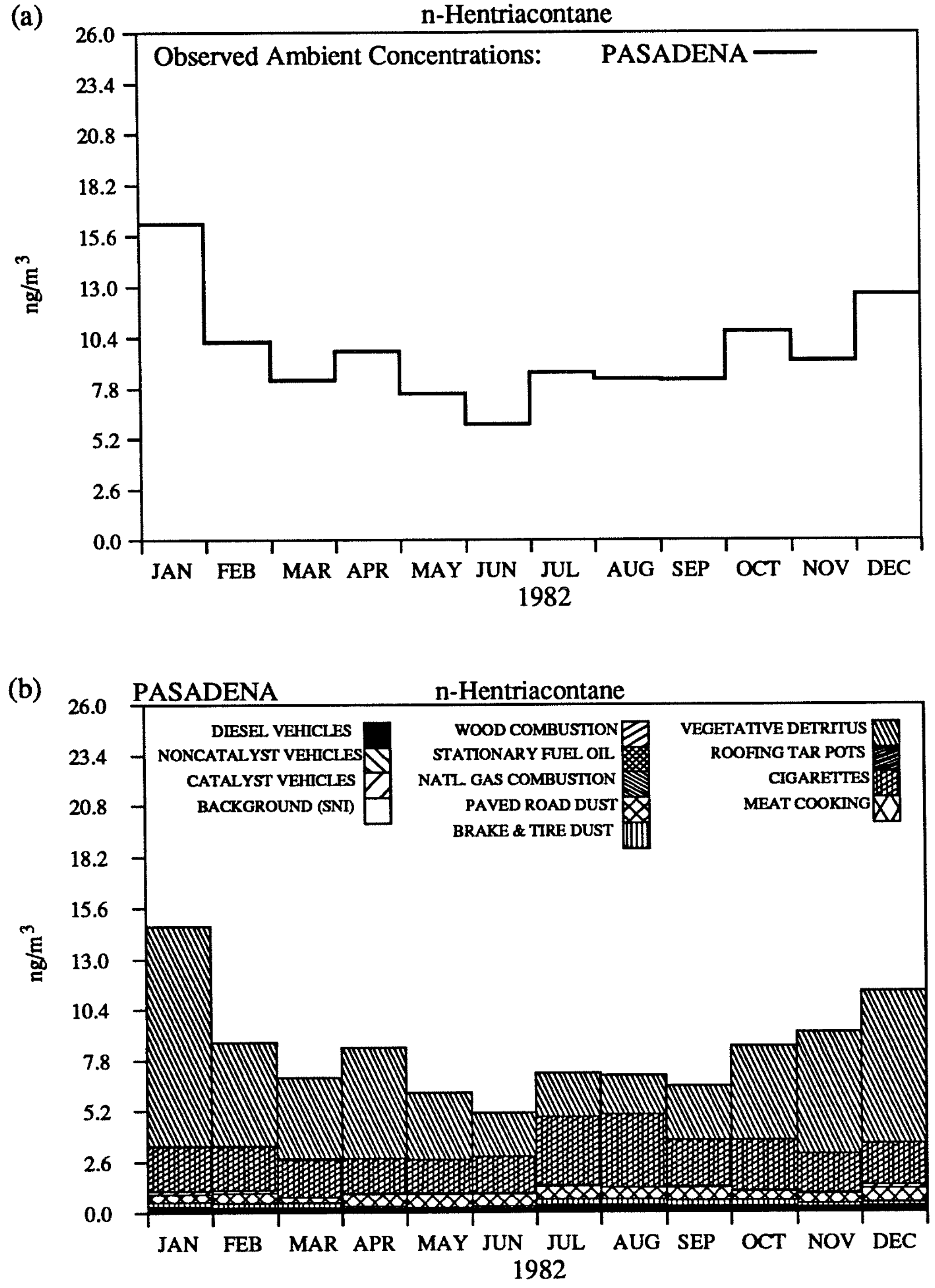


Fig. 12.15: Monthly mean *n*-hentriacontane (C_{31}) concentrations at Pasadena (1982): (a) observed, (b) predicted source contributions.

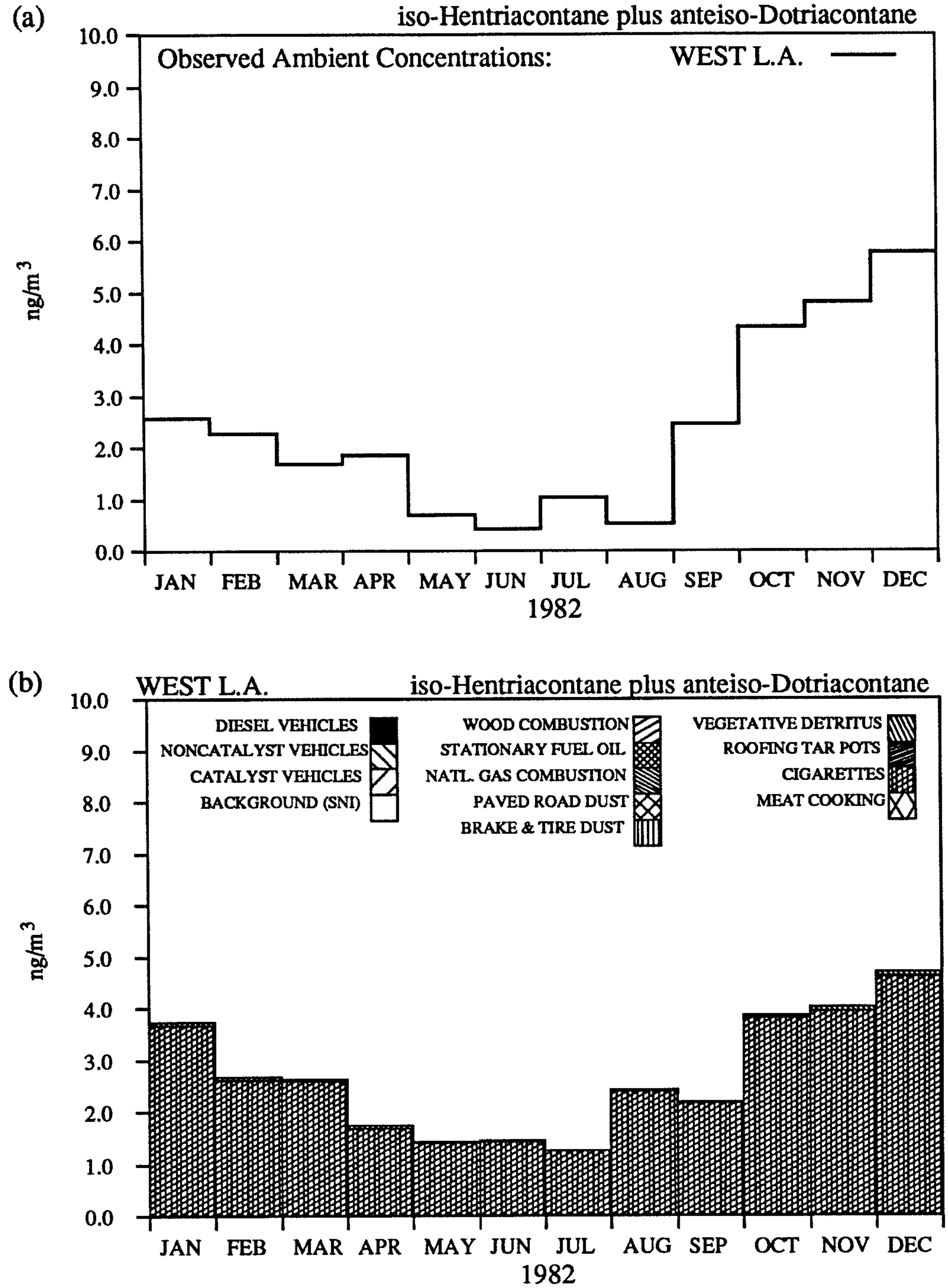


Fig. 12.16: The sum of monthly mean *iso*-hentriacontane (*iso*-C_{31}) plus *anteiso*-dotriacontane (*anteiso*-C_{32}) concentrations at West Los Angeles (1982): (a) observed, (b) predicted source contributions.

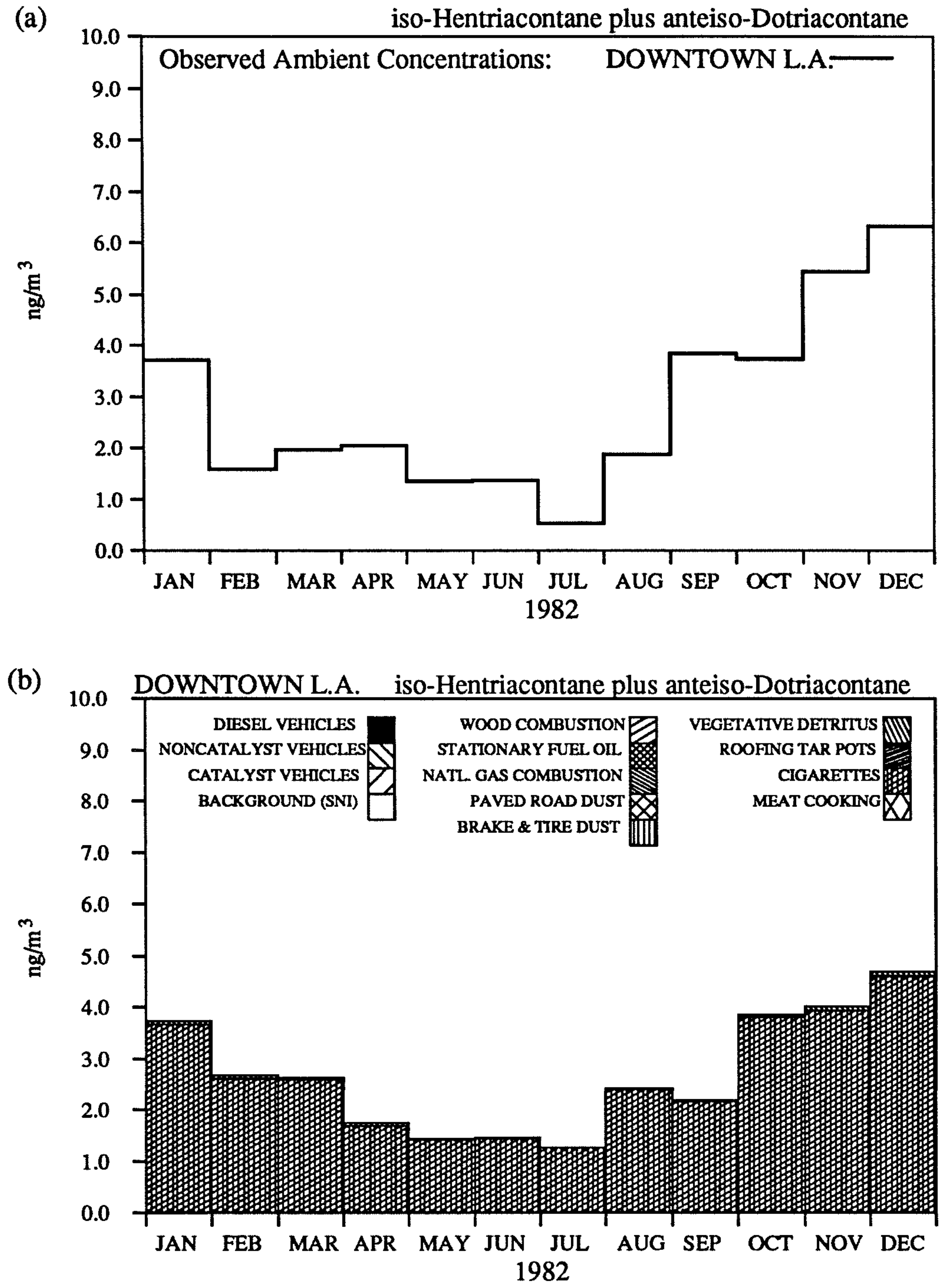


Fig. 12.17: The sum of monthly mean *iso*-hentriacontane (*iso*-C_{31}) plus *anteiso*-dotriacontane (*anteiso*-C_{32}) concentrations at Downtown Los Angeles (1982): (a) observed, (b) predicted source contributions.

