DETERMINATION OF KEY ORGANIC COMPOUNDS PRESENT IN THE PARTICULATE MATTER EMISSIONS FROM AIR POLLUTION SOURCES

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Executive Summary

Carbonaceous compounds constitute the largest contributor to the fine particulate matter in the atmosphere of highly industrialized and urbanized areas. Organic aerosol comprises 25% to 30% of total fine aerosol mass in the greater Los Angeles area. Fine particulate matter ($d_p \leq 2.0$ μm) is known to be easily inhalable and has been considered responsible, together with gaseous pollutants, for the possible health effects connected with air pollutants. Elevated concentrations of organic compounds in fine respirable particles measured in urbanized areas are of considerable concern because many of the organics present in the atmosphere are known mutagens and carcinogens. In order to design an advanced strategy for the control of fine primary organic particulate emissions, more knowledge is necessary regarding source/receptor relationships.

The purpose of this research is to provide a molecular characterization of the primary organic particulate matter emitted from urban pollution sources, to provide parallel data on the concentration of these compounds found in ambient air, and to use this information to compare emissions data to air quality data for many organic compounds. A dilution source sampling system was employed to collect primary fine aerosol emissions from 18 major urban source types that contribute close to 80% of the fine organic aerosol emitted in the Los Angeles area. Ambient fine particle samples were collected for one entire year at four urban locations and at one remote offshore sampling site. The identification and quantification of organic compounds present in these samples has been conducted by high resolution GC- and GC/MS- techniques. The identification of organic marker compounds that are characteristic of particular source types has been emphasized. These marker compounds then can be used along with source/receptor modeling tech-

niques to quantify the presence of the effluent from particular source types within ambient aerosol samples. The following sources will be characterized and their molecular source signatures discussed: charbroiling and frying of meat, noncatalyst and catalyst equipped automobiles, diesel trucks, paved road dust, brake lining dust, tire wear debris, vegetative detritus derived from the green and dead leaves of urban plants, natural gas home appliances, cigarette smoke, roofing tar pot fumes, distillate fuel oil combustion and woodsmoke.

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

Gasoline and diesel powered vehicles are known to contribute appreciable amounts of inhalable fine particulate matter to the atmosphere in urban areas. Internal combustion engines (stationary and mobile) burning gasoline and diesel fuel contribute more than 21% of the primary fine particulate organic carbon emitted to the Los Angeles atmosphere. In the present study, fine particulate ($d_p \leq 2\ \mu m$) exhaust emissions from six noncatalyst automobiles, seven catalyst-equipped automobiles, and two heavy-duty diesel trucks are examined by gas chromatography/mass spectrometry. The purposes of this study are: (a) to search for conservative marker compounds suitable for tracing the presence of vehicular particulate exhaust emissions in the urban atmosphere; (b) to compile quantitative source profiles on a molecular level which can be used to model vehicular source contributions to urban atmospheres; and (c) to study the contributions of fine organic particulate vehicular exhaust to the greater Los Angeles area atmosphere. More than 100 organic compounds are quantified, including n-alkanes, n-alkanoic acids, one n-alkenoic acid, benzoic acids, substituted benzaldehydes, polycyclic aromatic hydrocarbons and their oxygenated homologues, steranes, pentacyclic triterpanes, azanaphthalenes, and others. Although fossil petroleum markers such as steranes and pentacyclic triterpanes can be emitted from other sources that burn or process petroleum products, it can be shown that their ambient concentrations measured in the Los Angeles atmosphere are attributable mainly to vehicular exhaust emissions. Thus the hopanes and steranes are proposed as tracers for the presence of vehicle exhaust in ambient particulate matter samples.

Charbroilers and Meat Cooking

Meat cooking operations are a major source of organic aerosol emissions to the urban atmosphere, comprising up to 21% of the primary fine organic carbon particle emissions in the Los Angeles area. In the present study, the chemical composition of meat smoke aerosol is examined by high resolution gas chromatography and gas chromatography/mass spectrometry. The objective is to search for molecular markers which will confirm the presence of meat smoke aerosol in urban atmospheric samples. More than 75 organic compounds are quantified including the series of the *n*–alkanes, *n*–alkanoic acids, *n*–alkenoic acids, dicarboxylic acids, *n*–alkanals, *n*–alkenals, *n*–alkanones, *n*–alkanols, furans, lactones, amides, nitriles, polycyclic aromatic hydrocarbons, steroids, and pesticide residues. Prominent among the compounds emitted are *n*–hexadecanoic acid (i.e. palmitic acid), *n*–octadecanoic acid (i.e. stearic acid), *cis*–9–octadecenoic acid (i.e. oleic acid), nonanal, 2–octadecanal, 2–octadecanol, and cholesterol. Although cholesterol can be emitted from other sources, cholesterol concentrations measured in the West Los Angeles atmospheric aerosol are consistent with the cholesterol mass emission rates determined from meat cooking source tests.

Road Dust, Tire Debris, and Organometallic Brake Lining Dust

Particulate matter emitted to the atmosphere due to motor vehicles arises from several sources in addition to tailpipe exhaust. In this study, the organic constituents present in fine particulate ($d_p \leq 2.0\ \mu m$) road dust, brake lining wear particles, and tire tread debris (not size-segregated) are analyzed using gas chromatography/mass spectrometry. The objective is to characterize such traffic-related sources on an organic compound basis and to search for molecular markers that will assist the identification of traffic-associated dusts in the urban atmosphere. More than 100 organic compounds are quantified in these samples, including *n*-alkanes, *n*-alkanoic acids, *n*-alkenoic acids, *n*-alkanals, *n*-alkanols, benzoic acids, benzaldehydes, polyalkylene glycol ethers, PAH, oxy-PAH, steranes, hopanes, natural resins, and other compound classes. Paved road dust acts as a repository for vehicle-related particles, which can then be resuspended by the passing traffic. To evaluate the contributions from major urban sources to the road dust complex, source profiles representing different types of vehicle exhaust, brake dust, tire debris, and vegetative detritus are compared and their fractional contributions are estimated using several groups of organic tracer compounds. Likewise, the close relationship between airborne fine particulate organic constituents and road dust organic matter is discussed.

Particulate Abrasion Products from Leaf Surfaces of Urban Plants

Green and dead leaves from 62 plant species characteristic of the Los Angeles area were harvested and composited according to the actual leaf mass distribution for that area. To simulate leaf surface abrasion by the wind, the leaf composites were agitated in clean Teflon bags while a purified air stream flowed through. Fine particles ($d_p \leq 2\ \mu m$) shed from the leaf surfaces were extracted and analyzed using gas chromatography/mass spectrometry. Organic constituents including *n*-alkanes, *n*-alkanoic and *n*-alkenoic acids, *n*-alkanols, *n*-alkanals, terpenoid compounds, and trace amounts of PAH were identified and quantified. *n*-Alkanes showed similar concentrations in both dead and green leaf surface matter; mono-, sesqui-, and triterpenoids were depleted in dead leaf material while *n*-alkanoic acids were enriched in dead leaf abrasion products. It is shown that the higher molecular weight *n*-alkanes ($C_{27} - C_{33}$), with their pronounced odd/even carbon number predominance, provide a suitable marker compound assemblage for tracing vegetative detritus in the urban atmosphere.

Natural Gas Home Appliances

Fine particle emissions from the combined exhaust of a vented natural gas-fired residential space heater plus a water heater have been examined using GC/MS-techniques. Organic compounds such as n-alkanes, n-alkanoic acids, PAH, oxy-PAH, aza-arenes, and thia-arenes have been identified in the exhaust emissions. Total fine particle emission rates are fairly low, with 45.8 ng/kJ (± 17.4); thus residential natural gas combustion does not add much to the total fine particulate organic carbon (OC) mass emissions to the urban atmosphere (about 0.1% for the Los Angeles area). At least 22.5% of the particle mass emitted consists of PAH, oxy-PAH, aza-arenes, and thia-arenes, and many of these compounds are known or suspected carcinogens or mutagens. If tests of additional units should show comparable emission rates, then residential and small commercial natural gas combustion in the Los Angeles area in 1982 could have contributed amounts of PAH and oxy-PAH to the urban atmosphere that are comparable to that emitted from diesel vehicles, and that are about half as much as that released from catalyst-equipped automobiles. Therefore, in spite of its low mass emission rate, natural gas combustion aerosol may be of interest because of its high PAH content.

Cigarette Smoke in the Urban Atmosphere

Molecular marker compounds that can be used to trace cigarette aerosol in the outdoor urban atmosphere are identified. While the most abundant resolved organic compounds present are nitrogen-containing heterocyclics (e.g. nicotine), other potential tracers that will be more stable in the outdoor urban atmosphere also are found. *iso-* and *anteiso*-Alkanes ($C_{29} - C_{34}$) are enriched in cigarette smoke aerosol and 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. Relative to major leaf surface wax *n*-alkanes, these *iso-* and *anteiso*-alkanes are enriched by a factor of more than forty in tobacco and tobacco smoke particles as compared to leaf surface waxes from Los Angeles area plants. It is found that the *iso-* and *anteiso*-alkanes concentration pattern generated by cigarette smoke is preserved in the urban atmosphere and is measured at levels that are comparable to emissions estimates based on daily cigarette consumption. Using these marker compounds, ambient fine cigarette smoke particles are estimated to be present at a concentration of 0.57 to 0.72 μg m^{-3} in the Los Angeles outdoor air.

Hot Asphalt Roofing Tar Pot Fumes

The organic compounds present in fine particulate roofing asphalt tar fumes have been characterized using GC/MS-techniques. Most of the compound mass identified consists of *n*-alkanes (73%), while polycyclic aromatic hydrocarbons (PAH) and thia-arenes (S-PAH) contribute nearly 8% of the identified compound mass. The daily roofing tar pot contribution to the fine organic aerosol emissions in the greater Los Angeles area has been estimated. It has been found that hot process built-up roofing tarpot use contributed 3.1 kg of PAH on average per day in 1982. Roofing tar applications in the Los Angeles area emit quantities of PAH to that atmosphere that are comparable to the PAH emissions from diesel vehicles in Los Angeles.

Boilers Burning No.2 Distillate Fuel Oil

Fine particulate matter emitted from an industrial-scale boiler burning No.2 distillate fuel oil has been characterized on a molecular basis using GC/MS-techniques. Most of the identified compound mass consists of *n*-alkanoic acids (42.0–51.5%), aromatic acids (5.8–22.6%), and *n*-alkanes (6.7–25.0%). Polycyclic aromatic hydrocarbons (PAH) and oxygenated PAH (oxy-PAH) amount to 3.1–8.6% of the identifiable mass. Chlorine compounds in oil are known to promote PAH formation. Chloro-organic compounds are identified in the present source samples with emission levels that are similar to that found for PAH.

Wood Smoke

The fine organic particulate emissions from wood combustion in residential fireplaces has been characterized by GC/MS techniques. Pine, oak and synthetic log combustion was studied. More than 200 organic compounds were quantified including alkanes, alkenes, alkanals, alkanoic acids, alkenoic acids, dicarboxylic acids, resin acids, hydroxylated/methoxylated phenols, PAH, plus polycyclic aromatic ketones and quinones. Many of the resin acids and the substituted phenolic compounds can be used to trace the presence of wood smoke in the urban atmosphere.

Source Contributions to Airborne Organic Compound Concentrations

The organic compound emission rates from all sources acting together were computed for an 80 km x 80 km study area centered over Los Angeles. The relative emission rates for more than 100 individual compounds were compared to the relative abundance of the same compounds in the atmosphere. The predicted and measured relative abundances 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. Aliphatic dicarboxylic and aromatic polycarboxylic acids concentrations measured in the urban atmosphere are much greater than can be contributed by the primary emissions from the sources indicating that these acids 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 confirm whether or not the relative abundance of particulate organic compounds measured in ambient air at community receptor air monitoring sites.

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 emissions from all sources acting together are computed for an 80 km × 80 km area centered over Los Angeles. The relative abundance of the individual organic compounds emitted from the sources studied is compared with the average organic compound concentrations measured throughout 1982 at West Los Angeles, downtown Los Angeles, and Pasadena, as reported in Chapter 12. This comparison makes it possible to confirm that most of the primary organic compound emissions to the atmospheric aerosol complex are now understood. It also allows the identification 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 in concentrations that greatly exceed the direct emissions of those compounds from primary emission sources.

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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.

