Characterization of Fine Particle Emissions from Burning Church Candles

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A series of source tests were conducted on the combustion of paraffin and beeswax candles. An enclosed chamber sampling system was utilized, and fine particle samples were collected on both quartz fiber and Teflon filters. Electronic particle sizing was performed using an optical particle counter and a differential mobility analyzer. Filter samples were weighed to determine fine particle mass emission rates and then analyzed for elemental carbon and organic carbon by thermal evolution and combustion analysis and for organic chemical composition by GC/MS. Three modes of candle burning were observed with very different emission profiles: a "normal burning" mode characterized by low mass emission rates and particles smaller than 100 nm in diameter; a "sooting" behavior with high emission rates of predominantly elemental carbon particles; and a "smoldering" phase upon candle extinction during which most of the mass emissions occurred as white particles having diameters between 400 and 800 nm. The majority of emissions were organic compounds including alkanes, alkenes, alkanoic acids, wax esters, cyclohexylalkanes, and alkanals. Analysis of the unburned waxes revealed that while some of these compounds were thermally altered products of the unburned wax, many others were unaltered candle components emitted by direct volatilization. Thus, possible chemical tracers for candle burning may be easily identified by analyzing unburned wax material. The information provided in this study, in conjunction with future ambient indoor air sampling programs and receptor-oriented chemical mass balance techniques, can be used to determine the relative importance of candle burning to indoor soiling problems.

Introduction

The soiling of the interior surfaces of buildings that house cultural properties is an important issue in the field of art conservation. Many historical churches in Europe and elsewhere contain priceless works of art including frescoes, paintings, sculptures, and tapestries. Much of the damage to these artifacts is attributed to the deposition of airborne particles that can significantly darken or alter their appearance and possibly react chemically with the artistic medium (*1—3*). The surfaces of these objects are very expensive or impossible to clean or repair, and the damage is often irreversible. The recent costly restoration of Michelangelo's Sistene Chapel ceiling fresco at the Vatican is a prime example of the consequences of airborne particulate soiling (*4*).

The sources of indoor particles in historical churches include ambient outdoor particulate pollution that enters through doors and other openings in the building shell and the indoor burning of oil lamps and ritual candles (*3, 5*). Outdoor particle sources, such as diesel exhaust and wood smoke, have been characterized and quantified previously (*6—15*). However, to determine the relative importance of candle smoke to the interior soiling problem, the particle emissions from candle combustion must also be quantified.

Receptor-oriented chemical tracer techniques have been successful for determining the contribution of individual emission source types to outdoor particle concentrations (*16*). The same methods can be applied to study the sources and levels of indoor particles. The success of these methods depends on accurate source characterization including mass emission rates and in-depth chemical speciation to identify possible organic tracer compounds and chemical signatures that are unique to each source. The very few studies of candle emissions date back to Faraday's famous lecture series on "The Chemical History of a Candle" presented in 1860 (*17*). More recent studies have focused on particle size and hygroscopicity (*18*) or potential health effects from toxic compounds present in candle smoke such as PAH (*19*). More detailed analysis is needed, particularly with respect to organic compound emissions, if a unique source signature for candle smoke is to be found. To this end, a series of source tests were conducted in order to determine the particle emission rates, size distributions, and chemical compositions of candle smoke.

Experimental Methods

Source Tests. The source test apparatus used in these experiments is shown in Figure 1. Candles were placed in a burn chamber with a volume of approximately 0.64 m³. Filtered ultrapure air (Liquid Air Corp., ultra-zero grade air) was pumped into the bottom of the chamber through four air diffusers at a nominal flow rate of 100 L/min. Two Teflon glovebags mounted on the chamber wall allowed manipulation inside the chamber while maintaining a closed system. The bags also served to regulate the air pressure within the burn chamber. Minor adjustments of the air flow rate were used to keep the bags half inflated and thus ensure that the chamber was at ambient atmospheric pressure. Candles were lit with a butane lighter and extinguished with an inverted cup fashioned from clean aluminum foil.