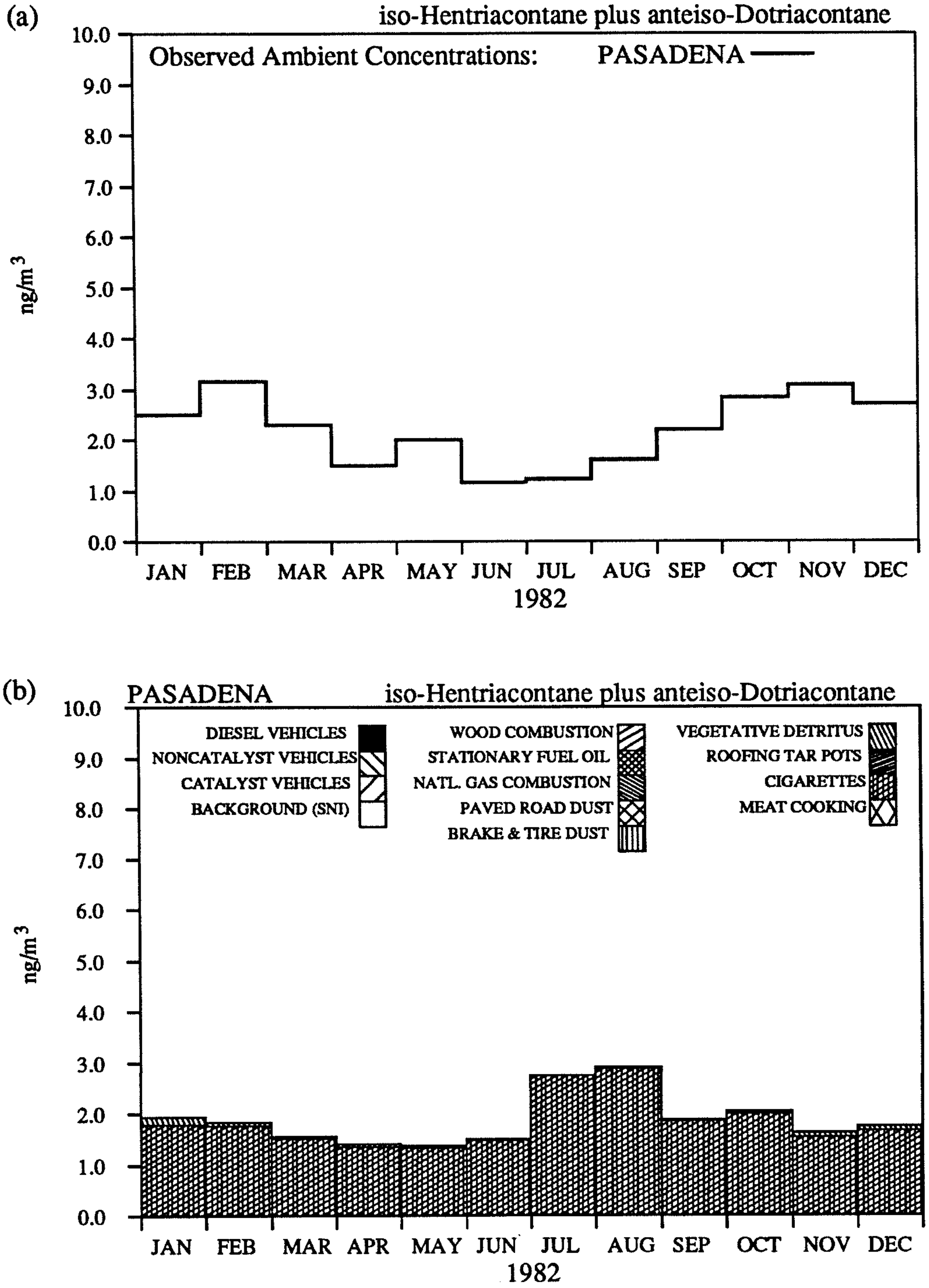


Fig. 12.18: Monthly mean *iso*-hentriacontane (*iso*-C_{31}) and *anteiso*-dotriacontane (*anteiso*-C_{32}) concentrations at Pasadena (1982): (a) observed, (b) predicted source contributions.

None of these studies distinguished PAH degradation in the gas-phase separately from heterogeneous reactions involving gas-phase attack on particle-phase organics. PAH cover a wide range of vapor pressures from $\sim 10^{-4}$ atm (naphthalene) to $\sim 10^{-15}$ atm (coronene) at 20 °C. These vapor pressures increase by approximately an order of magnitude when the ambient temperature increases by 20 °C (Murray et al., 1974). In the urban atmosphere, organic compounds with a vapor pressure of roughly 10^{-11} atm or less (at 20 °C) are exclusively found in the particle phase (Bidlemann, 1988).

If PAH degradation occurs in the gas-phase at an appreciable rate then the ambient concentrations of low molecular weight PAH could be drastically reduced in the reactive urban atmosphere over the course of one day. In contrast, PAH such as e.g., benzo[ghi]perylene and coronene that are completely in the particle-phase should be less affected by such degradation processes.

Figures 12.19a,b depict both measurements and model predictions for ambient coronene concentrations for each month during 1982 at West Los Angeles. The mathematical model predicts ambient coronene concentrations that typically approximate the measured ambient concentrations quite well except during the late summer months. The model calculations performed for inert elemental carbon (EC) and total carbon (TC) by Gray (1986) show a similar trend during late summer (compare to Figure 12.1c), suggesting that the overpredictions of primary species contributions during the summer is at least partially induced by transport calculations within the model itself. Unfortunately, the chromatographic separation of the samples acquired at the other sampling sites was stopped before coronene could elute from the column used; hence, coronene predictions for these sites can not be compared to measured ambient concentrations.

Benzo[ghi]perylene, another typical particle-phase PAH, produces a similarly good match between model predictions and measured values at West Los Angeles (see Figures 12.20a,b). At downtown Los Angeles (Figure 12.21a,b) and Pasadena (Figure 12.22a,b), the model predictions of monthly averaged benzo[ghi]perylene concentrations show a rather flat concentration profile throughout the year not matching the much higher measured winter concentrations. Both, coronene and benzo[ghi]perylene are nearly exclusively emitted from noncatalyst vehicles.

The annually averaged concentration of typical particle-phase PAH such as benzo[ghi]perylene and coronene are slightly overpredicted by the model when compared to the measured annual mean concentrations, as is displayed in Figures 12.23a,b for West Los Angeles. Lower molecular weight PAH ($\leq$ MW 252) that partition between the particle- and gas-phase show drastically depleted measured ambient concentration levels when compared to the concentrations that would be present of all particle-phase primary source emissions were conserved in the atmosphere. The discrepancy grows systematically with increasing vapor pressure. This result suggests that the highest molecular weight PAH that occur mainly in the particle phase are conserved in the atmosphere while the lower molecular weight PAH are depleted by volatilization and/or chemical reaction in the atmosphere. At downtown Los Angeles and Pasadena very similar results are found.

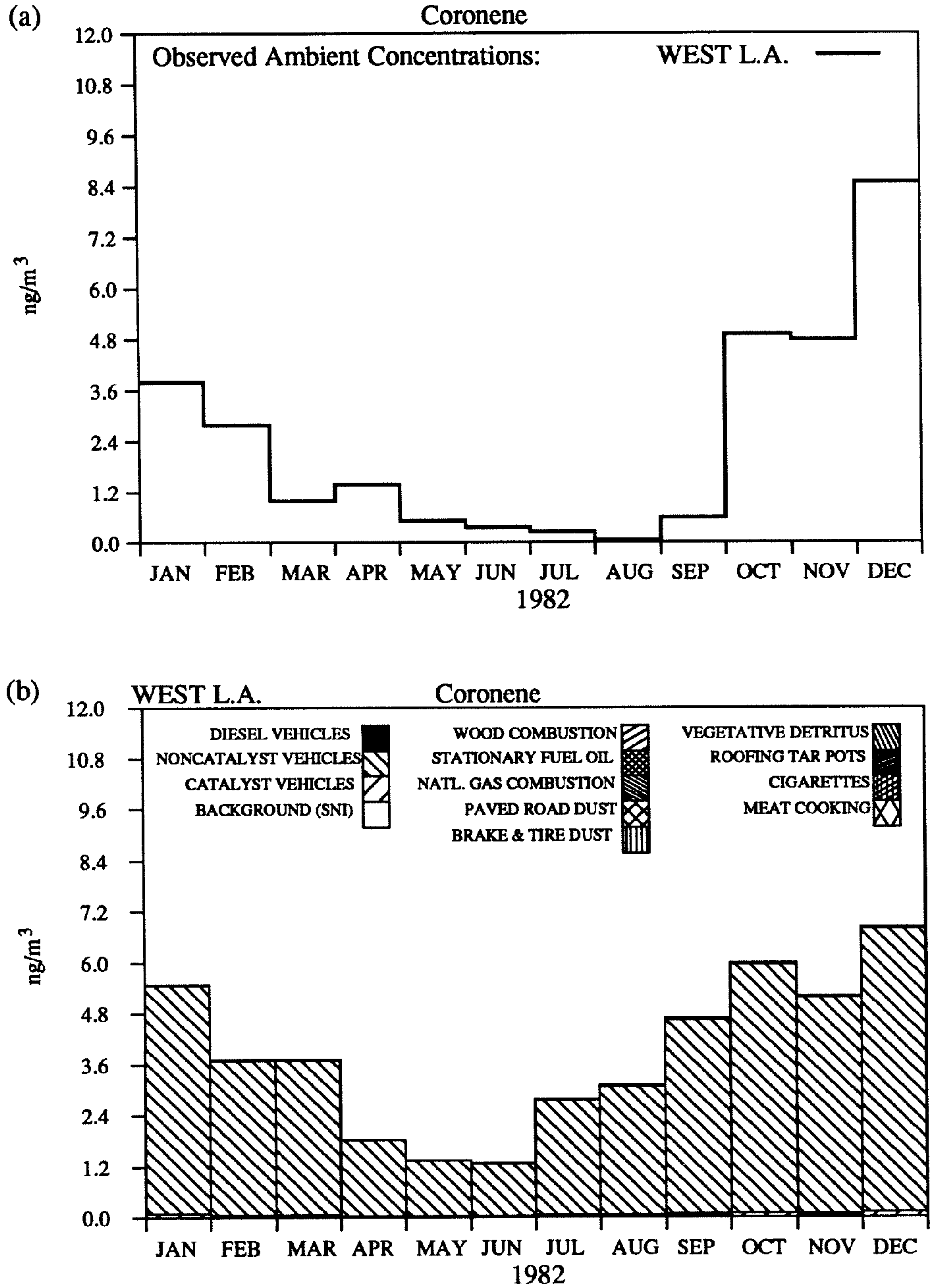


Fig. 12.19: Monthly mean coronene concentrations at West Los Angeles (1982): (a) observed, (b) predicted source contributions.

