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SOURCE APPORTIONMENT OF AIRBORNE PARTICULATE MATTER USING ORGANIC COMPOUNDS AS TRACERS

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Abstract—A chemical mass balance receptor model based on organic compounds has been developed that relates source contributions to airborne fine particle mass concentrations. Source contributions to the concentrations of specific organic compounds are revealed as well. The model is applied to four air quality monitoring sites in southern California using atmospheric organic compound concentration data and source test data collected specifically for the purpose of testing this model. The contributions of up to nine primary particle source types can be separately identified in ambient samples based on this method, and approximately 85% of the organic fine aerosol is assigned to primary sources on an annual average basis. The model provides information on source contributions to fine mass concentrations, fine organic aerosol concentrations and individual organic compound concentrations. The largest primary source contributors to fine particle mass concentrations in Los Angeles are found to include diesel engine exhaust, paved road dust, gasoline-powered vehicle exhaust, plus emissions from food cooking and wood smoke, with smaller contributions from tire dust, plant fragments, natural gas combustion aerosol, and cigarette smoke. Once these primary aerosol source contributions are added to the secondary sulfates, nitrates and organics present, virtually all of the annual average fine particle mass at Los Angeles area monitoring sites can be assigned to its source. Copyright © 1996 Elsevier Science Ltd

Key word index: Receptor models, organic aerosol, fine particles, source contributions, emissions.

INTRODUCTION

Suspected adverse health effects of even low levels of airborne particulate matter have led to increased concern over how fine particulate concentrations might best be controlled (Dockery *et al.*, 1993). The development of effective control strategies for fine particulate air pollution abatement in turn requires a knowledge of the relative importance of the various sources that contribute to the particulate matter concentrations at ambient air monitoring sites (Atkinson and Lewis, 1974; Harley *et al.*, 1989).

Two approaches can be employed to evaluate source contributions from source emissions data and ambient monitoring data: source-oriented models and receptor-oriented models. Source-oriented models use emissions data and fluid mechanically explicit transport calculations to predict pollutant concentrations at specific receptor air monitoring locations. This type of model is validated by comparison of the predicted spatial and temporal distribution of pollutant concentrations against measured concentrations (Bencala and Seinfeld, 1979; Liu and Seinfeld, 1975). Receptor-oriented models infer source contributions by determining the best-fit linear combination of emission source chemical composition profiles needed to reconstruct the measured chemical composition of ambient samples (Watson, 1984).

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Determination of source contributions from ambient monitoring data by receptor modeling techniques relies on the ability to characterize and distinguish differences in the chemical composition of different source types. The elemental composition of source emissions has been used on many occasions to identify separately different sources of airborne particles (Miller *et al.*, 1972; Hopke *et al.*, 1976; Gordon, 1980; Cooper and Watson, 1980; Cass and McRae, 1983). Unfortunately, a large number of sources that emit fine particulate matter do not produce emissions that have unique elemental compositions; instead, many sources emit principally organic compounds and elemental carbon. Examples of such sources include diesel engine exhaust, combustion of unleaded gasoline, the effluent from meat cooking operations, and cigarette smoke (Hildemann *et al.*, 1991). When such important sources of primary particle emissions cannot be identified in ambient samples, then much of the true nature of a particulate air pollution problem remains obscured.

Recent advances in source testing techniques make it possible to measure the concentrations of hundreds of specific organic compounds in the fine aerosol emitted from air pollution sources (Rogge *et al.*, 1991, 1993b–e; Rogge, 1993). By analogous methods, the organic compounds present in the fine aerosol collected at ambient sampling sites also can be determined (Rogge *et al.*, 1993a; Rogge, 1993). The relative distribution of single organic compounds in source emissions provides a means to fingerprint sources that cannot be uniquely identified by elemental composition alone. These advances in measurement methods therefore create the practical possibility of devising receptor models for aerosol source apportionment that rely on organic compound concentration data and that potentially can identify separately the contributions of many more source types than has been possible based on elemental data alone.

In the present paper, receptor modeling methods will be developed that use organic compound distributions in both source samples and in ambient samples to determine source contributions to airborne particulate matter samples. Two critical aspects of this work are (1) selection of the sources to be included in such a model and (2) identification of the organic compounds for which material balances can be written. Methods developed will be tested by application to data taken in southern California.

EXPERIMENTAL

Ambient samples

Throughout 1982, airborne fine particulate matter ($d_p < 2$ μm) samples were collected for 24 h every sixth day at 10 Los Angeles-area air quality monitoring sites and one upwind remote off-shore island (Gray *et al.*, 1986). The present study uses samples from four of these sampling sites: West Los Angeles, Downtown Los Angeles, Pasadena, and Rubidoux (see Fig. 1).

The ambient aerosol samples used in this study were collected downstream of an AIHL cyclone separator operated at 25.9 ℓ min^{-1} that removed particles with aerodynamic diameters larger than 2 μm (John and Reischl, 1980). Air leaving the cyclone was divided between four parallel 47 mm diameter filter assemblies: two containing quartz fiber filters (Pallflex Tissuequartz 2500 QAO), one containing a Teflon membrane filter (Membrana 0.5 μm pore size), and one containing a Nuclepore filter (0.4 μm pore size). Each of the quartz fiber filters was operated at an air flow rate of 10 ℓ min^{-1}, while the Teflon filters and the Nuclepore filters were operated at 4.9 and 1.0 ℓ min^{-1}, respectively. The quartz fiber filters were baked at 600°C for a minimum of 2 h prior to sample collection to lower residual carbon levels associated with untreated filters.

One quartz fiber filter from each day at each sampling site was analyzed for elemental carbon (EC) and organic carbon

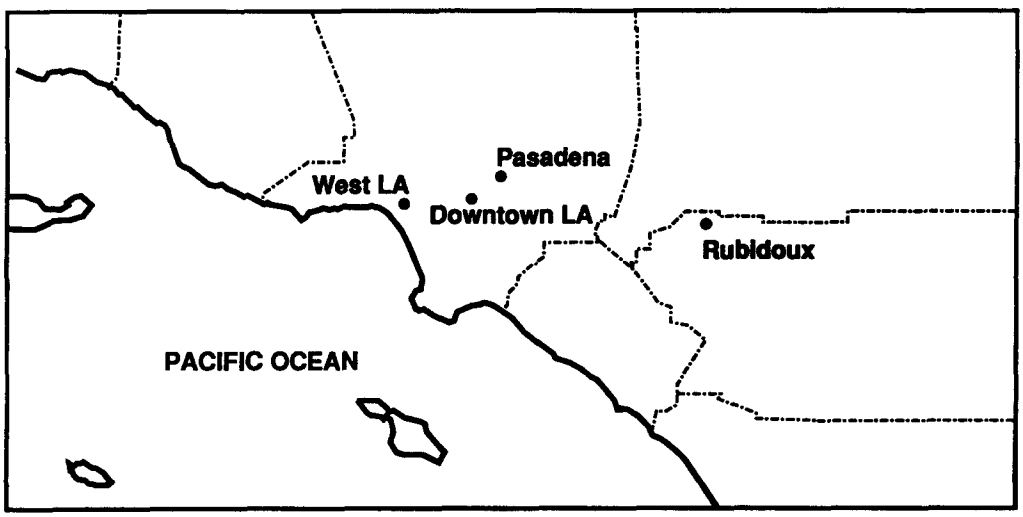

Fig. 1. Air quality monitoring sites in southern California used in the present study.

(OC) by the method of Huntzicker *et al.* (1982) and Johnson *et al.* (1981). Monthly composites formed by utilizing the second quartz fiber filter from each site on each day were reserved for the identification and quantification of the individual organic compounds present by high-resolution gas chromatography (HRGC) and gas chromatography/mass spectrometry (GC/MS) (Rogge *et al.*, 1993a; Rogge, 1993).

The particulate matter collected on the Teflon filters was used to determine total fine particulate mass concentrations by gravimetric analysis. The Teflon filters were also analyzed by X-ray fluorescence to quantify the concentrations of 34 trace elements including aluminum and silicon, which will be used in the present study. Samples collected on the Nuclepore filters were analyzed for sulfate and nitrate by ion chromatography (Mueller *et al.*, 1978), and for ammonium ion by the phenol–hypochlorite method (Solorzano, 1967).

Source samples

A source sampling program was undertaken in order to determine the mass emission rate and chemical composition of the fine particulate matter released from the most prominent sources of carbonaceous aerosol emissions in southern California. Fifteen source types were tested, as shown in Table 1, that accounted for approximately 80% of the fine carbonaceous aerosol emissions in the Los Angeles basin during the 1982 period for which ambient samples are available (Gray, 1986; Hildemann *et al.*, 1991). Detailed descriptions of the procedures used for fine particulate source sampling from each source have been presented previously (Hildemann *et al.*, 1991). Briefly, combustion source emissions were collected utilizing a dilution stack sampling system (Hildemann *et al.*, 1989). Dilution air, which was passed through a HEPA filter and an activated carbon bed, was mixed with source emissions to simulate the condensation process that occurs due to dilution and cooling as a plume enters the atmosphere. After sufficient residence time in the sampler, several streams of diluted emissions were drawn through AIHL cyclones at conditions designed to remove particles with aerodynamic diameters greater than 2 μm, followed by fine particle collection on appropriate filter substrates. Quartz fiber filters (Pallflex Tissuequartz 2500 QAO) were used in the same manner as described for ambient sampling for both EC/OC analysis and for identification and quantification of organic compounds by HRGC and GC/MS. Samples collected on Teflon filters (Gelman Teflo, 2 μm pore size) were used for gravimetric determination, X-ray fluorescence analysis, and for ion chromatography. The emissions from catalyst-equipped autos, non-catalyst autos, diesel trucks, oil-fired boilers, natural gas home appliances, meat charbroiling and frying, and fireplace combustion of wood were measured in this manner.

