Environ. Sci. Technol. **1994**, *28*, 1375–1388

Sources of Fine Organic Aerosol. 6. Cigarette Smoke in the Urban Atmosphere

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Molecular marker compounds that can be used to trace cigarette smoke particles in the outdoor urban atmosphere are identified. While the most abundant resolved organic compounds present are nitrogen-containing heterocyclics (e.g., nicotine), other potential tracers that will be more stable in the outdoor urban atmosphere also are found. Iso- and anteisoalkanes (C_{29}–C_{34}) are enriched in cigarette smoke particles and show a concentration pattern characteristic of tobacco leaf surface waxes that is distinctly different from leaf surface abrasion products shed from plant leaves that grow in the Los Angeles area. Relative to major leaf surface wax *n*-alkanes, these iso- and anteisoalkanes are enriched by a factor of more than 40 in tobacco and tobacco smoke particles as compared to leaf surface waxes from Los Angeles area plants. It is found that the iso- and anteisoalkanes concentration pattern generated by cigarette smoke is preserved in the urban atmosphere and is measured at levels that are comparable to emissions estimates based on daily cigarette consumption. Using these marker compounds, ambient fine cigarette smoke particles are estimated to be present at a concentration of 0.28–0.36 $\mu g\ m^{-3}$ in the Los Angeles outdoor air, accounting for 1.0–1.3% of the fine particle mass concentration.

Introduction

Cigarette smoke has been intensively researched in the last 3 decades. Studies that focus on the gaseous and particulate smoke constituents have been numerous, and substantial literature is available on both the chemical composition and possible health risks due to tobacco smoke (e.g., refs 1–7).

Previous investigations have developed nicotine, solanesol, *n*-alkanes, polycyclic aromatic hydrocarbons (PAH), and other organic constituents as marker compounds for the presence of cigarette smoke in indoor air (e.g., refs 8–19). The purpose of the present study is not to add additional knowledge to the extensive literature available for cigarette smoke compositon and indoor air quality. Instead, in this study, tobacco smoke is viewed as one of the many small sources contributing organic fine particulate matter to the outdoor urban atmosphere. Hildemann et al. (*20*) report that cigarette smoke accounted for about 2.7% of the fine organic aerosol emissions to the Los Angeles area atmosphere in 1982, and that reference can be consulted in order to place cigarette smoke emissions in a proper context versus other urban air pollution sources such as diesel engine exhaust.

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

Experimental Methods

Cigarettes Tested. Four different cigarette types —including regular (nonfilter), filter, light, and menthol cigarettes—have been tested, and the resulting particulate emission samples composited to closely represent the market share in the United States in 1981 for each of these cigarette types. For each cigarette type, one of the five most popular cigarette brands has been employed for this study including products carrying the Camel, Merit, Winston, and Benson & Hedges brand names. For more details, see Hildemann et al. (*20*).

Sampling. A specially designed vertically oriented dilution tunnel was used to collect the exhaled mainstream and sidestream smoke generated by human smokers (*20*). The size of the dilution tunnel and the flow rate through the tunnel (residence time of ca. 30 s) provided sufficient time for cigarette smoke to cool to ambient temperatures, allowing condensible organic compounds emitted in the vapor phase to equilibrate with the smoke particles prior to sampling. Since laboratory dilution tunnels cannot as a practical matter dilute the emissions as much as the outdoor atmosphere, it is possible that the most volatile compounds in the particle phase (e.g., nicotine) may be present to a greater degree in the particle phase under the test conditions than in the atmosphere, but the nonvolatile

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high molecular weight n-alkanes and branched alkanes of most interest to this paper will be found almost exclusively in the particle phase both under these test conditions and in the atmosphere.

Five AIHL-design cyclone separators were mounted at the downstream end of the dilution tunnel. Two of the cyclone separators were used for fine particle sampling and were operated at a flow rate of 27.9 ± 0.3 L min^{-1}, removing particles with an aerodynamic diameter >2.0 μm from the airstream. Fine particulate matter ($d_p \leq 2.0$ μm) next was collected by filtration downstream of each of those two cyclone separators using 3–4 parallel 47-mm diameter filter assemblies per cyclone, for a total of seven fine particle filter samples per cigarette type. Five of these fine particle cigarette smoke samples per test were collected on quartz fiber filters (Pallflex 2500 QAO) and were used for organics analysis. The other two fine particle samples per test were collected on Teflon filters (Gelman Teflo, 2.0-μm pore size) used for gravimetric analysis of fine particle mass emssion rates as well as elemental and ionic species analysis. All quartz fiber filters were annealed before use (750 °C for 2–4 h) to guarantee low contamination levels for organic compounds. Additional details of the experimental protocol are given elsewhere (*20*).

Bulk Chemical Analysis. Trace elements, ionic species, organic carbon (OC), and elemental carbon (EC) emission rates have been previously quantified in the cigarette smoke samples (*20*).

Sample Extraction. Organic compounds present in the cigarette smoke particle samples were extracted using the procedure developed for ambient fine particulate mater by Mazurek et al. (*21*) that subsequently has been used in several studies concerned with organic particulate matter emissions and ambient air quality (*22–29*). The extraction protocol can be described briefly as follows. Before sample extraction, fine particle cigarette smoke samples were composited according to their market share. Perdeuterated tetracosane (n-$C_{24}D_{50}$), which serves as an internal standard, next was spiked onto the filter composites. The composited quartz fiber filter samples were extracted in a sequential procedure that utilized hexane (2 × 30 mL) followed by benzene/2-propanol (2:1 mixture, 3 × 30 mL). Each extraction step was conducted for 10 min and supported by mild ultrasonic agitation. Following each extraction step, the extracts were filtered and combined using a transfer and filtering device that is described in detail by Mazurek et al. (*21*). A two-step rotary evaporation scheme followed by gentle high-purity N_2-stream evaporation was employed to reduce the combined sample extract volume to 200–500 μL. One portion of the sample extract was then processed with freshly produced diazomethane to convert organic acids to their methyl ester analogues and other compounds with susceptible hydroxy functionalities to their methoxyl analogues. The sample extracts were stored prior to GC/MS analysis in the dark at −21 °C.

Sample Analysis. A Finnigan 4000 quadrupole mass spectrometer connected to a gas chromatograph and interfaced with an INCOS data system was used for compound identification and quantification. Sample extracts were injected onto a conventional Grob splitless injector (300 °C), which was connected to a 30-m fused-silica DB-1701 column (J&W Scientific, Rancho Cordova, CA). Gas chromatography of the injected sample extract was carried out using the following temperature program: (1) isothermal hold at 65 °C for 10 min, (2) temperature increase at 10 °C/min for 21 min, and (3) isothermal hold at 275 °C for another 49 min. The mass spectrometric data were acquired while operating the mass spectrometer in the electron impact mode (electron energy of 70 eV). For supplemental studies, a Varian 4600 high-resolution gas chromatograph (HRGC) with FID detector was used and operated with the same physical column and temperature program as used during these GC/MS analyses (*24*). Additional information describing the analytical procedure can be found elsewhere (*21, 22, 25–27, 30*).

Quality Assurance. A series of quality control and monitoring steps were followed. The major steps include: field and laboratory blank testing; solvent testing to monitor possible contaminants; recovery experiments in which a large set of polar and nonpolar standard compounds were spiked onto test filters and then extracted; and dilution air testing. For a more detailed discussion, the reader is referred to accompanying source and ambient fine organic particle studies published elsewhere (*22, 25–27, 30*).

Compound Identification and Quantification. Compound identification was assigned using the National Institute of Standards and Technology (NIST) mass spectral library accessed by the INCOS Data System, by the NIST/EPA/NIH mass spectral database (PC Version 4.0) distributed by NIST, and by reference to authentic standards injected onto the GC/MS system used here. Compound identification was labeled accordingly: (a) *positive*, sample mass spectrum and authentic standard mass spectrum compared well and showed identical retention times; (b) *probable*, same as before, except no authentic standards were available, but the NIST or NIST/EPA/NIH library mass spectrum and the sample mass spectrum agreed well; (c) *possible*, same as above except that the sample spectrum contained information from other compounds but with minor overlap; (d) *tentative*, when the sample spectrum contained additional information from possibly several compounds (noise) with overlap; (e) iso- and anteisoalkanes are positively identified by monitoring their major ions at M-43 and M-29, respectively.

The compound quantification process was based on the application of n-$C_{24}D_{50}$ as an internal standard and 1-phenyldodecane as the co-injection standard. To correct for detector response to compounds having different structures and retention times, sets of known standard compounds were injected onto the analytical system to monitor their specific MS response. For more information, the interested reader is referred to Rogge et al. (*25, 26*).