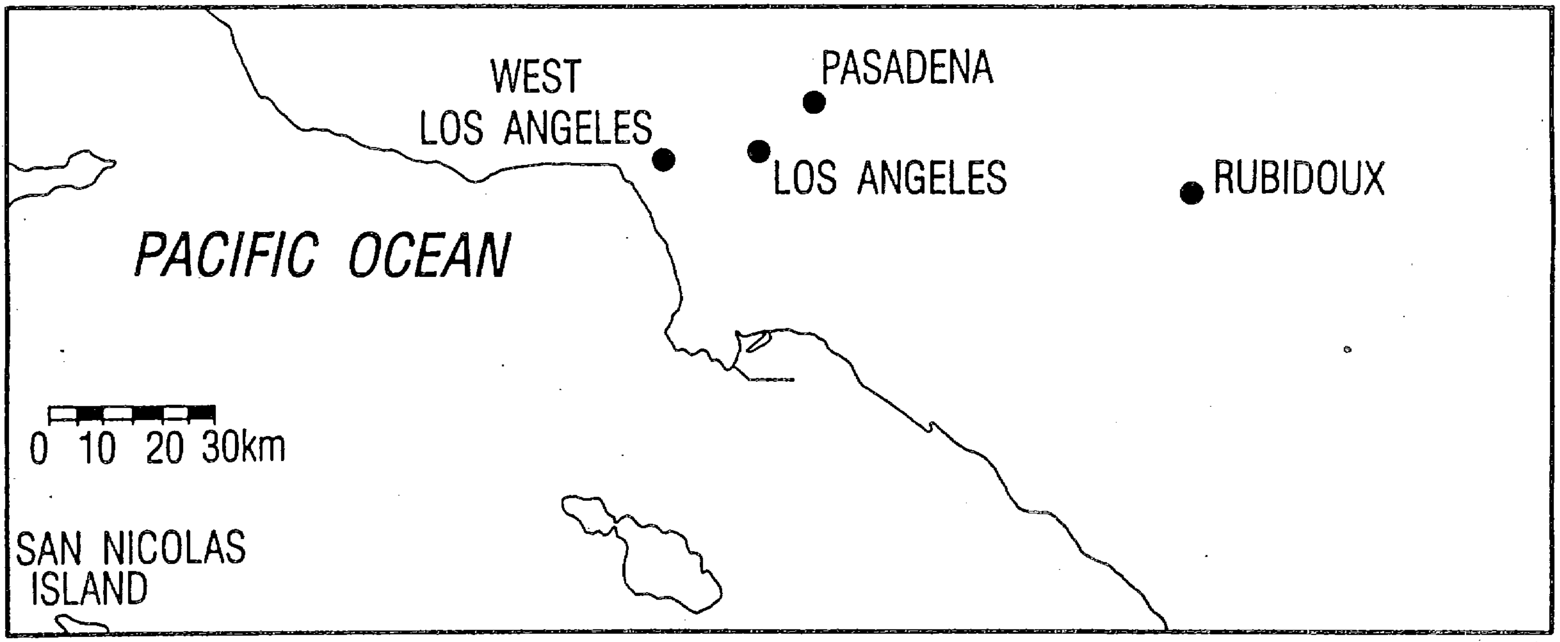

Figure 2.1: Sampling sites used throughout Southern California during the present study.

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 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 n-alkanes, n-alkanoic acids, one n-alkenoic acid, one 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).

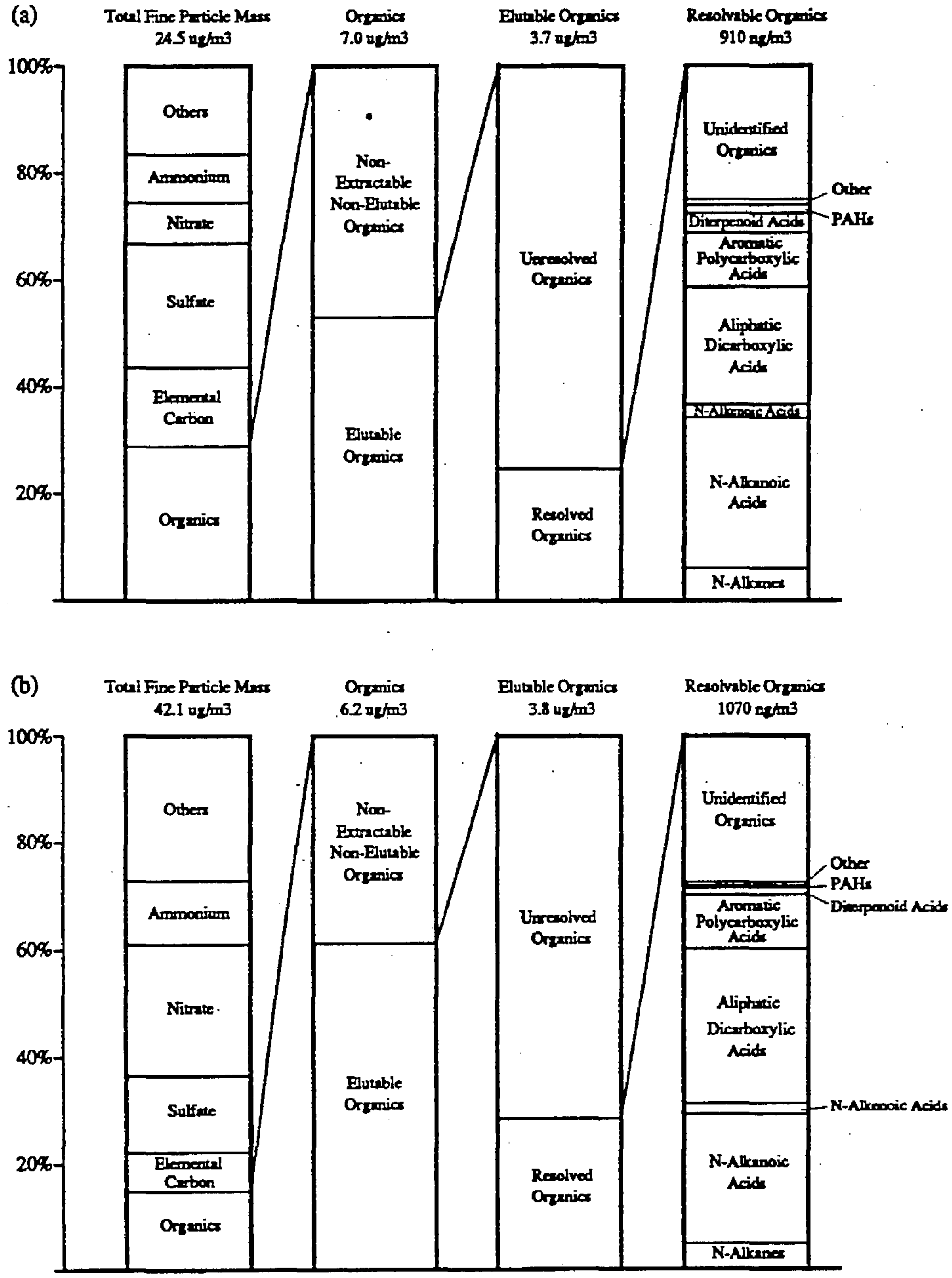

Fig. 2.2: Mass balance on the chemical composition of annual mean fine particle concentrations — 1982 for a) West Los Angeles and b) Rubidoux (Riverside).

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 (**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

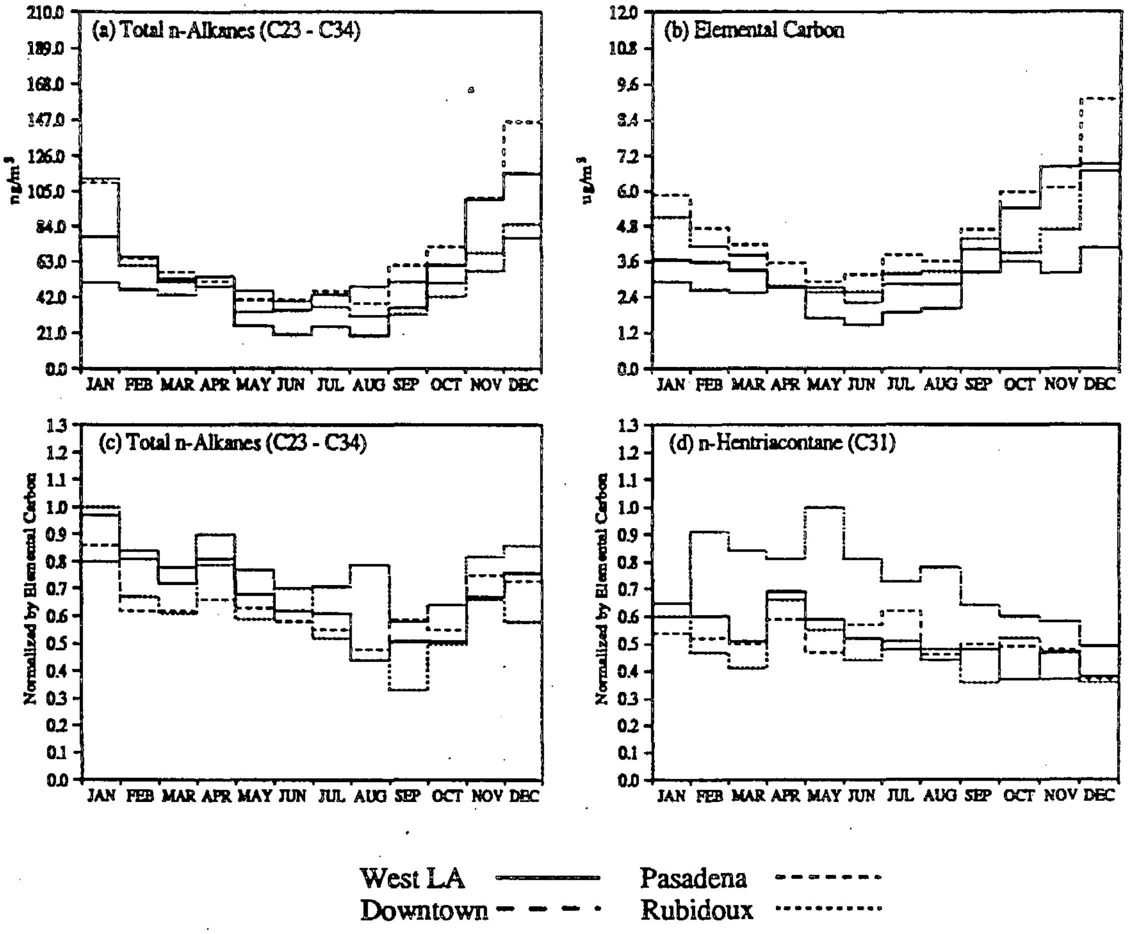

Fig. 2.3: Monthly averaged concentration profiles for (a) total n-alkanes (C_{23} - C_{34}) and (b) elemental carbon; monthly normalized concentration profiles for (c) total n-alkanes (C_{23} - C_{34}), and (d) n-hentriacontane (C_{31}).

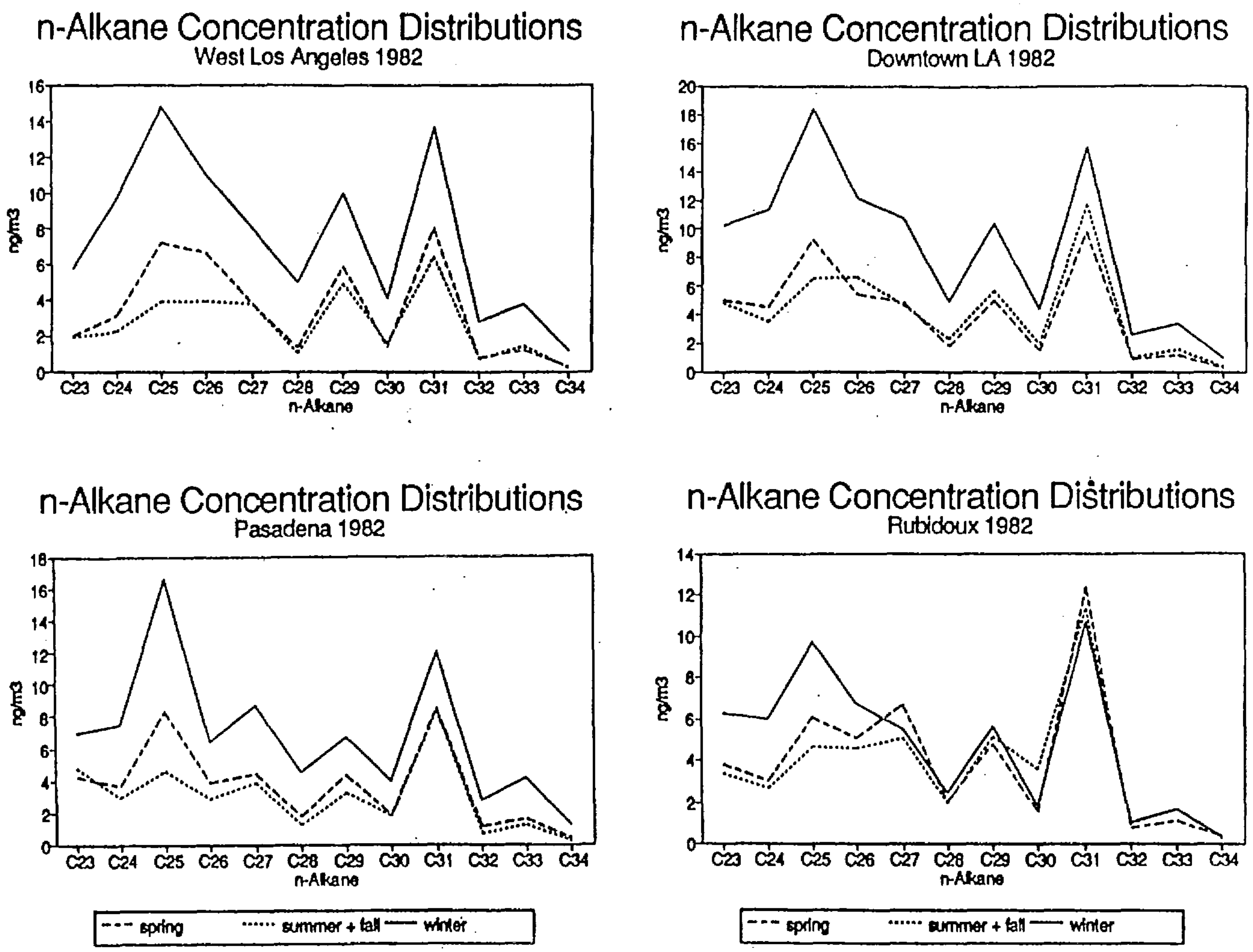

Figure 2.4: Seasonal n-alkane concentration distributions (spring: March - May; summer + fall: June - October; winter: November - February)—1982.

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 $\underline{n}$-nonanoic acid (C_9) to $\underline{n}$-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 $\underline{n}$-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 $\underline{n}$-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 $\underline{n}$-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} $\underline{n}$-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 $\underline{n}$-alkanoic acids, with $\underline{n}$-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.