The diesel trucks tested by Hildemann *et al.* (1991) represented vehicles newer than the fleet of diesel trucks in operation in the Los Angeles basin in 1982, when the ambient samples used in this study were collected. Comparison of the Hildemann *et al.* source test data for newer trucks to source test data on older diesel trucks summarized by Gray (1986) shows that the organic compound emission rates from both the newer and older trucks are similar, while the elemental carbon emissions from the older trucks are much higher than for the newer trucks. For this reason, the elemental carbon emissions rate used in the present study to represent diesel-powered vehicles in 1982 is taken from Gray *et al.* (1986), while the emissions rate and distribution of the organic compounds is taken from Hildemann *et al.* (1991).

Cigarette smoke and roofing tar pot emissions were sampled with a modified dilution sampler (Hildemann *et al.*, 1991) that employed the same cyclone and filter collection

Table 1. Estimate of fine aerosol organic carbon (OC) emissions within an 80 × 80 km square study area centered over Los Angeles for 1982 (Gray, 1986; Hildemann *et al.*, 1991)

Source type	OC emitted ($kg\,d^{-1}$)	Profile no. of source tested in this study	Source profile used to represent source for inventory purposes[a]
(1) Meat-cooking operations			
Charbroiling	4938	1[b]	1
Frying	1393	2	2
(2) Paved road dust	4728	3	3
(3) Fireplaces			
Pine wood	3332	4	4
Oak wood	840	5	5
Synthetic logs	n.k.		
(4) Non-catalyst gasoline vehicles			
Automobiles	2088	6	6
Other vehicles[c]	1372		6
(5) Diesel vehicles			
Heavy-duty trucks	1242	7	7
Other vehicles[d]	617		7
(6) Surface coating	1433		
(7) Forest fires	877		
(8) Cigarettes	802	8	8
(9) Catalyst-equipped gasoline vehicles			
Automobiles	780	9	9
Other vehicles[e]	79		9
(10) Organic chemical processes	692		
(11) Brake lining wear debris	690	10	10
(12) Roofing tar pots	556	11	11
(13) Tire wear debris	414	12	12
(14) Misc industrial point sources	393		
(15) Natural gas combustion			
Residential/commercial	30	13	13
Other sources[f]	262		13

Table 1. (continued)

Source type	OC emitted ($kg\,d^{-1}$)	Profile no. of source tested in this study	Source profile used to represent source for inventory purposes[a]
(16) Misc petroleum industry processes	278		
(17) Primary metallurgical processes	228		
(18) Railroad (diesel oil)	211		7
(19) Residual oil stationary sources[g]	206		14
(20) Refinery gas combustion	195		13
(21) Secondary metallurgical processes	167		
(22) Mineral industrial processes	158		
(23) Other organic solvent use	106		
(24) Jet aircraft	92		
(25) Asphalt roofing manufacturing	81		11
(26) Coal burning	76		
(27) Wood processing	74		
(28) Residual oil-fired ships	66		
(29) Structural fires[h]	63		4
(30) Distillate oil stationary sources			
Industrial[i]	13	14	14
Other[j]	23		14
(31) Vegetative detritus			
Green leaf abrasion products[k]	1000	15	15
Dead leaf abrasion products	n.k.		
(32) Other sources[l]	226		6,7
Total	30,822		

n.k. = not known.

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

[b] Charbroiling regular hamburger meat with a fat content of 21%.

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

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

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

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

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

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

[i] Test no. 2 is used (see Rogge, 1993).

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

[k] The emissions of vegetative detritus within the inventory area are estimated from a small chemical mass balance receptor modeling calculation based on silica, alumina, and alkanes from vegetation, road dust and cigarette smoke, with vegetation emissions then scaled from the known cigarette smoke emission rate in proportion to their relative ambient concentrations.

[l] Other sources included in emission inventory: diesel powered ships (42.1 $kg\,d^{-1}$), industrial rubber and plastics operations (35.7 $kg\,d^{-1}$), petroleum refining FCC units (24.5 $kg\,d^{-1}$), fugitive emissions from livestock feedlots (20.4 $kg\,d^{-1}$), industrial waste burning (20.2 $kg\,d^{-1}$), industrial internal combustion engines using gasoline (19.0 $kg\,d^{-1}$), industrial internal combustion engines using digester gas (18.6 $kg\,d^{-1}$), industrial printing operations (12.9 $kg\,d^{-1}$), aviation gas mobile sources (9.6 $kg\,d^{-1}$), residential and high priority commercial LPG combustion (7.8 $kg\,d^{-1}$), industrial degreasing operations (5.1 $kg\,d^{-1}$), industrial food and agricultural operations (5.0 $kg\,d^{-1}$), agricultural burning operations (2.5 $kg\,d^{-1}$), industrial textile manufacturing (1.8 $kg\,d^{-1}$), non-refinery industrial/ low priority commercial LPG combustion (1.3). Of these, the diesel ships have been assigned to profile 7, the gasoline engines have been assigned to profile 6, and the remaining sources are not used in the model.

equipment that was used for the hot ducted combustion sources. Vehicular brake dust, paved road dust, and vegetative detritus were collected following particle resuspension in clean Teflon bags. The resuspended particulate matter was passed through AIHL cyclones to remove particles with aerodynamic diameters greater than 2 μm, followed by collection on quartz fiber and Teflon filters as described above for the hot source samples. Due to the electrostatic nature of tire dust, resuspension within the Teflon bags is not possible. For this reason, the chemical composition of the tire dust samples was analyzed from total particulate matter samples, which included coarse particles (Hildemann *et al.*, 1991). This should not pose a problem for the relative chemical composition data needed here since tire tread is a well-mixed industrial material.

Organic compound identification and quantification

Both ambient samples and source samples collected on quartz fiber filters were subjected to identical filter handling and analytical protocols to identify and quantify the organic compounds present. The methods used were developed for trace level quantification of organics in airborne particulate matter by HRGC and GC/MS techniques and have been discussed extensively elsewhere (Mazurek *et al.*, 1987, 1989, 1991; Rogge *et al.*, 1991). Briefly, the composited filters were

spiked with an internal recovery standard, perdeuterated tetracosane (n-$C_{24}D_{50}$). The samples were extracted twice with hexane, followed by three successive benzene/2-propanol (2:1) extractions. Extracts were combined and each final extract mixture was reduced to 200–500 μl total volume. An aliquot of the concentrated extract was derivatized with diazomethane to convert organic acids to their methyl ester analogues (Mazurek *et al.*, 1987). Then the concentrations of the 100 individual organic compounds, listed in Table 2, were quantified in the ambient fine particulate samples by GC/MS techniques (Rogge *et al.*, 1993a; Rogge, 1993). The same compounds plus other readily identified organics were sought in the source samples. Tracer compound mass concentrations in both source and ambient samples were corrected for recovery efficiency during extraction (see Mazurek *et al.*, 1987 for example) such that the total tracer content of each sample was measured. Single compound mass emission rates from each of the 15 source types studied are reported by Rogge *et al.* (1991, 1993b–e, 1994) and by Rogge (1993). These references by Rogge *et al.* when combined with gravimetric mass concentration data and total carbon data reported by Gray *et al.* (1986) and Hildemann *et al.* (1991) yield source profiles and ambient aerosol composition data that show the fine particle mass, overall organic carbon and elemental carbon content, extractable organics content, individual organic compound content and trace element content of each sample. The source profile and ambient data used in the present study also can be obtained in consolidated form from the authors.

Confidence intervals for the organic compound quantification procedures used in this study were estimated from analysis of the variance of the historical ambient data along with more recent experiments conducted in our laboratory.

