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QUANTIFICATION OF URBAN ORGANIC AEROSOLS AT A MOLECULAR LEVEL: IDENTIFICATION, ABUNDANCE AND SEASONAL VARIATION

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Abstract—Organic aerosol samples collected systematically throughout a complete annual cycle at four urban sites in southern California are examined by high-resolution gas chromatography and gas chromatography/mass spectrometry. More than 80 organic compounds are quantified and their seasonal ambient concentration patterns are discussed. Primary organic aerosol constituents are readily identified, revealing an annual pattern, with high winter and low summer concentrations. In contrast, aliphatic dicarboxylic acids of possible secondary origin show a reverse pattern, with high concentrations in late spring/early summer. Concentration patterns similar to the secondary dicarboxylic acids also are found for aromatic polycarboxylic acids, certain lower molecular weight *n*-alkanoic acids, nonanal and other compounds. Molecular markers characteristic of woodsmoke are identified, and their concentrations change by season in close agreement with prior estimates of the seasonal use of wood as a fuel. This data set can be used to evaluate the predictions of mathematical models for the atmospheric transport and reaction of organic aerosol constituents defined at a molecular level.

Key word index: Hydrocarbons, organic acids, alkanals, PAH, oxy-PAH, woodsmoke markers, steroids, primary organic aerosol, secondary organic aerosol, seasonal distribution, spatial distribution.

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 1970s 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 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 analysed 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.

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Additional samples collected at an offshore island are used to establish pollutant concentrations upwind of the city.

In companion studies (Hildemann *et al.*, 1991a, b; Rogge *et al.*, 1991), primary organic aerosol emitted from the most important sources in the Los Angeles area are analysed 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-h periods at 6-day intervals for the entire calendar year 1982 at each site. The sampling equipment consisted of low volume ($25.9\ \ell\,\mathrm{min}^{-1}$) 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 analysed for 34 trace elements, elemental carbon (EC), organic carbon (OC) and ionic species. The fourth filter holder was operated at $10\ \ell\,\mathrm{min}^{-1}$ 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 Fig. 1) were designated for organic compound identification and quantification by means of HRGC and GC/MS.

Extraction protocol for ambient samples

All glassware used for sample extraction was annealed at 550°C for at least 8 h. 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 five 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 (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.

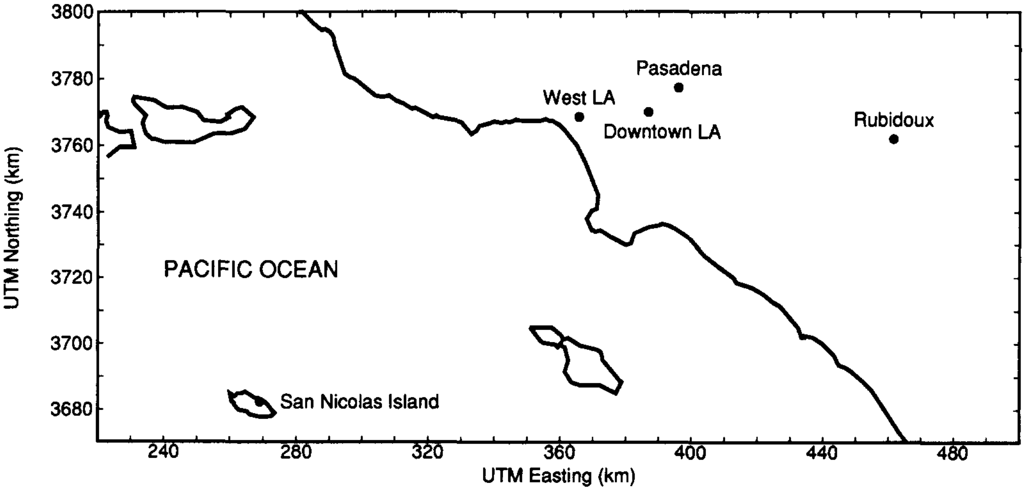

Fig. 1. Sampling sites used throughout southern California during the present study.

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 3–5 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 300–500 μl. Following volume determination using a 500-μl syringe ($\pm$10-μl 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.

HRGC and GC/MS analysis. Extracts from the fine carbon particle samples were analysed 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-m 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 s^{-1}, ranging from 50 to 550 Da. 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 with 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 aluminum 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 reanalysed in our laboratory prior to use to assure that any contaminants present were quantified. Procedural blanks were analysed 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 eight-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 Figs 2a and 2b. 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