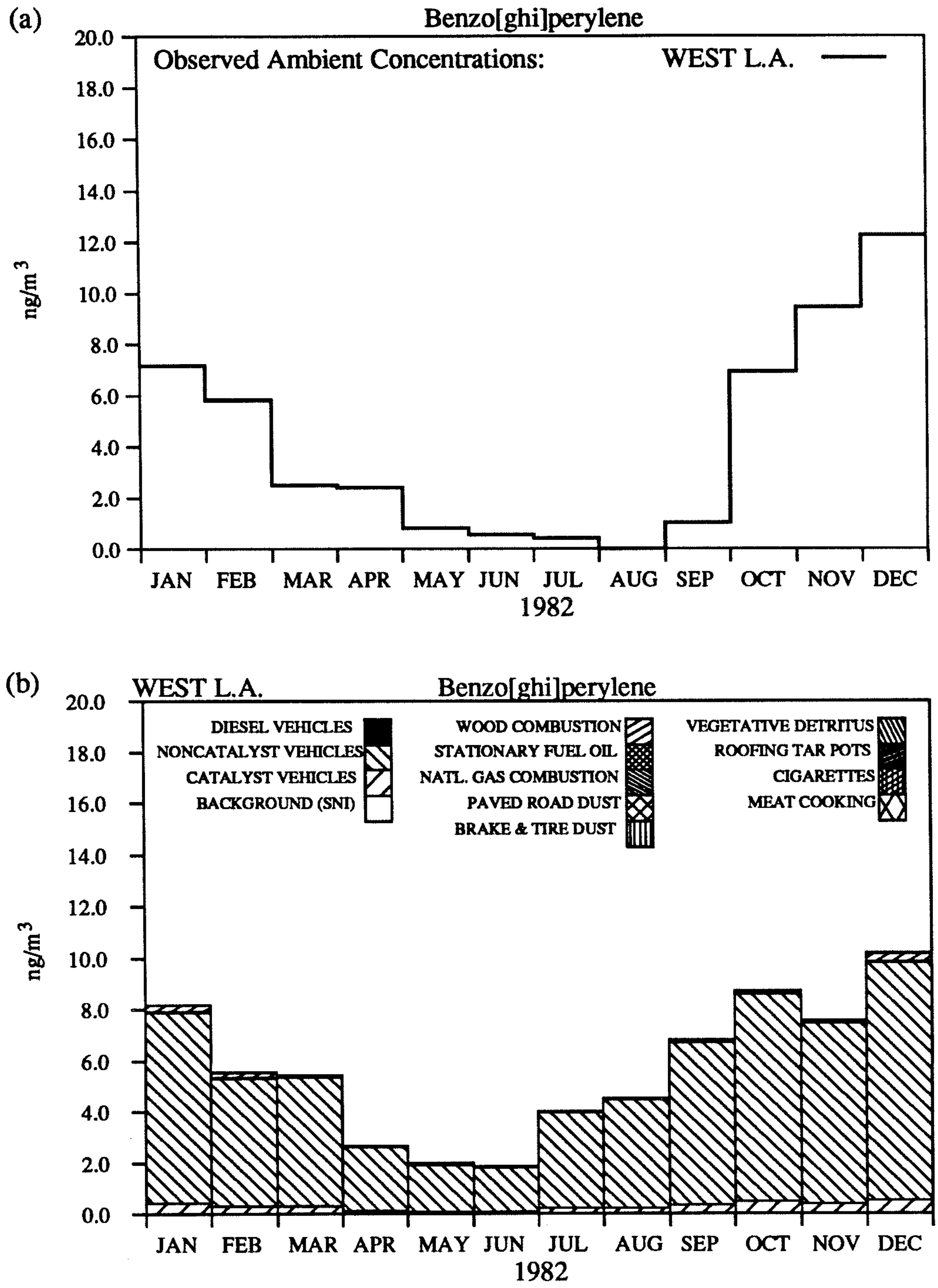


Fig. 12.20: Monthly mean benzo[ghi]perylene concentrations at West Los Angeles (1982): (a) observed, (b) predicted source contributions.

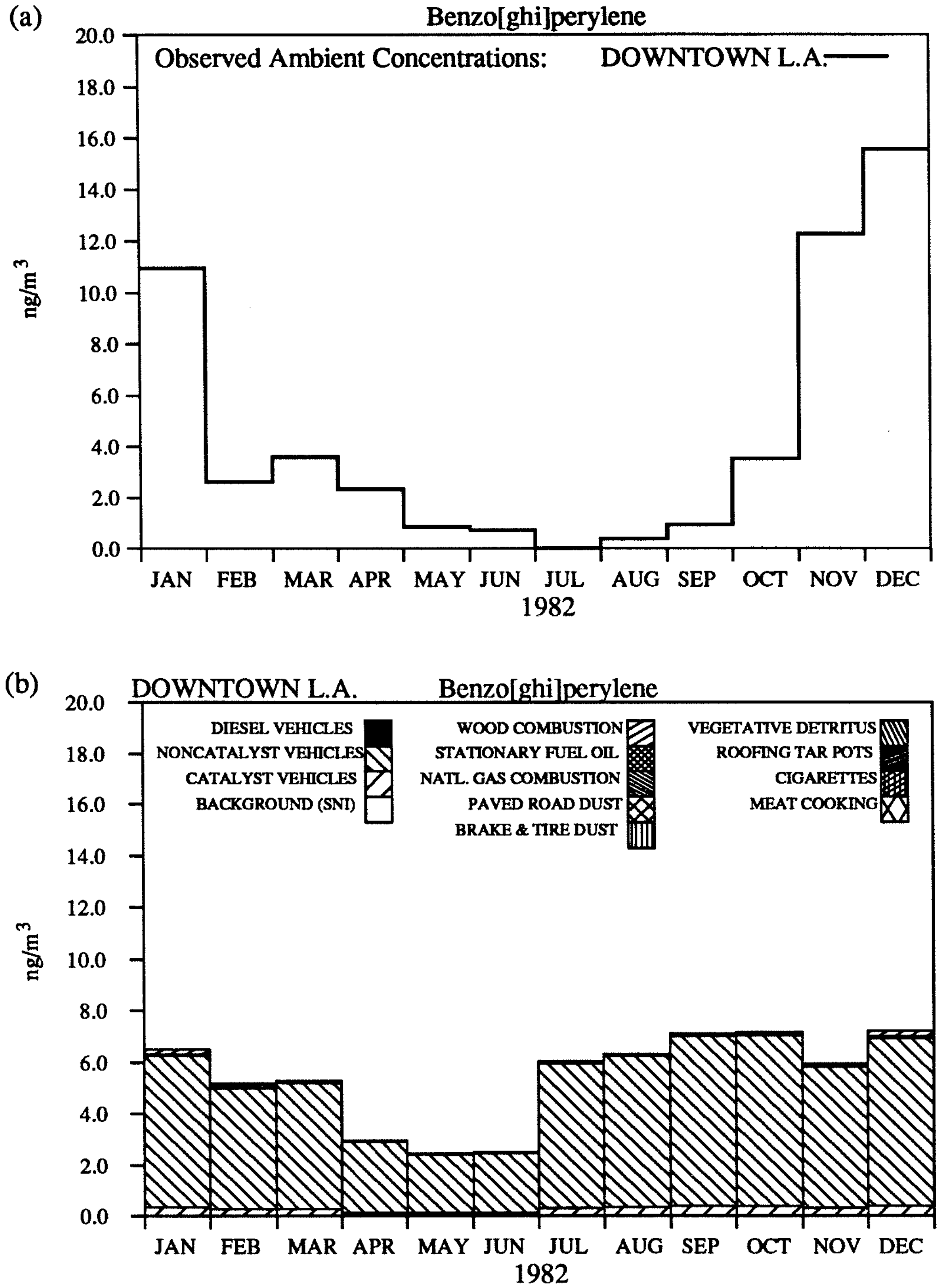


Fig. 12.21: Monthly mean benzo[ghi]perylene concentrations at downtown Los Angeles (1982): (a) observed, (b) predicted source contributions.

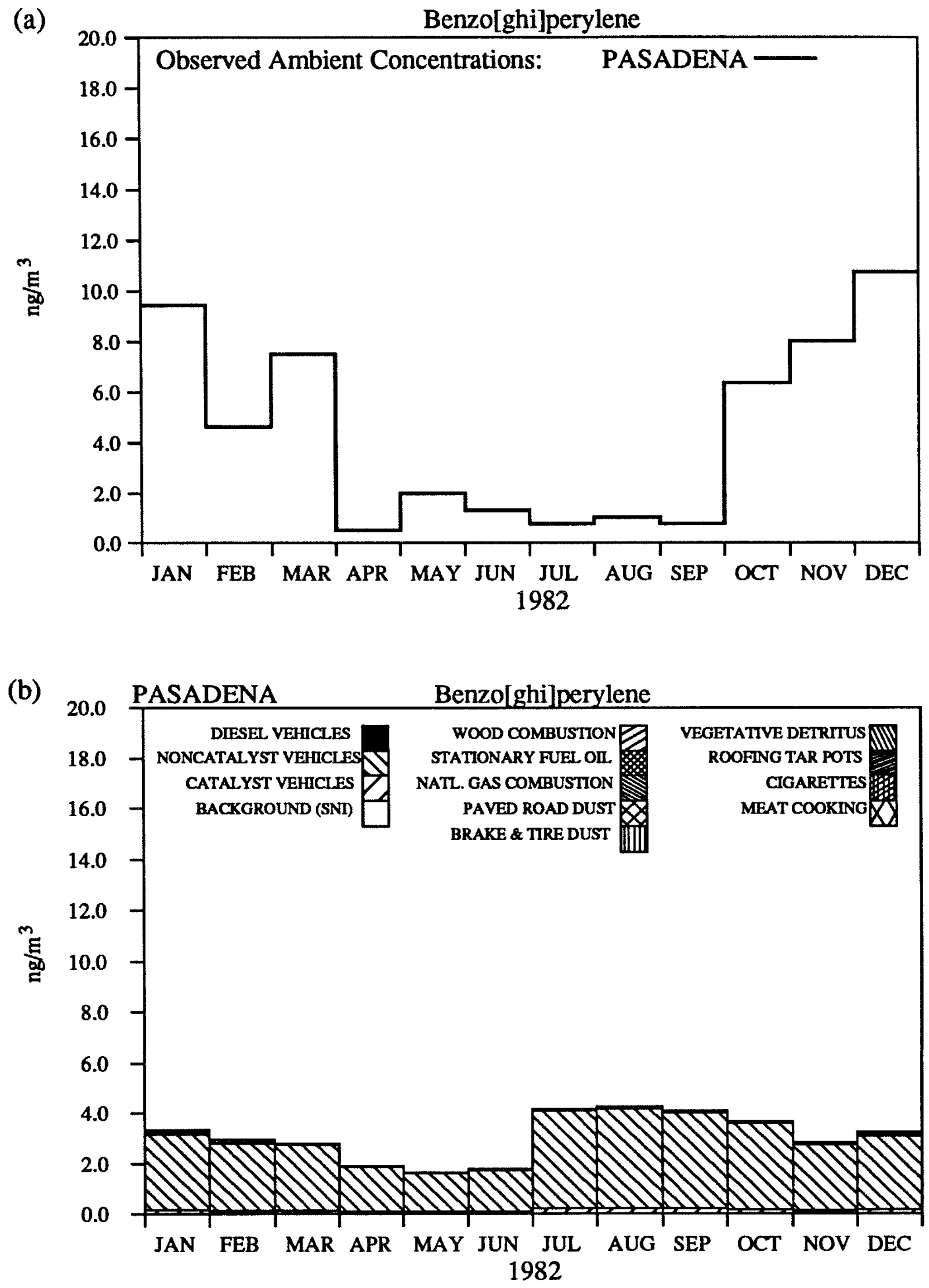


Fig. 12.22: Monthly mean benzo[ghi]perylene concentrations at Pasadena (1982): (a) observed, (b) predicted source contributions.