Table 2. List of compounds available for possible use in the receptor model-1982, Los Angeles

Compound name	Range of annual average ambient fine particulate concentration (ng m^{-3})	Used in receptor model	Reason not used
n-Alkanes			
n-Tricosane	3.2–6.7	Yes	
n-Tetracosane	3.9–5.0	Yes	
n-Pentacosane	6.7–11.2	Yes	
n-Hexacosane	4.3–8.2	Yes	
n-Heptacosane	5.2–6.7	Yes	
n-Octacosane	2.1–3.1	Yes	
n-Nonacosane	4.7–7.1	Yes	
n-Triacontane	2.4–2.7	Yes	
n-Hentriacontane	9.3–12.6	Yes	
n-Dotriacontane	1.0–1.5	Yes	
n-Tritriacontane	1.5–2.3	Yes	
n-Tetratriacontane	0.36–0.68	Yes	
iso- and anteiso-Alkanes			
anteiso-Triacontane	< 0.03–0.23	Yes	
iso-Hentriacontane	0.73–1.50	Yes	
anteiso-Hentriacontane	< 0.03–0.12	Yes	
iso-Dotriacontane	< 0.03–0.13	Yes	
anteiso-Dotriacontane	0.89–1.31	Yes	
iso-Tritriacontane	0.30–0.33	Yes	
Hopanes and steranes			
20S&R-5α(H),14β(H),17β(H)-Cholestanes	0.34–1.18	Yes	
20R-5α(H),14α(H),17α(H)-Cholestane	0.34–1.23	Yes	
20S&R-5α(H),14β(H),17β(H)-Ergostanes	0.51–1.75	Yes	
20S&R-5α(H),14β(H),17β(H)-Sitostanes	0.52–1.67	Yes	
22,29,30-Trisnorneohopane	0.32–0.93	Yes	
17α(H),21β(H)-29-Norhopane	0.66–2.42	Yes	
17α(H),21β(H)-Hopane	1.32–4.02	Yes	
22S-17α(H),21β(H)-30-Homohopane	0.52–1.42	Yes	
22R-17α(H),21β(H)-30-Homohopane	0.36–1.06	Yes	
22S-17α(H),21β(H)-30-Bishomohopane	0.33–0.84	Yes	
22R-17α(H),21β(H)-30-Bishomohopane	0.20–0.58	Yes	
n-Alkenoic acids			
cis-9-n-Octadecenoic acid	17.3–26.0	Yes	
Aldehydes			
Nonanal	5.7–9.5	Yes	
n-Akanoic acids			
n-Nonanoic acid	3.3–9.9	No	a
n-Decanoic acid	1.3–3.1	No	a
n-Undecanoic acid	2.8–6.0	No	a
n-Dodecanoic acid	3.7–7.0	No	a
n-Tridecanoic acid	3.3–4.9	No	a

Table 2. (continued)

Compound name	Range of annual average ambient fine particulate concentration (ng m^{-3})	Used in receptor model	Reason not used
n-Tetradecanoic acid	14.4–22.8	No	a
n-Pentadecanoic acid	4.3–6.1	No	a
n-Hexadecanoic acid	118–141	No	a
n-Heptadecanoic acid	3.4–5.2	No	a
n-Octadecanoic acid	41.1–59.2	No	a
n-Nonadecanoic acid	0.79–1.1	No	a
n-Eicosanoic acid	3.1–6.1	No	a
n-Heneicosanoic acid	1.4–2.3	No	a
n-Docosanoic acid	5.7–9.9	No	a
n-Tricosanoic acid	1.5–2.5	No	a
n-Tetracosanoic acid	9.2–16.5	No	a
n-Pentacosanoic acid	1.1–1.6	No	a
n-Hexacosanoic acid	5.3–9.3	No	a
n-Heptacosanoic acid	0.47–0.81	No	a
n-Octacosanoic acid	2.7–4.9	No	a
n-Nonacosanoic acid	0.33–0.57	No	a
n-Triacontanoic acid	1.0–2.2	No	a
Dicarboxylic acids			
Propanedioic acid	28.0–51.0	No	b
2-Butenedioic acid	0.58–1.3	No	b
Butanedioic acid	51.2–84.1	No	b
Methylbutanedioic acid	11.6–20.3	No	b
Pentanedioic acid	28.3–38.7	No	b
Methylpentanedioic acid	15.5–23.7	No	b
Hydroxybutanedioic acid	7.8–22.1	No	b
Hexanedioic acid	14.1–24.3	No	b
Octanedioic acid	2.5–4.1	No	b
Nonanedioic acid	22.8–44.7	No	b
Aromatic carboxylic acids			
1,2-Benzenedicarboxylic acid	53.5–60.6	No	b
1,3-Benzenedicarboxylic acid	2.1–3.4	No	b
1,4-Benzenedicarboxylic acid	0.88–2.8	No	b
4-Methyl-1,2-benzenedicarboxylic acid	15.2–28.8	No	b
1,2,4-Benzenetricarboxylic acid	0.45–0.84	No	b
1,3,5-Benzenetricarboxylic acid	11.3–22.6	No	b
1,2,4,5-Benzenetetracarboxylic acid	0.40–0.80	No	b
Wood smoke markers			
Dehydroabietic acid	10.2–23.6	No	b
13-Isopropyl-5α-podocarpa-6,8,11,13-tetraen-16-oic acid	0.30–1.2	No	b
8,15-Pimaradien-18-oic acid	0.07–1.1	Yes	
Pimaric acid	0.94–4.8	Yes	
Isopimaric acid	0.71–2.3	Yes	
7-Oxodehydroabietic acid	1.9–4.1	No	b
Sandaracopimaric acid	0.60–2.2	No	b
Retene	0.01–0.10	Yes	
Polycyclic aromatic hydrocarbons			
Fluoranthene	0.07–0.15	No	b
Pyrene	0.12–0.26	No	b
Benz[a]anthracene	0.09–0.29	No	b
Cyclopenta [cd] pyrene	0.04–0.41	No	b
Benzo[ghi]fluoranthene	0.11–0.39	No	b
Chrysene/triphenylene	0.23–0.61	No	b
Benzo[k]fluoranthene	0.33–1.20	Yes	
Benzo[b]fluoranthene	0.68–1.23	Yes	
Benzo[e]pyrene	0.38–0.97	Yes	
Benzo[a]pyrene	0.18–0.44	No	b
Indeno[1,2,3-cd]pyrene	0.07–0.43	Yes	
Indeno[1,2,3-cd]fluoranthene	0.26–1.09	Yes	
Benzo[ghi]perylene	1.12–4.47	Yes	
Coronene	2.41[c]	Yes	

Table 2. (continued)

Compound name	Range of annual average ambient fine particulate concentration (ng m^{-3})	Used in receptor model	Reason not used
PAH ketones and quinones			
7H-Benz[de]anthracen-7-one	0.25–0.84	Yes	
Benz[a]anthracene-7,12-dione	0.12–0.25	Yes	
Benzo[cd]pyren-6-one	0.02–1.24	Yes	
Steroids			
Cholesterol	1.9–2.7	No	c
N-containing compounds			
3-Methoxypyridine	0.46–1.4	No	b
Isoquinoline	0.61–1.1	No	b
1-Methylisoquinoline	0.24–1.1	No	b
1,2-Dimethoxy-4-nitrobenzene	0.22–3.9	No	b
Inorganic elements			
Elemental carbon	3030–4870	Yes	
Particulate aluminum	249–330	Yes	
Particulate silicon	336–600	Yes	

[a] Significant source not in model.
[b] Species fails check for apparent conservation in the atmosphere (it behaves as if it is formed or depleted).
[c] Some monitoring sites have missing data.

The annual average ambient organic compound concentrations represent the mean of 12 monthly composites of daily samples taken at six day intervals. The uncertainties in the annual means of these atmospheric samples ($\pm 1\sigma$) typically are approximately $\pm 20\%$, and arise mainly from the fact that not all days of the year were sampled. The quantifiable uncertainties in the source samples are principally analytical uncertainties and also average approximately $\pm 20\%$ ($\pm 1\sigma$).

SOURCE/RECEPTOR RECONCILIATION

Chemical mass balance approach

The chemical composition of the emissions from individual sources can be used to estimate source contributions to atmospheric samples taken at receptor air monitoring sites (Hidy *et al.*, 1974; Miller *et al.*, 1972; Friedlander, 1973; Cass and McRae, 1983). One useful method for assigning ambient particulate matter concentration increments to the sources from which they originate is the chemical mass balance (CMB) technique. In the CMB method, a mass balance is constructed in which the concentration of specific chemical constituents in a given ambient sample is described as arising from a linear combination of the relative chemical compositions of the contributing sources. The concentration of chemical constituent i at receptor site k, c_{ik}, can be expressed as:

$$c_{ik} = \sum_{j=1}^{m} f_{ijk} a_{ij} s_{jk} \qquad (1)$$

where s_{jk} is the increment to total particulate mass concentration at receptor site k originating from source j, a_{ij} is the relative concentration of chemical constituent i in the emissions from source j, and f_{ijk} is the coefficient of fractionation that represents the modification of a_{ij} during transport from source j to receptor k. The fractionation coefficient accounts for selective loss of constituent i due to processes such as gravitational settling, chemical transformation, or evaporation; it can also be used to account for selective gains in constituent i due to chemical formation or condensation. In the present study, chemical constituents which do not have fractionation coefficients near unity will not be used in mass balance calculations. With the chemical composition of both the source samples (a_{ij}) and the ambient samples (c_{ik}) known from experimental measurements and with f_{ijk} near unity for each chosen chemical substance, the system of equations (1) can be solved for the unknown source contributions, s_{jk}, to the ambient pollutant concentrations.

If the number of chemical constituents included in the mass balance calculations exceeds the number of sources then the system of equations (1) is overdetermined, and exact agreement between the ambient concentrations and a unique linear combination of the source profiles is not expected due to the presence of small measurement errors. In this usual case, an ordinary least-squares solution to the system of equations (1) can be employed. Alternatively, an effective variance weighted least-squares solution, which takes advantage of known uncertainties in ambient measurements and emissions data, can be used to solve the linear system of equations (Watson *et al.*, 1984). In the present study, the system of equations (1) will be solved using the CMB7 source–receptor modeling computer program (Watson *et al.*, 1990) that employs

this effective variance weighted least-squares technique.