All effluent from the chamber was pumped out through one stainless steel sample port and then split into four parallel sample lines. On three of the lines, the sample was drawn through AIHL-design cyclone separators (*20*) at a nominal rate of 30 L/min each. The cyclones removed coarse particles with aerodynamic diameters greater than 1.8 μm and allowed fine particles to pass through. The filter assembly downstream of one cyclone separator consisted of two Teflon (47 mm diameter, Gelman Sciences Teflo, 2 μm pore size) and two quartz fiber filters (47 mm diameter, Pallflex, 2500-QAO-UP) operated in parallel. The nominal flow rates were 10 L/min each for one Teflon and one quartz filter and 5 L/min each for the second Teflon and quartz filters, thus maintaining the desired 30 L/min flow rate while providing samples having different mass loadings as required for different analyses. Air flows through the filters were controlled with critical orifices located between the filters and the pump. The Teflon

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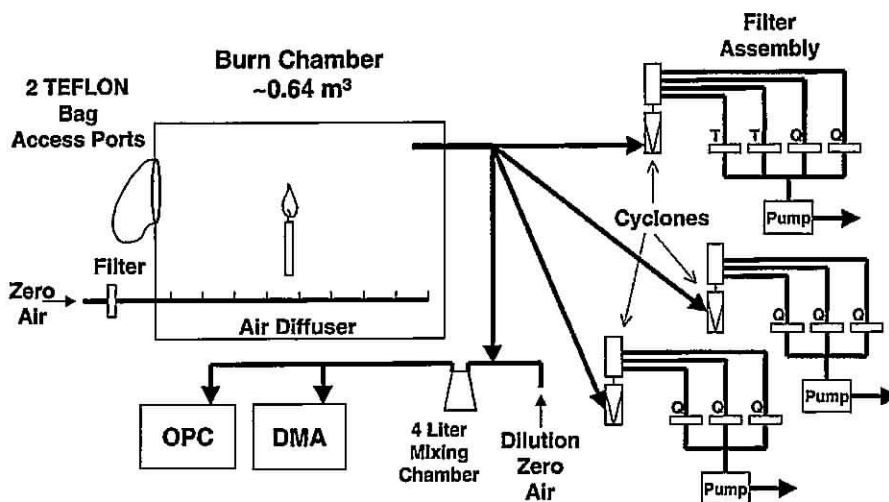
FIGURE 1. Experimental apparatus. OPC, laser optical particle counter; DMA, TSI differential mobility analyzer/condensation nucleus counter combination; T, Teflon filter; Q, quartz fiber filter.

filters allow the fine particle mass emission rate to be determined gravimetrically by repeated weighing of the filters before and after use. The quartz fiber filters were used for carbon particle analyses. Two additional cyclone/filter assemblies containing three 47 mm diameter quartz fiber filters per cyclone were also used, with sample drawn at a rate of 10 L/min through each of the six filters. Through the fourth sample line, smoke was drawn from the burn chamber at 0.5 L/min and subsequently diluted with ultrapure air by a factor of 10. After being mixed in a 4-L chamber to average the fluctuations in the particle concentrations, the sample was then drawn into two particle sizing instruments. The residence time in the burn chamber was on the order of 10 min, the residence time in the 4-L mixing chamber was about 45 s, and the residence time in the tubing connecting the apparatus was about 15 s. The size distribution of particles less than 200 nm in diameter was measured by a TSI 3071 differential mobility analyzer (DMA) connected to a TSI 3760 condensation nucleus counter and operated in scanning mode by a personal computer. The size distribution of larger particles was measured with a PMS-ASASP-X laser optical particle counter (OPC). The electronic instruments were also used to confirm the absence of particles in the chamber prior to and after sampling.

All quartz fiber filters were baked at 550 °C for a minimum of 12 h to reduce residual carbon levels. All cyclone parts, filter holders, and fittings were cleaned by sonication in dichloromethane. Stainless steel tubing was rinsed in dichloromethane, and the interior of the burn chamber was cleaned with methanol. Flow rates were measured before and after each test using a rotameter calibrated with an electronic bubble flowmeter (Gilian Instrument Corp. model 800268).