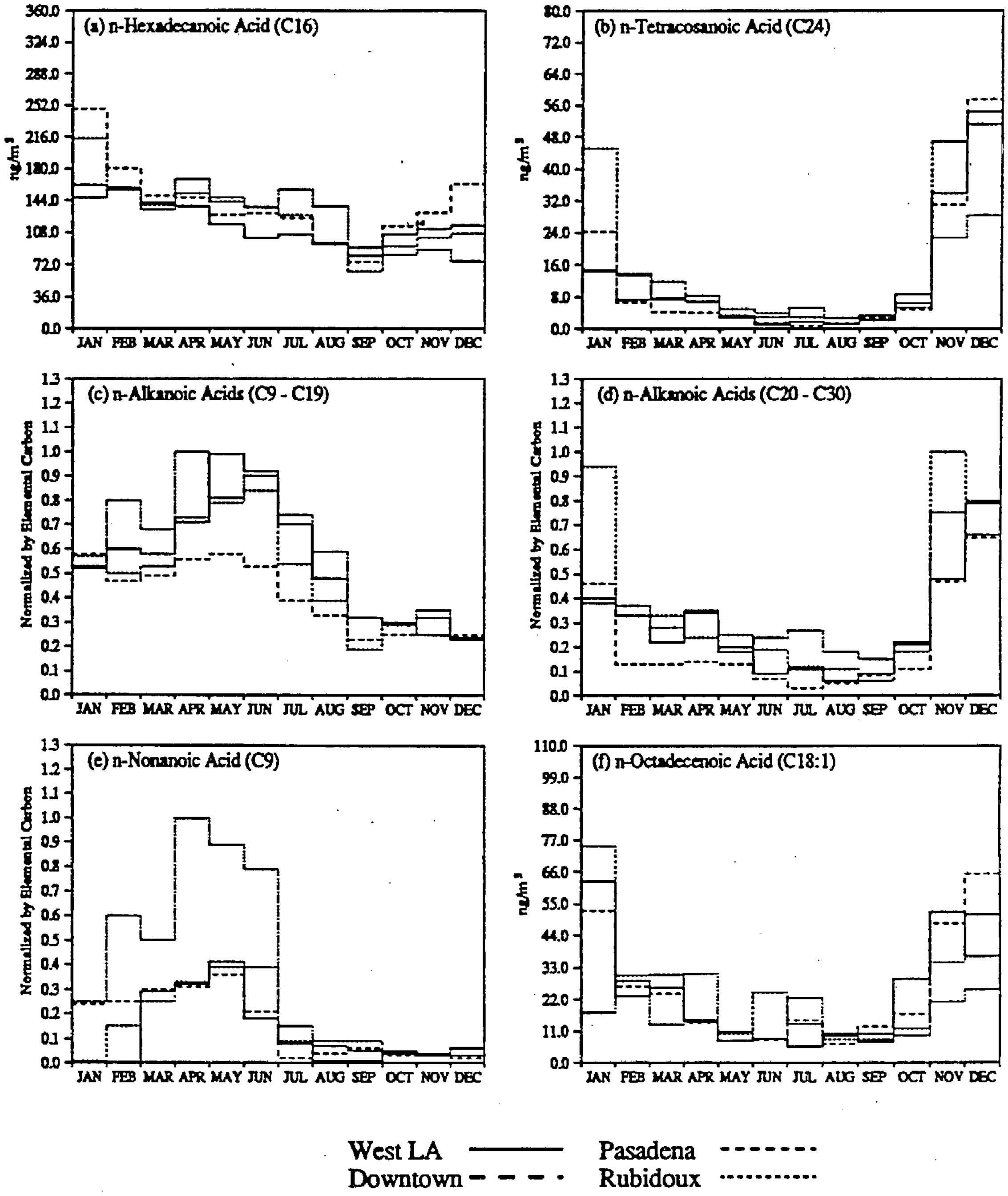

Fig. 2.5: Monthly averaged concentration profiles for a) n-hexadecanoic acid (C_{16}) and b) n-tetracosanoic acid (C_{24}); monthly normalized concentration profiles for c) n-alkanoic acids (C_9 - C_{19}), d) n-alkanoic acids (C_{20} - C_{30}), and e) n-nonanoic acid (C_9); monthly averaged concentration 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

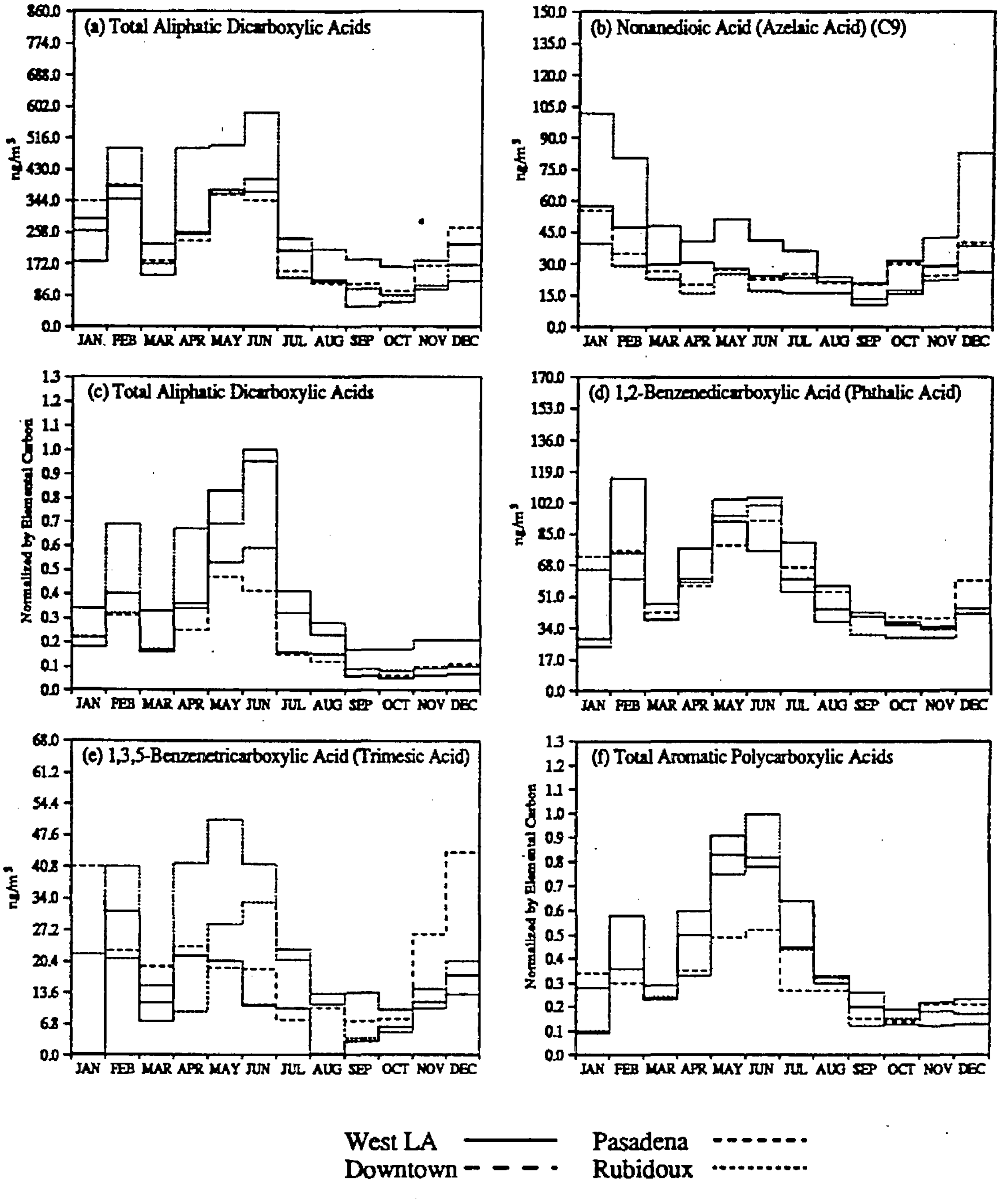

Fig. 2.6: Monthly averaged concentration profiles for a) total aliphatic dicarboxylic acids and b) nonanedioic acid (azelaic acid); monthly normalized concentration profile for c) total aliphatic dicarboxylic acids; monthly averaged concentration profiles for d) 1,2-benzenedicarboxylic acid (phthalic 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 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

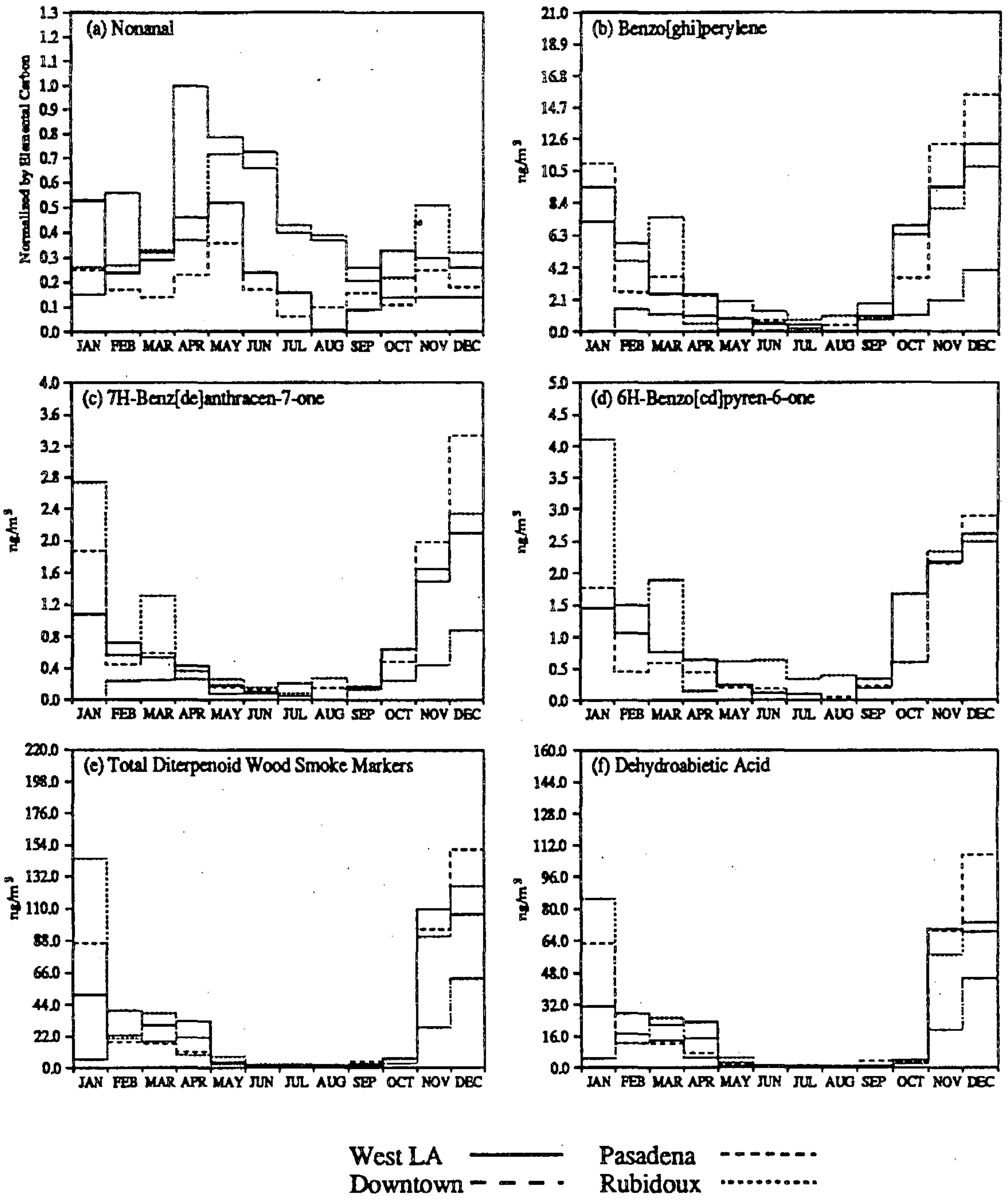

Fig. 2.7: Monthly normalized concentration profile for a) nonanal; monthly averaged concentration profiles for b) benzo[ghi]perylene, c) 7H-benz[de]anthracen-7-one, d) 6H-benzo[cd]pyrene-6-one, e) total diterpenoid wood smoke markers, and f) dehydroabietic acid. (Normalization was achieved by dividing 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 n-alkanoic acid concentrations in winter is dominated by the higher carbon number homologues (C_{20} – C_{30}). The higher molecular weight 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 n-alkanoic acids (C_{20} – C_{30}) during the winter season.