Standard Compounds. Confirmation and quantification of organic compounds was obtained through the use of more than 150 authentic standards (see ref 27). The following standard mixtures were injected onto the GC/MS system: (1) normal alkanes ranging from n-C_{10} to n-C_{36}; (2) normal alkanoic acids as methyl esters ranging from n-C_6 to n-C_{30}; (3) unsaturated aliphatic acids such as oleic acid and linoleic acid as methyl esters; (4) normal alkanols ranging from n-C_{10} to n-C_{30}; (5) several phenolic compounds, benzaldehydes, and substituted aromatic acids; (6) a suite of 39 aromatic and polycyclic aromatic hydrocarbons (PAH); (7) 10 polycyclic aromatic ketones and quinones; (8) a set of eight aromatic and polycyclic aromatic N- and S-substituted compounds; (9) steroids including cholesterol and cholestane; (10) a set of four

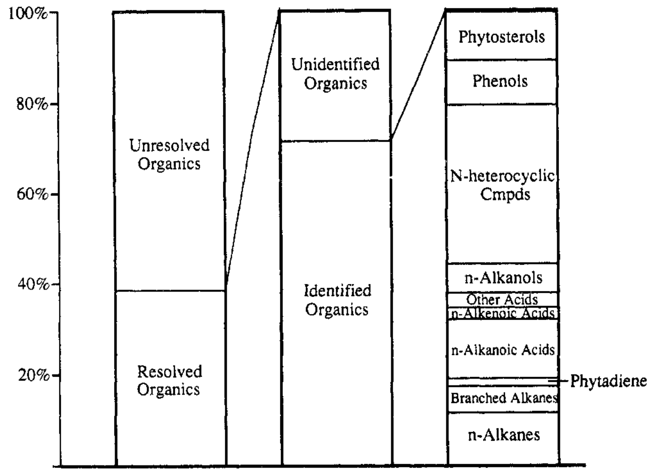

Figure 1. Mass balance for elutable organic matter contained in fine cigarette smoke particles.

phytosterols; (11) several natural resins; (12) plasticizers; (13) a suite of 11 aliphatic dicarboxylic acids (C_3–C_{10}); (14) a suite of seven aromatic di- and tricarboxylic acids, all as their methyl ester analogues; and (15) nicotinic acid, nicotine, myosmine, and other compounds that are characteristic of cigarette smoke.

Results and Discussion

Mass Balance for Elutable Organics in Fine Cigarette Smoke Particles. A material balance has been constructed for the elutable and extractable portion of the organic matter associated with cigarette smoke particles and is shown in Figure 1. Of the extractable and elutable organic mass, 38.3% could be resolved chromatographically as single compound peaks. The remainder is made up of organic compounds eluting closely together, forming an unresolvable accumulation of compounds known as the unresolved complex mixture (UCM) and present in the GC/MS chromatograms as a "hump" (*31*). Using GC/MS techniques, 71.6% of the resolved organic mass could be identified and attributed to known single organic compounds. As seen from Figure 1, the major portion (35.6%) is made up of N-heterocyclic compounds, especially alkaloids such as pyridines, pyrrolidines, and pyrroles. Nicotine, the most common pyridine alkaloid in cigarette smoke, constitutes close to 69% of the N-heterocyclic compound class (see also Table 1). Phytosterols (10.7%), phenolic compounds (8.2%), *n*-alkanols (6.6%), carboxylic acids (19.0%), normal (11.6%) and branched (6.1%) alkanes, plus neophytadiene (an isoprenoid alkene; 1.7%) have been identified and quantified in the fine particulate matter collected from exhaled mainstream plus sidestream cigarette smoke.

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

Alkanes and Alkenes. *n*-Alkanes ranging from C_{20} to C_{35} have been identified and quantified (see Table 1). The emission rate profile (μg/cigarette; exhaled mainstream plus sidestream smoke particles) reflects the typical leaf surface wax *n*-alkanes distribution commonly found in the leaf surface waxes of vascular plants (*32–40*) with a pronounced odd-to-even carbon number predominance as shown in Figure 2a. The highest emission rates were found for the C_{27}, C_{29}, C_{31}, and C_{33} *n*-alkanes with C_{31} as the dominant *n*-alkane, closely resembling results from prior studies (*18, 41–44*); see Table 1 for the comparison.

Iso-(2-methyl-) and anteiso- (3-methyl-) alkanes are leaf wax constituents that are preferentially found in tobacco leaf surface waxes (*6, 41–46*). They are also found to a much lesser degree in leaf waxes typical of urban vegetation, as will be shown in a later section (*29, 33, 34, 36, 47–49*). Isoalkanes found in the cigarette smoke particles show a preference for odd-carbon-numbered homologues, whereas anteisoalkanes are present at the highest concentrations for even-numbered homologues, a result that is closely linked to the route of their biosynthesis in the plant leaves (*34, 41*). In Figure 2a, the normal and branched alkane profiles (C_{25}–C_{34}) obtained from cigarette smoke during the present study are compared to the results published by Mold et al. (*41*) for direct extraction of leaf waxes from unburned tobacco leaves. The *n*-alkane, iso-, and anteisoalkane concentration profiles of both studies agree rather well, indicating that each alkane-type compound is transferred at about the same rate from the tobacco leaf waxes into the cigarette smoke particles. This observation concurs with prior studies in which the transfer of these and other organic tobacco constituents into the cigarette smoke has been investigated (*6, 41, 42, 45*).

Acyclic isoprenoid-type alkenes (unsaturated and branched) constitute another compound class commonly found in tobacco and tobacco smoke (*2, 6, 42, 50, 51*). Several isoprenoid compounds are tobacco-specific and often are also found in cigarette smoke (*2, 6, 44*). Here, neophytadiene (a diunsaturated and branched alkene) has been identified, and its concentration is comparable to that found in earlier studies, see Table 1 (*42, 51*).

Carboxylic Acids. *n*-Alkanoic acids and their unsaturated homologues are found in the leaf surface waxes of vascular plants, including tobacco leaves (*23, 26, 29, 32, 35, 37–40, 52, 53*). As a result of their biosynthesis, *n*-alkanoic acids show a preference for even-carbon-numbered homologues, as shown in Figure 2b. In this study, particle-phase *n*-alkanoic acids have been identified ranging from C_8 to C_{34}. In contrast to leaf surface waxes of other vascular plants that typically show increased concentrations of the higher molecular weight *n*-alkanoic acids > C_{20}, cigarette smoke is exclusively enriched in lower molecular weight C_{14}, C_{16}, and C_{18} *n*-alkanoic acids (*3, 29, 34, 40, 54, 55*). Of the three unsaturated fatty acids identified, linoleic acid ($C_{18:3}$) is most abundant, which agrees with prior published data (*45, 56*).

Dicarboxylic acids also have been identified in our cigarette smoke samples, of which succinic acid is most abundant. Likewise, cyclic acids such as furancarboxylic acids, phenylacetic acid, and nicotinic acid have been quantified. For comparison to the results of other researchers, see Table 1.

***n*-Alkanols.** Several acyclic alcohols have been identified in the exhaled mainstream plus sidestream tobacco smoke particles investigated here, and the results are included in Table 1. *n*-Alkanols are often the major compound class identified in leaf waxes and commonly show a preference for even-carbon-numbered homologues (*29, 31, 34, 35, 38, 57, 58*). However, Severson et al. (*42*) have reported that the *n*-alkanols content in tobacco smoke is low because the *n*-alkanols content of tobacco leaf waxes is lower than for many other plants. In this study, the