Selection of sources and organic compounds: an emissions inventory assisted approach

For the use of a chemical mass balance receptor model to be successful, several criteria must be met. First, if the coefficient of fractionation, f_{ijk}, in equation (1) is to be set to unity, then the chemical species for which material balance equations are written must be sufficiently stable that they are conserved during transport from their sources to the receptor air monitoring sites. The species must not be significantly depleted from the fine particulate fraction by volatilization or chemical reaction, and the species concentration must not be significantly increased by atmospheric chemical formation processes. Second, all major sources of each chemical species used in the mass balance must be included in the model, and the relative chemical compositions of the emissions from different source types that are included in the model must be different from each other in a statistical sense such that the problems of source profile collinearity are avoided. Little prior experience exists to show how a chemical mass balance receptor model based on organic tracer compounds should be constructed in order to exclude compounds that are insufficiently stable chemically, to assure that all major source types are included, and to detect and deal with source profiles from sources that are so similar to each other that collinearity problems would arise. In the following sections of the present paper, these issues are addressed within the context of example calculations in the Los Angeles area. In general, the methods used are similar to the emissions inventory-assisted chemical mass balance modeling procedures developed previously for data sets involving trace metals by Cass and McRae (1983).

A test for apparent chemical stability. One hundred organic compounds, listed in Table 2, were quantified both in source emissions and in fine aerosol samples collected at the four urban air monitoring sites used in this study (Rogge *et al.*, 1993a; Rogge, 1993). An individual organic compound listed in Table 2 can be used successfully in the present CMB model only if it is conserved during transport from source to receptor ($f_{ijk} \simeq 1$). Since the atmospheric stability of many of these organic compounds has not been examined in this light previously, the first step in our analysis is to perform an initial screening to identify and exclude compounds that do appear to be significantly modified during transport from source to receptor. The approach taken is to examine the ratio of the average atmospheric concentration to the area-wide emission rate for each organic compound studied. Fine elemental carbon particles have been employed previously as a nearly conserved tracer because they are not depleted by chemical reaction and because, by virtue of their small size (Ouimette and Flagan, 1982; Venkataraman and Friedlander, 1994), they are not depleted rapidly by dry deposition (Sehmel, 1980). Those organic compounds in fine particles that likewise are conserved in the atmosphere ought to show a ratio of ambient concentration to source emission rate that is fairly similar to that for elemental carbon particles. Those compounds that are formed by atmospheric reactions will have a much higher than average ratio of atmospheric concentration to mass emissions, while those compounds that are depleted rapidly by evaporation or chemical reaction will show lower average ratios of their ambient concentrations to emissions than is the case for a conserved species like elemental carbon.

The first step in this procedure for screening the compounds to be used is to construct a comparison of area-wide emissions and ambient concentrations for each chemical substance. Table 1 provides an emissions inventory for fine organic aerosol mass within an 80×80 km area centered over the city of Los Angeles for 1982 (Hildemann *et al.*, 1991). The sources sampled by Hildemann *et al.* (1991) and analyzed by Rogge *et al.* (1991, 1993a–d, 1994; Rogge, 1993) are indicated in Table 1. Several sources which were not tested by Hildemann *et al.* (1991) can be approximated, for purposes of an emissions inventory, by sources for which detailed emissions data are available (see Table 1). Including untested sources which can be represented by a tested source, the speciated emissions inventory data account for approximately 84% of the fine organic aerosol emissions within the 80×80 km inventory area. Using the atmospheric organic compound concentration data of Rogge *et al.* (1993a), along with chemical composition profiles generated by Hildemann *et al.* (1991) and Rogge *et al.* (1991, 1993b–e, 1994; Rogge, 1993) a quantitative comparison of emissions and ambient concentrations for each compound can be constructed. Figures 2a and b show the ratio of average airborne organic aerosol compound concentrations to the area-wide emissions rate within the 80×80 km inventory area for each of the 100 fine aerosol organic compounds in Table 2, plus fine particle silicon, fine particle aluminum, and fine particle elemental carbon. For our inert indicator species, fine elemental carbon, fine silicon, and fine aluminum, there exists reasonable consistency between estimated area-wide emission rates and the average ambient concentration at the three central basin air monitoring sites that are within the emission inventory area: West Los Angeles, Downtown Los Angeles and Pasadena. Organic compounds having a ratio of ambient concentration to primary emission rate in the same range as seen for fine elemental carbon, silicon, and aluminum will pass our initial screening check that $f_{ijk} \simeq 1$ over the relatively short distance from source to receptor that exists in the western and central portions of the Los Angeles basin. To formalize that concept, an organic compound having an atmospheric concentration to emission rate ratio falling within a specific interval will be considered to be sufficiently stable that it can be used for mass balance

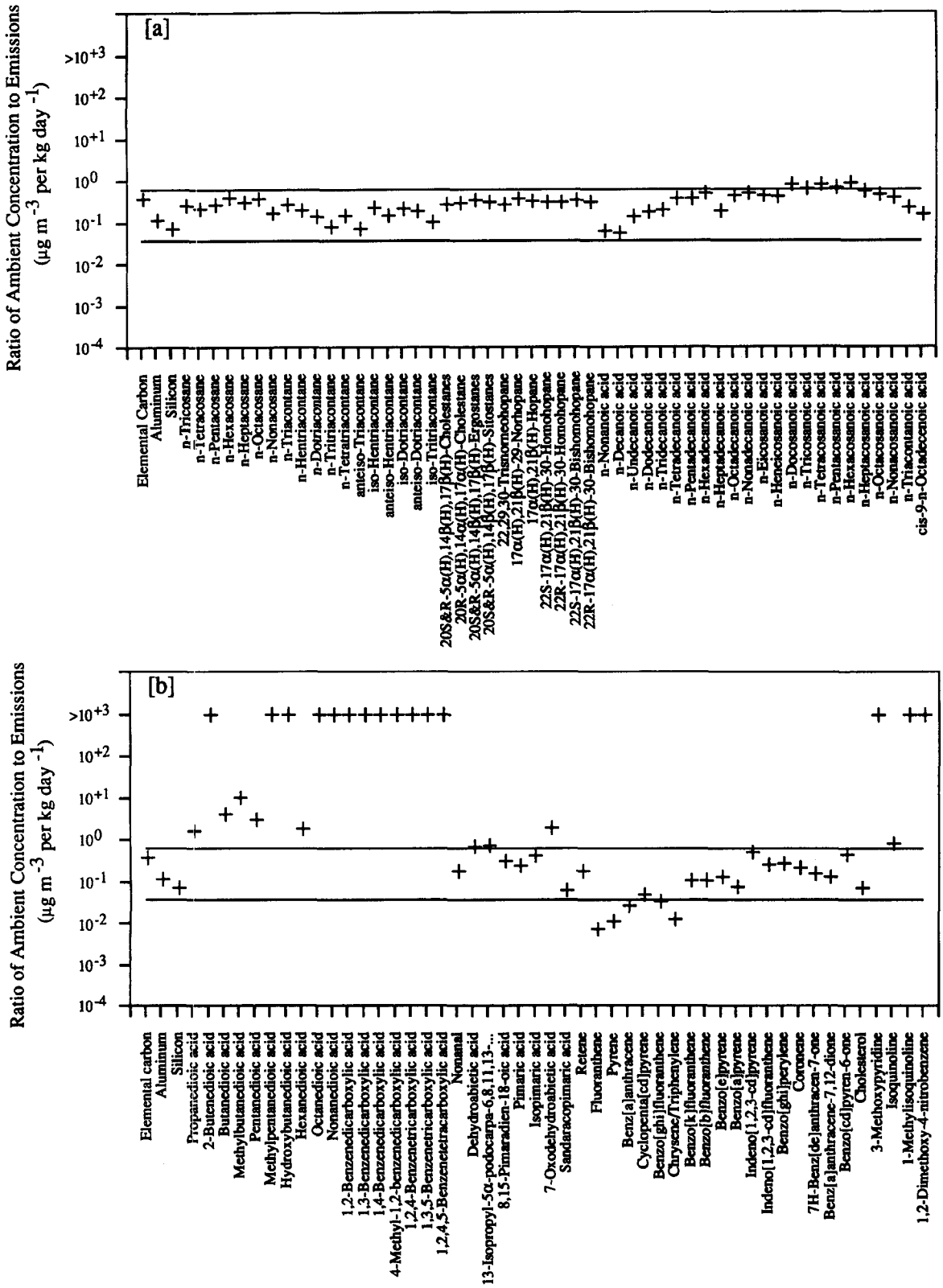

Fig. 2. Central basin 1982 annual average ambient compound concentrations divided by compound emissions within the 80 × 80 km emissions inventory area centered over Downtown Los Angeles (Hildemann *et al.*, 1991). Solid lines represent the average ± two standard deviations of the ratio of concentration to emission rate observed for the conserved reference materials: elemental carbon, fine particle aluminum, and fine particle silicon. Central basin average ambient concentrations include all data from within the emissions inventory area: Pasadena, West Los Angeles, and Downtown Los Angeles. Values shown at 10^3 are greater than or equal to 10^3.

calculations. That interval is defined by the mean of the ambient concentration to emissions ratio seen for the inert reference species elemental carbon, fine aluminum and fine silicon, plus and minus two standard deviations of that population of three reference species ratios. This range is shown between the horizontal solid lines in Figs 2a and b. Emissions inventories for elemental carbon, fine aluminum and fine silicon are taken from Gray (1986).