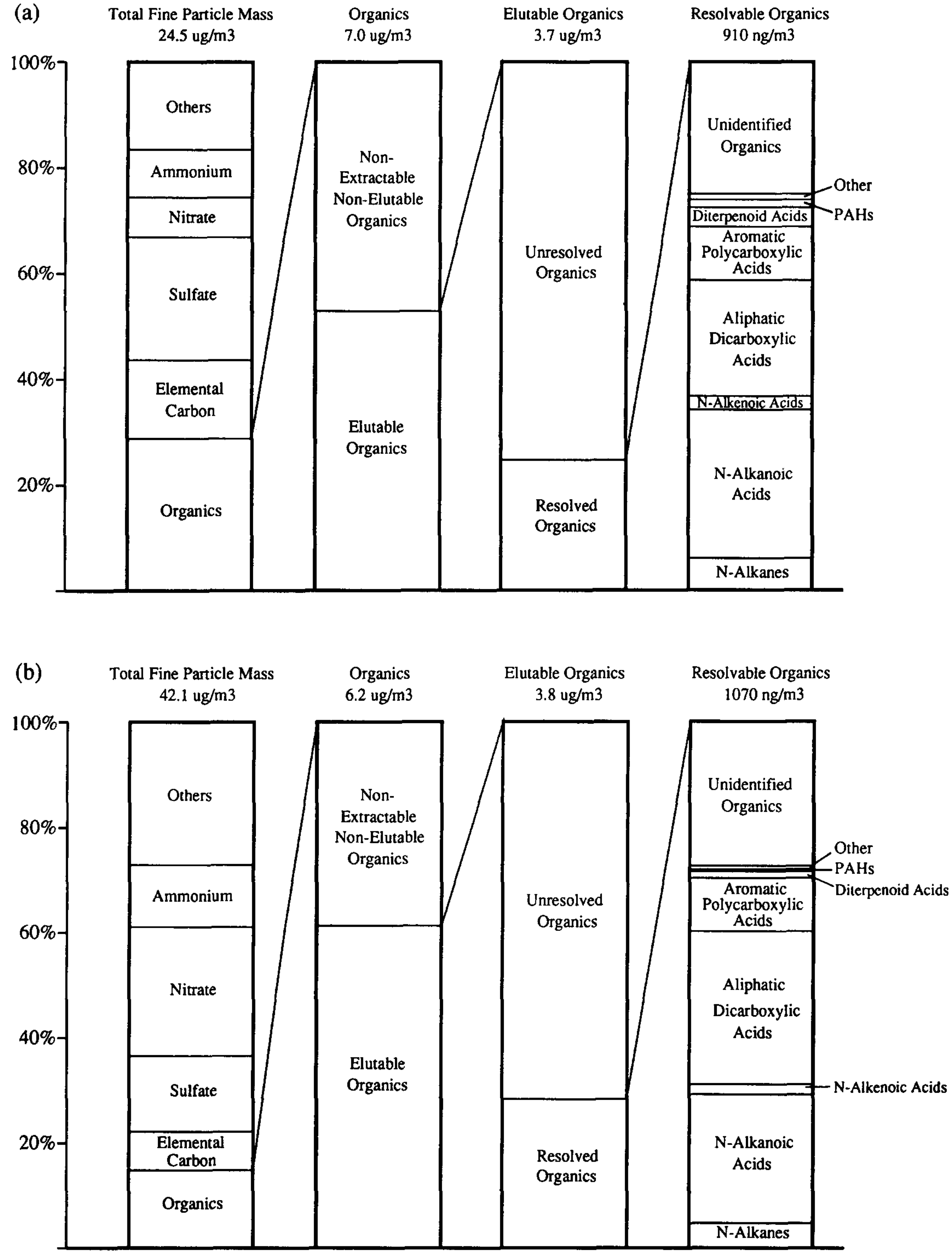

Fig. 2. Mass balance on the chemical composition of annual mean fine particle concentrations, 1982, for (a) West Los Angeles and (b) Rubidoux (Riverside).

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 2a and 2b 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 Figs 2a and 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 $\mathrm{ng\,m^{-3}}$ on average at West L.A. to more than 300 $\mathrm{ng\,m^{-3}}$ at Rubidoux).

In Table 1, the annual average material balance on identified organic compounds shown in Fig. 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.

Normal 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 $\mathrm{m\,s^{-1}}$ 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 ($\mathrm{CPI_{odd}}$), organic matter of recent biogenic origin shows a preference for odd carbon numbered *n*-alkanes with $\mathrm{CPI_{odd}}$ 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 $\mathrm{CPI_{odd}}$ 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 $\mathrm{CPI_{odd}}$ 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 $\leqslant C_{19}$ in both

Table. 1. Ambient annual average concentrations (ng m^{-3}) for fine particle organic compounds found at West Los Angeles, downtown Los Angeles, Pasadena, Riverside and San Nicolas Island for 1982

Compound name	West L.A.	Downtown L.A.	Pasadena	Rubidoux	San Nicolas Island* (July–Dec.)	Compound identification†
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
Total *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
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
Total *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
Total aliphatic dicarboxylic acids (C_3–C_9)	198.98	230.26	213.8	312.24		
Diterpenoid acids and retene‡						
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
Total woodsmoke 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
Total 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

Table 1. (Continued)

Compound name	West L.A.	Downtown L.A.	Pasadena	Rubidoux	San Nicolas Island* (July–Dec.)	Compound identification†
Benzo[*b*]fluoranthene	0.77	1.23	0.85	0.68	<0.01	a
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	NM	NM	NM	<0.01	a
Total 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
Total polycyclic aromatic ketones and quinones	1.77	1.82	2.33	0.39		
Steroids						
Cholesterol	2.7	ND	1.9	ND	<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
Total N-containing compounds	3.21	4.03	6.64	1.93		

* Sample analyses were completed only for July to December 1982.