Table 1. Emission Rates for Single Organic Compounds Found in Fine Particulate Cigarette Smoke

	emission rates in µg/cigarette			
		other studies[b]		
	this study,[a] exhaled MS + SS	SS	MS	compd ID[c] for this study
	n-Alkanes			
heneicosane	5.6		6–19[g]	a
docosane	5.3		6–22[g]	a
tricosane	6.7		4–9[g]	a
tetracosane	7.6		3–105[g]	a
pentacosane	13.2		3–31[g]	a
hexacosane	11.1		3–32[g]	a
heptacosane	59.2	66–87[f]	21–131[g]	a
octacosane	11.3		3–23[g]	a
nonacosane	58.0	28–39[f]	30–104[g]	a
triacontane	23.8		37–101[g]	a
hentriacontane	200.6	148–197[f]	164–341[g]	a
dotriacontane	38.3		97–194[g]	a
tritriacontane	102.3	44–62[f]	73–268[g]	a
tetratriacontane	3.2			a
pentatriacontane	2.8			a
total class mass concentration	549.0		450.0–1380.0[g]	
	Iso- and Anteisoalkanes			
isononacosane	14.1			e
isotriacontane	4.9			e
isohentriacontane	78.7			e
isodotriacontane	7.2			e
isotritriacontane	39.5			e
isotetratriacontane	1.8			e
anteisotriacontane	40.7			e
anteisohentriacontane	10.5			e
anteisodotriacontane	79.1			e
anteisotritriacontane	6.2			e
anteisotetratriacontane	6.5			e
total class mass concentration	289.2			
	Isoprenoid Alkanes			
neophytadiene	81.6	70–421[h]	61–308[h–j]	b
total class mass concentration	81.6			
	n-Alkanoic Acids[d]			
nonanoic acid	6.9			a
decanoic acid	2.9			a
undecanoic acid	3.6			a
dodecanoic acid (lauric acid)	3.9		up to 34[k]	a
tridecanoic acid	3.2			a
tetradecanoic acid (myristic acid)	22.8		4–38[k]	a
pentadecanoic acid	18.0			a
hexadecanoic acid (palmitic acid)	344.4		44–312[j–l]	a
heptadecanoic acid	13.7			a
octadecanoic acid (stearic acid)	73.0		9–107[j–l]	a
nonadecanoic acid	2.3			a
eicosanoic acid	26.2			a
heneicosanoic acid	5.4			a
docosanoic acid	19.4			a
tricosanoic acid	8.4			a
tetracosanoic acid	11.9			a
pentacosanoic acid	3.6			a
hexacosanoic acid	4.5			a
heptacosanoic acid	2.0			a
octacosanoic acid	12.3			a
nonacosanoic acid	4.0			a
triacontanoic acid	9.4			a
hentriacontanoic acid	3.3			a
dotriacontanoic acid	12.1			a
tritriacontanoic acid	0.12			a
tetratriacontanoic acid	0.19			a
total class mass concentration	617.51			
	n-Alkenoic Acids[d]			
cis-9-octadecenoic acid (oleic acid)	22.3		21–108[l]	a
9,12-octadecadienoic acid (linoleic acid)	39.8		50–146[l]	a
9,12,15-octadecatrienoic acid (linolenic acid)	62.0		52–329[l]	b
total class mass concentration	124.1			

Table 1 (Continued)

	emission rates in μg/cigarette			
		other studies[b]		
	this study,[a] exhaled MS + SS	SS	MS	compd ID[c] for this study
Dicarboxylic Acids[d]				
butanedioic acid (succinic acid)	30.7	65–70[m]	112–163[m]	a
methylbutanedioic acid (methylsuccinic acid)	3.6	1–13[m]	4–20[m]	a
pentanedioic acid (glutaric acid)	3.7	6–18[m]	10–58[m]	a
1,2-benzenedioic acid	0.35			a
total class mass concentration	38.35			
Other Aliphatic and Cyclic Acids[d]				
4-oxopentanoic acid	11.1			b
furancarboxylic acid (furoic acid)	15.5	25–60[m]	44–107[k,m]	b
2-methyl-2-furancarboxylic acid	1.0			b
benzeneacetic acid (phenylacetic acid)	46.5	11–30[m]	0.6–41[k,m]	b
nicotinic acid	42.6			a
total class mass concentration	116.6			
n-Alkanols				
pentadecanol	21.4			b
hexadecanol	24.8			b
heptadecanol	38.8			a
octadecanol	28.3			a
nonadecanol	23.7			a
eicosanol	21.6		1.7–3.7[j]	a
heneicosanol	26.8			b
docosanol	23.8		5.6–12.4[j]	a
tricosanol	12.7			b
tetracosanol	36.7		0.6–1.0[j]	a
pentacosanol	39.4			a
hexacosanol	12.7			a
total class mass concentration	310.7			
Phenols[e]				
1-ethenyl-4-hydroxybenzene	16.3			b
1,2-benzenediol (catechol)	12.7	138–292[m]	148–362[m]	a
1,4-benzenediol (hydroquinone)	283.5	91–285[m]	114–300[m]	b
4-methyl-1,2-benzenediol (4-methylcatechol)	49.6	25–55[m]	29–80[m]	a
2-methyl-1,4-benzenediol	21.4			b
4-ethenyl-1,2-benzenediol	3.1			b
total class mass concentration	386.6			
Phytosterols				
cholesterol	23.3	18.8[n]	8.5–22.0[j,n]	a
cholest-5-en-3β-ol acetate	28.2			b
campesterol	92.8	25.8[n]	42.7[n]	a
stigmasterol	252.2	53.6[n]	78.0[n]	a
β-sitosterol	100.4	28.0[n]	27.1–59.3[j,n]	a
total class mass concentration	496.9			
Triterpenoids				
β-amyrin	8.7			b
total class mass concentration	8.7			
N-Containing Compounds				
nicotine (total: gas plus particle phase)		2987–6588[h,i,o,p]	799–4229[h,i,o,p]	
nicotine (particle filter sample only)	1159.0	970–1320[o]	550–1620[o]	a
cotinine	52.8			b
2,3-bipyridyl	34.3	35–76[h,p]	16–22[h,p]	b
3-pyridinol	57.8			b
1-(2-pyridinyl)ethanone	4.6			b
1-(1-methyl-1*H*-pyrrol-2-yl)ethanone	17.2			b
3-hydroxypyridine[e]	128.6	157–172[h]	90–211[h]	b
1-methyl-2,5-pyrrolidinedione (*N*-methylsuccinimide)	30.2			b
1-methyl-2(1*H*)-pyridione	7.4			a
4-methylbenzhydrazide	8.0			b
3-(3,4-dihydro-2*H*-pyrrol-5-yl)pyridine (myosmine)	177.9	73–224[m]	8.8–53.4[i,m]	a
1-methyl-9*H*-pyrido[3,4-*b*]indole (harman)	4.9	1.9–3.5[q]	1.1–3.1[q]	b
N-isooctanoylnornicotine	8.5			b
total class mass concentration	1691.2			
Polycyclic Aromatic Hydrocarbons				
phenanthrene	2.6	2.1[r]	0.075[r]	a
anthracene	0.76	0.67[r]	0.024[r]	a
methyl(phenanthrenes, anthracenes)	3.5		0.16[s]	b

Table 1 (Continued)

	emission rates in μg/cigarette			
		other studies[b]		
	this study,[a] exhaled MS + SS	SS	MS	compd ID[c] for this study
fluoranthene	0.95	0.67[r]	0.061[r]	a
pyrene	1.0	0.47[r]	0.043[r]	a
benzacenaphthylene	0.30			b
2-phenylnaphthalene	0.37			b
methyl(fluoranthenes, pyrenes)	1.3		0.11[s]	b
benzo[*a*]fluorene/benzo[*b*]fluorene	0.54	0.20[r]	0.021[r]	a
benz[*a*]anthracene	0.27	0.20[r]	0.013[r]	a
chrysene/triphenylene	0.67	0.49[r]	0.020[r]	a
methyl(benz[*a*]anthracenes, -chrysenes, -triphenylenes)	0.69			b
dimethyl(fluoranthenes, pyrenes)	0.55	*t*		b
total class mass concentration	13.5			
	Others			
6,7-dihydroxy-2*H*-1-benzopyran-2-one	7.3			b
vitamin E	0.88			b
total class mass concentration	8.18			

[a] This study: exhaled MS + SS (exhaled mainstream and sidestream fine particulate matter). [b] Other studies: if not otherwise indicated, the measurements include particle plus gas-phase components together (condensate); data for refs 42, 52, and 60 are reported in μg/1 g of tobacco smoked (depending on the cigarette type, the tobacco content ranges on average from 0.6 to 1.1 g/cigarette); mainstream (MS) and sidestream (SS) smoke in the cited studies were generated in laboratory test apparatus. [c] For more details see text. a, positive: authentic standard verification; b, probable: library spectrum verification; c, possible; d, tentative; e, iso- and anteisoalkanes are positively identified by monitoring their major ions at M-43 and M-29, respectively. [d] Detected as methyl ester in the derivatized sample aliquot. [e] Compound detected as methoxy homologue in the derivatized sample aliquot. [f] Ramsey et al. (*18*), sidestream particulate matter of different filter cigarettes was collected using a dilution sampler. [g] Spears et al. (*43*), mainstream condensate of nonfilter cigarettes. [h] Sakuma et al. (*51*), mainstream and sidestream condensate of nonfilter cigarettes. [i] Matsushima et al. (*50*), mainstream particulate matter from nonfilter cigarettes. [j] Severson et al. (*42*), mainstream condensate of nonfilter cigarettes (concn in μg/g of tobacco). [k] Elmenhorst (*52*), mainstream condensate of nonfilter cigarettes (concn in μg/g of tobacco). [l] Hoffmann and Woziwodzki (*56*), mainstream condensate of nonfilter cigarettes. [m] Sakuma et al. (*59*), mainstream and sidestream condensate of nonfilter cigarettes. [n] Schmeltz et al. (*60*), mainstream and sidestream condensate of nonfilter cigarettes (concn in μg/g of tobacco). [o] Browne et al. (*63*), mainstream and sidestream particulate and gaseous nicotine. [p] Sakuma et al. (*65*), mainstream and sidestream condensate of nonfilter cigarettes. [q] Klus and Kuhn (*15*), mainstream and sidestream condensate of filter and nonfilter cigarettes. [r] Grimmer et al. (*67*), mainstream and sidestream particle samples of nonfilter cigarettes (gas-phase PAH also were measured and usually consisted of 1% of the amount that was found for the particle phase). [s] Lee et al. (*68*), mainstream condensate of standard cigarettes. [t] Grimmer et al. (*67*), particle phase only.

n-alkanols range from C_{15} to C_{26} with no obvious carbon number predominance.