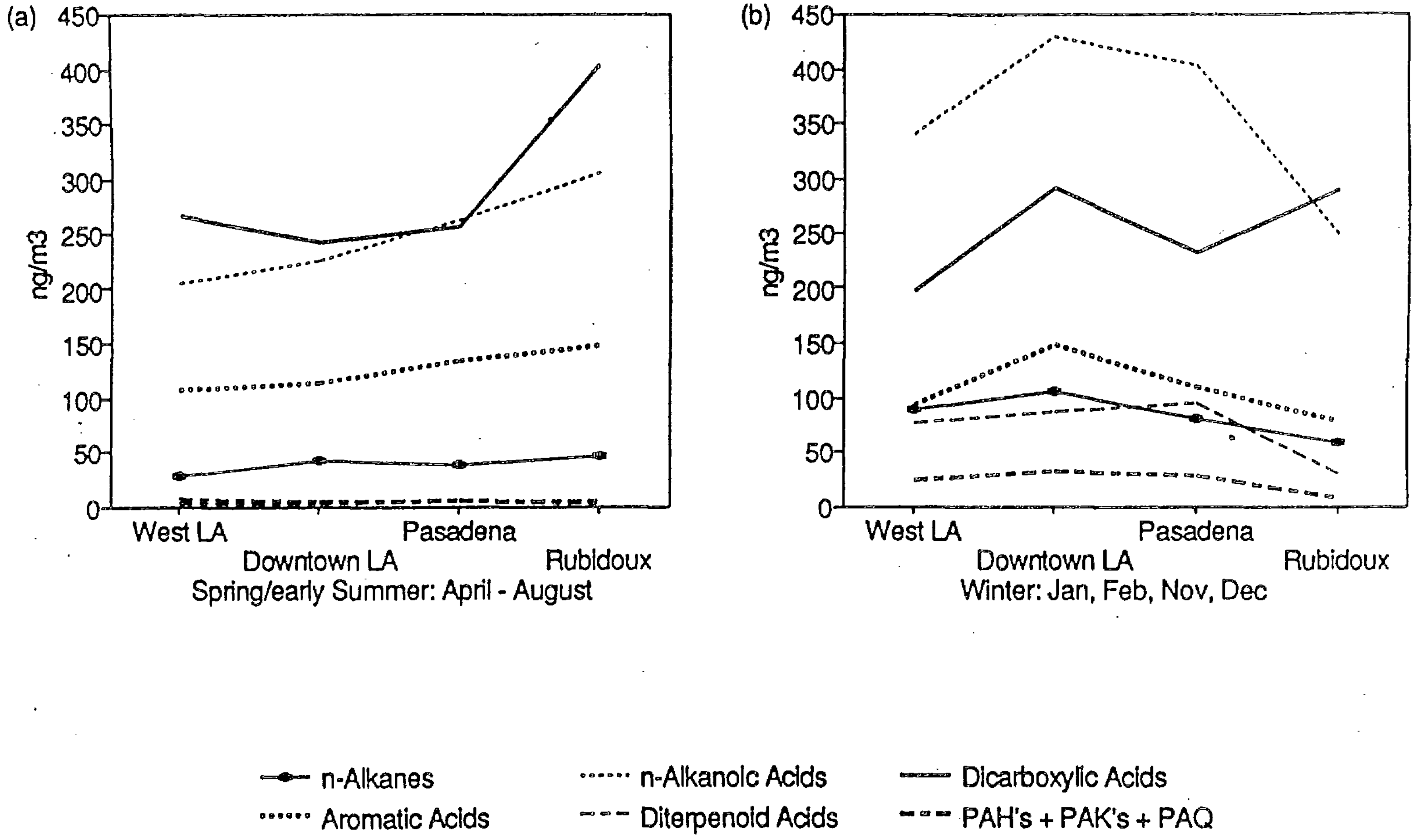

Figure 2.8: Seasonal and spatial concentration patterns of fine particle associated organic compounds for a) April through August and b) January, February, November and December—1982.

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.

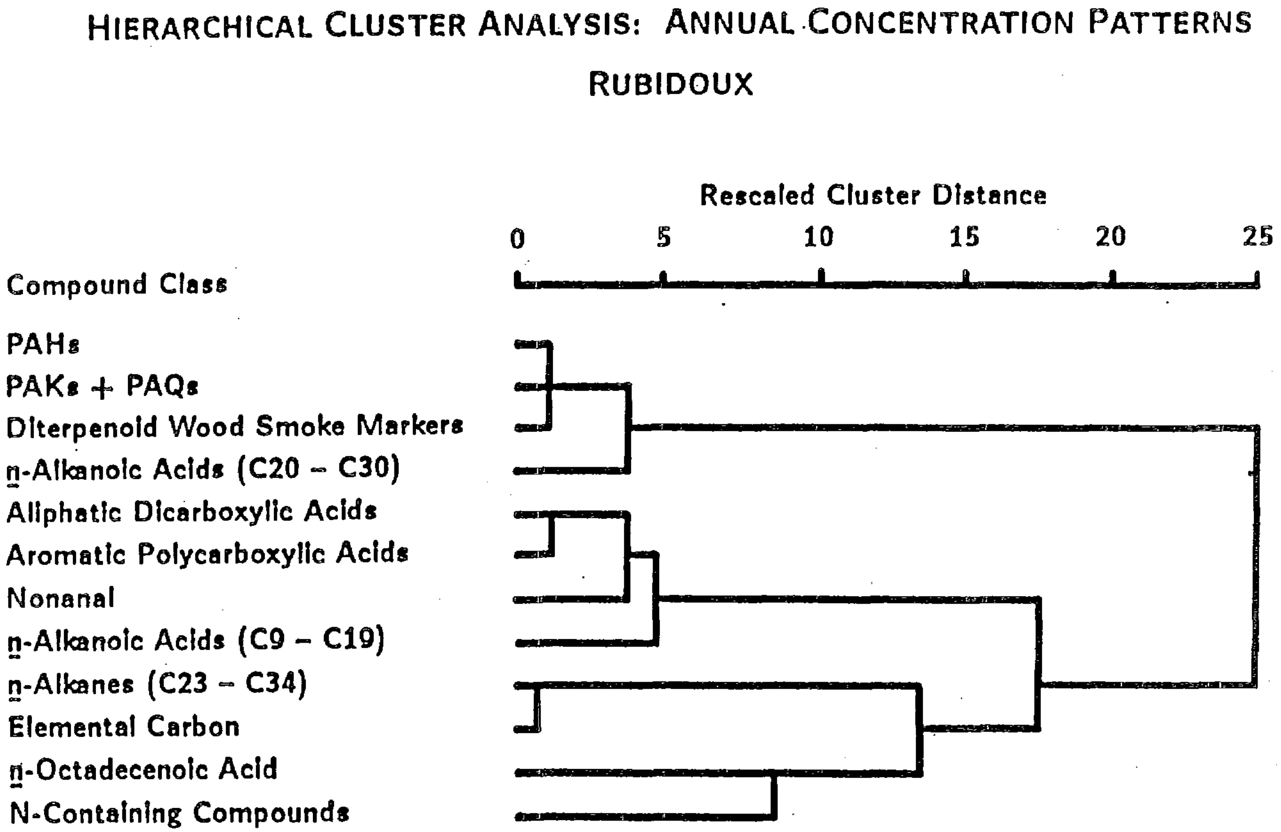

Figure 2.9: Hierarchical cluster analysis to determine similarities in the seasonal variations of monthly average concentrations measured at Rubidoux.

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 ($d_p \leq 2\ \mu m$) 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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Reference: Rogge, W.F.; Mazurek, M.A.; Hildemann, L.M.; Cass, G.R.; Simoneit, B.R.T. *Environ. Sci. Technol.*, 1991, 25, 1112–1125.

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%]–cyanopropylphenyl 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 n–C_{10} to n–C_{36}; 2) normal alkanoic acids as methyl esters from n–C_6 to 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

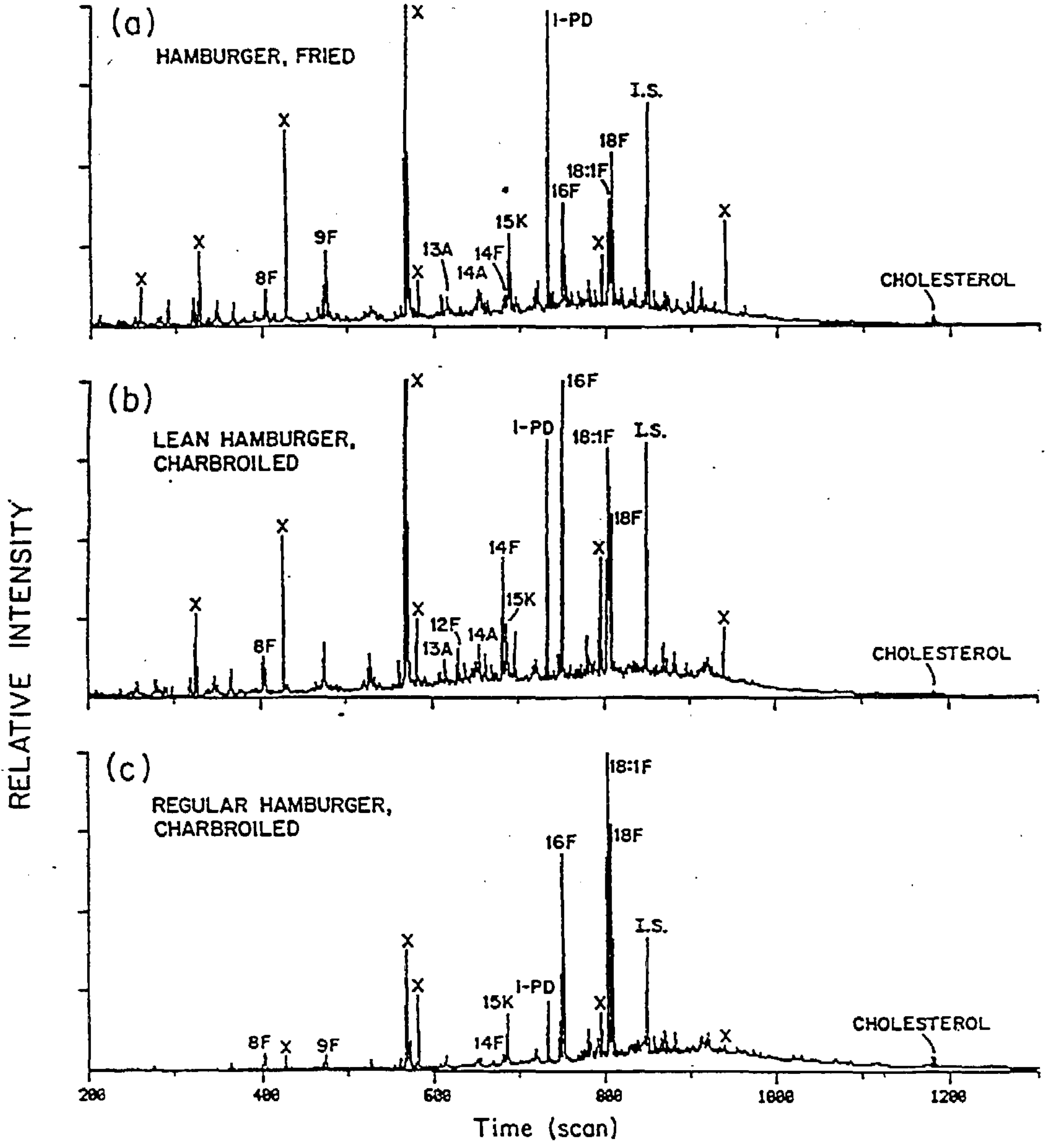

Figure 3.1: Total ion current traces from GC/MS data (equivalent to HRGC traces) for the smoke aerosol from hamburger cooking: (a) frying extra-lean/regular meat 50%/50% (15.5% fat), (b) gas-broiling extra-lean meat (10% fat), (c) gas-broiling regular meat (21% fat). Numbers refer to carbon chain length 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 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 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 n–C_{24} and 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

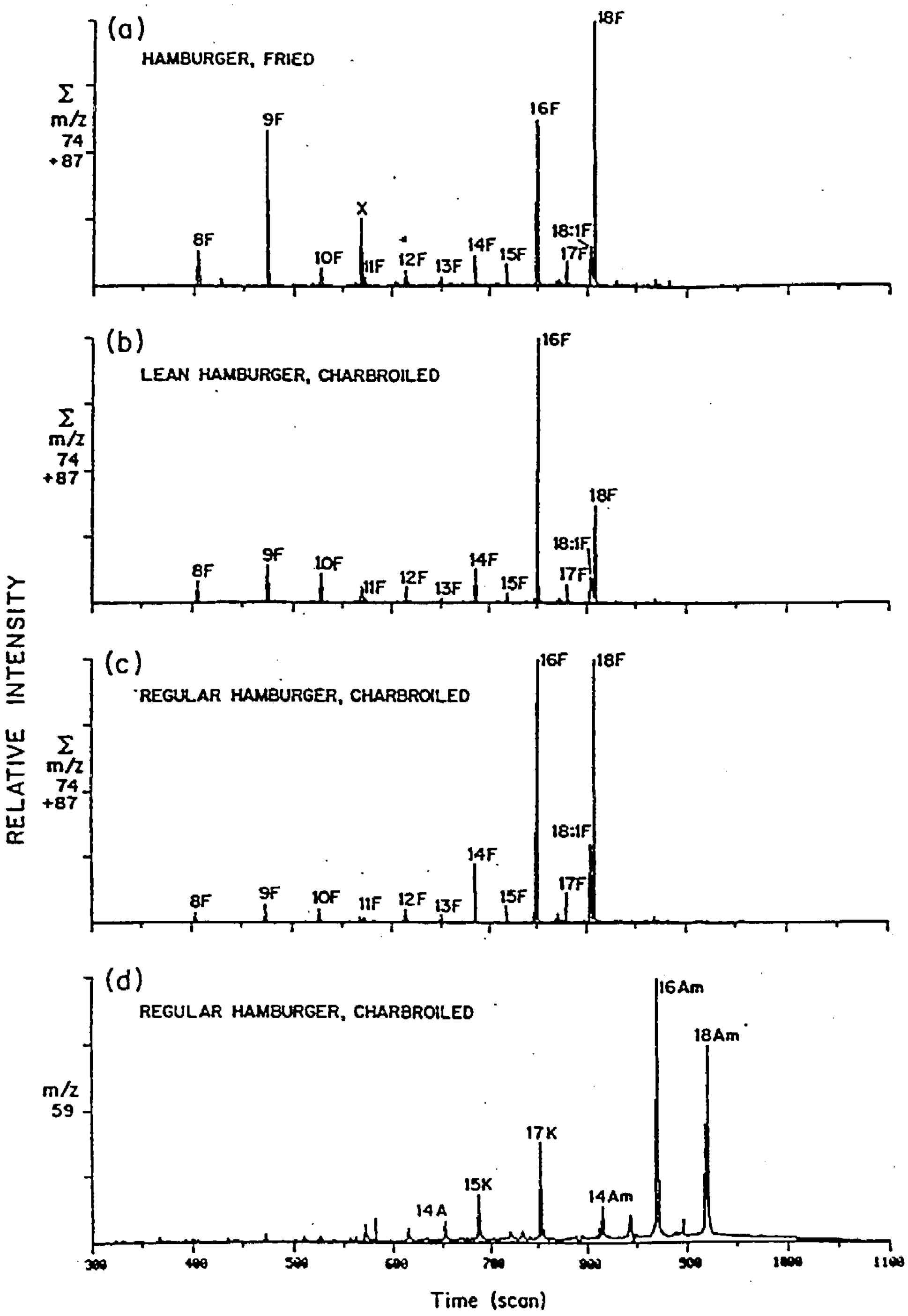

Figure 3.2: Selected mass fragmentograms for n–alkanoic acids as methyl esters (a)–(c), showing summed m/z 74 + 87, and amides (d), showing m/z 59 for the smoke aerosol from hamburger cooking: (a) frying, (b) gas–broiling extra–lean meat, (c) gas–broiling regular meat, (d) gas–broiling regular meat (numbers 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