† For more detail see text; a = positive, b = probable, c = possible, d = tentative.

‡ Woodsmoke 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.

NM = not measured; since coronene elutes very late from the column used in this study, coronene data were taken only at West L.A.

ND = not detected.

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 $\geqslant C_{26}$. 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 July–September composite sample to the October–December composite sample (1.3 vs 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 Fig. 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 (20–40 ng m^{-3}) were found during the summer months (May–August 1982). As seen in Fig. 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 Fig. 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

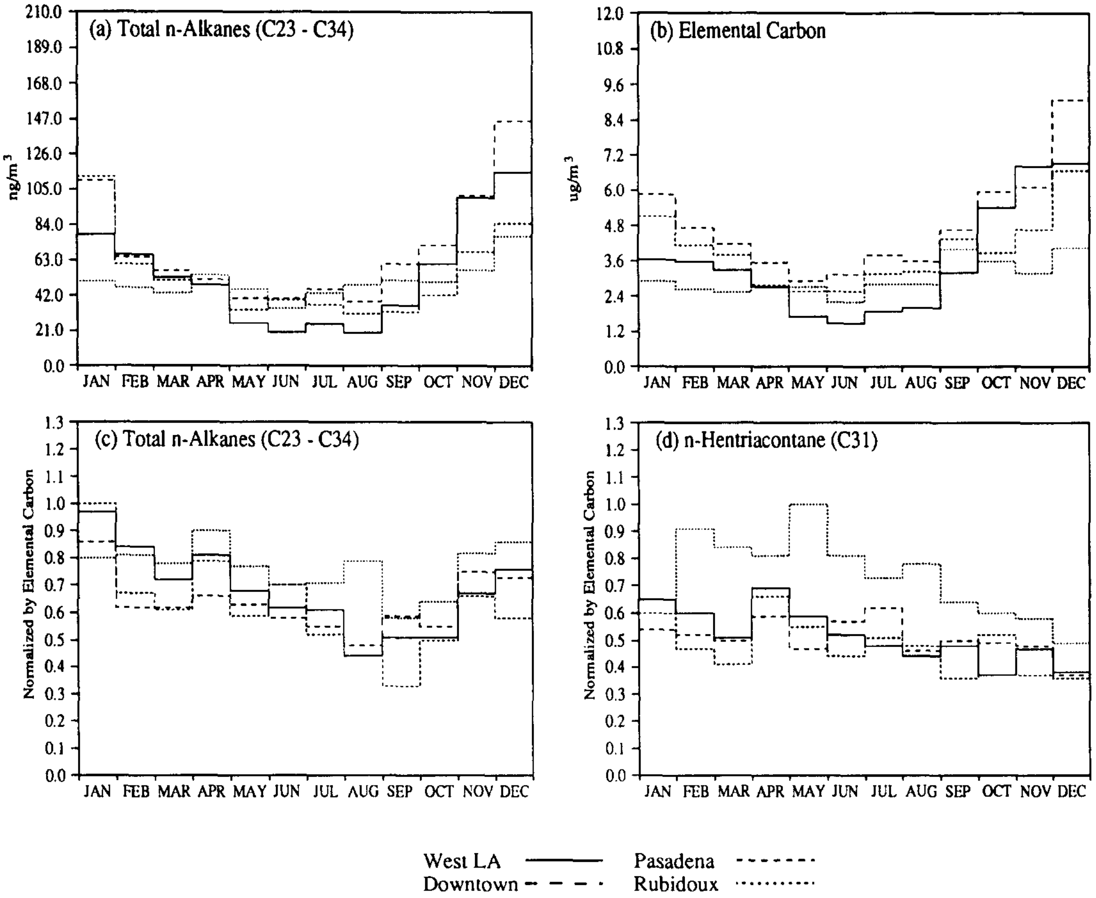

Fig. 3. Monthly averaged concentration profiles for (a) total *n*-alkanes (C_{23}–C_{34}) and (b) elemental carbon; monthly normalized concentration profiles for (c) total *n*-alkanes (C_{23}–C_{34}) and (d) *n*-hentriacontane (C_{31}). Normalization was achieved by dividing the time series of monthly averaged compound concentrations by the time series of elemental carbon concentrations for each site followed by rescaling as explained in the text.