Phenols. A great number of phenols and polyphenols are known to be present in cigarette smoke (*2, 3, 6, 59*). Here, only a few have been quantified in the fine cigarette smoke particles. *p*-Cresol and *o*-cresol, two rather volatile phenols, have been found in traces in the particulate cigarette smoke. One of the prominent phenols quantified in Table 1, hydroquinone (1,4-benzenediol), is emitted at a rate of 283.5 μg/cigarette, an emission rate comparable to that found by Sakuma et al. (*59*).

Phytosterols. Tobacco plants, similar to other higher plants, contain C_{28} and C_{29} phytosterols such as campesterol, stigmasterol, and β-sitosterol as the major sterols. Cholesterol (C_{27}), a typical zoosterol (from animals, especially vertebrates) that is commonly found only in traces in plant materials, is somewhat more pronounced in tobacco leaf waxes when compared to the typical phytosterols than is the case for most other plants (*42, 60*). Stigmasterol, emitted at a rate of more than 250 μg/cigarette, was the most abundant phytosterol, followed by β-sitosterol. Data drawn from the literature on mainstream and sidestream cigarette smoke phytosterols show concentration ranges similar to our data and are included in Table 1 for comparison (*42, 60*).

N-Containing Compounds. When burning a cigarette, about 60% of the nicotine in tobacco undergoes degradation and conversion (*61*). Portions of the tobacco alkaloids are converted to pyridines, indoles, quinolines, arylnitriles, aromatic hydrocarbons, and other compounds (*1, 3, 6, 62*). Due to its volatility, nicotine is mainly found in the gas phase and then primarily in sidestream smoke (*10, 50, 51, 63–65*). Nonetheless, one of the most abundant single compounds identified in the fine particle-associated cigarette smoke samples can be nicotine. Nicotine was collected at a rate of 1159 μg/cigarette under our sampling conditions, but would be present in smaller amounts given greater dilution. Comparable nicotine concentrations in the particle phase also have been reported by Browne et al. (*63*) (see also Table 1). Besides nicotine, several other alkaloids commonly found in cigarette smoke (*1, 3, 6, 62*) have been identified and are summarized in Table 1. While most of these N-containing compounds are partitioned between the gas and the particle phase, the N′-acylalkaloids have high enough molecular weights to be found exclusively in the particle phase (*66*) and, thus, might serve as potential tracers for particle-phase cigarette smoke. One of the more abundant members of this compound class, *N*′-isooctanoylnornicotine, was identified in our cigarette smoke samples, but in fairly low concentrations (see Table 1).

Polycyclic Aromatic Hydrocarbons. While most of the compounds discussed so far are released mainly by distillation from the tobacco during combustion (with some accompanying partial degradation), the polycyclic aromatic hydrocarbons (PAH) are typical pyrolysis products formed during combustion in zones of relatively low oxygen content (*1, 61, 67–69*). In Table 1, the PAH identified in this study are listed and compared to results from a study by Grimmer et al. (*67*) in which PAH emission rates were reported for the particle and gas phase in mainstream as

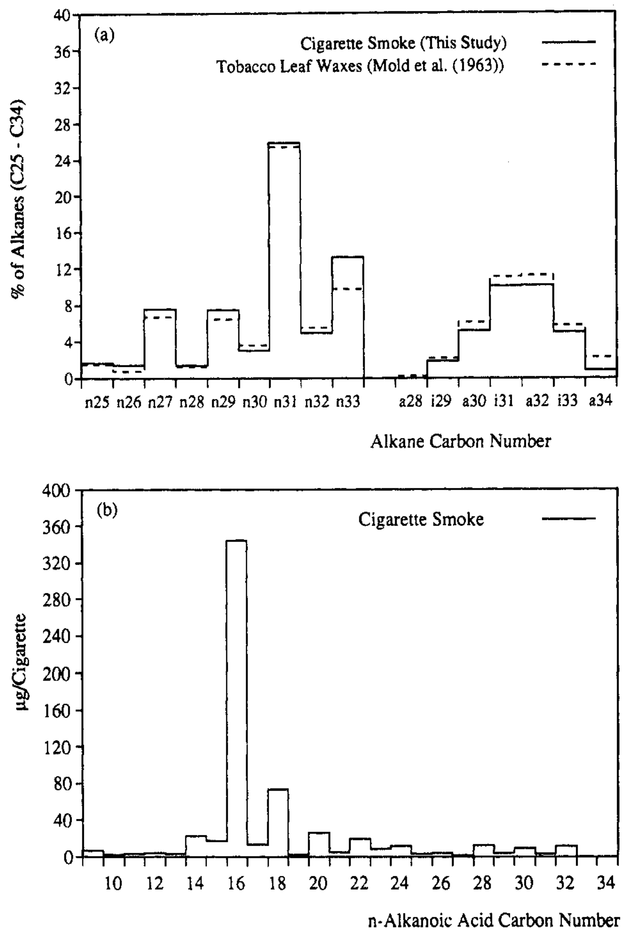

Figure 2. Concentration distributions for cigarette smoke constituents: (a) *n*-alkanes in cigarette smoke (this study) compared to the tobacco leaf wax darta of Mold et al. (*41*) (in mass % relative to total alkanes in the range from C_{25} to C_{36}), and (b) *n*-alkanoic acids in cigarette smoke (this study).

well as in sidestream cigarette smoke separately. From their experimental data (see Table 1), Grimmer and coworkers concluded that most of the PAH are formed between puffs and, consequently, are found primarily in the sidestream cigarette smoke. Total particle-phase PAH concentrations of 13.5 μg/cigarette were measured in this study, which compares well with the measurements of Grimmer et al.

Tracing Cigarette Smoke Particles In Urban Atmospheres. Because people spend on the average most of their time indoors (e.g., ref 70) where restricted airflow limits the indoor/outdoor air exchange, cigarette smoke exposure studies in the past have been concerned mainly with elevated indoor pollutant concentrations caused by cigarette smoking (*2, 4, 5, 7, 11, 71*). To apportion the tobacco smoke contributions to an indoor environment with several potential indoor air pollution sources, a number of organic marker compounds such as nicotine, 3-ethenylpyridine, solanesol, PAH, and *n*-alkanes have been utlized in the past (*8, 9, 13, 16, 18, 19, 72, 73*).

In order to trace tobacco smoke particles in a reactive outdoor urban atmosphere that is influenced by a great number of different emission sources, organic marker compounds for tobacco smoke must meet several requirements: The tracer compounds must be (1) source specific, (2) detectable in urban air, (3) exclusively in the particle phase, (4) chemically stable over transport times between the source and the atmospheric measurement sites, and (5) present in known ratio to the traced quantity which in this case is the fine particulate mass concentration increment due to cigarette smoke.

Nicotine, a possible tobacco smoker tracer, is known to partition between the gas and particle phase. Because nicotine is primarily associated with the gas phase (*8, 10, 17, 19*) and is susceptible to photodegradation (*10*), it is not a reliable quantitative tracer for cigarette smoke particles in the urban atmosphere, although it might be useful as a qualitative tracer for whole cigarette smoke if both gas- plus particle-phase constituents were of interest. If nicotine can be detected in urban atmospheric fine particulate matter, it should be viewed as a supportive indication that cigarette smoke indeed is present, while quantification of that cigarette smoke particulate matter should be based on more stable tracers. 3-Ethenylpyridine, a combustion product of nicotine, also is mainly found in the gas phase but is more stable in the presence of UV radiation than nicotine (*10, 64, 74*); we would still decline to use it as a tracer because of its volatility and potential for degradation by atmospheric chemical reactions.

Solanesol, a long-chain ($C_{45}H_{74}O$) trisesquiterpenoid alcohol, is characteristic of cigarette smoke and completely in the particle phase under normal conditions; hence, it has been suggested as an indoor cigarette smoke tracer (*19, 73*). Because solanesol is an isoprenol with nine double bonds, the probability that it will degrade rapidly in a photochemically reactive atmosphere is high (e.g., due to O_3 or photodegradation). Tang and co-workers (*19*) have shown that tobacco smoke-associated solanesol reacts rapidly when exposed to UV light simulating midday solar radiation. Hence, although it may be suitable to trace tobacco smoke in indoor environments, solanesol probably is not suitable as a tobacco smoke tracer in the outdoor urban atmosphere.