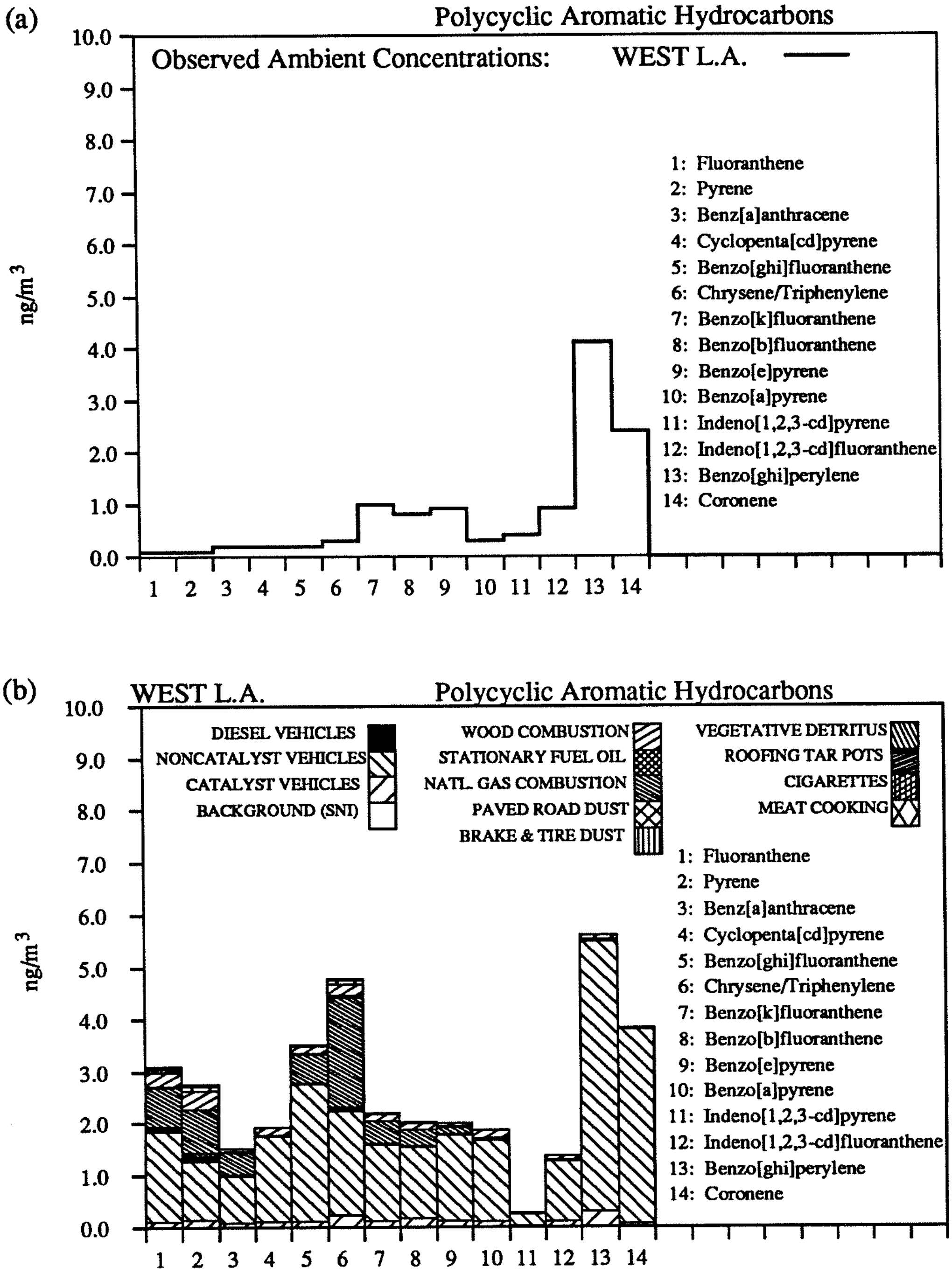


Fig. 12.23: Annually mean polycyclic aromatic hydrocarbon (PAH) concentrations at West Los Angeles (1982): (a) observed, (b) predicted source contributions if no further volatilization or atmospheric chemical reactions were to take place.

Hopanes and Steranes

Recently it has been suggested that fossil petroleum compounds such as steranes and hopanes serve as tracer compounds that can be used to estimate vehicular source contributions to ambient fine particulate matter concentrations (Rogge et al., 1993b). Like coronene and benzo[ghi]perylene, these fossil petroleum markers are exclusively in the particle-phase and consequently are useful indicators for testing model performance. For West Los Angeles, Figures 12.24a,b compare the measured and predicted total hopanes and steranes concentrations. Several emission sources contribute to ambient concentrations, with vehicles as the main emitters (Rogge et al., 1993b,c,g). The agreement between measured concentrations and model predictions is as good as was found for coronene and benzo[ghi]perylene. Again, the late summer concentrations predicted by the atmospheric transport model are somewhat higher than the observed values. At downtown Los Angeles (Figure 12.25a,b) and Pasadena (Figure 12.26a,b), the elevated measured winter concentrations are not matched by the model, a situation that has been discussed before for EC, TC, *n*-alkanes, and higher molecular weight PAH.

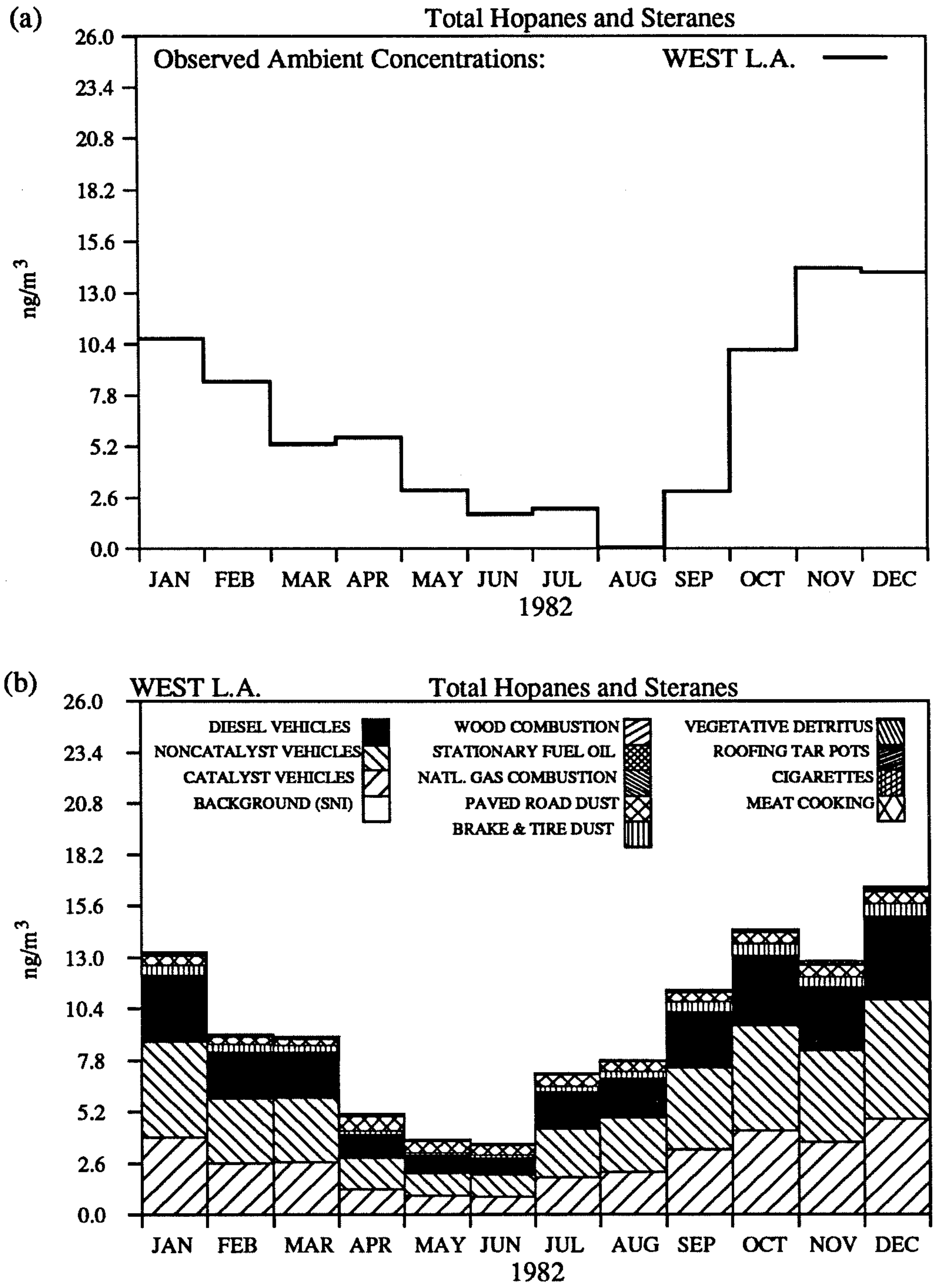


Fig. 12.24: Monthly mean total hopanes and steranes concentrations at West Los Angeles (1982): (a) observed, (b) predicted source contributions.

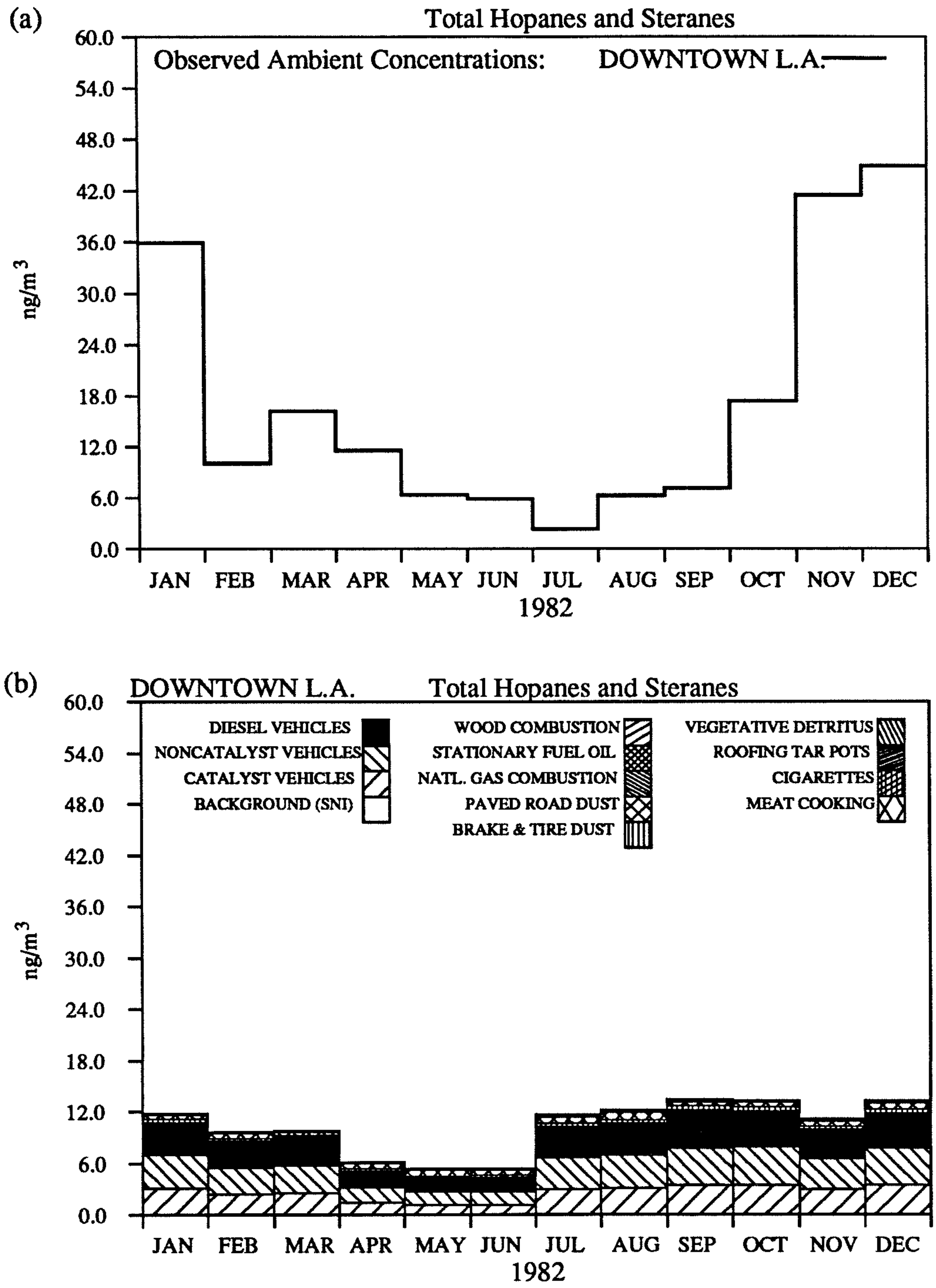


Fig. 12.25: Monthly mean total hopanes and steranes concentrations at downtown Los Angeles (1982): (a) observed, (b) predicted source contributions.