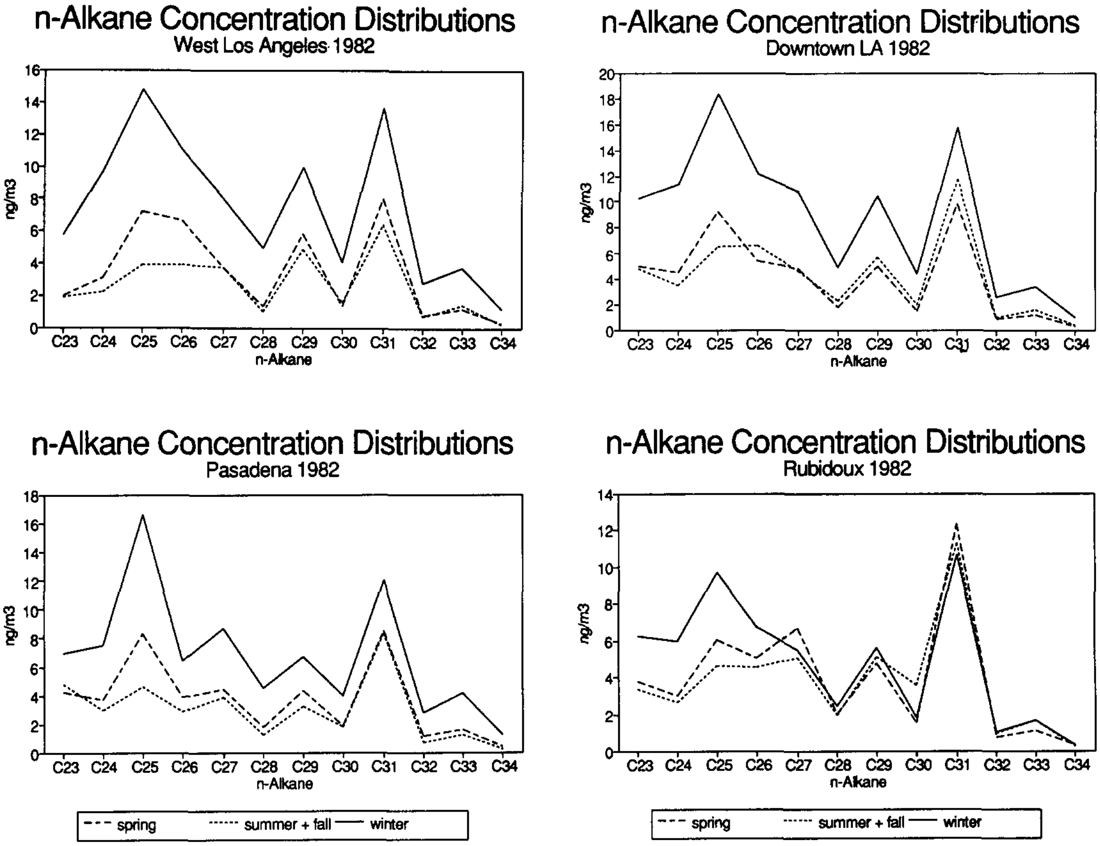

Fig. 4. Seasonal *n*-alkane concentration distributions (spring: March–May; summer+fall: June–October; winter: November–February), 1982.

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 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 ($d_p \leqslant 2.1$ μm). 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 (Fig. 3a vs 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 (Fig. 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 (Fig. 3d).

Normal 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 $\leqslant n\text{-}C_{20}$ (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 $n\text{-}C_{16}$, $n\text{-}C_{18}$, 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, $\Delta^9\text{-}C_{18:1}$, undergoes photochemically induced oxidation yielding ω-oxocarboxylic acids, aldehydes, carboxylic acids and dicarboxylic acids with predominantly C_9 species. Experimental observations of the reaction of oleic acid as its methyl ester with ozone in the liquid phase have demonstrated that aldehydes, carboxylic acids and dicarboxylic acids form the final reaction products (Killops, 1986). The major reaction products were the C_9-aldehyde (nonanal), C_9-ester-aldehyde (9-oxononanoate) and C_9-acid (nonanoic acid), depending on the ozone concentrations used. The extent to which these results can be applied to the atmospheric aerosol is not yet clear. It is speculated that similar reaction pathways also occur in the atmosphere.

Normal alkanoic acids ranging from *n*-nonanoic acid (C_9) to *n*-triacontanoic acid (C_{30}) have been identified during the present study at the remote (San Nicolas Island) and urban sampling locations. At the background station on San Nicolas Island, the measured total *n*-alkanoic acid concentrations summed to 19.5 $ng\,m^{-3}$ during summer versus 25.6 $ng\,m^{-3}$ during the October–December time period. The urban total *n*-alkanoic acid concentrations during the summer season were as low as 150 $ng\,m^{-3}$ (August, September), whereas during wintertime concentrations were more than tripled (550 $ng\,m^{-3}$). As shown in Fig. 5a, the highest concentrations of single *n*-alkanoic acids for all sites and seasons were found for the C_{16} acid (100–250 $ng\,m^{-3}$), followed by C_{18} acid (30–100 $ng\,m^{-3}$). Both the C_{16} and C_{18} *n*-fatty acids show relatively constant concentrations throughout the year at the West L.A., downtown L.A. and Pasadena sampling sites. Figure 5b shows a distinctly different annual concentration profile typical of the higher molecular weight *n*-alkanoic acids, with *n*-tetracosanoic acid (C_{24}) as an example, revealing very low summer concentrations with pronounced higher winter concentrations. Trace amounts for 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.