PAH have been used as well in indoor environments to assess the contribution of cigarette smoke to indoor air pollution (e.g., refs 9, 12, 16, and 75). In the absence of indoor heating sources such as wood burning stoves or kerosene heaters, indoor PAH concentrations may track the exposure to tobacco smoke. In the urban atmosphere, PAH are contributed by virtually all combustion sources and are known to degrade photochemically in the presence of UV light (e.g., refs 26, 27, and 76–78). Consequently, PAH are not suitable as tracers for cigarette smoke in the urban atmosphere.

Higher molecular weight *n*-alkanes (C_{27}, C_{29}, C_{31}, and C_{33}) have been used to monitor tobacco smoke particles in indoor environments (*18*). While the odd-carbon-numbered *n*-alkane concentration pattern in a smoker's home might be mainly due to tobacco smoke, the odd-to-even carbon-numbered *n*-alkane concentration pattern found in ambient outdoor suspended fine particulate matter is mainly controlled by the release of vegetative detritus in the form of abraded waxy leaf surface particles shed by outdoor plants (*26, 29, 31, 35, 40*). Hence, the high molecular weight odd carbon *n*-alkanes cannot be used to identify cigarette smoke in outdoor air.

A more promising compound class that shows properties similar to the *n*-alkanes consists of the branched alkanes such as iso- (2-methyl-) and anteiso- (3-methyl-) alkanes. These iso- and anteisoalkanes show a characteristic concentration pattern in tobacco leaf surface waxes and consequently in tobacco smoke (see Figure 2a). To serve as cigarette smoke markers in the urban atmosphere, either the iso- and anteisoalkane concentration patterns in tobacco smoke particles must be distinctly different from those found in the leaf surface abrasion products of urban plants or the emission rates should be higher such that tobacco smoke-derived iso- and anteisoalkanes will dominate the outdoor concentrations of such compounds. The latter requirement, if met, would guarantee that possible interferences due to iso- and anteisoalkane release from urban vegetation to the atmosphere are minor. If the concentration patterns are different *and* the cigarette smoke mass emissions dominate, then the iso- and anteisoalkanes would be particularly robust tracers for cigarette smoke. In order to determine whether cigarette smoke particles dominate the emissions of iso- and anteisoalkanes to the urban environment, it is first necessary to characterize the emissions of such compounds from plants growing outdoors.

Release of fine particulate leaf surface abrasion products from plants typical of the Los Angeles area has been characterized on a molecular level by Rogge et al. (*29*). Green and dead leaves from the 62 most common plant species growing in the Los Angeles area, including broadleaf trees, conifers, palms, shrubs, and grasses, were collected during a harvesting campaign in 1988 (*20*). The collected green and dead leaves were each composited according to the mass fraction of leaf material attributed to each species in the Los Angeles area as determined by Miller and Winer (*80*) and Winer et al. (*81*). The green leaf and the dead leaf composites were separately agitated to release particulate matter shed from their surface when the leaves brush against each other as would occur naturally by the wind. The abraded waxy leaf surface material was subsequently collected as fine particulate matter on quartz fiber filters downstream of cyclone separators, and the samples then were extracted by the same methods used in the present study (*24*, *29*). Additional information on the sampling campaign including the plant species collected is summarized by Hildemann et al. (*20*).

Organic compounds present in these Los Angeles dead and green leaf abrasion product samples were analyzed by GC/MS (*29*). While many compound classes show altered concentrations in the dead leaf abrasion products, it was found that the *n*-, iso-, and anteisoalkane concentrations present in the fine particulate leaf surface abrasion products were very similar when comparing green leaf with dead leaf surface abrasion products. This in turn indicates that the high molecular weight wax-type alkanes are rather stable in the urban environment, since the dead leaf material had aged for quite some time between the end of wax synthesis by the leaf and the time that particular samples were collected. Iso- and anteisoalkanes were found in the leaf abrasion products in the range from C_{29} to C_{34}. Comparing the amount of iso- and anteisoalkanes to the amount of *n*-alkanes in the same carbon range (C_{29}–C_{34}), such iso- and anteisoalkanes together only amount to 1.5–1.6% of the respective *n*-alkanes found in the dead leaf or green leaf surface abrasion products. Similar results also have been reported by other researchers for several plant species (e.g., refs 33, 48, and 82).

In contrast, the same branched alkanes in the tobacco smoke samples investigated here comprise close to 68% of the respective *n*-alkane mass (C_{29}–C_{34}) found in the smoke particles, a 40 times higher relative abundance than found for the leaf abrasion products of urban vegetation. Similar results have been found for tobacco leaves (*6*, *8*, *41–43*, *45*) and tobacco smoke (*6*, *34*, *41*, *42*, *45*). Typical ion chromatograms characteristic of the alkanes are shown in Figure 3a,b for green leaf surface abrasion products and tobacco smoke particles. These figures clearly demonstrate enrichment in iso- and anteisoalkanes relative to *n*-alkanes in the tobacco smoke samples when compared to Los Angeles green leaf surface abrasion products. Figure 4a,b shows the concentration of iso- and anteisoalkanes measured in green leaf and dead leaf abrasion products (μg/g of fine particulate abraded leaf surface material) and fine tobacco smoke particles (μg/cigarette). On comparing these two graphs, it can be seen that: (1) isohentriacontane (iso-C_{31}) in the cigarette smoke samples is found at about the same concentration level as anteisodotriacontane (anteiso-C_{32}), which differs noticeably from the Los Angeles area vegetative leaf composite surface waxes (iso-C_{31} > anteiso-C_{32}); (2) while isotritriacontane (iso-C_{33}) is the dominant branched alkane in the Los Angeles leaf surface wax composites, anteisodotriacontane (anteiso-C_{32}) is the dominant branched alkane in tobacco smoke followed closely by iso-C_{31}. The concentration ratio of anteiso-C_{32} to iso-C_{33} is 2.0 for cigarette smoke. The same compound ratio for Los Angeles leaf abrasion products is 0.34, a pronounced difference that distinguishes cigarette smoke from the leaf abrasion products. Thus, the characteristic tobacco leaf surface iso- and anteisoalkane concentration patterns, preserved in the cigarette smoke particles, might be useful to trace such emissions in the atmosphere of urban areas.

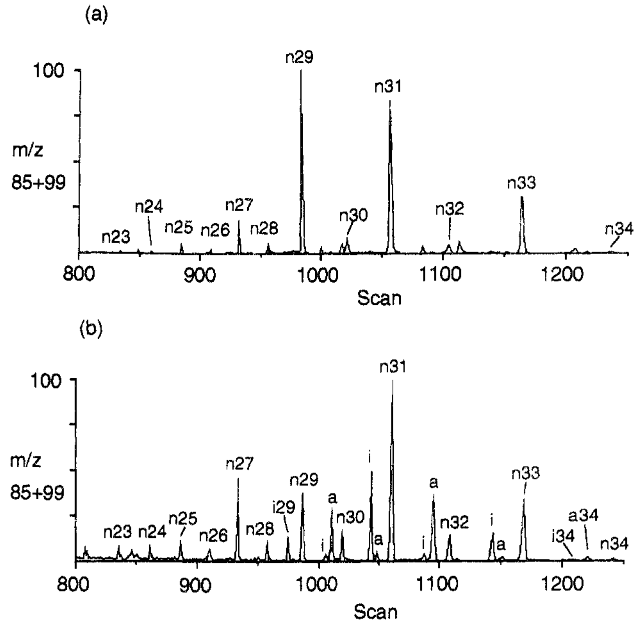

Figure 3. Selected mass fragmentograms for *n*-, iso-, and anteisoalkanes (sum: *m/z* 85 + 99) found in (a) leaf abrasion products from green leaf composites typical of the Los Angeles area and (b) cigarette smoke particles. Numbers refer to the carbon chain length of the molecules. Letters refer to the following: n, *n*-alkanes; i, isoalkanes; a, anteisoalkanes. For simplicity, only the major compound peaks are labeled.

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

The fine particulate emissions from gasoline and diesel-powered vehicles have been characterized by Rogge et al.