Figure 2 shows that on a yearly average the normal alkanes are not removed from fine aerosols any more rapidly than inert substances such as elemental carbon, fine aluminum, or fine silicon over the time scale of transport between sources and receptors in the western and central Los Angeles basin. Similarly, regular steranes, pentacyclic triterpanes, iso-alkanes, and anteiso-alkanes show the same basic relationship between emission rates and ambient concentrations and therefore do not appear to have major selective losses or gains from the fine aerosol fraction. This empirical result is consistent with the expected decay rates of these species. All of the above-noted conserved organic compounds are considered to react relatively slowly. On a yearly average their fractionation coefficient can be taken to be close to one. Therefore, these compounds will be included in the base case CMB model.

In contrast, the polycarboxylic aromatic acids, the dicarboxylic acids, 3-methoxypyridine, 1-methylisoquinoline, and 1,3-dimethoxy-4-nitrobenzene show very high values of the ratio of their ambient concentration to their emissions rate within the area-wide primary particle emissions inventory. The concentrations of these compounds are thought to be dominated by secondary formation due to atmospheric chemical reactions. Aliphatic dicarboxylic acids are known to be formed from gas-phase precursors under photochemical smog conditions (Appel *et al.*, 1980; Cronn *et al.*, 1977; Grosjean, 1977; Grosjean and Friedlander, 1980; Satsumabayashi and Kurita, 1989). Emissions of aromatic polycarboxylic acids are below detection limits in all of the sources tested here, and cluster analysis applied to atmospheric concentration data shows that the concentrations of these compounds follow the behavior of the aliphatic dicarboxylic acids (Rogge *et al.*, 1993a). Thus, aromatic polycarboxylic acids are also believed to be formed by atmospheric chemical reactions. These compounds that appear to be formed by atmospheric chemical reactions will not be used within the model.

The selective loss of many of the lower molecular weight primary particle-phase polycyclic aromatic hydrocarbons (PAH) is suggested by Figs 2a and b. All of the PAH with molecular weights less than benzo[k]fluoranthene, with the possible exception of cyclopenta[cd]pyrene, have normalized ambient concentrations that are much lower than is exhibited by the conserved species. The lighter of these compounds, fluoranthene, pyrene, and benz[a]anthracene, would be expected to be lost from the fine particle phase due to volatilization. The losses of some of these PAH also are believed to result from heterogeneous reactions in the particle phase (Kamens *et al.*, 1988), although little data exist to quantify the rate of these reactions under ambient conditions. Kamens *et al.* (1988) measured the reactivity of several PAH on wood soot particles in a smog chamber and found a semi-empirical correlation for reactivity that depends on temperature, total solar radiation intensity, and humidity. Cyclopenta[cd]pyrene, benz[a]anthracene, and benzo[a]pyrene were found to have the fastest reaction rates under the conditions tested by Kamens *et al.* (1988) on wood soot particles. For that reason, these three compounds will be excluded as fitting species in the base case CMB model, even though the average particle composition and the atmospheric conditions of the Kamens *et al.* tests may be very different than the annual average particle composition and atmospheric conditions experienced in the Los Angeles basin. For these reasons, all of the PAH with molecular weights less than 252 (i.e. those having lower molecular weights than benzo[k]fluoranthene) are also not used as mass balance species in the CMB model.

For the PAH with molecular weights of 252 or greater (except for benzo[a]pyrene), there is insufficient data to allow a sharp dividing line to be drawn between individual compounds that should be included or excluded from our analysis. For this reason, two cases have been investigated. In the base case, all of the PAH with molecular weights greater than or equal to 252 (i.e. PAH having molecular weights at least as great as that of benzo[k]fluoranthene), except benzo[a]pyrene, are included as if they were stable compounds in the mass balance calculations. In an alternative case, only the four highest molecular weight PAH are included: indeno[1,2,3-cd]pyrene, indeno[1,2,3-cd]fluoranthene, benzo[ghi]perylene, and coronene. While Fig. 2 suggests that the longer list of PAH can be used as if they were conserved species over the short distance transport within the central Los Angeles basin, a similar analysis shows that benzo[k]fluoranthene, benzo[b]fluoranthene, and benzo[e]pyrene can be depleted over the longer transport distance to downwind Rubidoux.

Kamens *et al.* (1988, 1989) also have examined the stability of several polycyclic aromatic ketones and quinones (oxy-PAH) and a wood smoke marker, retene, in smog chamber experiments. Retene was found to react at a rate comparable to benzo[a]pyrene on wood smoke particles under conditions of high solar irradiance, humidity, and temperature, but showed much lower relative reactivity at lower solar irradiance, humidity, and temperature. Since retene appears from Fig. 2 to be conserved based on the relationship of its emissions and ambient concentration, retene is used as a mass balance species in our model. Of the remaining wood smoke components, only 8,15-pimaradien-18-oic acid, pimaric acid, isopimaric acid, and sandaracopimaric acid pass the initial screening

test. As seen in Fig. 2, sandaracopimaric acid does not cluster with the three other wood smoke components just mentioned above and therefore will not be included in the base case model application. Dehydroabietic acid, 13-isopropyl-5α-podocarpa-6,8,11,13-tetraen-16-oic acid, and 7-oxodehydroabietic acid, all have ratios of ambient concentrations to emission rates that fail the initial screening test.

The several oxy-PAH tested by Kamens *et al.* (1989) were found to be stable both in the absence of sunlight and in the absence of appreciable ozone on wood smoke particles. The three oxy-PAH shown in Fig. 2, 7H-benz[de]anthracen-7-one, benz[a]anthracene-7,12-dione, and benzo[cd]pyren-6-one, appear to be conserved over short transport distances within the central Los Angeles basin, but a further analysis shows that they are not very well conserved over longer downwind transport to Rubidoux. These three oxy-PAH are emitted predominantly by natural gas home appliances and non-catalyst gasoline-powered vehicles in Los Angeles, while the Kamens *et al.* results apply to oxy-PAH adsorbed onto wood smoke particles. Our analysis in Fig. 2 plus the work of Kamens *et al.* (1989) suggest that these compounds are reasonably well conserved over short distance transport. For this reason, these compounds are included as mass balance compounds in the base case air quality model.

Oleic acid appears from Fig. 2 to be present in about the expected quantity in airborne fine particles even though oleic acid is an olefinic compound susceptible to ozone attack. This compound is a key tracer for aerosols from food cooking and therefore should not be excluded from the present model unless it is absolutely clear that it must be excluded. Thus, oleic acid is used as a mass balance species in this study. The sensitivity of the CMB model results to this assumption will be discussed later.

Although cholesterol is thought to be an excellent marker for the aerosol released from meat cooking (Rogge *et al.*, 1991), quantification of trace cholesterol concentrations in ambient samples was not possible for some samples. Cholesterol is therefore not included in the base case model as a mass balance component. Alternative case models, which include cholesterol as a mass balance compound, will be presented later for the apportionment of sources contributing to the two air monitoring sites for which cholesterol data are available, West Los Angeles and Pasadena. Coronene elutes very late from the chromatographic column used here and was only quantified in the West Los Angeles samples. Coronene is only included in the model for that site. Similarly, the anteiso-C_{30} and C_{31} alkanes and the iso-C_{32} alkane were not identified in the Downtown Los Angeles and Rubidoux ambient samples and thus are also not included in the base case model at those sites. Table 2 summarizes those compounds that are included in the base case model.

Elimination of collinearity between source profiles. Use of the chemical mass balance model requires that the source profiles be sufficiently different from each other. Therefore, several steps were taken to remove collinearities. Elemental carbon plus silicon and aluminum measurements from the source sampling program (Hildemann *et al.*, 1991) and the ambient sampling program (Gray *et al.*, 1986) were added to the database. The aluminum and silicon data when combined with the organics yield a distinguishing fingerprint for paved road dust. The elemental carbon data when combined with the organic compound concentrations provides a unique fingerprint for diesel engine exhaust. There are three generic source types that each have two source profiles in our data base: gasoline-powered vehicles, fireplace combustion of wood, and meat cooking. Within pairs, these source profiles are sufficiently similar that each pair was combined to form a single emissions-weighted average source profile. Catalyst-equipped gasoline-powered vehicle emissions and non-catalyst gasoline-powered vehicle emissions were combined in proportions equivalent to their contributions to the fine organic aerosol emissions inventory to produce a single emissions-weighted overall source profile for gasoline-powered vehicles. Similarly, source profiles for fireplace combustion of hardwood and softwood were combined to form an emissions-weighted average wood smoke source profile. The source profiles for meat charbroiling and meat frying also were combined into a single emissions-weighted average meat cooking source profile. Following creation of these combined source profiles, a total of 12 separate source profiles remain for use in the CMB model.