Two types of candles were tested: a yellow paraffin wax candle purchased from the supply in use at an historical church in Thessaloniki, Greece, and a beeswax candle made of rolled honeycomb from Casa Blanca, Chile, that is typically used in local churches. In each experiment, the candle was ignited, burned for 15 min, extinguished, and then the air in the chamber was sampled for an additional 15 min to collect all airborne particles remaining in the chamber. Five tests were conducted for each candle. In two experiments of each set, two MOUDI impactors were employed in place of the additional cyclones in order to take samples that could be analyzed to obtain size-resolved chemical speciation data. Results from the MOUDI impactor measurements are not presented here. The remaining three experiments used the additional cyclone/filter assemblies described above and

shown in Figure 1. These six additional filters remained in place through three consecutive tests in order to collect sufficient particle mass for organic compound speciation by gas chromatography/mass spectrometry (GC/MS).

Chemical Analyses. A 1.5-cm² punch from a quartz fiber filter from each test was processed to determine the elemental and organic carbon (EC/OC) content of the candle smoke by thermal evolution and combustion analysis (*21*). Organic carbon mass was multiplied by a factor of 1.2 to obtain an estimate of organic compound mass (*22*). This conversion factor is justified by the detailed organic compound speciation results presented below, which show that the predominant compounds in our samples have molecular weight to carbon weight ratios between 1.17 and 1.23.

Organic compound identification and quantification by GC/MS was based on methods developed previously by our research group (*7–15, 23*). Six quartz fiber filter samples were taken for GC/MS analysis that collectively represented three consecutive combustion experiments on each type of candle. These filters were then combined in a prebaked sample jar into a single composite sample for each candle type. All filters were stored in a freezer at −21 °C before and after sampling.

Before extraction, the composite filter samples were spiked with a mixture of eight deuterated internal recovery standards: n-decane-d_{12}, n-pentadecane-d_{32}, n-tetracosane-d_{30}, n-hexanoic acid-d_{11}, n-decanoic acid-d_{19}, phenol-d_5, benzoic acid-d_5, and benzaldehyde-d_6. Samples were extracted by successive 10-min sonications twice in hexane followed by three extractions in benzene/2-propanol (2:1). Extracts were filtered, combined, and reduced by gentle nitrogen blowdown to a nominal volume of 1 mL. The sample was then split into two fractions: one ready for GC injection and intended for use in measuring nonpolar organic compounds and a second fraction derivatized with diazomethane to convert organic acids to their methyl ester analogues prior to injection and intended for use in analysis of polar organic compounds. In addition to the filter samples, unburned candle wax of each type was dissolved in a hexane/benzene/2-propanol solution, and a fraction was derivatized by the same method as the filter extracts.

Derivatized and underivatized sample fractions were analyzed by GC/MS (Hewlett-Packard GC model 6890, MSD model 5973) using a 30 m × 0.25 mm diameter HP-1701 capillary column (splitless injection, 50–550 Da mass range, 2.94 scans/s, held at 65 °C for 10 min, 10 °C/min ramp to 275 °C, and held for 39 min). Heavier compounds, specifically the wax esters, were analyzed using a 30 m × 0.25 mm

diameter HP-5MS capillary column that allowed for higher elution temperatures (50–800 Da mass range, 2.00 scans/s, held at 65 °C for 10 min, 10 °C/min ramp to 325 °C, and held for 34 min). Sample injection was accompanied by 1-phenyldodecane used as a co-injection standard to normalize overall instrument response. Extraction efficiency was determined by the recovery of the deuterated n-alkane internal standards. The deuterated acids served to verify that the diazomethane derivatization reactions had been driven to completion.

Identification and quantification of organic compounds were facilitated by additional injections of more than 100 authentic standards. When specific quantitative standard compounds were not available, compound identification was based on published relative retention times for compounds in the same homologous series and interpretation of ion fragmentation patterns. Quantification of compounds for which primary standards were not available was estimated from the response of authentic standards in the same compound class and other compounds with similar retention times. Previous work has determined that the uncertainties ($\pm 1\sigma$) in the quantification procedures used are in the range of ±20% (16).