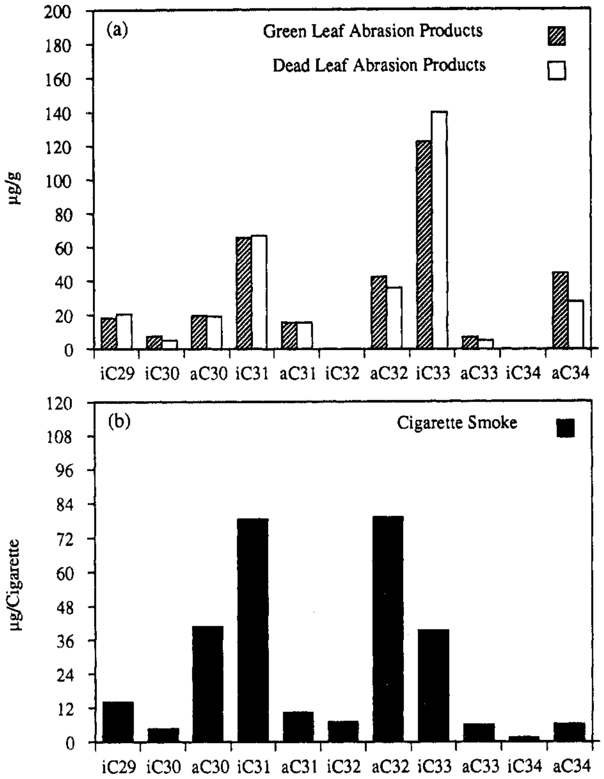

Figure 4. *n*-, iso-, and anteisoalkane concentrations measured in (a) leaf surface abrasion products from green leaf and dead leaf composites typical of the Los Angeles area and (b) cigarette smoke particles collected in this study.

(*27*) using methods essentially identical to those employed in the present study. None of the iso- and anteisoalkanes discussed here could be detected in that or other studies (e.g., ref 83). This result agrees well with the observation that long-chain alkanes from higher plants are typically not found in crude oils as a result of the diagenic and catagenic processes ongoing during crude oil formation (*84, 85*). Kissin (*86*) reported that monomethyl-substituted alkanes found in crude oils are the result of chemical processes occurring during catagenesis, with methyl groups approximately equally substituted in all positions of the alkane molecules, primarily below C_{20}. Biogenically-derived or human-controlled biogenic sources, such as meat cooking, wood combustion, aerial dispersion of bacteria or resuspension of insect fragments, likewise need to be examined to see if they interfere with these possible cigarette smoke tracers. Meat cooking (*25*) does not produce detectable amounts of higher molecular weight branched alkanes. Wood combustion, already very low in *n*-alkane emissions, also does not emit any branched alkane-type compounds (*87*). Likewise, bacteria that might become airborne and that are smaller than 2.0 μm in diameter do not contain the higher molecular weight iso- and anteisoalkanes studied here (C_{28}–C_{34}). Instead, such bacteria do contain complex mixtures of unsaturated and branched (iso- and anteiso-) alkenes in the range from C_{23} to C_{29} (*88, 89*) and iso- and anteisoalkanoic acids (C_{12}–C_{17}) (*90*).

The cuticula of insects are usually covered with a thin layer of waxy compounds including *n*-alkanes, and mono-, di-, and trimethylalkanes ranging from C_{26} to about C_{43} (*91–96*). The series of iso- and anteisoalkanes in the carbon range of interest (C_{28}–C_{34}) is typically incomplete. The members of these series are usually minor compared to *n*-alkanes and dimethyalkanes and typically show a different concentration pattern than is found in tobacco leaf waxes and, consequently, in cigarette smoke (*91–96*). It is unlikely that insect debris would be confused with cigarette smoke in airborne particulate matter in particle sizes smaller than 2.0 μm in diameter.

Estimated Emission Rates for Cigarette Smoking in Los Angeles. Whether or not cigarette smoke particles can be traced in the urban atmosphere depends in part on the total emission rates for cigarette smoke constituents. Consequently, the first step is to estimate the emission rates of particle-associated cigarette smoke constituents that have been released during indoor and outdoor activities combined. Using total cigarette sales data for the entire United States in 1982 (*2*) together with population data for the same year (*97*), the average number of cigarettes per capita smoked in the United States in 1982 was determined to be 2700. In this study, total cigarette smoke compound emissions during 1982 were estimated for an 80 × 80 km study area centered over downtown Los Angeles [see map in Rogge et al. (*25*)], an area smaller than the entire South Coast Air Basin but rather an area that encompasses the urban core of the metropolitan area. Any subsequent year could have been chosen. However, the present study is part of a larger investigation that encompasses measurements of emission rates from the major primary fine particle emission sources (*20*), creation of emission inventories for primary fine particulate organic carbon (OC) and elemental carbon (EC) (*20, 98*), ambient OC and EC data (*99*), ambient fine particulate organic compound concentrations determined at several sites within that Los Angeles area during 1982 (*26, 100*), and characterization of the organic chemical composition of the source emissions (*25, 27–29, 76*). The database available for testing proposed organic tracer techniques during 1982 is the most advanced data set available.

Fine particle-associated organic compound class emission rates from cigarette combustion during 1982 within our Los Angeles study area as computed from cigarette sales plus the source test data of Table 1 are given in Table 2. Many of these cigarettes, of course, are smoked inside of buildings. From model calculations and experiments, Nazaroff et al. (*101*) determined that only 0.1–0.5% of the particles having diameters in the range 0.2–0.5 μm, a size range typical for cigarette smoke, that enters a building with outdoor air will ultimately deposit on indoor surfaces. Consequently, depositional losses are small, and much of that cigarette smoke will reach the outdoor atmosphere as the air is exchanged between buildings and the outdoors.

Considerable effort has been expended to characterize the penetration of particulate matter present in the outdoor atmosphere into the indoor air of buildings in Los Angeles (*101–103*) and elsewhere (*104–107*). From these studies of the penetration of fine particles into buildings from outdoors, estimates can be made of the ease with which indoor-generated fine particle cigarette smoke will escape to the outdoor atmosphere. Particle penetration into and out of both private homes and commercial buildings should be considered, as the ventilation strategies for those two types of structures differ substantially.

Spengler et al. (*105*) and Dockery and Spengler (*104*) have used respirable sulfate particles present in outdoor air to examine fine particle penetration into 55 private homes in six different cities. Measuring from Figure 4 of

Table 2. Daily Cigarette Smoke Particle Emissions for Single Compound Classes within the Urbanized (80 × 80 km) Los Angeles Study Area for 1982

compound class	emission rates[a] (kg day^{-1})
n-alkanes	36.2
iso- and anteisoalkanes	19.1
isoprenoid alkanes	5.4
n-alkanoic acids	40.7
n-alkenoic acids	8.2
dicarboxylic acids	2.5
other organic acids	7.7
n-alkanols	20.5
phenols	25.5
phytosterols	32.8
triterpenoids	0.57
N-containing compds (e.g., alkaloids)	111.5
polycyclic aromatic hydrocarbons	0.89
other identified compounds	0.54
total identified	312.1

[a] Daily compound class emission rates to the metropolitan 80 × 80 km area centered over Los Angeles were estimated as follows: the compound emission rates from Table 1 were multiplied by the average number of cigarettes sold per capita in the United States in 1982 (2700 cigarettes) times the population in the 80 × 80 km study area in 1982 (8 910 400) and then divided by 365 days. The number of cigarettes sold per capita was determined from total cigarette sales in the United States in 1982 [624 billion, IARC (*2*)] divided by the population of the United States in 1982 [231 million, U.S. Bureau of the Census (*97*)]. To estimate the population in the 80 × 80 km study area in 1982, the population data for 1980 for the study area as determined by Gray (*98*) were used along with an assumed 1% population growth per year according to the nationwide average [U.S. Bureau of the Census (*97*)]. The mass emission rates appearing in this table represent upper limits on the release to the outdoor atmosphere, with the actual release smaller by the amount of smoke removed within buildings (see text).