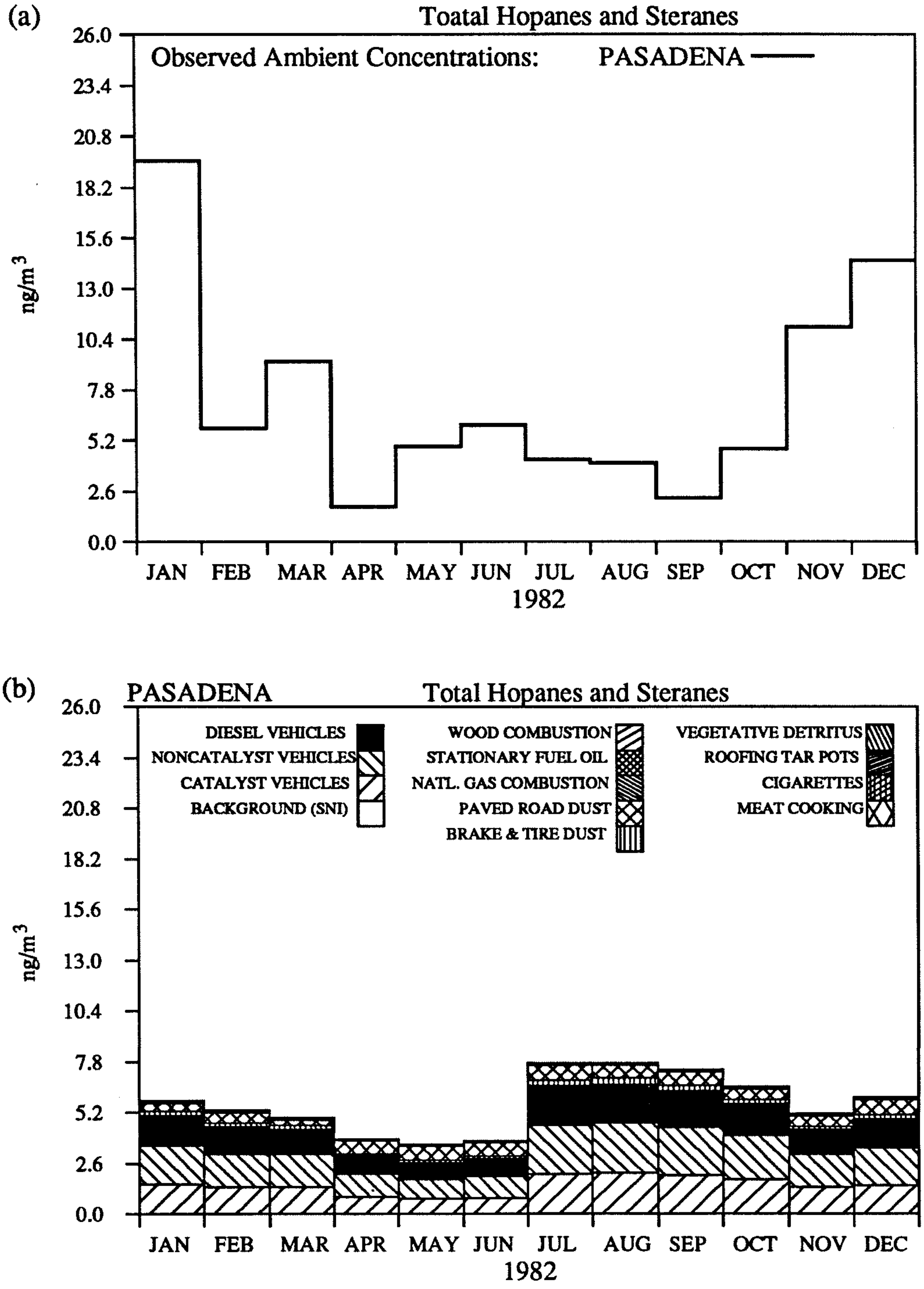


Fig. 12.26: Monthly mean total hopanes and steranes concentrations at Pasadena (1982): (a) observed, (b) predicted source contributions.

Alkanoic and Alkenoic Acids

n-Alkanoic acids ranging from C_9 to C_{30} constitute the compound class with the highest measured ambient concentrations. Typically, *n*-alkanoic acids show a concentration profile in which the even carbon numbered homologues are predominant. The single most abundant *n*-alkanoic acid is *n*-hexadecanoic acid (C_{16}), followed by *n*-octadecanoic acid (C_{18}).

The measured and predicted annual mean *n*-alkanoic acid concentrations at West Los Angeles are shown in Figures 12.27a,b. The predicted and observed concentration patterns for *n*-alkanoic acids $> C_{13}$ are very similar although the predicted ambient concentrations fall short of the measured values by about 50%. It is possible that cooking with seed oils that are rich in saturated and unsaturated fatty acids account for an appreciable portion of the observed differences between predictions and observations for the C_{16} and C_{18} fatty acids.

While *n*-alkanoic acids $< C_{13}$ are mainly contributed from vehicular emissions, *n*-hexadecanoic acid shows a multitude of source contributions, most importantly meat cooking emissions. Higher *n*-alkanoic acids $> C_{18}$ are typically contributed from wood combustion. The observed and predicted *n*-alkanoic acid concentration distributions at downtown Los Angeles and Pasadena are very similar to that for West Los Angeles and therefore are not shown here.

n-Octadecenoic acid (oleic acid) is a monounsaturated fatty acid typically released from cooking operations and wood combustion. Figures 12.28a,b show predicted concentration levels that are higher than measured values during the summer season, indicating that oleic acid concentrations in the reactive urban atmosphere are depleted by atmospheric chemical reactions as proposed by several researchers (Kawamura and Gagosian, 1987; Kawamura and Kaplan, 1987;

Killops, 1986). *n*-Octadecenoic acid is typically released together with its saturated homologue that has been underpredicted by the model, probably due to the lack of emissions data for cooking with vegetable oils. Consequently, the daily emission rate of oleic acid is probably higher than in the present emission inventory, suggesting an even greater rate of atmospheric degradation than would be infered by reference to Figure 12.28 alone.

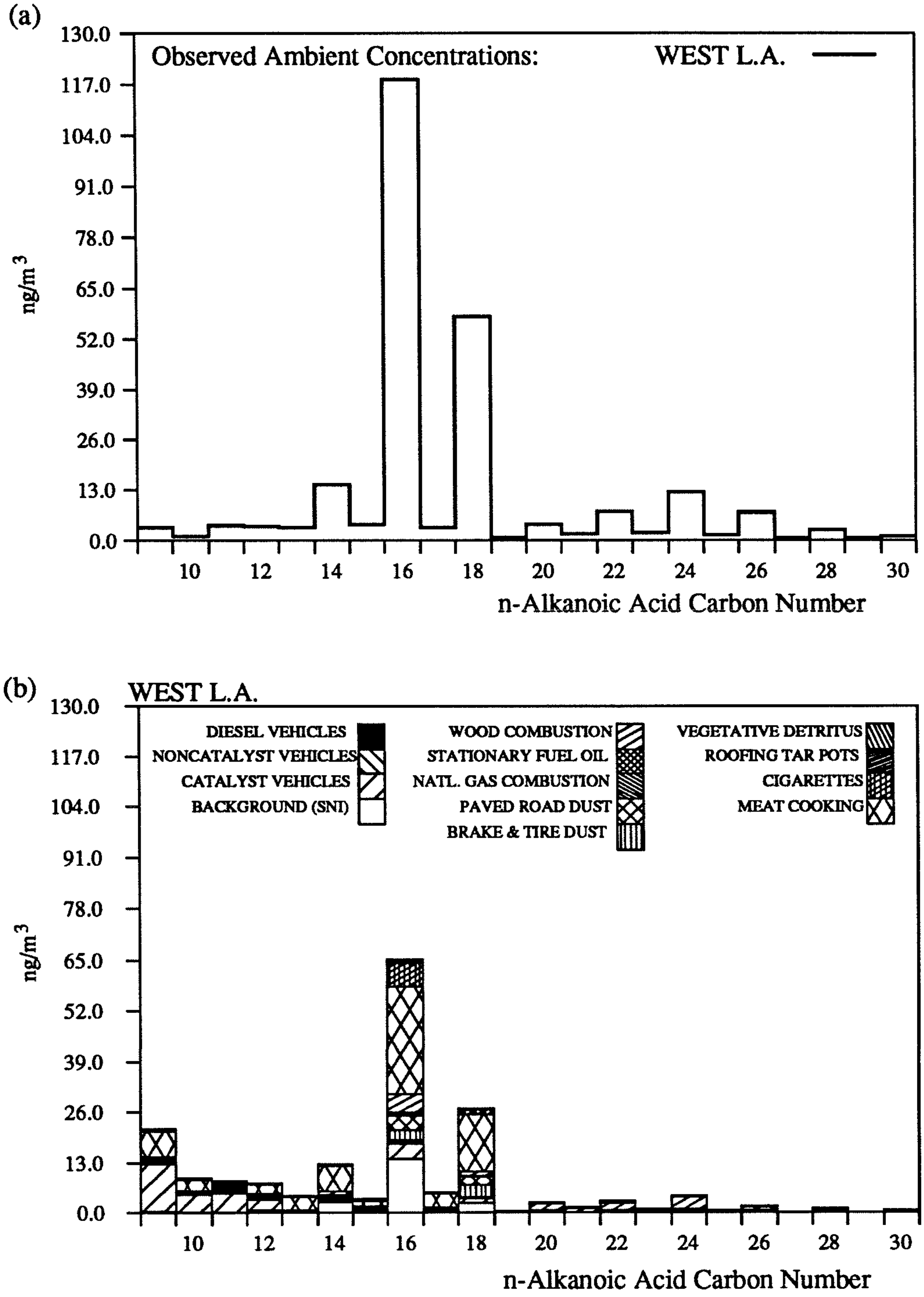


Fig. 12.27: Annually mean n-alkanoic acid concentrations at West Los Angeles (1982): (a) observed, (b) predicted source contributions.