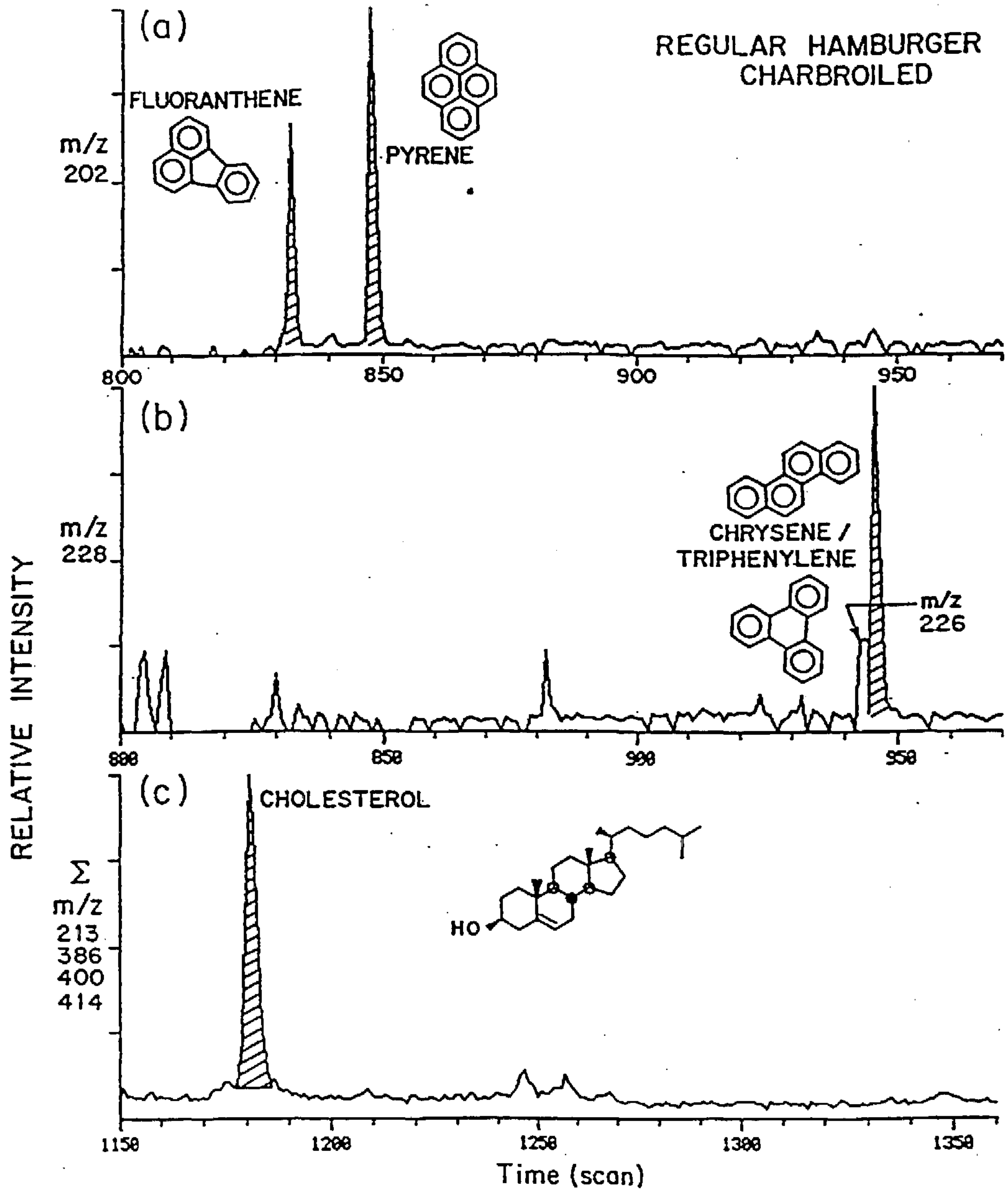

Figure 3.3: Selected mass fragmentograms for PAH ((a) + (b) —m/z 202 and 228, respectively) and sterols ((c) —summed m/z 213, key ion and m/z 386, 400, and 414, molecular ions of C_{27} to C_{29} sterols).

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

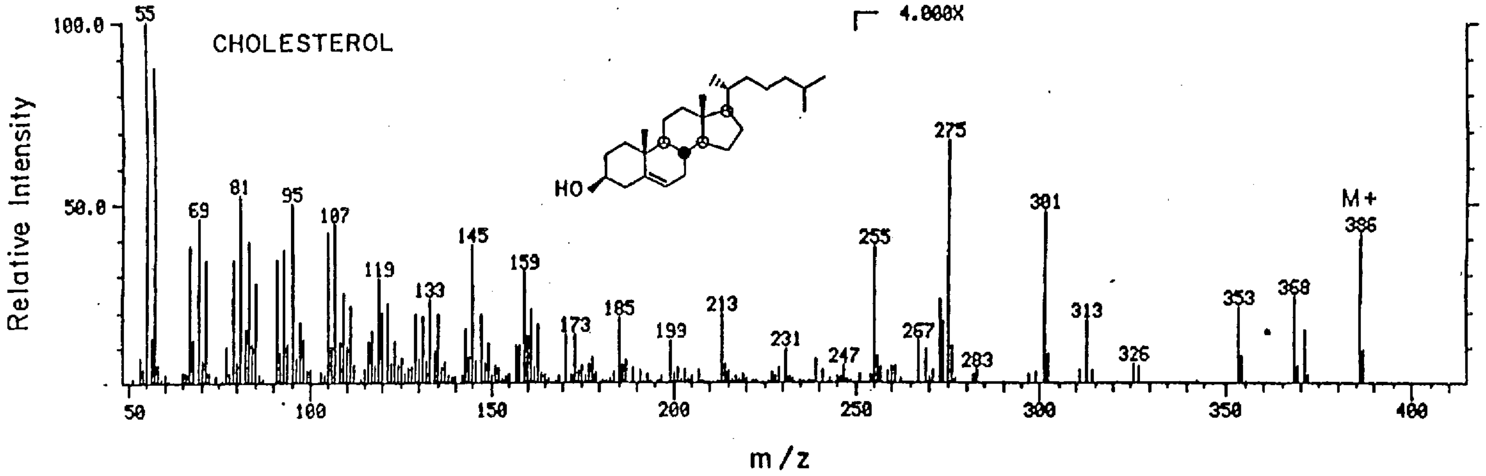

Figure 3.4: An example mass spectrum of underivatized cholesterol present in the smoke aerosol from hamburger cooking.

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.

PART A	Emission Rates[a] in $\mathrm{mg\ kg^{-1}}$ of Meat Cooked			
	Frying	Charbroiling		Compound ID[b]
	extralean & regular meat	extralean meat	regular meat	
	—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	
	—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	
	—n–Alkenoic Acids[c]—			
cis–9–hexadecenoic acid (palmitoleic acid)	0.8	4.6	52.0	b
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	Charbroiling		Compound
	extralean & regular meat	extralean meat	regular meat	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[c]—				
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**	**Charbroiling**		Compound
	[a] **extralean & regular meat**	**extralean meat**	**regular meat**	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] (extralean/reg.)	Case 2[b] (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 (80×80 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 $\times$ 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 $\times$ 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

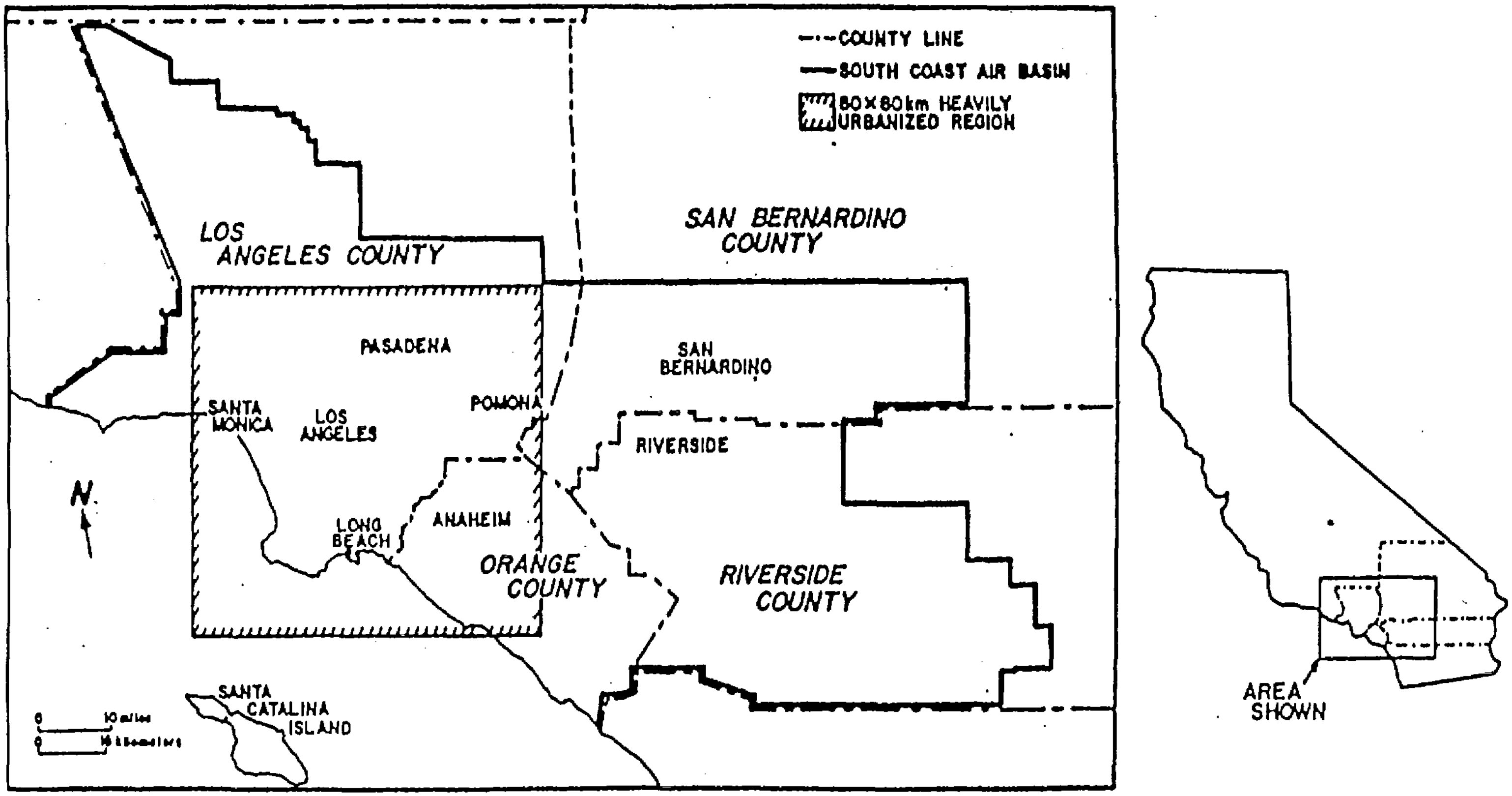

Figure 3.5: Geographic outline of the South Coast Air Basin, showing an 80×80 km square area that contains 83% of the basin's population in 1982.