Spengler et al. (*105*), one sees that indoor/outdoor sulfate ratios vary from a high of approximately 95% in Topeka, KS, and Watertown, MA, to a low of approximately 55% in Steubenville, OH. The indoor/outdoor sulfate ratio averaged over six cities appears to be approximately 77% from their measured values (*105*), and model calculations suggest a mean infiltration rate for outdoor fine particles of approximately 0.7 (*104*). These results are consistent with those of Leaderer et al. (*106*), who found indoor particulate sulfur concentrations in the range 69–62% of those outdoors in Suffolk and Onondaga Counties, New York, homes that did not possess any indoor air pollution sources of such materials. Moschandreas et al. (*107*) demonstrated that indoor fine sulfur-containing particle concentrations are about 80% of those outdoors, and they track the outdoor concentrations closely over time. Measurements of the penetration of black soiling particles into two private homes have been conducted by Yocom et al. (*108*) using tape samplers and show that indoor/outdoor ratios are in the range 0.67–1.19 with an overall average indoor/outdoor ratio of 0.88. Soiling measurements made using tape samplers in fact respond principally to the fine black elemental carbon particles present in the atmosphere (*109*) and as such again may provide a useful surrogate for smoke-size particles penetration through the building shell. Particle migration through Sepulveda House, a well-ventilated former private residence in downtwon Los Angeles that lacks any deliberate particle filtration system, has been examined using chemically-resolved fine particle filter samples and high-resolution optical particle counters (*101, 102*). Indoor fine particle levels at Sepulveda House are measured to be nearly identical to those outdoors (*102*). Experiments and modeling calculations that examine the fate of fine particles present in that building show that they are vented back to the outdoor atmosphere with greater than 90% efficiency (*101*). Fine aerosol penetration into, and hence out of, private homes thus is measured to lie in the range of approximately 0.55–0.95; an overall mean value of ca. 0.8 would be suggested in the present paper based on the pooling the values of Dockery and Spengler (*104*) and Leaderer et al. (*106*) of about 0.7 with the higher values of about 0.8 reported by Moschandreas et al. (*107*) and still higher values of about 0.9 observed by Yocum et al. (*108*) in Connecticut and by Nazaroff et al. (*101*) and Ligocki et al. (*102*) at Sepulveda House in Los Angeles. The important point is that fine particles generated indoors within private residences in Los Angeles in general will be exchanged easily with the outdoors.

Commercial buildings with conventional air conditioning systems having low-efficiency particle filters (single pass efficiency of roughly 15–35% for removing particles of 0.1–0.5-μm diameter, accompanied by several passes of air recirculated through the filters for each pass of outdoor makeup air) have indoor fine particle levels in the range of 20–60% as high as those outdoors (*102, 103*). Only a very small fraction of the fine particles present inside such buildings are collected by deposition on indoor surfaces: instead, nearly all fine particles are either collected by the ventilation system filters or are exhausted to the outdoor atmosphere (*103*). For a standard commercial building with 25% of its ventilation system flow contributed by outdoor makeup air and 75% of its airflow contributed by indoor air recirculated through filters with a single pass removal efficiency for fine particles of ca. 35% per pass, roughly half of the fine particle cigarette smoke emitted inside that building will be exhausted to the outdoor atmosphere (*103*). If the single pass filtration efficiency for fine particles is only 15%, then approximately two-thirds of any fine cigarette smoke particles generated indoors will be exhausted to the outdoor air. Yocom et al.'s (*108*) examination of two air conditioned office buildings shows indoor/outdoor ratios for black soiling particles that are in the range 0.55–0.89 with an overall mean of 0.74. For commercial buildings, the data just discussed suggest that a broad range of outcomes are possible, with between 0.2 and 0.9 of the cigarette smoke generated indoors exchanged from the building. A grand average over all commercial buildings would fall somewhere in the middle of this range, probably between 0.5 and 0.6. Taking into consideration cigarette smoke generation within a mix of homes and commercial buildings, approximately 0.5–0.8 of the cigarette smoke will be exhausted to the outdoors, depending on building type and ventilation scheme. A central value of 0.7 falling within the range observed in both homes and commercial buildings would seem to be a reasonable overall estimate for the fraction of indoor-generated cigarette somke that escapes to the outdoor atmosphere. The daily compound class emission rates in the Los Angeles study area given in Table 2 thus represent upper limits on their release to the outdoor atmosphere, with the actual release being smaller by the amount of smoke removed within buildings.

It can be seen from Table 2 that the dominant compound class in particle-associated cigarette smoke emitted to the Los Angeles atmosphere in 1982 consists of semivolatile pyridine alkaloids (e.g., nicotine) and other N-containing compounds. Because nicotine is rather volatile and unstable in the urban atmosphere, ambient fine particle-associated nicotine concentrations, if measurable, may not be found in the atmosphere in known proportions to whole tobacco smoke particle concentrations. Up to 19 kg of the more stable and nonvolatile high molecular weight iso- and anteisoalkanes were emitted per day to the atmosphere of the 80 × 80 km Los Angeles study area from cigarette smoking in 1982. For the two most prominent branched alkanes (iso-C_{31}, anteiso-C_{32}) alone, the daily emission rates totaled 10.4 day^{-1}.

Using the emission inventory for fine particulate organic carbon (OC) for the 80 × 80 km area centered over Los Angeles that was compiled for 1982 (*20, 98*), the emissions of primary particulate organic carbon (OC) from all sources combined was estimated to total 29 820 kg day^{-1}. Expressed as total organic compound mass (organic compounds $\simeq$1.2 × organic carbon), this amounts to 35 800 kg day^{-1} of equivalent organic compound mass. Thus, the two branched alkanes considered, when combined, account for 0.029% of the fine particulate organic compound emissions.

Gray et al. (*99*) published annual mean ambient fine particulate mass concentration data determined gravimetrically and particulate OC data for the area of interest. Fine particle mass concentrations averaged 24.4 $\mu g\ m^{-3}$ at West Los Angeles, 32.5 $\mu g\ m^{-3}$ at downtown Los Angeles, and 28.2 $\mu g\ m^{-3}$ at Pasadena during 1982. That data set can be used to compute the annual mean fine particle-associated total organic compound concentrations, yielding 6.94 $\mu g\ m^{-3}$ at West Los Angeles, 8.63 $\mu g\ m^{-3}$ at downtown Los Angeles, and 8.06 $\mu g\ m^{-3}$ at Pasadena during 1982. If 0.029% of that ambient fine particulate organic compound mass at each of the three sampling sites were present as the iso-C_{31} plus the anteiso-C_{32} alkane, then the ambient fine particle concentrations of these two branched alkanes together would account for the following: in West Los Angeles, 2.0 ng m^{-3}; in downtown Los Angeles, 2.5 ng m^{-3}; and in Pasadena, 2.3 ng m^{-3} during 1982.

Cigarette Smoke Particles in the Los Angeles Atmosphere. Fine particulate organic compound concentrations during the year 1982 have been measured as part of the present study (*26, 100*) at sites within the 80 × 80 km greater Los Angeles study area discussed earlier. Filter samples taken during the study by Gray et al. (*99*) were extracted beginning during 1983 and were then injected onto a GC/MS system. Reexamination of the magnetic tapes from those GC/MS runs permits *n*-, iso-, and anteisoalkane concentrations and nicotine concentrations in the particle phase to be quantified. Sampling techniques, analytical protocols, and compound identification procedures were essentially the same as those applied to the source samples described in the present study, except that samples were drawn directly from the atmosphere. Figure 5a,b shows the ambient concentration pattern for iso- and anteisoalkanes measured at West Los Angeles and Pasadena during October and November 1982. The annual average iso- and anteisoalkane concentrations are shown in Figure 5c. The major peak heights in Figure 5 have been set approximately to two-thirds of full scale so that the relative abundance of the various iso- and anteisoalkanes in ambient air can be easily compared to the relative abundance of such compounds in cigarette smoke as shown in Figure 4b. During the winter months, particle-associated nicotine concentrations also were high enough to be measured in the outdoor atmosphere at West Los Angeles (January, 2.9 ng m^{-3}; November, 8.1 ng m^{-3}; December, 1.6 ng m^{-3}) and at Pasadena (January, 10.7 ng m^{-3}).