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 $\geqslant C_{20}$ 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 $\geqslant C_{20}$ during the winter of that year (see Figs 5c and 5d). 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 simil-

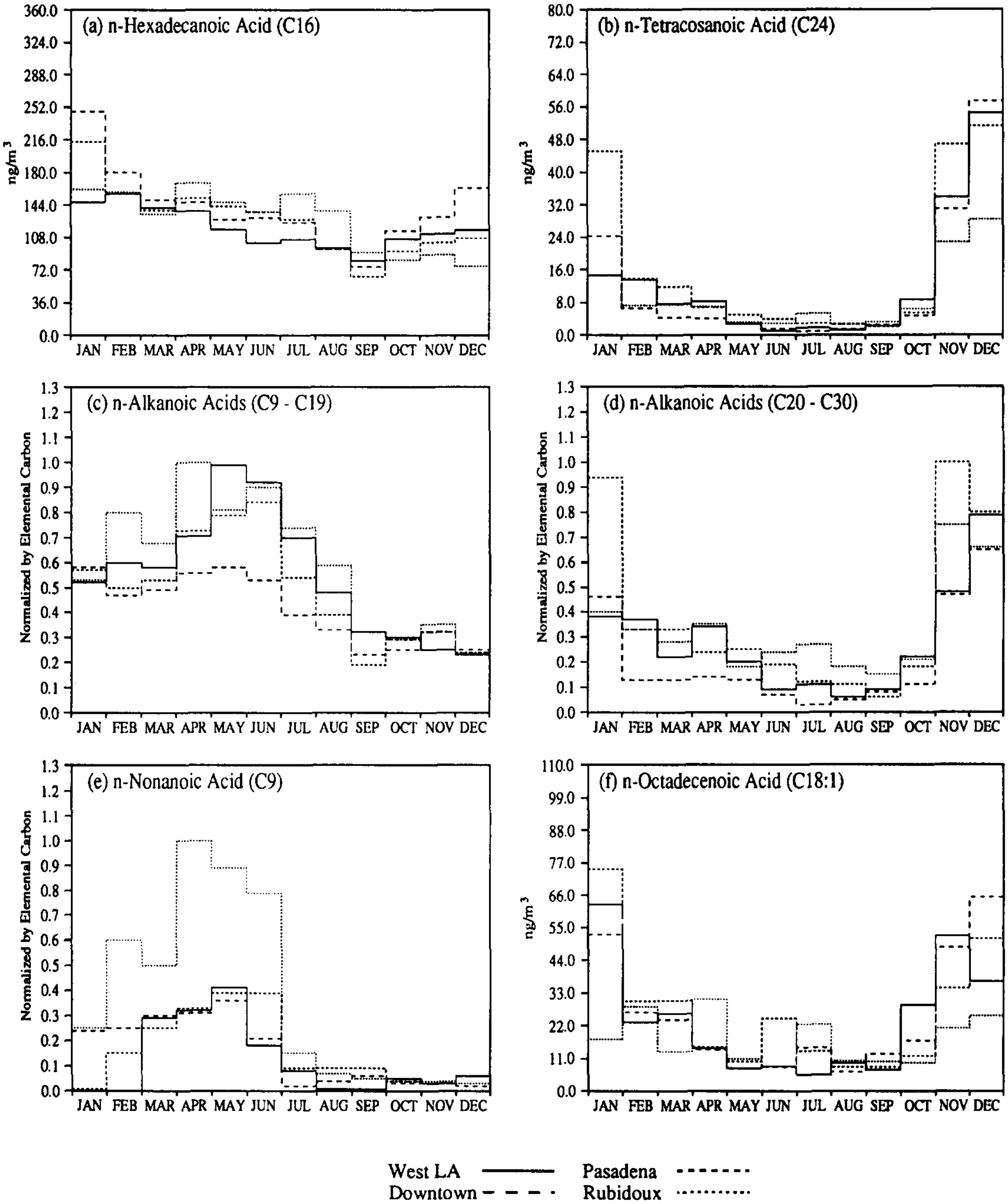

Fig. 5. Monthly averaged concentration profiles for (a) *n*-hexadecanoic acid (C_{16}) and (b) *n*-tetracosanoic acid (C_{24}); monthly normalized concentration profiles for (c) *n*-alkanoic acids (C_9–C_{19}), (d) *n*-alkanoic acids (C_{20}–C_{30}) and (e) *n*-nonanoic acid (C_9); monthly averaged concentration 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.

arities 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 (Fig. 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 analysed during the present study. No palmitoleic acid (Δ^9-$C_{16:1}$) 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 Fig. 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 to C_{10} have been identified in gasoline and diesel engine exhaust (Kawamura and Kaplan, 1987). The highest emission rates of particle-phase dicarboxylic acids ($\geqslant C_3$) 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 rain water of urbanized areas (Kawamura and Kaplan, 1983; Simoneit and Mazurek, 1989). Mono- and polyhydroxy-substituted 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 U.S.A. (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 hydrolysed 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 co-workers (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 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 to C_9, including branched and substituted dicarboxylic acids (see Table 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 Fig. 6a). This contrasts with the concentration profiles