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

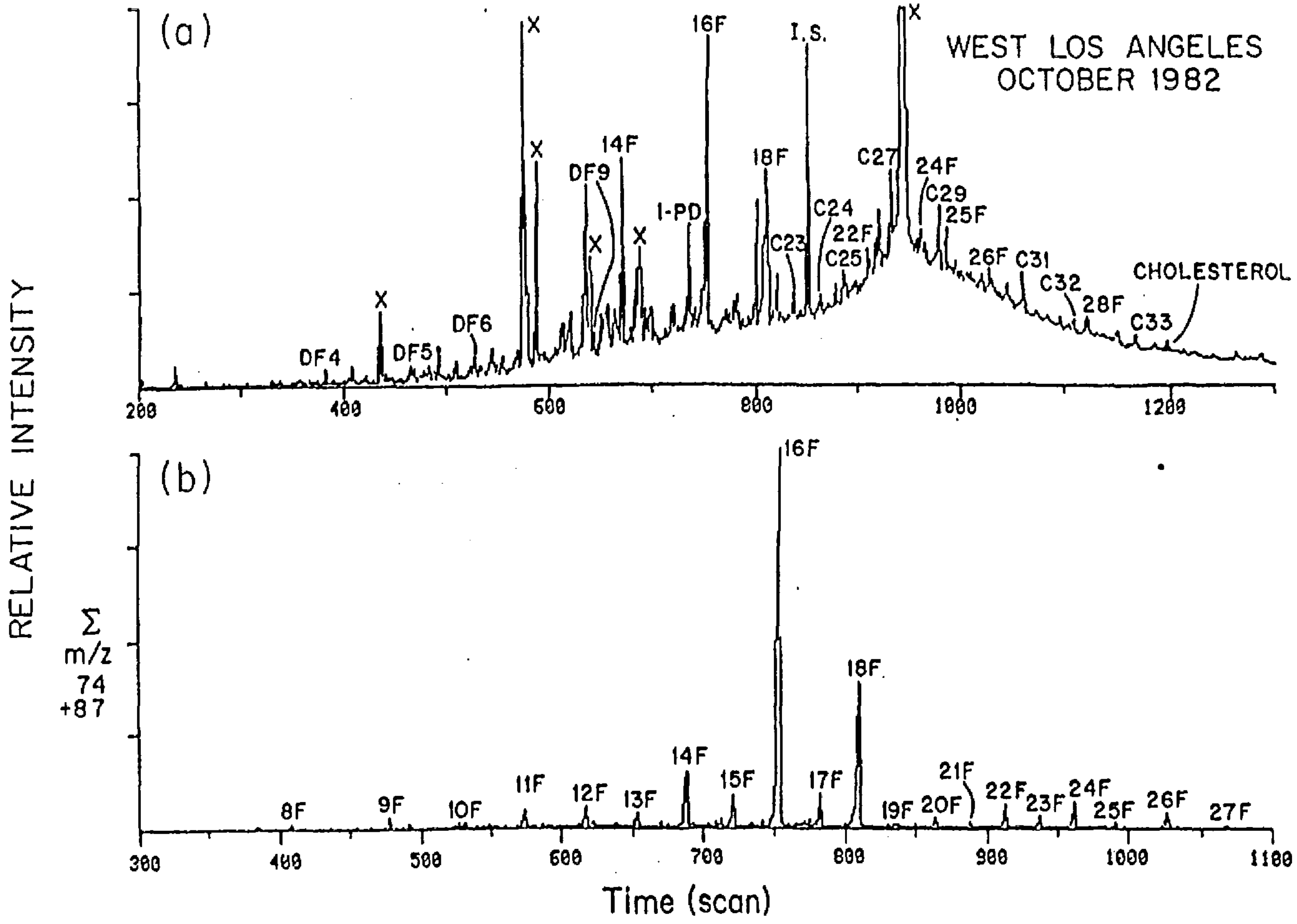

Figure 3.6: Total ion current (a) and summed m/z 74 + 87 traces (b) for the GC/MS data from the acid + neutral fraction of the fine ambient aerosol from West Los Angeles in October 1982 ($d_p \leq 2.0$ μm). Peak labels as in Figure 3.1, and DF = dicarboxylic acid; C_i = n-alkane.

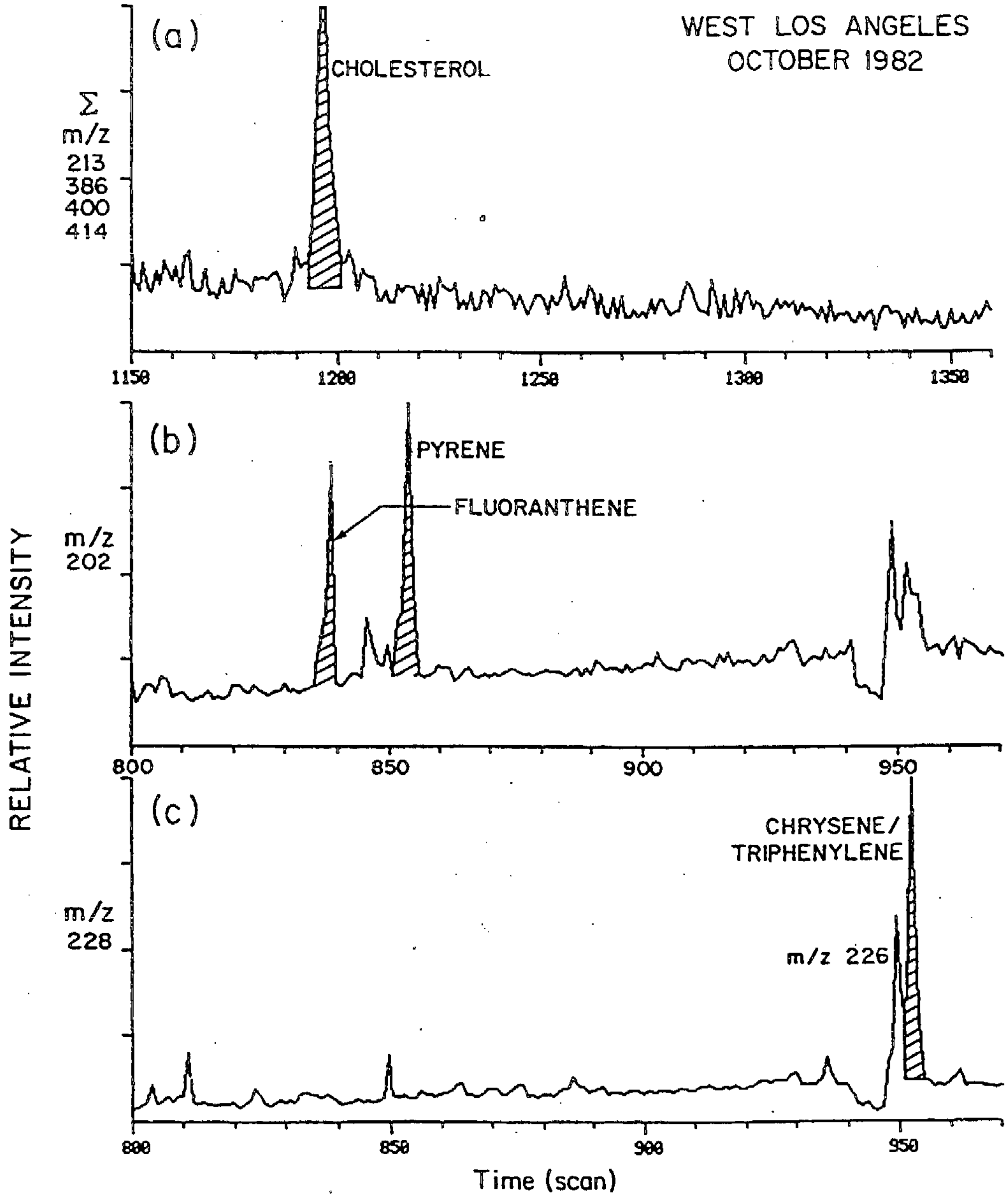

Figure 3.7: Selected mass fragmentograms for sterols (a) and for PAHs (b) + (c) in the acid + neutral fraction of the fine ambient aerosol ($d_p \leq 2.0\ \mu m$) from West Los Angeles in October 1982 (same plot parameters as Figure 3.3).

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 ($d_p \leq 2\ \mu m$) 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 × 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

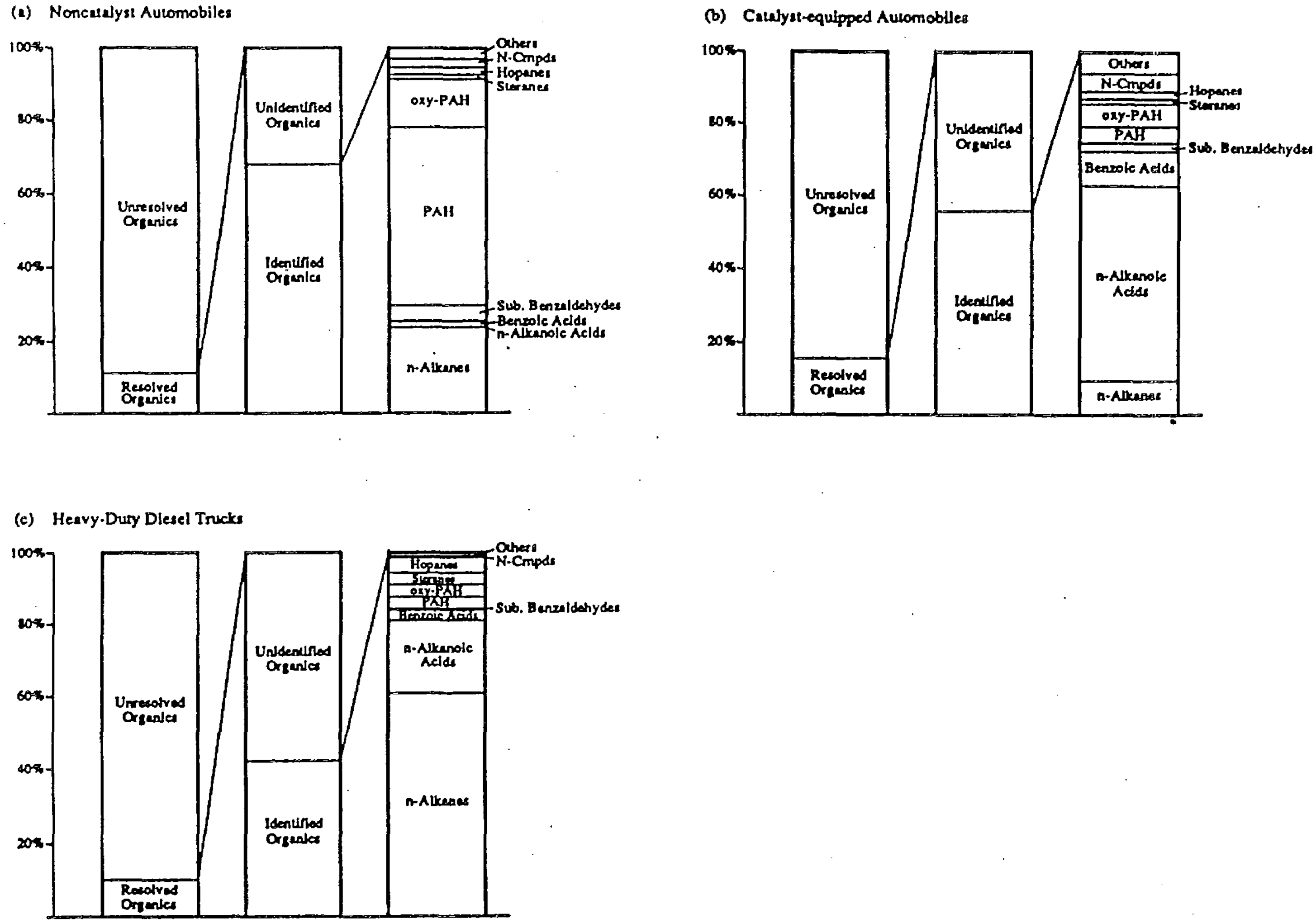

Figure 4.1 Mass balance for elutable organic matter in the fine particle emissions from: (a) automobiles without catalytic converters, (b) catalyst-equipped automobiles, and (c) heavy-duty diesel trucks.

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)

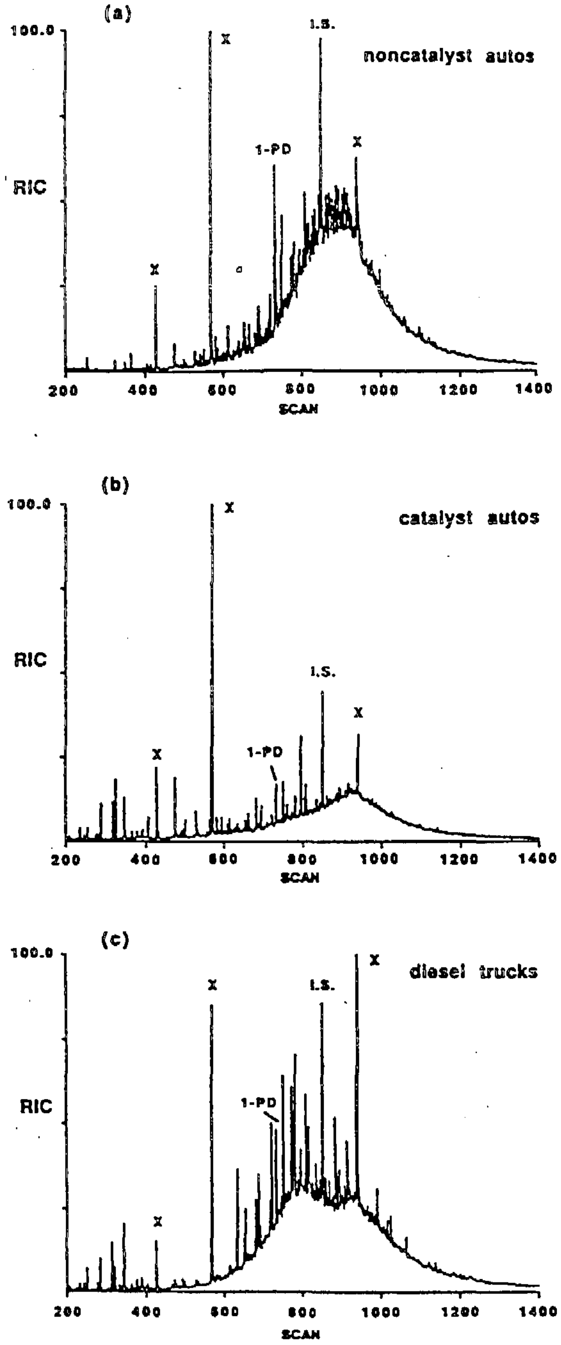

Figure 4.2 Total reconstructed ion current (RIC) for the fine particle organics emitted from the vehicles tested: (a) automobiles without catalytic converters, (b) catalyst-equipped automobiles, and (c) heavy-duty diesel trucks. I.S. is the internal standard ($\underline{n}$-$C_{24}D_{50}$); 1-PD is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