Results

Emission Rates and Particle Size Distributions. The combustion behavior of the candle flame was observed to be sporadic. Through visual observation and electronic particle sizing measurements, the flame behavior was divided into three modes of burning defined as follows:

"normal burn"—a small stable flame with no visible particle emissions

"sooting"—a larger flickering flame with visible black particle emissions

"smoldering"—occurs after flame extinction with visible white particle emissions

The extent of sooting behavior qualitatively appeared to depend on the air flow around the flame. A candle in a quiescent atmosphere creating its own air flow through buoyancy forces tended to undergo normal burn. A forced air flow around the flame caused sporadic sooting behavior. To a lesser extent, wick position also affected the amount of sooting observed. The extent of smoldering after the flame was extinguished varied from none at all to a case with visible emissions for 25 s. During smoldering, a small red ember at the tip of the wick was often observed. When the ember burnt out, the visible smoldering emissions ceased. It was also observed that the beeswax candle flame was generally smaller in size than the paraffin candle flame.

Figure 2 displays typical particle size distributions over 90-s sampling intervals for each of the three modes of burning. A normal burn (Figure 2a) was characterized by very low particle mass emission rates peaking at a particle diameter of about 50 nm. One should note that the candles were burned in particle-free air in order to prevent background contamination of the samples. Under real-world conditions, the presence of ambient aerosol in the vicinity of the candle, when the candle itself is emitting comparatively few particles, may provide sites for the condensation of semivolatile vapors, and thus, the size distribution of a normal burning candle may differ somewhat from our laboratory results. All the candle tests resulted in similar particle size distributions in the absence of significant sooting behavior. This is consistent with other studies of fine particle emissions from candle combustion (18). When the flame begins to undergo sooting behavior (Figure 2b), fine particle emissions increase by over an order of magnitude. The normal burn peak is still present, but larger particles are now detected up to the upper-limit detection diameter of the DMA. These particles are visibly black and thus are predominantly composed of elemental
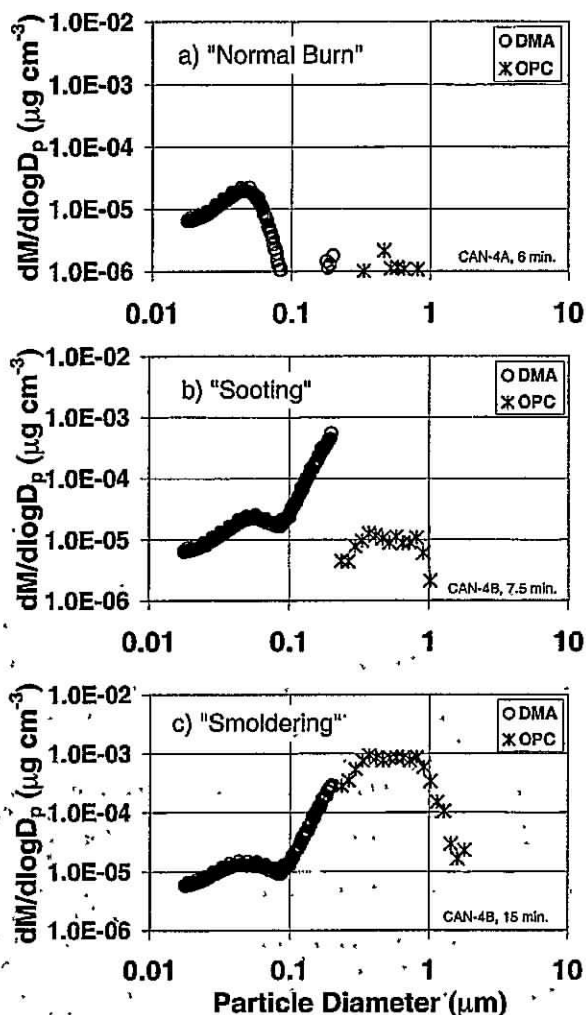