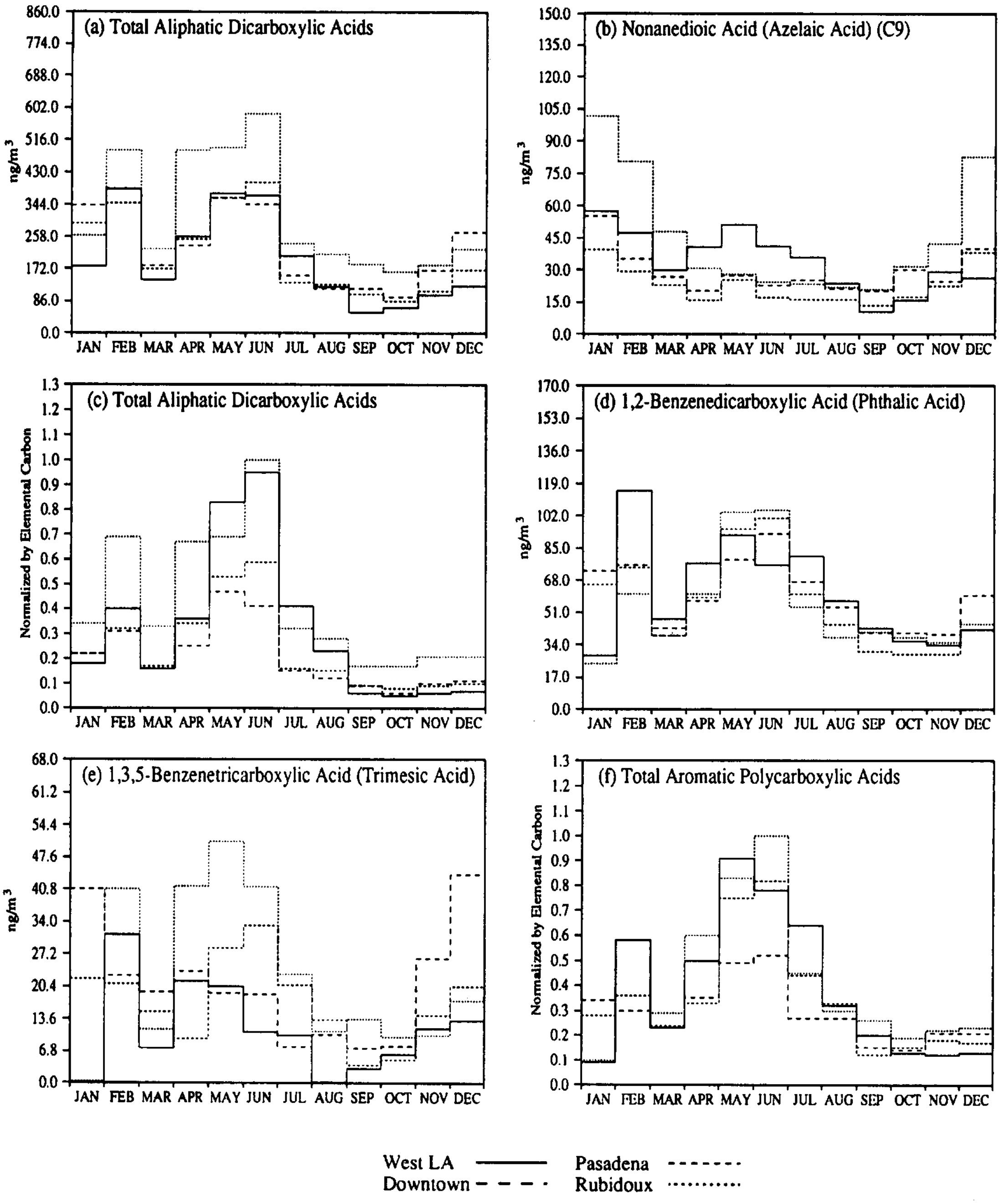

Fig. 6. Monthly averaged concentration profiles for (a) total aliphatic dicarboxylic acids and (b) nonanedioic acid (azelaic acid); monthly normalized concentration profile for (c) total aliphatic dicarboxylic acids; monthly averaged concentration profiles for (d) 1,2-benzenedicarboxylic acid (phthalic acid) and (e) 1,3,5-benzenetricarboxylic acid (trimesic acid); monthly normalized concentration profile for (f) total aromatic polycarboxylic acids. Normalization was achieved 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.

for *n*-alkanes and higher *n*-alkanoic acids, which peak during the winter months as seen in Figs 3a, 5b and 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 (Fig. 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} (Fig. 6a). Normalization relative to elemental carbon concentrations further emphasizes the mid-year enrichment in dicarboxylic acid concentrations (Fig. 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 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} (Fig. 6d), followed by trimesic acid (1,3,5-benzenetricarboxylic acid) (Fig. 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 Figs 6d–6f) closely resemble the total aliphatic dicarboxylic acid concentration profiles (Figs 6a and 6c), indicating that aromatic di-, tri- and tetracarboxylic acids may well be the products of atmospheric chemical reactions.