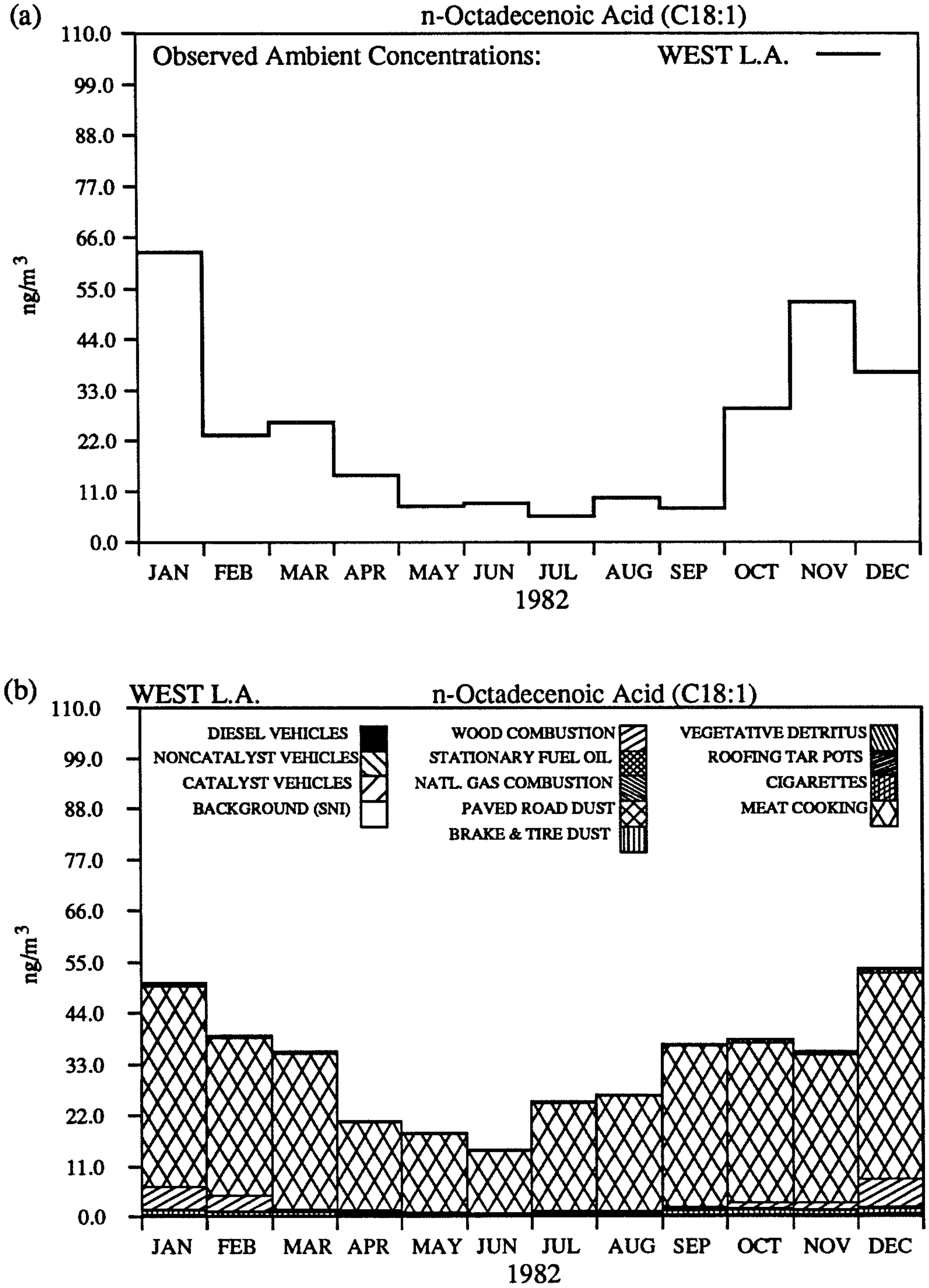


Fig. 12.28: Monthly mean n-octadecenoic acid (n-$C_{18:1}$) concentrations at West Los Angeles (1982): (a) observed, (b) predicted source contributions in the absence of atmospheric chemical reactions.

Aliphatic Dicarboxylic and Aromatic Polycarboxlic Acids

Aliphatic dicarboxylic acids are known to be formed under photochemical smog conditions from gas-phase precursor compounds. These atmospheric reaction products have very low vapor pressures, and thus condense onto preexisting particulate matter (Appel et al., 1980; Cronn et al., 1977; Grosjean, 1977; Grosjean and Friedlander, 1980; Rogge et al., 1993a; Satsumabayashi et al., 1989).

Aromatic polycarboxylic acids also have been reported in airborne particulate matter (Cautreels and Van Cauwenberghe, 1976; Matsumoto and Hanya, 1980; Rogge et al., 1993a; Satsumbayashi et al., 1989; Yokouchi and Ambe, 1986). They may result from atmospheric PAH degradation (Rogge et al., 1993a). Phthalic acid, in particular, may result from degradation of phthalate esters (plasticizers) (Rogge et al., 1993a).

The direct primary emission of aliphatic dicarboxylic acids and aromatic polycarboxylic acids from sources has not been extensively investigated in the past. During the source emissions characterization program conducted as part of the present study (Rogge et al., 1991, 1993b-i) the aliphatic dicarboxylic and aromatic polycarboxylic acids present in primary source emissions were measured and were found only in trace amounts. Using these source emission data, model predictions can be compared to actual measured ambient concentrations. Figures 12.29a,b show the measured and predicted annual mean ambient concentration levels for individual aliphatic dicarboxylic acids, ranging from propanedioic acid to nonanedioic acid. The predicted ambient dicarboxylic acids concentrations due to primary source emissions are far below the measured levels, indicating indeed that most of the aliphatic dicarboxylic acids found in airborne particles are the product of atmospheric chemical reactions that occur in photochemical smog. The same results have been found at downtown Los Angeles and Pasadena. The only sources that release detectable amounts of aliphatic dicarboxylic acids are fireplace combustion of wood and meat cooking operations. The measured ambient aliphatic dicarboxylic acid concentrations are shown in Figure 12.30a revealing low concentrations in most winter months and high concentrations during late spring and early summer (1982). In contrast, the primary source emissions indicated in Figure 12.30b show very low ambient concentrations, with an ambient concentration pattern over the seasons that is typical of most other primary source emissions in the Los Angeles air basin.

The primary source contributions to aromatic polycarboxylic acids concentrations are even smaller than that computed for the aliphatic dicarboxylic acids. The measured ambient concentrations reveal a seasonal concentration pattern similar to that found for the aliphatic dicarboxylic acids and again suggest that the aromatic polycarboxylic acids are produced mainly by atmospheric chemical reactions. For the measured ambient concentrations of aromatic polycarboxylic acids, the interested reader is refered to Rogge et al. (1993a) (see Chapter 2).

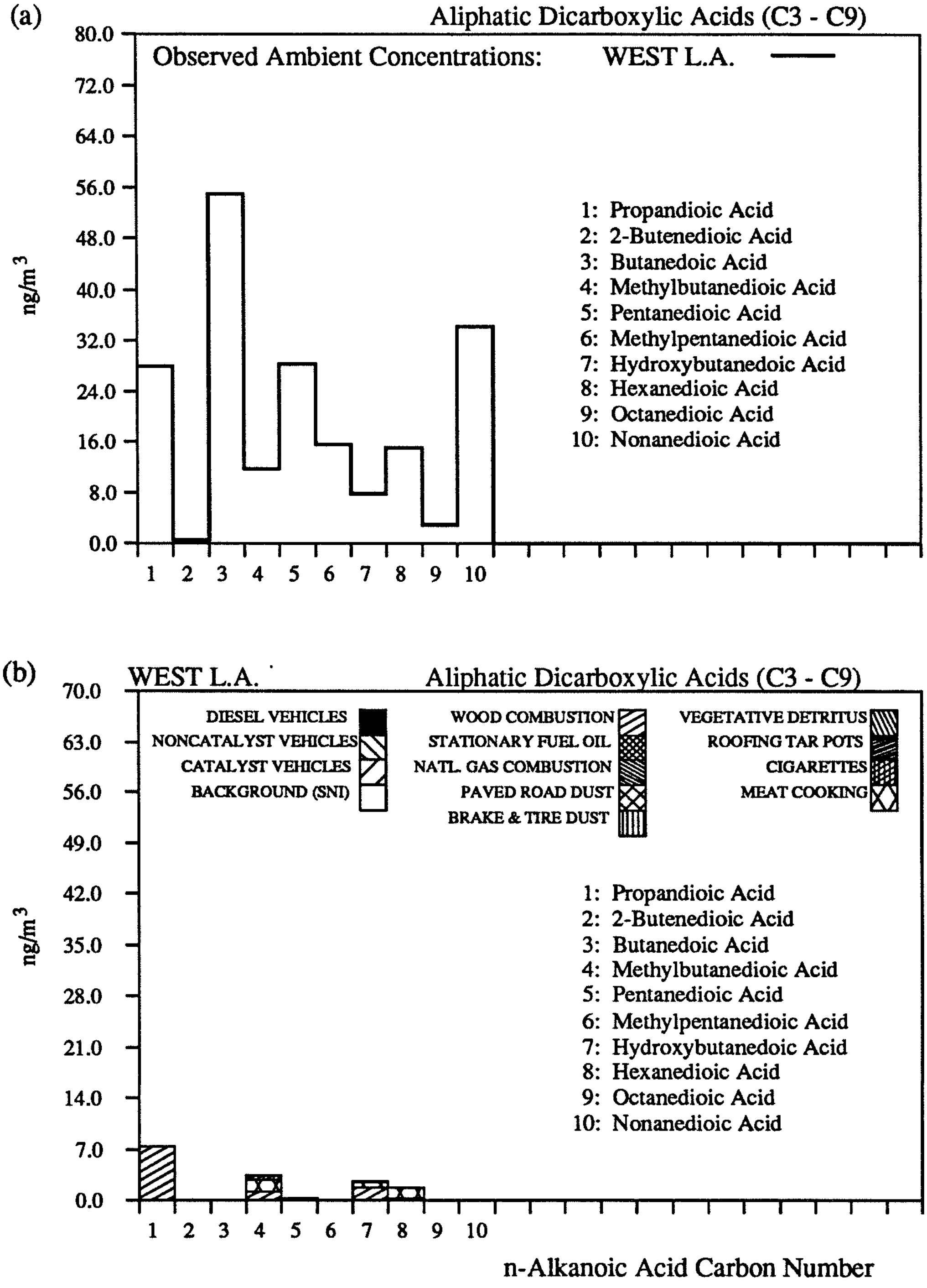


Fig. 12.29: Annual mean aliphatic dicarboxylic acid (C_3 - C_9) concentrations at West Los Angeles (1982): (a) observed, (b) predicted source contributions due to primary aerosol sources alone without any secondary aerosol formation.

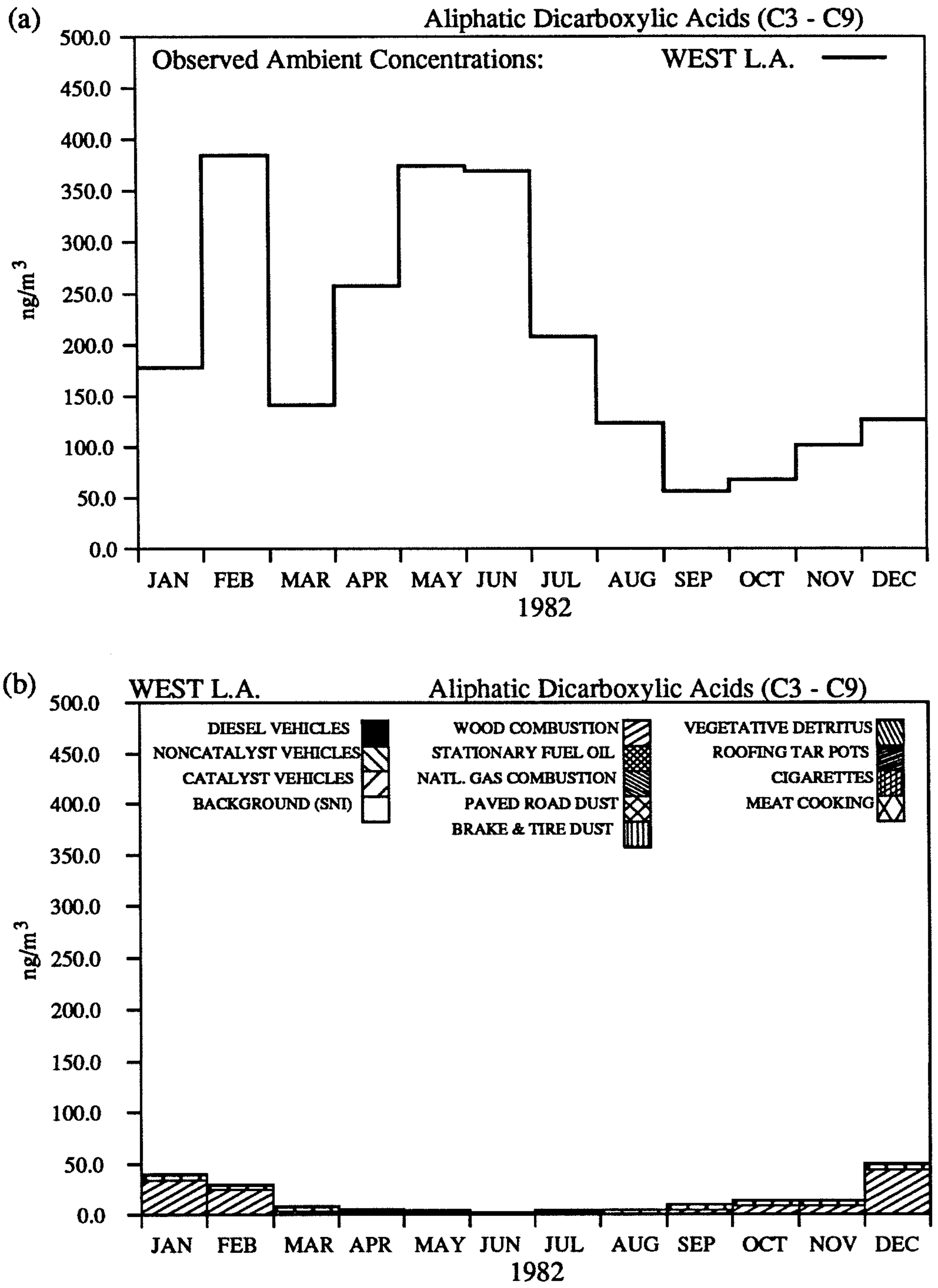


Fig. 12.30: Monthly mean aliphatic dicarboxylic acid (C_3 - C_9) concentrations at West Los Angeles (1982): (a) observed, (b) predicted source contributions.