FIGURE 2. Typical particle size distributions for the three observed modes of burning. Particles were assumed to be spherical and of unit density. OPC data for the sooting candle should be disregarded as the OPC is not intended to measure particles having a high light absorption cross section.

carbon (confirmed by EC/OC analysis as discussed below). The OPC cannot accurately size these particles since they have a very different index of refraction and shape than the polystyrene latex spheres used to calibrate the OPC. Furthermore, the DMA measures an aerodynamic diameter that does not correspond exactly with particle size for nonspherical agglomerates such as soot. Thus, the exact particle size distribution of the sooting mode remains uncertain. However, a greatly increased mass emission rate is still revealed by the DMA results.

Figure 2c shows a typical particle size distribution for a smoldering candle. The mass emission rate is over 2 orders of magnitude greater than that of the normal burn peak still visible at the left of that graph. The particle diameter peaks between 400 and 800 nm as measured by the OPC, which can more accurately size these visibly white particles that have optical properties closer to the OPC calibration aerosol. The particle mass distribution decreases dramatically in particle sizes greater than 1 μm in diameter, thereby justifying the use of cyclones with a 1.8-μm cutoff.

Table 1 summarizes the results of the candle tests including mass emission rates along with elemental carbon and particulate organic compound emission rates. Observations of sooting are from both visual and electronic detection.

TABLE 1. Summary of Results Including Fine Particle Mass Emission Rates

exp no.	candle type	burn time (min)	observations sooting	observations smoldering time (s)	mass burned (g)	burn rate (mg/min)	total mass emission rate (μg/g burned)	org compd emission rate (μg/g burned)	elemental C emission rate (μg/g burned)
CAN-2	paraffin	120	excessive	none	14.28 ± 0.01	119 ± 0.1	3720 ± 260	195 ± 18	3370 ± 240
CAN-4A	paraffin	15	some	~10	1.52 ± 0.01	101 ± 1	970 ± 80	1060 ± 100	120 ± 40
CAN-4B	paraffin	15	some	~10	1.54 ± 0.01	103 ± 1	1030 ± 80	1100 ± 110	180 ± 40
CAN-4C	paraffin	15	negligible	~2	1.15 ± 0.01	77 ± 1	520 ± 80	770 ± 90	<40
CAN-4D	paraffin	15	negligible	~15	1.12 ± 0.01	75 ± 1	730 ± 70	1040 ± 110	<40
CAN-4E	paraffin	15	some	~15	1.26 ± 0.01	84 ± 1	1060 ± 60	1400 ± 120	90 ± 40
CAN-5A	beeswax	15	negligible	~25	0.95 ± 0.01	63 ± 1	1840 ± 90	1820 ± 170	<60
CAN-5B	beeswax	15	negligible	~25	1.05 ± 0.01	70 ± 1	2010 ± 90	2260 ± 200	<60
CAN-5C	beeswax	15	negligible	~20	0.79 ± 0.01	53 ± 1	1460 ± 120	1820 ± 180	<60
CAN-5D	beeswax	15	negligible	~20	0.87 ± 0.01	58 ± 1	1820 ± 100	2110 ± 180	<60
CAN-5E	beeswax	15	negligible	~20	0.89 ± 0.01	59 ± 1	2040 ± 100	2380 ± 210	<60

Smoldering time was taken as the time between the extinction of the flame and the disappearance of visible white smoke emissions from the tip of the candle wick. Experiment CAN-2 was performed at a higher air flow rate through the burn chamber (~200 L/min) in order to induce sooting behavior. The very high elemental carbon emission rate in that case confirms that a sooting candle produces predominantly elemental carbon particles. The other 10 experiments were performed under the same low air flow rate conditions (~100 L/min) when sooting was much less active. A comparison of the candle burn rate with the observations of sooting and the EC results suggests that a sooting candle burns slightly faster than a normal burning candle.