Completeness of the Source Profile Library

More than 70 different carbon particle emissions source types can be identified in the Los Angeles area (Cass *et al.*, 1982; Gray, 1986). As a practical matter, receptor models based on elemental composition data seldom can resolve as many as a half dozen separate source contributions within a real application. The species selected for use in a mass balance model that seeks to resolve less than the full set of sources actually present must be chosen carefully so that the sources included in the model in fact do complete a mass balance on the subset of chemical species entered into the model. As a starting point, such a check for the completeness of the set of sources used can be constructed based on emissions inventory data. Using the set of 15 source profiles available together with the knowledge that they represent more than 80% of the primary organic aerosol emissions within the Los Angeles airshed, emission inventories were constructed for each chemical compound listed in Table 2 that was found in the source emissions. The contributions of the individual sources to the emissions of each organic compound are shown in Figs 3a–c. Before running the CMB7 computer code, these figures were used to perform consistency checks to assure that if

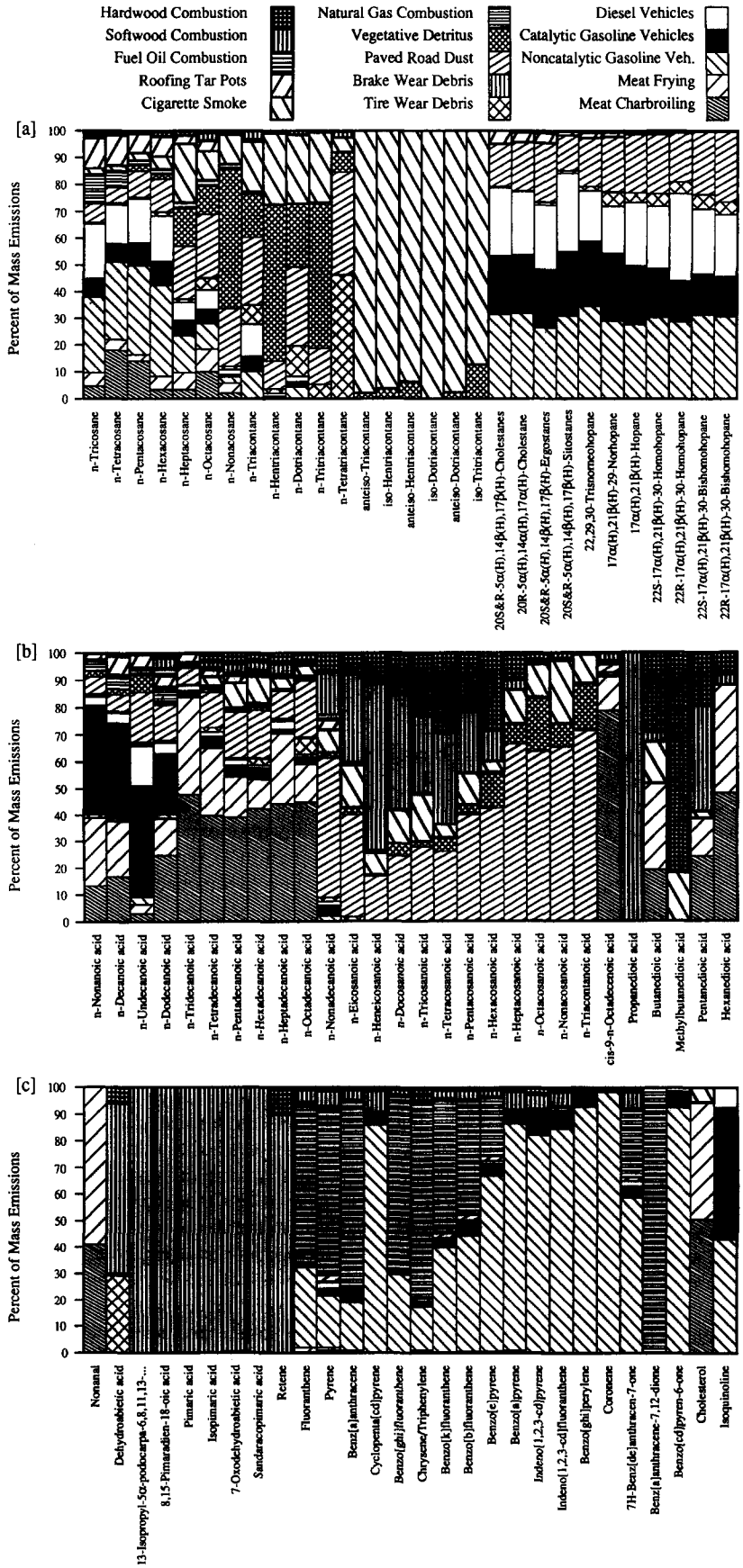

Fig. 3. Distribution of particulate organic compound emissions by source type within the Los Angeles basin, 1982.

a source profile must be deleted from the model (e.g. because it makes an insignificant contribution to the ambient aerosol), then at no time a species remained as a mass balance component when a significant known source of that compound was missing from the model. No compounds had to be deleted from the list of mass balance species due to this screening step.

The alkanoic acids shown in Fig. 2 appear to be stable enough chemically to be used in receptor modeling calculations. However, we suspect that cooking with seed oils is a significant source of *n*-alkanoic acids emissions to the urban atmosphere (Eckey, 1954), and the emission rate from such activities is not presently known. For that reason, we have not included the *n*-alkanoic acids in the base case model.

Following the application of the above consistency checks, 45 organic compounds plus data on silicon, aluminum, and elemental carbon concentrations remain for use in the model, and 12 separate source profiles remain.

RESULTS

The chemical mass balance model constructed above was tested by application to the southern California database. Compounds included as mass balance species in the base case model are listed in Table 2. As previously indicated, coronene and three of the iso- and anteiso-alkanes were eliminated from the mass balance calculations on a site-by-site basis in those cases where ambient data were not available.

A comparison of the modeled and measured ambient concentrations of each of the mass balance species at Downtown Los Angeles is given in Fig. 4. Generally, excellent agreement is obtained between observations and model predictions across the 45 diverse organic compounds used, plus aluminum, silicon, and elemental carbon. For each group of chemically similar tracers, the mean of the ratio of measured to predicted concentrations as well as the standard error of that ratio for the population of tracers in each chemical class was computed as follows: *n*-alkanes (0.88 ± 0.29), iso- and anteiso-alkanes (1.03 ± 0.42), hopanes and steranes (0.85 ± 0.14), alkenoic acids (1.00), aldehydes (1.09), conifer resin acids and their thermal alteration products (1.01 ± 0.26), PAH (1.14 ± 0.35), and oxy-PAH (0.87 ± 0.34).

Source contributions to annual average particulate organics mass and overall fine particulate mass concentrations that are statistically different from zero with greater than 95% confidence can be determined at West Los Angeles, at Downtown Los Angeles and at Pasadena for nine separate source types: diesel engine exhaust, paved road dust, gasoline-powered vehicle exhaust, emissions from food cooking and wood smoke, natural gas combustion aerosol, cigarette smoke, plant fragments, and tire dust as shown in Table 3. At the Rubidoux site, contributions from

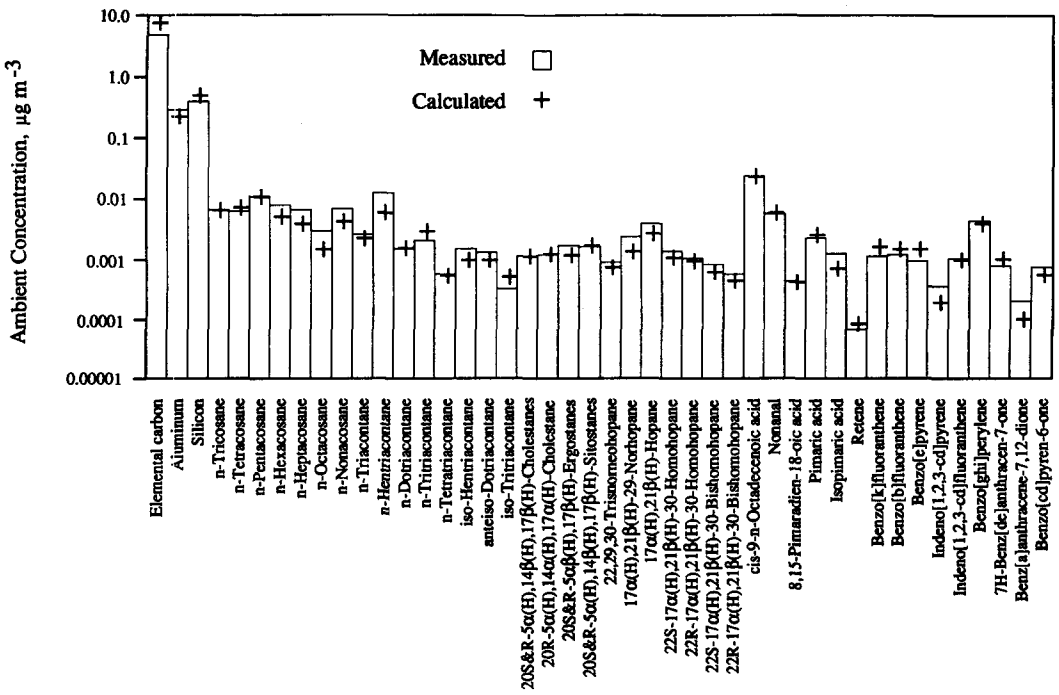

Fig. 4. Comparison of model predictions to measured ambient concentrations for the mass balance compounds — Downtown Los Angeles, 1982 annual average.