Resin Acids Wood Smoke Markers

In the northern hemisphere, the combustion of pine wood is considered to be the most important source of resinous organic acid emissions to the atmosphere (Rogge et al., 1993i; Simoneit and Mazurek, 1982; Standley and Simoneit, 1987; 1990). The combustion of wood for space heating and for home recreational purposes in the Los Angeles area occurs during the winter months and consists mainly of the combustion of wood logs in open fireplaces.

Air quality predictions for wood smoke markers are compared to measured ambient concentrations in Figures 12.31a.b – 12.33a,b. At all three urban sites considered, the predicted concentrations follow the seasonal use of wood as a domestic fuel. At West Los Angeles, the predicted concentrations closely follow the measured concentration levels. At Pasadena, the model predictions are far lower than the measured values, suggesting greater use of wood fuels in Pasadena than is typical of Los Angeles as a whole (which is likely considering the unusually large number of trees and fireplaces in Pasadena). At all three monitoring sites, wood use for space heating seems to be underpredicted during the month of November.

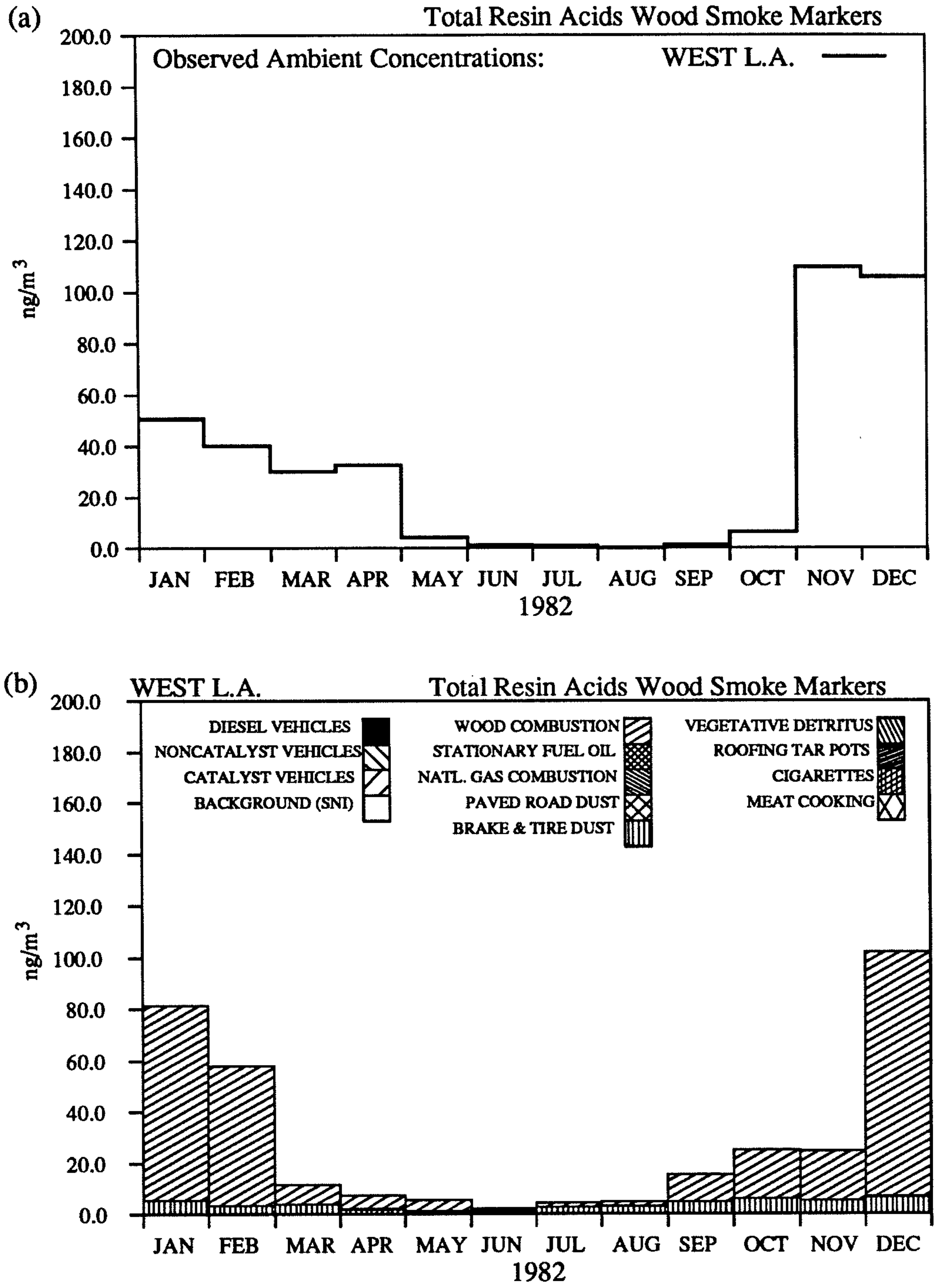


Fig. 12.31: Monthly mean total total resin acids wood smoke marker concentrations at West Los Angeles (1982): (a) observed, (b) predicted source contributions.

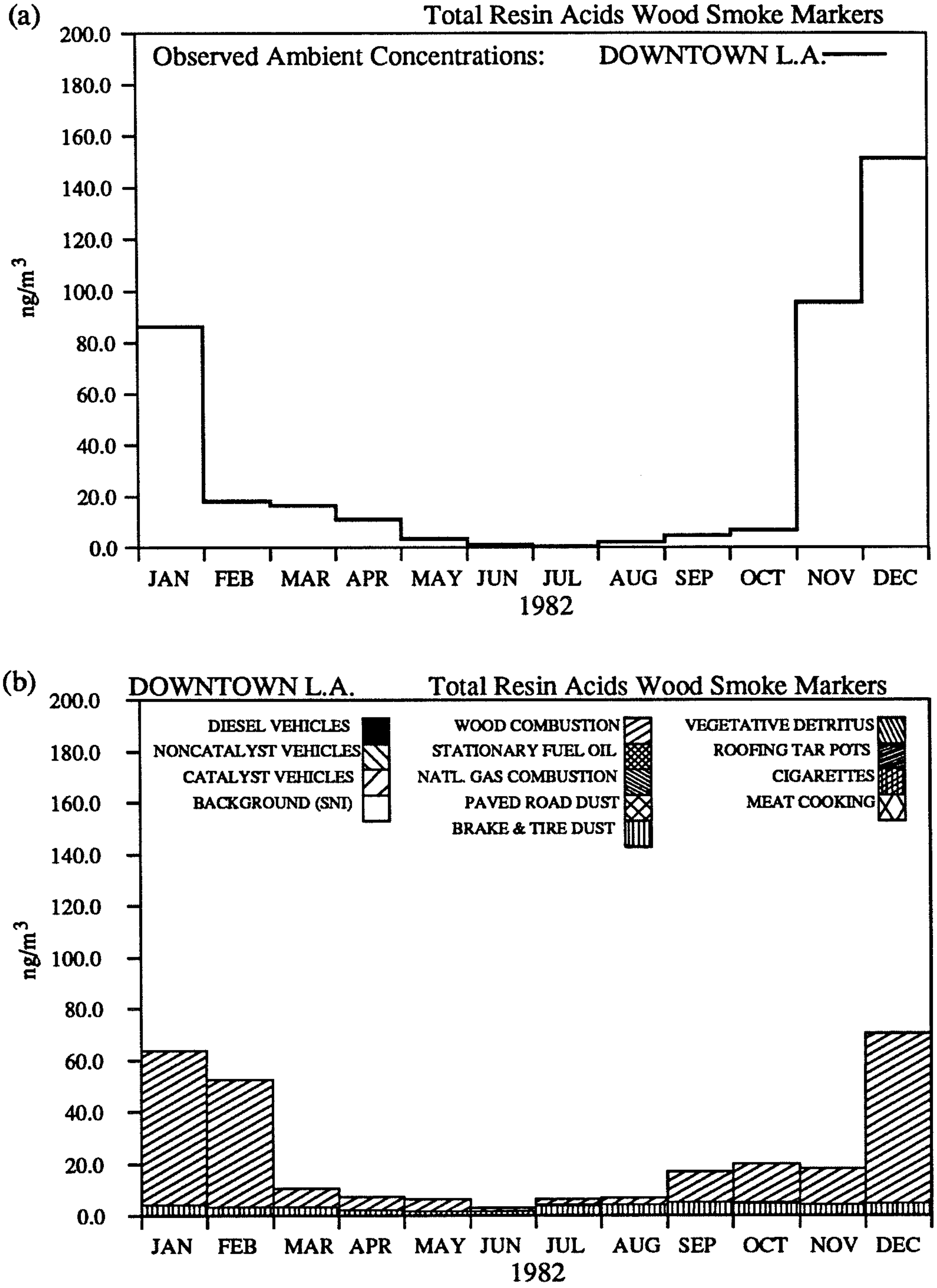


Fig. 12.32: Monthly mean total resin acids wood smoke marker concentrations at downtown Los Angeles (1982): (a) observed, (b) predicted source contributions.