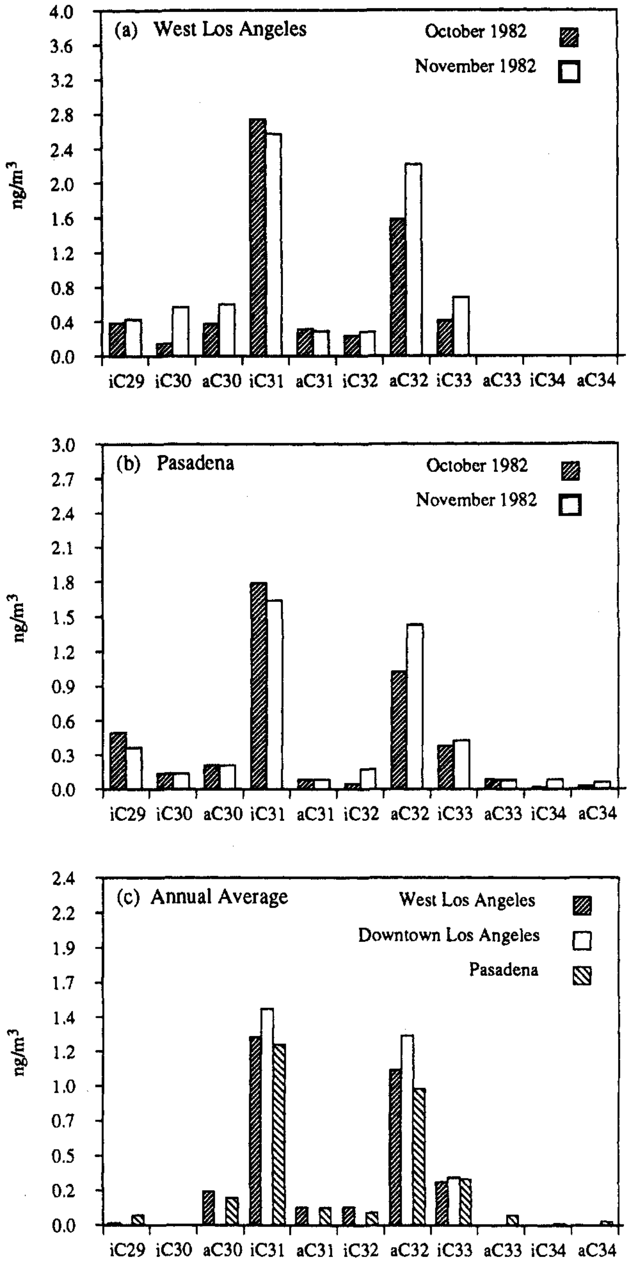

Figure 5. Ambient *n*-, iso-, and anteisoalkane concentrations measured (a) at West Los Angeles and (b) at Pasadena, both in October and November 1982, and (c) annual average concentrations measured at West Los Angeles, downtown Los Angeles, and Pasadena during 1982.

The ambient iso- and anteisoalkane concentration patterns (Figure 5a–c) can be compared with the concentration pattern found for cigarette smoke (Figure 4b), and similarly with green and dead vegetative detritus (Figure 4a). It is seen that the atmospheric particulate matter concentration profiles most closely resemble cigarette smoke (iso-C_{31} $\simeq$ anteiso-C_{32}; anteiso-C_{30} and iso-C_{33} smaller; anteiso-C_{34} minor) while the Los Angeles vegetative detritus is different (iso-C_{33} $\gg$ iso-C_{31} or anteiso-C_{32}). Consequently, the ambient iso- and anteisoalkane concentration profile does not match that of leaf surface abrasion products from the plant communities growing in Los Angeles. Instead it compared well to the concentration profile found in cigarette smoke particles. Further, the measured ambient annual average concentration of the iso-C_{31} plus anteiso-C_{32} alkanes during 1982 totals 2.4 ng m^{-3} at West Los Angeles, 2.8 ng m^{-3} at downtown Los Angeles, and 2.2 ng m^{-3} at Pasadena. This is very close to the 2.0–2.5 ng m^{-3} concentration range estimated earlier in this paper based on previously published emissions and ambient organic particulate matter concentrations. Working backward using a fine particle mass emission rate of 20.4 mg/cigarette (20) and an emission rate of 158 μg/cigarette for the iso-C_{31} plus anteiso-C_{32} alkanes (Table 1), an ambient iso-C_{31} plus anteiso-C_{32} alkane concentration of 2.2–2.8 ng m^{-3} would correspond to an ambient fine particle contribution from cigarette smoke of 0.28–0.36 μg m^{-3} at the maximum (or 1.0–1.3% of the total ambient fine particle mass).

The absolute mass emission rate of vegetative detritus to the Los Angeles urban atmosphere has not been measured directly. But to test the hypothesis that urban plants are not the major source of urban atmospheric iso- and anteisoalkane concentrations in Los Angeles, the following consistency check can be performed. Assume that all iso- and anteisoalkanes (C_{29}–C_{34}) measured in this urban atmosphere were completely due to the leaf surface abrasion products of common vegetation typical of the Los Angeles area. Then it would be possible to estimate from the ambient iso- and anteisoalkane concentrations the hypothetical ambient *n*-alkane concentration contributions that must be present from vegetative detritus using the ratio between branched vs *n*-alkanes found in the leaf surface abrasion product composites discussed earlier. It was found from these calculations (using the iso-C_{31} alkane compared to the C_{29}–C_{34} *n*-alkanes) that the urban C_{29}–C_{34} *n*-alkane concentrations measured on average in the greater Los Angeles area would have to be roughly 20-fold higher than actually observed if all iso- and anteisoalkanes found in the airborne fine particulate matter were solely due to urban vegetation. Conversely, the contribution from urban plant detritus to the measured Los Angeles atmospheric iso- and anteisoalkane concentrations must be 5% or less based on the upper limit posed by the ambient C_{29}–C_{34} *n*-alkane concentration. Therefore, airborne vegetative detritus in Los Angeles will not interfere substantially with the use of the iso- and anteisoalkanes concentration pattern characteristic of cigarette smoke to accurately trace cigarette smoke particles in the Los Angeles atmosphere.

The above estimates of cigarette smoke particulate matter concentrations in the Los Angeles atmosphere will hold true provided that other possible interferences can be eliminated. As stated earlier, other conventional air pollution sources, such as motor vehicle exhaust, have been examined and were found not to emit significant quantities of the branched alkanes that are used here as tracers. Burning of vegetative waste is prohibited in the Los Angeles area, thereby eliminating any possible interference from open burning or incineration. There were no major forest fires on our sampling days near our sampling sites. Ambient organic fine particle concentrations were measured during 1982 at San Nicolas Island upwind of Los Angeles. It was found that iso- and anteisoalkane concentrations were below our detection limits in the San Nicolas Island background air, thereby eliminating contributions from upwind air masses as a major source of interferences (*100*).

Therefore, we conclude that the iso- and anteisoalkane concentration pattern characteristic of cigarette smoke can be used as a marker assemblage to accurately trace cigarette smoke particulate matter in the Los Angeles atmosphere. Since the ratio of branched alkanes tracer concentration to cigarette smoke particle mass emitted has been established at the source, this procedure can be applied to other urban areas in which interfering sources can be eliminated as was the case in Los Angeles. Of course, cigarette smoke particulate matter concentrations will be found to vary from place to place.

Conclusions. A study has been conducted to identify marker compounds that can be used to trace cigarette smoke particles in the outdoor Los Angeles urban atmosphere. The organic compounds present in cigarette smoke particle samples from exhaled mainstream plus sidestream smoke were examined by gas chromatography/mass spectrometry. The compound emission rates agree with literature values, thereby validating the sampling and analytical methods applied here. It was shown that the iso- and anteisoalkanes concentration pattern characteristic of tobacco leaf surface waxes is preserved in cigarette smoke particles. To verify whether or not this iso- and anteisoalkane concentration pattern found in the cigarette smoke particles is sufficiently unique that it can be used to trace cigarette smoke emissions in the urban atmosphere, common anthropogenic and biogenic emission sources likewise have been investigated. Particulate matter dislodged from the waxy leaf surfaces of urban plants by wind and weather show on average an iso- and anteisoalkane concentration pattern that is different than that found for the cigarette smoke particles. It was shown that the ratio of iso- and anteisoalkanes to *n*-alkanes in tobacco smoke is about 40 times larger than that found in the leaf surface abrasion products from urban vegetation. Other major emission sources ranging from vehicular emissions to meat cooking do not show any detectable amounts of iso- and anteisoalkanes in the carbon range from C_{29} to C_{34}, when analyzed by the same methods as used for the cigarette smoke and leaf surface waxes.

Using national cigarette sales data and population data for Los Angeles in 1982, ambient cigarette smoke branched alkane tracer concentrations were estimated that closely resemble concentrations measured in ambient air throughout the greater Los Angeles area. Considering all avenues investigated, the iso- and anteisoalkane concentration pattern found in cigarette smoke particles is unique and is preserved in this urban atmosphere. Atmospheric sampling at an offshore island upwind of Los Angeles showed that iso- and anteisoalkanes are below detection limits in the upwind background air. It can be concluded that cigarette smoke particles can indeed be traced in this urban atmosphere, and the tracer assemblage can be used to quantitatively estimate the ambient cigarette smoke concentrations outdoors. On average in 1982 in the Los Angeles area, the outdoor ambient fine particle cigarette smoke concentration determined by this technique averaged approximatley 0.28–0.36 μg m^{-3}.

Acknowledgments

We thank Ed Ruth for his assistance with the acquisition of the mass spectrometry data and Christos Christoforou as well as Joseph Fontana for their assistance during the cigarette smoke experiments. This research was supported by the California Air Resources Board under Agreement

A932-127. Portions of the work benefited from research supported by the U.S. Environmental Protection Agency under Agreement R-813277-01-0 and by the South Coast Air Quality Management District. Partial funding also was provided by the U.S. Department of Energy under Contract DE-AC02-76CH00016. The statements and conclusions in the report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products. This paper has not been subject to the EPA's peer and policy review and, hence, does not necessarily reflect the views of the EPA.

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Received for review February 4, 1994. Accepted March 1, 1994.⊗

⊗ Abstract published in *Advance ACS Abstracts*, April 1, 1994.