Normal 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 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 L.A. and downtown L.A. 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 Fig. 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 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 u.v. solar radiation or O_3 has been found to yield polycyclic aromatic ketones (PAK) and polycyclic aromatic quinones (PAQ) during photo-oxidation 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 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 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) (Fig. 7c), 6H-benzo[*cd*]pyren-6-one (Fig. 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

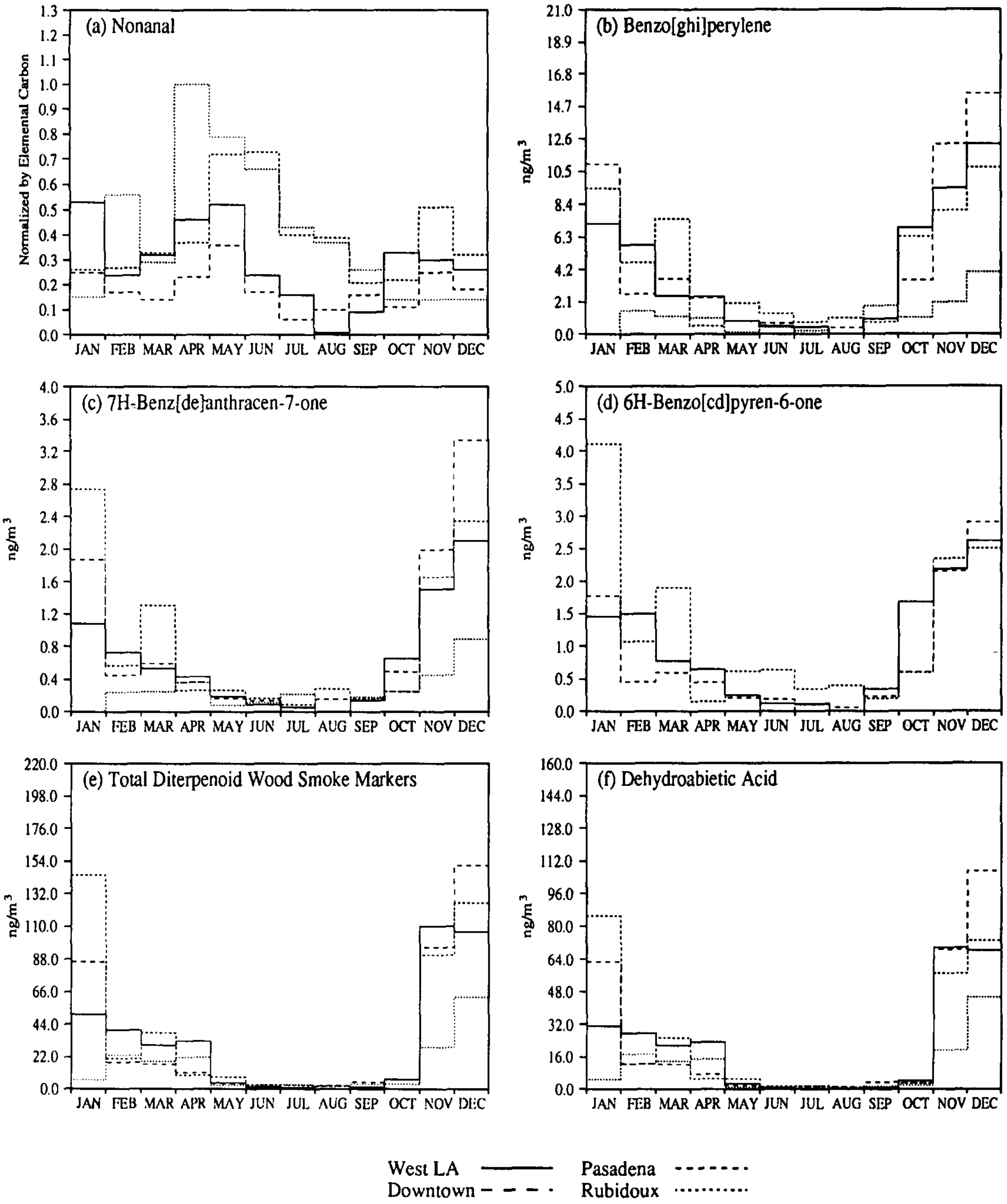

Fig. 7. Monthly normalized concentration profile for (a) nonanal; monthly averaged concentration profiles for (b) benzo[*ghi*]perylene, (c) 7H-benz[*de*]anthracen-7-one, (d) 6H-benzo[*cd*]pyrene-6-one, (e) total diterpenoid woodsmoke markers and (f) dehydroabietic acid. Normalization was achieved by 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.