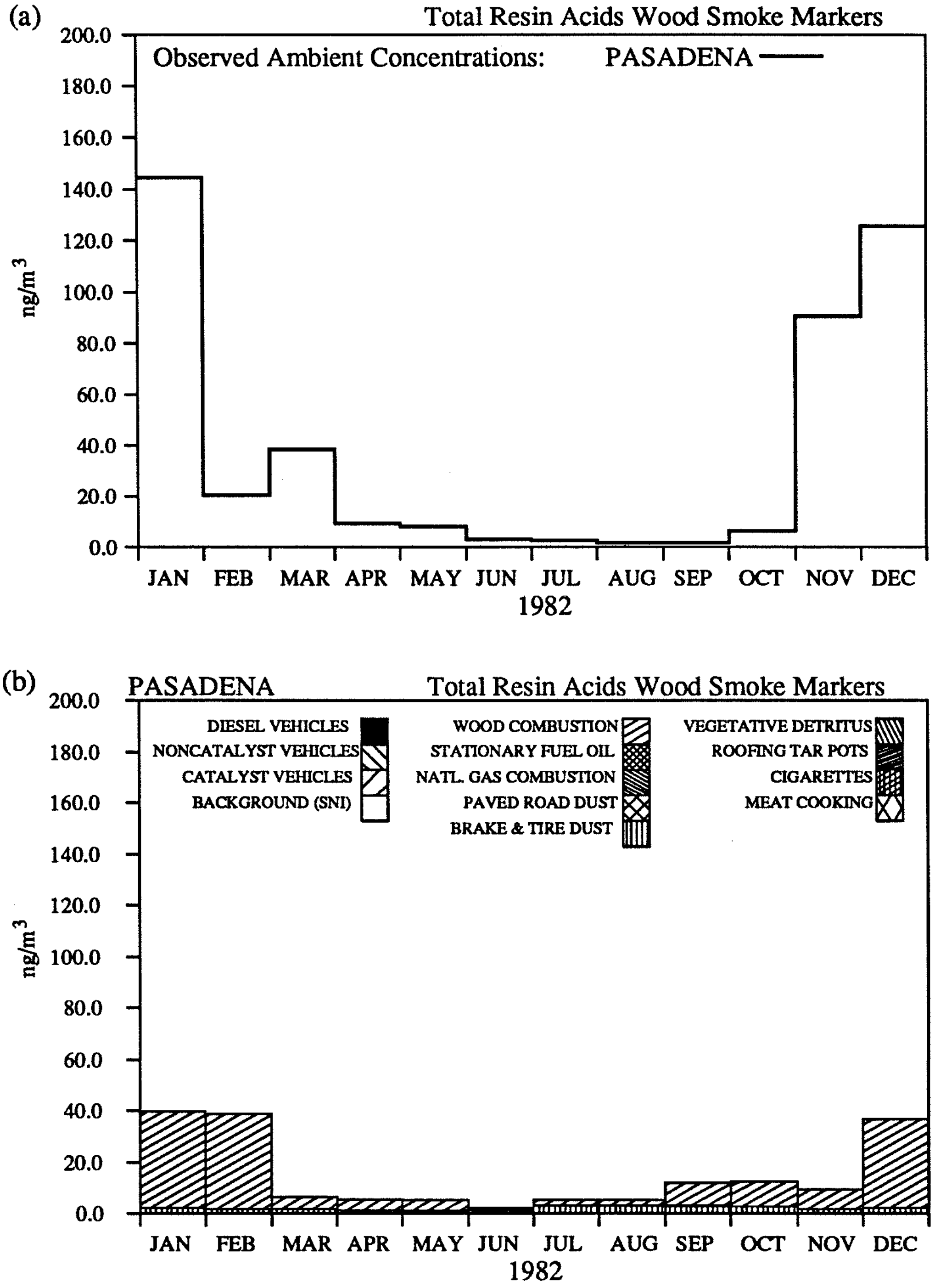


Fig. 12.33: Monthly mean total resin acids wood smoke markers concentrations at Pasadena (1982): (a) observed, (b) predicted source contributions.

Conclusions

A mathematical model that simulates pollutant advection and dispersion has been used to predict source contributions to monthly averaged fine particle-bound organic compound concentrations at three sites within an 80 km × 80 km modeling domain centered over Los Angeles. Typically good agreement between measured concentration levels and air quality model predictions has been found for stable organic compounds that are exclusively present in the particle-phase such as *n*-alkanes, *iso-* and *anteiso*-alkanes, higher molecular weight PAH (e.g., coronene, benzo[ghi]perylene), and fossil petroleum compounds including hopanes and steranes.

Vegetative detritus released as fine particles shed from waxy leaf surfaces contribute together with cigarette smoke to the higher molecular weight *n*-alkane concentration levels measured throughout the studying area. *Iso-* and *anteiso*-alkanes, characteristic markers for cigarette smoke, show predicted concentrations that agree well with measured concentration levels. High molecular weight PAH such as benzo[ghi]perylene and coronene show predicted and measured monthly concentration levels that are in particularly good agreement at West Los Angeles. Low molecular weight PAH concentrations are drastically overpredicted by the model, when further volatilization and/or atmospheric chemical reactions are neglected.

n-Alkanoic acid concentrations are typically underpredicted by the model, suggesting that other sources, not yet considered, such as cooking with vegetable oils could contribute significant amounts of *n*-alkanoic acids. Aliphatic dicarboxylic acids and aromatic polycarboxylic acids are released only in small amounts to the urban atmosphere from primary aerosol sources indicating that such compounds are indeed mainly the result of atmospheric formation processes that occur in photochemical smog.

Resin acids wood smoke marker concentration predictions reveal a seasonal pattern that follows the use of wood as a domestic fuel. The model predictions suggest that the use of wood in residential fireplaces is underestimated during November 1982 at all three sampling sites and at Pasadena during the whole heating season.

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Chapter 13

Summary and Conclusions

Fine organic aerosol samples collected systematically throughout a complete annual cycle at 4 urban sites in Southern California have been examined by gas chromatography/mass spectrometry. More than 100 organic compounds were quantified and their seasonal ambient concentration patterns were discussed. Primary organic aerosol constituents revealed an annual ambient concentration pattern with high winter and low summer concentrations. In contrast, aliphatic dicarboxylic acids and aromatic polycarboxylic acids of possible secondary origin showed a reverse pattern, with high concentrations in late spring/early summer. Molecular markers characteristic of several source types have been identified that would permit back calculation of the contribution of specific sources to the ambient aerosol if the concentration of these tracers in source emissions were known. In pursuit of such data on tracer concentrations in source emissions, fine organic aerosol emissions from 18 different source types were characterized using sampling and analytical techniques that were comparable to those employed during the ambient aerosol characterization campaign. The source samples investigated here were collected using a dilution sampler that simulates the cooling and dilution processes that occur in the atmosphere immediately downwind of a hot emission source, allowing condensible organic compounds emitted in the vapor-phase to condense onto particles prior to filter sampling.

Together, more than 400 different organic compounds have been identified and quantified in the source emissions studied here. It has been shown that meat cooking operations contribute substantial amounts of fine particle-bound organics to the ambient atmosphere. Cholesterol, a constituent in the fatty portion of meat, is proposed as a marker compound for the smoke from meat cooking operations and has also been identified in the urban atmosphere.

The emissions from 13 motor vehicles, including noncatalyst and catalyst-equipped automobiles, and heavy-duty diesel trucks, have been examined. It has been shown that the organic particulate exhaust emissions differ greatly from vehicle type to vehicle type. The identifiable portion of the organic aerosol emitted from gasoline-powered noncatalyst automobiles, for example, was dominated by polycyclic aromatic hydrocarbons (PAH), whereas the particle-phase organic compounds in the exhaust from catalyst-equipped automobiles included large amounts of organic acids dominated by *n*-alkanoic acids. The fine particulate matter emitted from diesel truck exhaust showed high concentrations of *n*-alkanes. More than 100 different organic compounds have been identified in the vehicular exhaust emissions, including fossil petroleum markers such as steranes and pentacyclic triterpanes (hopanes) that likewise have been found in ambient fine aerosol samples. It has been shown that the ambient concentrations of hopanes and steranes measured in the Los Angeles atmosphere are attributable mainly to vehicular exhaust emissions. Thus hopanes and steranes act as useful tracers for motor vehicle exhaust that can be used in future source/receptor reconciliation studies.

Paved road dust, an agglomerate of multiple source contributions and in turn an appreciable source for airborne fine particulate matter, has been examined. Contributions to the paved road dust deposits from vehicular exhaust emissions, tire wear, and vegetative detritus, coming from nearby plants and trees, have been estimated using authentic source profiles generated during the course of the present source characterization study.

In order to trace biogenic emissions, fine particles shed from leaf surfaces were investigated. Leaf composites were made up that represent green leaves (and separately; dead leaves) from 62 different plant species that are characteristic of vegetation in the Los Angeles area. It has been shown that fine particle leaf surface abrasion products exhibit a concentration pattern of higher molecular weight *n*-alkanes (C_{27} – C_{33}) with a pronounced odd/even carbon number predominance that is preserved in the urban atmosphere. This marker assemblage of higher molecular weight *n*-alkanes has been demonstrated in the air quality modeling part of this study as a means for tracing the contribution of vegetative detritus emissions to the urban atmosphere.

Cigarette smoke, a typical fugitive urban emission source, has been studied previously in indoor environments. In this study, molecular marker compounds such as *iso*- and *anteiso*-alkanes (C_{29} – C_{34}) have been identified that are enriched in cigarette smoke aerosol and that show a concentration pattern characteristic of tobacco leaf surface waxes that is distinctly different from leaf surface abrasion products shed from plant leaves that grow in the Los Angeles area. When this finding is applied to the ambient aerosol, it has been shown that cigarette smoke contributes 0.57 to 0.72 μg m^{-3} of the fine particulate matter measured in the outdoor Los Angeles area atmosphere on an average during 1982 (or 2.0 to 2.5% of the total fine ambient particle mass).

The combustion of natural gas in residential home appliances also has been investigated. Previous studies indicated that natural gas combustion shows fairly low fine particulate emission rates and consequently the chemical composition was not identified in the past. Here, it has been shown that at least 22.5% of the particle mass emitted from natural gas combustion in residential home appliances consists of PAH-tpye compounds. Applying the source test results to natural gas consumption data for the Los Angeles study area, it has been estimated that natural gas combustion in residential homes and commercial establishments emits amounts of PAH and oxy-PAH to the urban atmosphere that are comparable to that from all types of diesel vehicles or about half the amount emitted from catalyst-equipped automobiles on a daily basis.

The source and ambient data sets just described have have been used together with a long-term average Lagrangian particle-in-cell air quality model to predict ambient aerosol-associated organic compound concentrations within an 80 km x 80 km study area centered over Los Angeles during the year 1982. Typically, the predicted and measured ambient concentrations for stable particle-phase organic compounds such as higher molecular *n*-alkanes, PAH, hopanes, and steranes agree well. *n*-Alkanoic acid concentrations predicted by the air quality model fall short of observed values by roughly 50%, suggesting that other sources not yet included in the model, e.g., cooking with seed oils, may emit substantial amounts of *n*-alkanoic acids. Aliphatic dicarboxylic acids and aromatic polycarboxylic acids, that have been suggested to be the products of atmospheric chemical reactions involving gaseous precursor compounds, show only small amounts of primary source contributions to the ambient aerosol. The current study underlines that indeed such oxygenated organic compounds must be synthesized in the reactive urban atmosphere in the form of secondary aerosols because they are simply not present in primary source emissions in anywhere near the quantities needed to explain the observed ambient concentrations.

Volatile low molecular weight PAH show ambient concentration levels predicted by the air quality model that by far exceed measured ambient concentration levels. In contrast, higher molecular weight PAH that do not partition between the gas- and particle-phase show predicted and measured ambient concentrations that agree quite well. It is concluded that particle-bound high molecular weight PAH indeed show life times at least as long as it takes for transport from the sources to the receptor air monitoring sites, while the lower molecular weight PAH are stripped from the particle-phase by volatilization and/or chemical reaction over the same time scale.

Many of the most important molecular markers identified in the present study, for example, hopanes and steranes that act as tracers for vehicular emissions, or *iso*- and *anteiso*-alkanes ($C_{29} - C_{34}$) that act as tracers for cigarette smoke, show good agreement between measured concentrations and the concentrations predicted by the air quality model used here. This consistency between predicted and observed molecular marker concentrations adds support to the notion that these compounds do indeed act as conserved tracers for the particular sources identified in the present study.

Recommendations for Future Research

Although the data sets provided here on organic compounds identified in the urban atmosphere and in the source emissions are substantial, many questions remain that cannot be answered without further experimental investigations.

In order to evaluate chemically reactive models for the dynamics of primary aerosols and secondary aerosol formation in the urban atmosphere, ambient measurements of shorter duration (e.g., a few hours) are necessary. Semi-volatile compounds exist that must be better understood in order to bridge the gap that exists between aerosol research and gas-phase research. New sampling devices and measurement methods have to be developed that enable researchers to follow the complex interactions ongoing between the gas- and particle-phases. A new sampling device for particulate matter needs to be developed that allows particulate matter samples to be drawn from the urban atmosphere without disturbing the gas-/particle-phase partitioning that prevailed in the atmosphere at the time of sampling. Chemical extraction methods need to be developed that are capable of retaining the more volatile compounds during the extraction of particulate matter samples.

If these measurement challenges can be mastered, then air quality models can be developed and tested that consider both the gaseous and particulate pollutant emissions simultaneously.