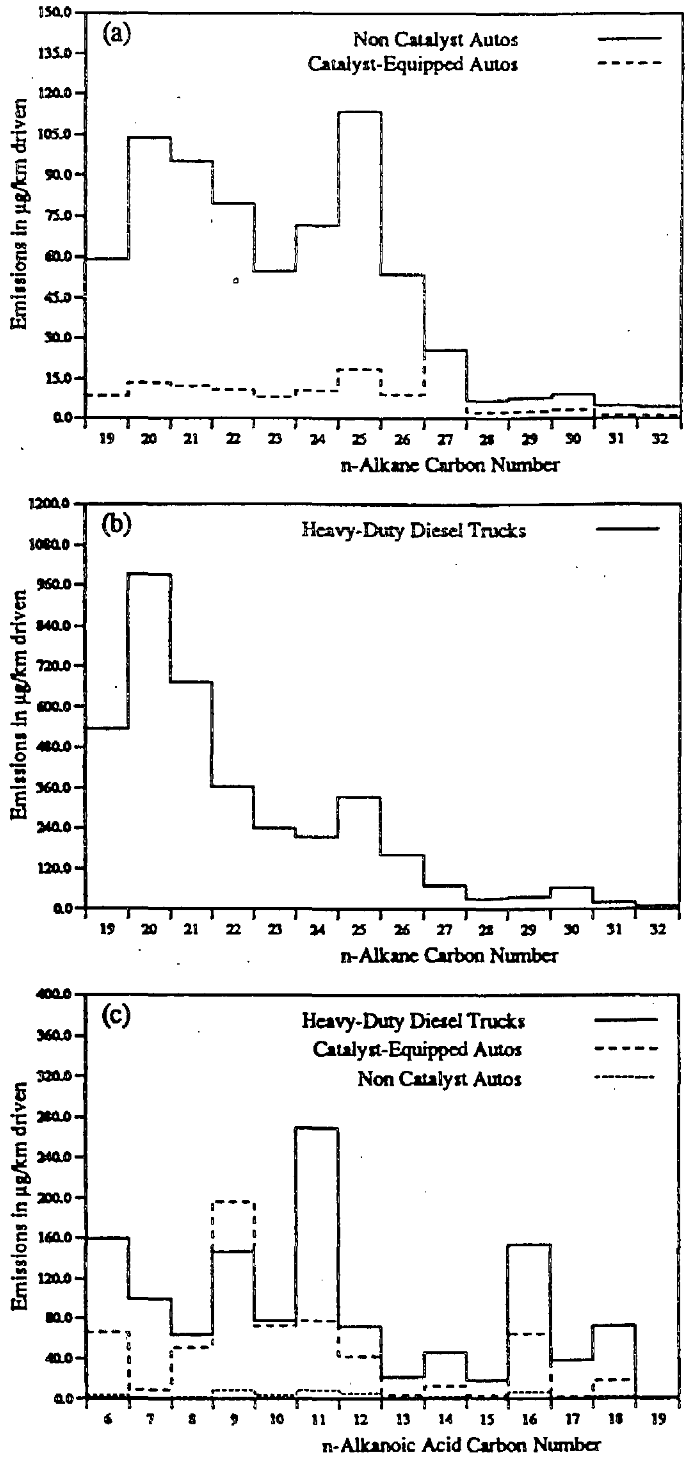

Fig. 4.3: Vehicular emission profiles for fine particle associated n-alkanes and n-alkanoic acids: (a) n-alkanes from automobiles with and without catalytic converters, (b) n-alkanes from heavy-duty diesel trucks, and (c) n-alkanoic acids from the 3 vehicle types tested.

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

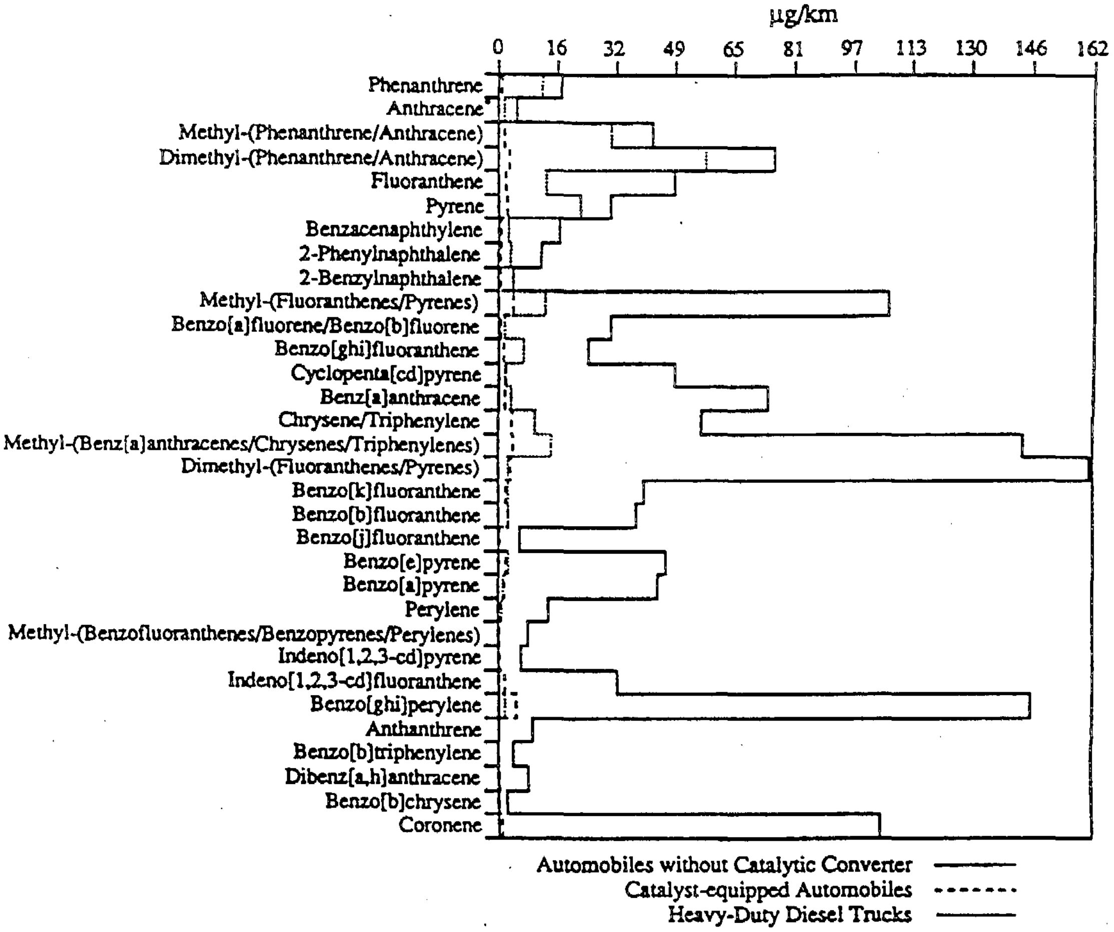

Figure 4.4 Vehicular emission profiles for fine particle polycyclic aromatic hydrocarbons (PAH).

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).

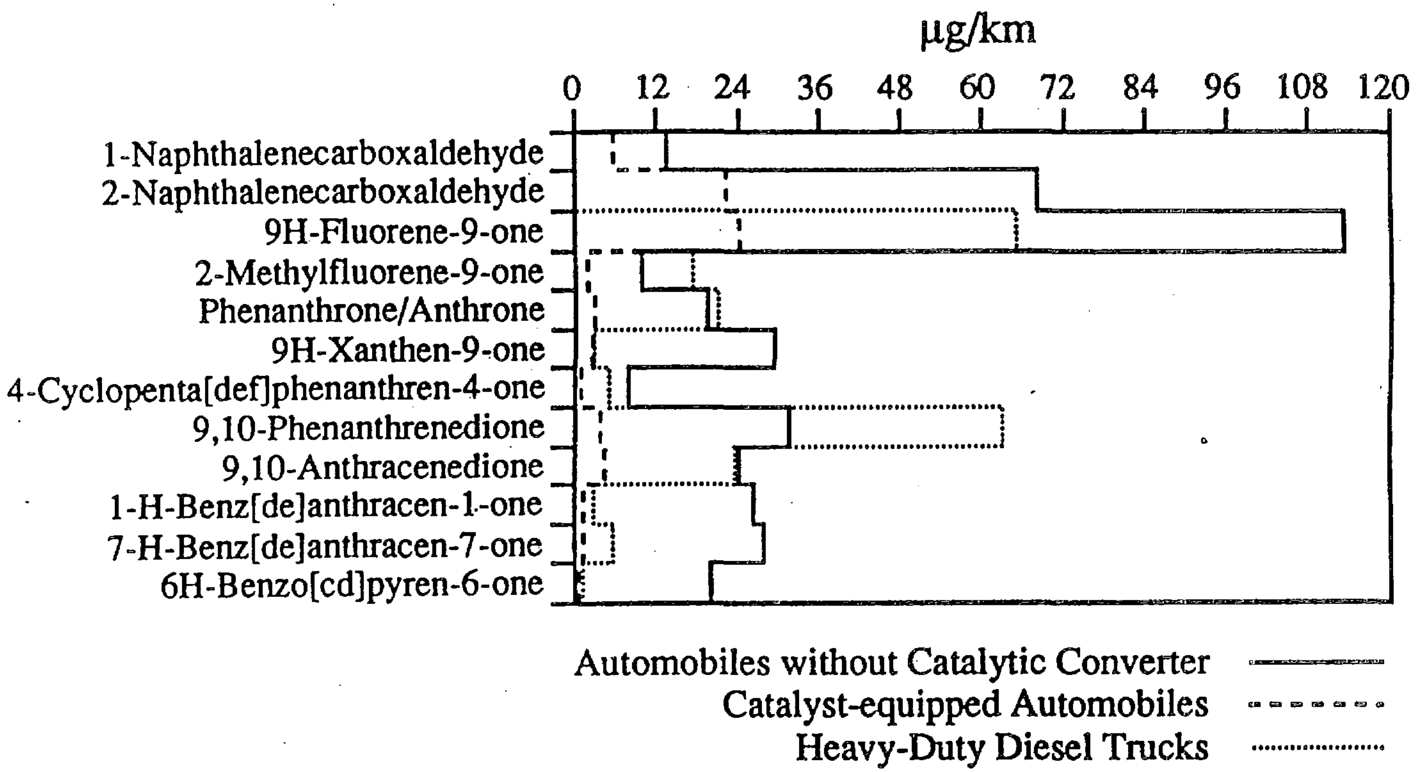

Figure 4.5 Vehicular emission profiles for fine particle oxygenated polycyclic aromatic hydrocarbons (oxy-PAH).

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

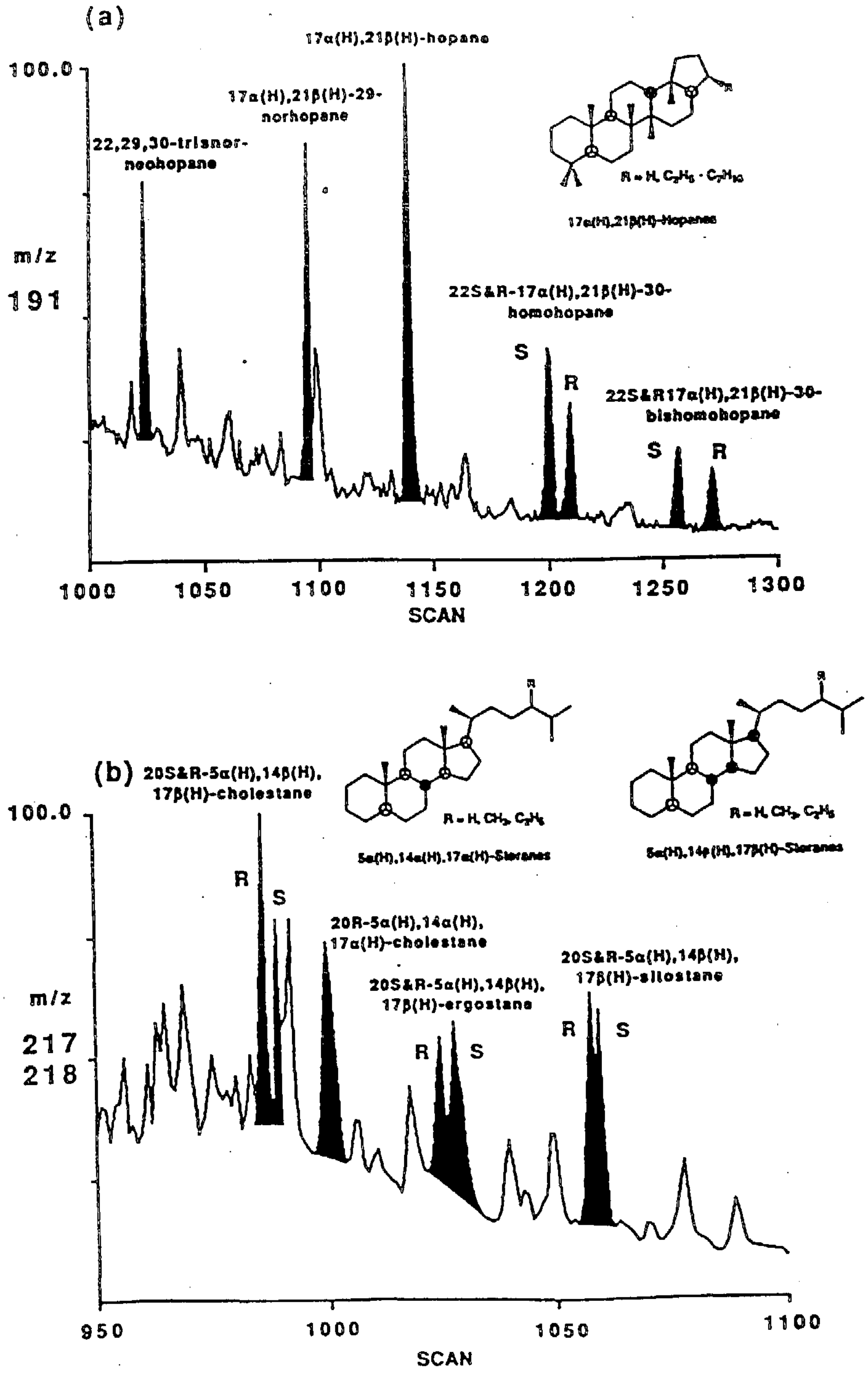

Figure 4.6 Selected mass fragmentograms for fine particle organic aerosol emissions from heavy-duty diesel trucks, (a) m/z 191: indicator for pentacyclic triterpanes, (b) m/z 217 + 218: key fragment ions for steranes.