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 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 woodsmoke aerosol (Hawthorne *et al.*, 1988; Ramdahl, 1983a, b; 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 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 wood smoke 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 woodsmoke markers (seven identified diterpenoid acids and retene) is shown in Fig. 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} (Fig. 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 woodsmoke 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 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 L.A. 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 (Fig. 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 (Fig. 8b). The increase in *n*-alkanoic acid concentrations in winter is dominated by the

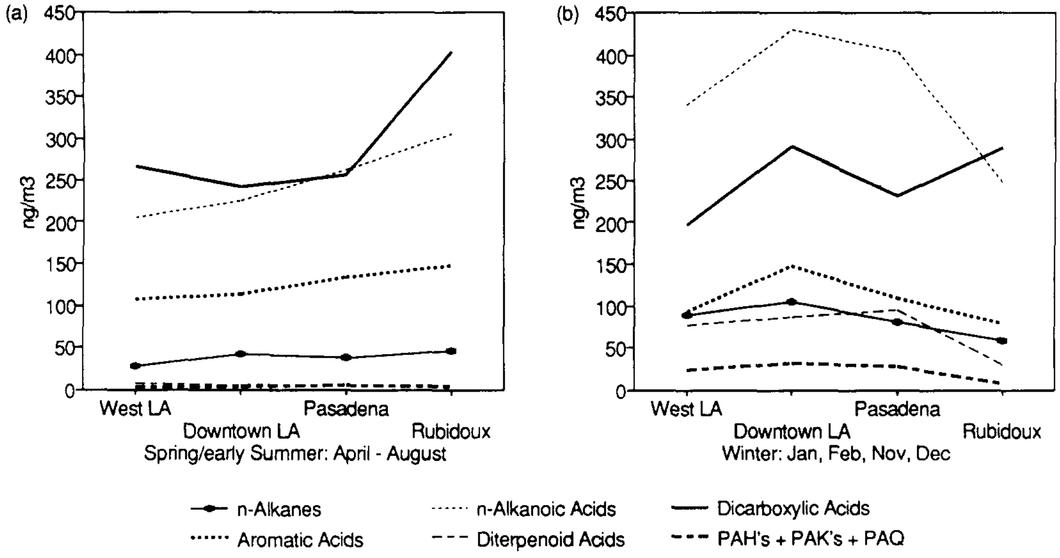

Fig. 8. Seasonal and spatial concentration patterns of fine particle associated organic compounds for (a) April–August and (b) January, February, November and December, 1982.

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 Fig. 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.

Similarities in ambient concentration patterns

Hierarchical cluster analysis was employed to evaluate quantitatively 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 Fig. 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 woodsmoke 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 woodsmoke markers is plausible. Second, all compound classes of this cluster are subject to depletion in the summer months. Diterpenoid woodsmoke 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

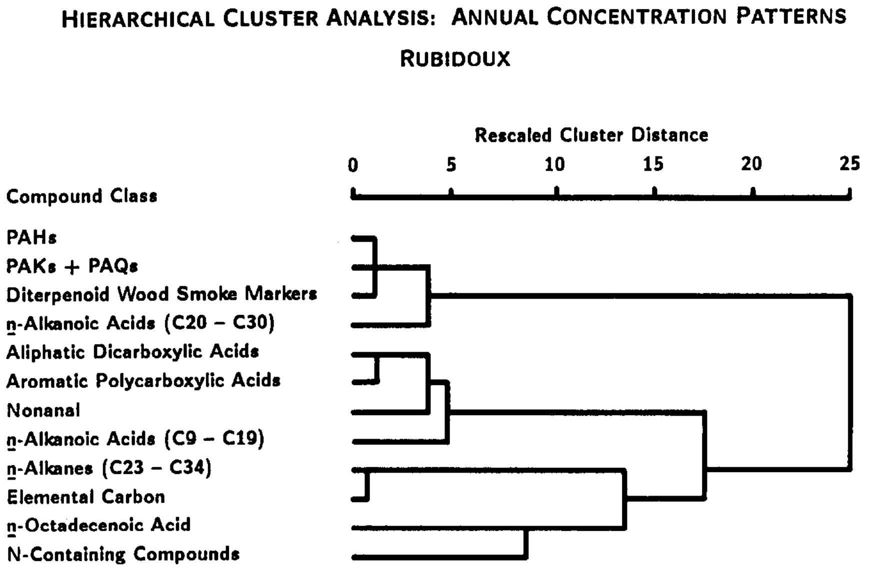

Fig. 9. Hierarchical cluster analysis to determine similarities in the seasonal variations of monthly average concentrations measured at Rubidoux.

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 22–43% 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, 40–61% are extractable and elute under the GC conditions used here. Resolved compounds comprise 23–29% of the elutable organics mass. Single compounds identified in the present study account for 74–81% 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 (250–300, 200–300 and *ca* 100 ng m^{-3} annual average, respectively). Smaller quantities of *n*-alkanes, *n*-alkenoic acids, alkanals, woodsmoke 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 woodsmoke 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, 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.

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