Table 3. Source apportionment of primary fine organic aerosol: 1982 annual average determined by chemical mass balance (avg ± std in $\mu g\ m^{-3}$)

Source	Pasadena	Downtown LA	West Los Angeles	Rubidoux
Diesel exhaust	1.24 ± 0.17	2.72 ± 0.28	1.02 ± 0.15	1.26 ± 0.12
Tire wear debris	0.13 ± 0.046	0.096 ± 0.040	0.11 ± 0.040	[a]
Paved road dust	0.56 ± 0.070	0.59 ± 0.075	0.49 ± 0.063	0.89 ± 0.099
Vegetative detritus	0.13 ± 0.039	0.095 ± 0.046	0.15 ± 0.043	0.071 ± 0.033
Natural gas combustion aerosol	0.048 ± 0.020	0.041 ± 0.019	0.035 ± 0.016	0.029 ± 0.008
Cigarette smoke	0.13 ± 0.018	0.19 ± 0.033	0.14 ± 0.020	0.13 ± 0.023
Meat charbroiling and frying	1.69 ± 0.32	1.22 ± 0.24	1.42 ± 0.27	1.35 ± 0.25
Catalyst and non-catalyst gasoline-powered vehicle exhaust	1.20 ± 0.14	1.56 ± 0.17	1.06 ± 0.12	0.25 ± 0.040
Wood smoke	1.57 ± 0.25	1.07 ± 0.18	1.54 ± 0.24	0.31 ± 0.060
Sum	6.68 ± 0.41	7.58 ± 0.38	5.97 ± 0.37	4.30 ± 0.27
Measured[b]	8.14 ± 0.52	8.72 ± 0.66	7.00 ± 0.61	6.24 ± 0.35

[a] Not statistically different from zero with greater than 95% confidence.
[b] Includes secondary organic aerosol; receptor model results should be less than or equal to measured total fine particle organic concentration.

the first eight of the above sources can be identified. The emissions from industrial boilers burning distillate fuel oil, vehicular brake lining wear, and roofing tar pot effluent could not be identified in the ambient samples. Each of these is a minor source according to the emissions inventory. The nine sources that remain in the model account for approximately 80% of the primary aerosol organic carbon emissions according to the emissions inventory. The standard errors of the source contribution estimates reported for each source type in Table 3 are smaller than the standard error of the combined source contributions estimated for any linear combination of these source profiles, as judged by the absence of any similarity/uncertainty clusters within the CMB7 program results (see Watson *et al.*, 1990).

In an alternative model calculation, three PAH with questionable stability were removed from the base case list of compounds: benzo[k]fluoranthene, benzo[b]fluoranthene and benzo[e]pyrene. For all four monitoring sites, this alternative model calculation produced the same result as the base case within 95% confidence limits.

A second alternative case examined cholesterol as a marker for meat cooking operations. Cholesterol data are only available for two sites, West Los Angeles and Pasadena. Generally, cholesterol concentrations in the atmosphere are less than would be expected from the ambient concentrations of compounds largely derived from meat cooking operations, oleic acid, nonanal, and the C_{23}–C_{27} normal alkanes. If we add cholesterol data to the base case model compounds, we find that the quantity of ambient meat cooking aerosol predicted by the model is decreased. For West Los Angeles, the results of this alternative case were not statistically different from the base case, while for Pasadena the ambient aerosol mass concentration increment assigned to meat cooking was decreased by 0.78 $\mu g\ m^{-3}$ and none of the other source contributions changed significantly from the base case model results.

Computed source contributions to the annual average fine organic aerosol at each monitoring site are shown in Fig. 5. The contribution from "other sources," which includes secondary organic aerosol formation, is obtained by subtracting the concentration increments due to identified sources from the annual average fine organic compound concentration measurements reported by Gray *et al.* (1986) (organic compounds $\simeq 1.2 \times OC$).

The dominant sources of fine organic aerosol were found to be diesel exhaust, gasoline-powered vehicle exhaust, meat cooking operations, and wood combustion. Paved road dust is the next largest contributor followed by four smaller sources: tire wear, vegetative detritus, natural gas combustion, and cigarette smoke. The relative and absolute contributions are very similar for West Los Angeles and Pasadena, while the Downtown Los Angeles site is noticeably different from the other two sites in the western portion of the air basin. The diesel exhaust contribution to the Downtown Los Angeles site is approximately twice the value seen at the other two more residential sites in the western basin. This increase is believed to be a result of the higher density of commercial trucking and the presence of a major railroad yard near the Downtown Los Angeles sampling site. Auto exhaust aerosol is also significantly increased near the Downtown Los Angeles sampling site.

The quantity of organic aerosol that cannot be attributed to the nine primary sources resolved by the model places an upper limit on the annual average secondary organic aerosol concentration that could be present due to gas-to-particle conversion processes in the atmosphere. Both qualitative consideration of transport direction and airmass aging plus quantitative analysis of the ambient samples used here to determine the concentrations of likely secondary

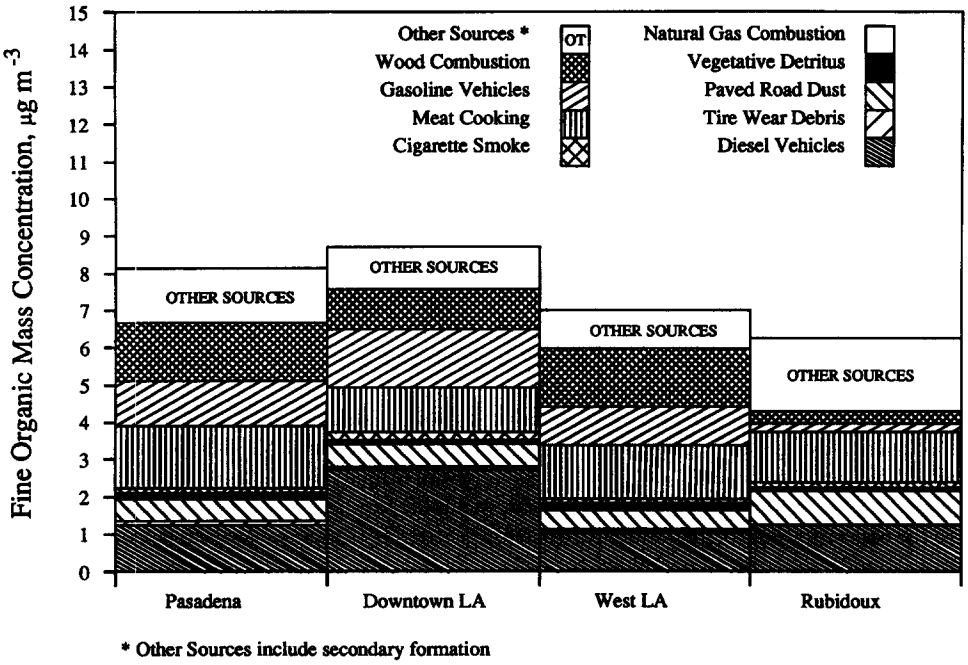

Fig. 5. Source apportionment of ambient fine organic aerosol mass concentration — 1982 annual average.

Table 4. Source apportionment of fine particulate mass concentration: 1982 annual average determined by chemical mass balance (avg ± std in $\mu g\,m^{-3}$)

Source	Pasadena	Downtown LA	West Los Angeles	Rubidoux
Diesel exhaust	5.27 ± 0.72	11.6 ± 1.19	4.36 ± 0.64	5.35 ± 0.51
Tire wear debris	0.29 ± 0.11	0.22 ± 0.09	0.25 ± 0.09	[a]
Paved road dust	3.46 ± 0.43	3.62 ± 0.46	3.00 ± 0.39	5.50 ± 0.61
Vegetative detritus	0.33 ± 0.10	0.24 ± 0.12	0.38 ± 0.11	0.18 ± 0.08
Natural gas combustion aerosol	0.047 ± 0.02	0.040 ± 0.019	0.034 ± 0.016	0.029 ± 0.008
Cigarette smoke	0.18 ± 0.03	0.26 ± 0.045	0.20 ± 0.028	0.19 ± 0.032
Meat charbroiling and frying	2.41 ± 0.46	1.74 ± 0.34	2.03 ± 0.39	1.94 ± 0.35
Catalyst and non-catalyst gasoline-powered vehicle exhaust	1.63 ± 0.20	2.12 ± 0.23	1.44 ± 0.16	0.34 ± 0.05
Wood smoke	2.70 ± 0.43	1.85 ± 0.31	2.65 ± 0.41	0.54 ± 0.10
Organics (other + secondary)	1.46 ± 0.66	1.16 ± 0.76[b]	1.03 ± 0.71[b]	1.94 ± 0.44
Sulfate ion (secondary + background)	5.9 ± 0.60	6.6 ± 0.65	5.9 ± 0.60	5.8 ± 0.51
Secondary nitrate ion	2.1 ± 0.27	3.0 ± 0.54	1.9 ± 0.29	10.4 ± 1.2
Secondary ammonium ion	2.6 ± 0.34	3.0 ± 0.37	2.3 ± 0.23	5.1 ± 0.59
Sum	28.3 ± 1.5	35.5 ± 1.9	25.3 ± 1.4	37.3 ± 1.8
Measured	28.2 ± 1.9	32.5 ± 2.8	24.5 ± 2.0	42.1 ± 3.3