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 $\mu g\ km^{-1}$			
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} Automobiles Noncatalyst	 Catalyst	 Heavy-Duty Diesel Trucks	Compound ID^b
—*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 $\mu g\ km^{-1}$			
	Automobiles		Heavy-Duty Diesel Trucks	Compound ID[b]
	Noncatalyst	Catalyst		
—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.**

	Emission Rates in $\mu g\ km^{-1}$			
Compound Name[a]	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).**

Mobile Sources	Fine Particulate Emissions[a] in kg day^{-1}: Organic Carbon (OC)	Fine Particulate Emissions[a] in kg day^{-1}: 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 × 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 × 80 km) Los Angeles Study Area for 1982.**

	Emission Rates in kg day^{-1}		
	Gasoline Vehicles[a]		**Diesel**
Compound Class	**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 × 80 km area in 1982: noncatalyst autos 53.7×10^6 km; catalyst autos 140.0×10^6 km, and heavy-duty diesel trucks 9.4×10^6 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 $17\alpha(H), 21\beta(H)$-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 × 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 $\mu g\ m^{-3}$, downtown Los Angeles 8.63 $\mu g\ m^{-3}$, and Pasadena 8.06 $\mu g\ m^{-3}$ during 1982 (organic compound concentrations $\simeq$ 1.2 × 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.

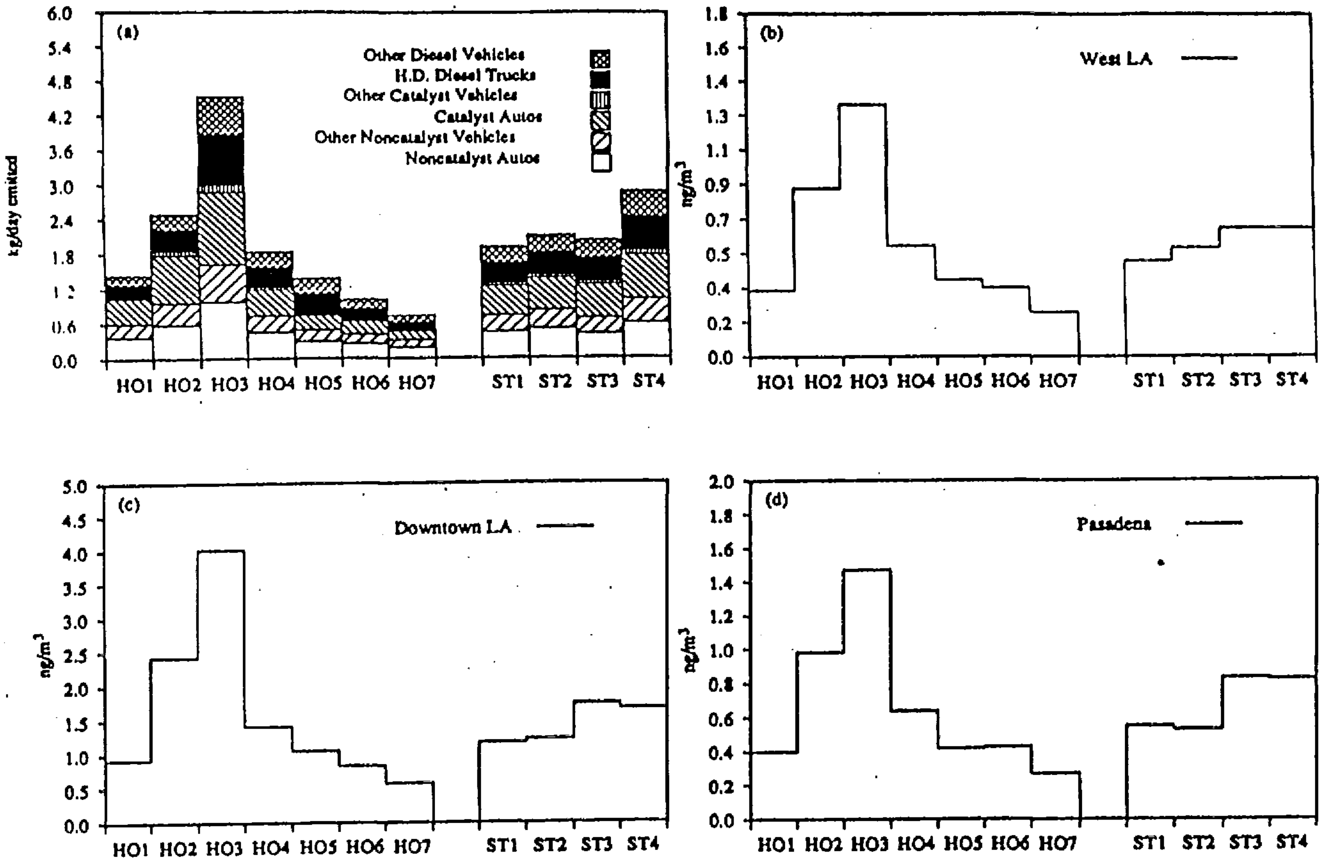

Figure 4.7 Vehicular emission profiles and ambient concentration profiles of fine particle fossil fuel markers: (a) 1982 emission rates for the 80 × 80 km greater Los Angeles area; measured 1982 annual average concentrations at (b) West Los Angeles, (c) downtown Los Angeles, and (d) Pasadena. HO1: 22,29,30-trisnorneohopane;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

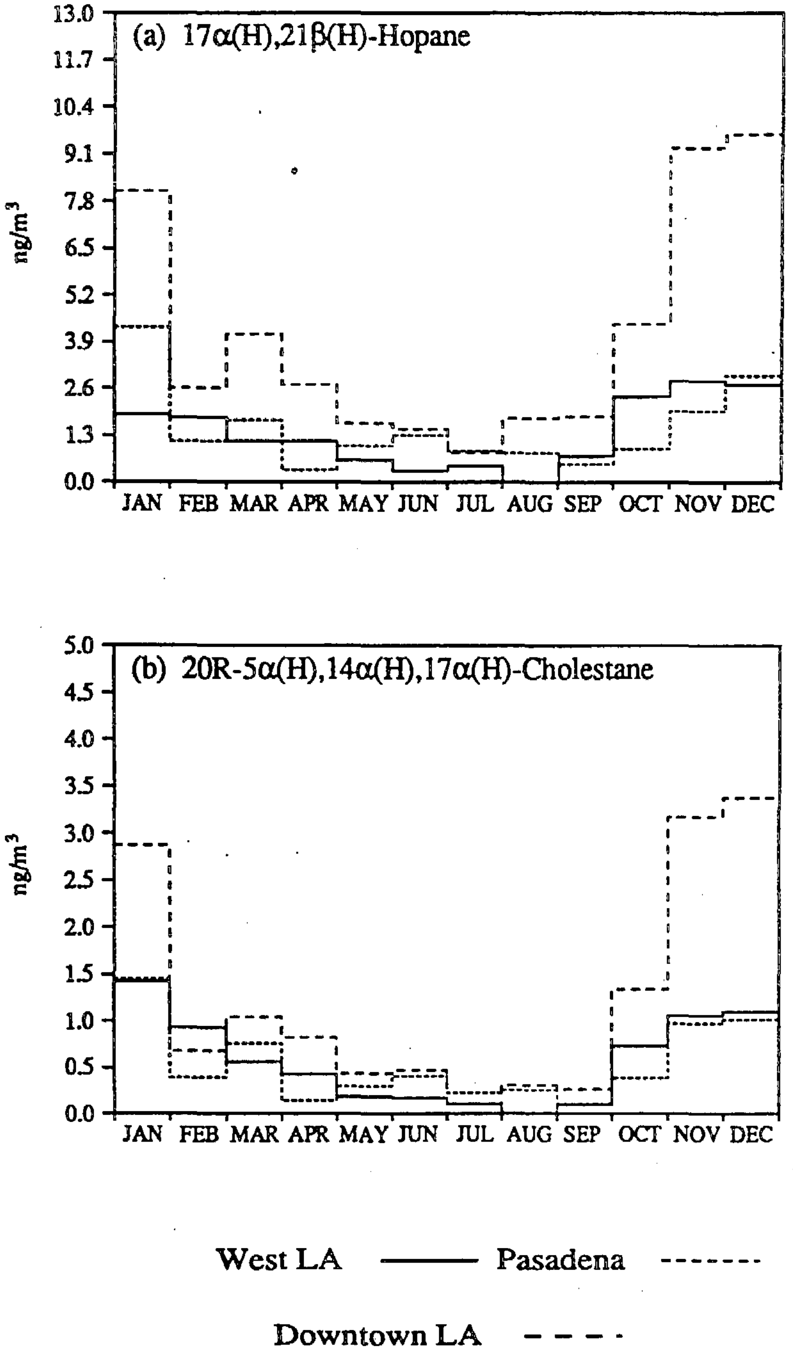

Fig. 4.8: Measured monthly average ambient fine particle concentrations for two fossil fuel markers during 1982. (a) 17α(H),21β(H)-hopane; (b) 20R–5α(H),14α(H),17α(H)–cholestane.

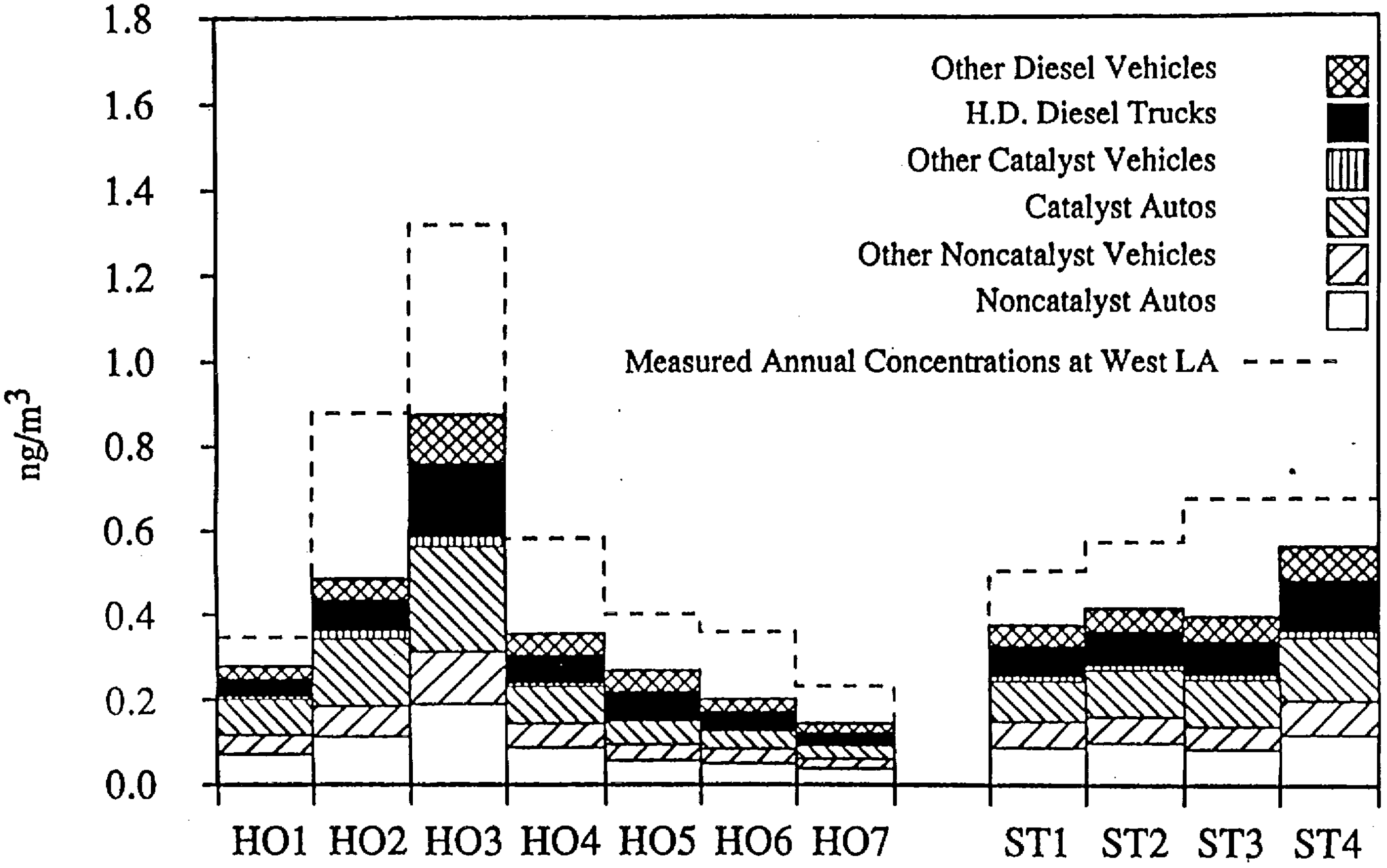

Figure 4.9 Estimated and measured ambient annual averaged concentrations of fine particle fossil fuel markers at West Los Angeles. HO1–HO7 and ST1–ST4 as in Fig. 4.7.

Conclusion

The chemical composition of organic fine particulate matter ($d_p \leq 2$ μm) 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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