[a] Not statistically different from zero with greater than 95% confidence, and therefore removed from CMB model.
[b] Not statistically different from zero with greater than 95% confidence.

aerosol reaction products (e.g. dicarboxylic acids, see Rogge *et al.*, 1993a) suggest that the secondary aerosol levels should be highest at the far downwind site at Rubidoux. The model results indeed show that 31% of the organic aerosol at Rubidoux cannot be attributed to the major primary sources. This places an upper limit of 31% on the contribution of secondary organic aerosol at that site. At West Los Angeles, Downtown Los Angeles, and Pasadena, the comparable upper limit on secondary organic aerosol concentrations in 1982 is in the range of 15–18% of the fine organic aerosol. These estimates can be compared to previous work. Based on the ratio of organic carbon to elemental carbon in ambient samples and in source emissions, Gray *et al.* (1986) estimated that 27–38% of the organic aerosol at Rubidoux in 1982 was

secondary in origin. The photochemical trajectory modeling study by Pandis *et al.* (1992) placed secondary organic aerosol concentrations as a fraction of total organic aerosol during a 1987 summer smog episode in the Los Angeles area at 5–8% at near-coastal sites and at about 15–22% at Claremont, CA (located approximately half-way between Pasadena and Rubidoux). Based on differences observed between ambient organic aerosol concentrations vs primary source contributions to acidic organics calculated using a Lagrangian transport model, Hildemann *et al.* (1993) estimated as an upper limit that 18–27% of the organic aerosol was secondary in origin at the three western basin sites studied here. The upper limits on secondary organic aerosol concentrations established by the present study are consistent with these prior estimates.

The relative contribution of the various primary sources to the concentrations of individual particulate organic compounds also can be computed from the model. The percentage of the modeled individual organic compound concentrations predicted to be due to each of the primary sources studied is illustrated for Downtown Los Angeles in Fig. 6.

Total fine particulate mass apportionment

The ratio of single organic compound concentrations to both the total organic aerosol mass concentration and to the overall fine particulate mass concentration is known for both the source emissions and ambient data sets used here (Gray *et al.*, 1986; Rogge *et al.*, 1993a; Hildemann *et al.*, 1991). Therefore, the receptor model can be used to apportion total fine particulate mass concentrations between contributing sources. The results of that calculation are shown in Fig. 7. In that figure, the sulfate, nitrate and ammonium ion increments shown are obtained from the SO_4^{2-}, NO_3^-, and NH_4^+ ion concentrations reported by Gray *et al.* (1986) after subtracting the primary sulfate, nitrate and ammonium ion concentrations that accompany the direct emissions from the primary sources studied here according to the source emission profiles of Hildemann *et al.* (1991). The sulfate, nitrate and ammonium ion increments shown in Fig. 7 are largely due to local secondary aerosol formation, but also include contributions from background air transported from upwind plus possible small increments from primary SO_x sources that are not included in the model (e.g. refinery FCC Units; see Cass, 1981). The secondary organic aerosol is contained within the Other Organics category as discussed earlier. The total fine particulate mass concentrations assigned to the sources studied by the model plus secondary aerosol are not statistically different from the total fine particulate mass concentrations measured by Gray *et al.* (1986). Within ± 1–$2\ \mu g\,m^{-3}$, all major sources of airborne fine particulate mass are accounted for in the model at West Los Angeles, Downtown Los Angeles and Pasadena; results at Rubidoux are still within $\pm 2\sigma$ of closing a material balance on the origin of the entire fine aerosol. As seen in Fig. 7, the major primary fine particulate source contributions are

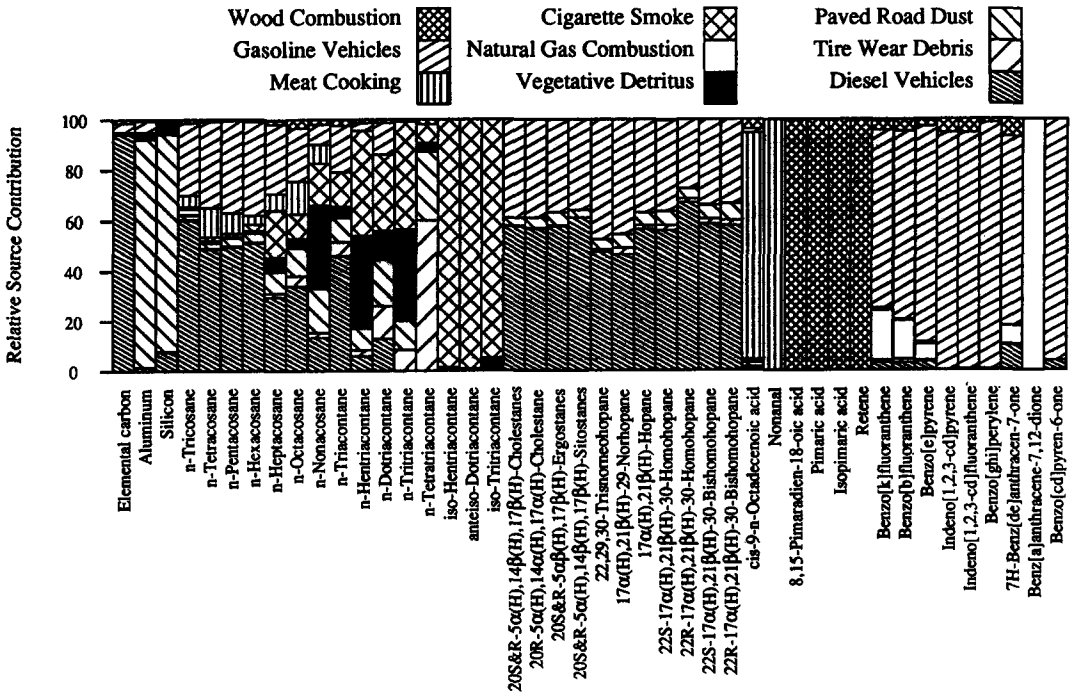

Fig. 6. Relative source contribution to modeled ambient concentrations of organic compounds used in the mass balance at Downtown Los Angeles — 1982 annual average.

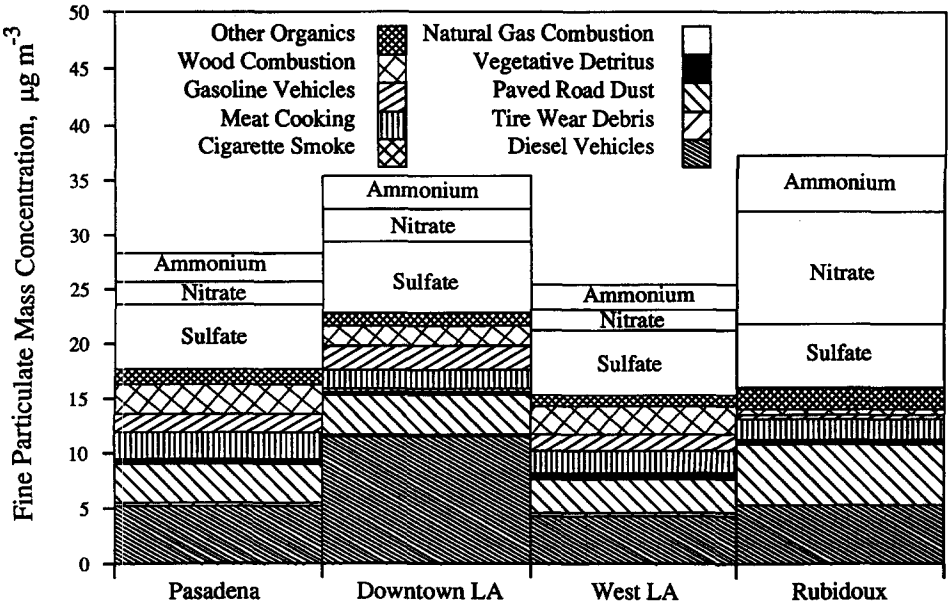

Fig. 7. Source apportionment of fine mass concentrations — 1982 annual average.

attributed to diesel soot, paved road dust, gasoline-powered motor vehicles exhaust, food cooking operations and wood smoke with small but quantifiable contributions from cigarette smoke, natural gas combustion aerosol, tire wear debris, and plant fragments. Secondary aerosol concentrations again are highest at the farthest downwind site at Rubidoux, as expected.

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SUPPLEMENTAL MATERIALS

Tables containing 1982 annual average ambient concentration data for the air quality monitoring sites used in this study are contained in the references by Rogge *et al.* (1993a), Rogge (1993), and Gray (1986) and also can be obtained in consolidated form from the authors of the present article. Source profiles showing the organic compound distributions in primary source emissions are reproduced in the references cited, and also can be obtained in consolidated form from the authors of the present article.

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