In Table 1, the particle mass emission rates per mass of candle material burned are presented. However, the electronic particle size distribution data suggest that sooting and smoldering modes of burning account for almost all of the particle mass emissions from candle combustion. The mass of candle burned and the time of burning in the normal burn mode are almost inconsequential to the amount of fine particle mass emitted. The low EC emission rates during the low air flow experiments suggest that sooting was infrequent; most of the mass emitted was during the 2–25 s of smoldering at the end of each low air flow experiment. Thus, the mass emissions could be more accurately normalized by smoldering time rather than by the mass of candle material burned. Unfortunately, there is no way to predict the smoldering time as the same candle can behave quite differently during successive experiments. The beeswax candle had higher emission rates per mass of wax burned than the paraffin candle due to lower burn rates and longer smoldering times.

On occasion (e.g., experiment CAN-4D), the quantity of organic compounds measured on the quartz fiber filter exceeds the gravimetrically determined mass emission rate. This could result from the adsorption of vapor phase organic compounds on the quartz fiber filters as has been observed in previous studies (24). In any case, the results indicate that carbonaceous species emissions account for nearly all of the fine particle mass emitted from both the paraffin and beeswax candles.

Organic Compound Mass Balance. For each candle type, smoke samples were drawn through six quartz fiber filters that were left in place for three test periods. Each set of six filters was combined in a jar and extracted prior to GC/MS analysis. The results of GC/MS analysis of the candle smoke samples and the unburned wax are summarized in an organic compound mass balance shown in Figure 3. Total fine organic compound mass is estimated from the EC/OC analysis of other filters collected in parallel with those used for extraction. The unburned waxes were assumed to consist of 100% organic compounds.

For the unburned paraffin wax, 78% of the mass was extractable and eluted from the GC column in the derivatized

sample. All eluted compounds were positively identified and quantified. Alkanes accounted for 93% of the identifiable compounds in the paraffin wax with minor mass contributions from alkanoic acids (6%) and cyclohexylalkanes (1%). The alkane predominance agrees well with other analyses of commercial waxes (25). The organic acids content is from substances that are commonly added to candle waxes as hardening agents (26, 27). The cyclohexylalkanes are remnants from the unrefined petroleum distilled to produce the paraffin candles (28). From the unburned beeswax, 76% was extractable and elutable, all of which was identified as specific organic compounds. Consistent with other analyses (29–31), the predominant components were long chain wax esters, which accounted for over 67% of the identified mass. Alkanes and alkanoic acids were also detected making up 14% and 15% of the identified mass, respectively, while the remaining mass was identified as alkenes.

Of the total fine particle organic compound mass emitted from combustion of the paraffin candle, 41% was extractable and elutable. Of this, 59% was resolved and identified as single compounds by GC/MS with the remainder designated as an unresolved complex mixture (UCM) of branched and cyclic hydrocarbons appearing as a broad hump in the total ion chromatogram. Of the identified organic compounds in the smoke from the paraffin wax candle, alkanes are the predominant compound class (68%) with lesser amounts of alkanoic acids (10%), alkanals (long-chain aldehydes, 17%), alkenes (5%), and cyclohexylalkanes (<1%). The fine particle organic compound mass emitted from the beeswax candle was 36% extractable and elutable, with 65% of this identified at the single compound level. The identified organics were composed of comparable amounts of alkanes (24%), alkanoic acids (23%), alkanals (15%), wax esters (19%), and alkenes (19%).

An examination of the results in Figure 3 suggests that many of the particulate organic compounds emitted in candle smoke consist of unburned wax components. The heavy alkane predominance in the paraffin candle smoke can be explained by volatilization of the mostly alkane wax material and subsequent condensation into the particle phase. The presence of wax esters in the beeswax candle emissions can also be ascribed to this volatilization process. Some of the other compounds found in the emissions are pyrolysis products from the candle flame. These assertions are supported by the detailed speciation of each organic compound class discussed below. Although all organic compounds from the candle emissions collected on the quartz fiber filters are described as being in the smoke particles, it is possible that some portion of the lower molecular weight compounds were collected as part of the vapor-phase adsorption artifact described above. Previous studies of other sources suggest that collection of vapor-phase organics on the particle filter is most important for

Paraffin Wax

Beeswax

Paraffin Candle Emissions
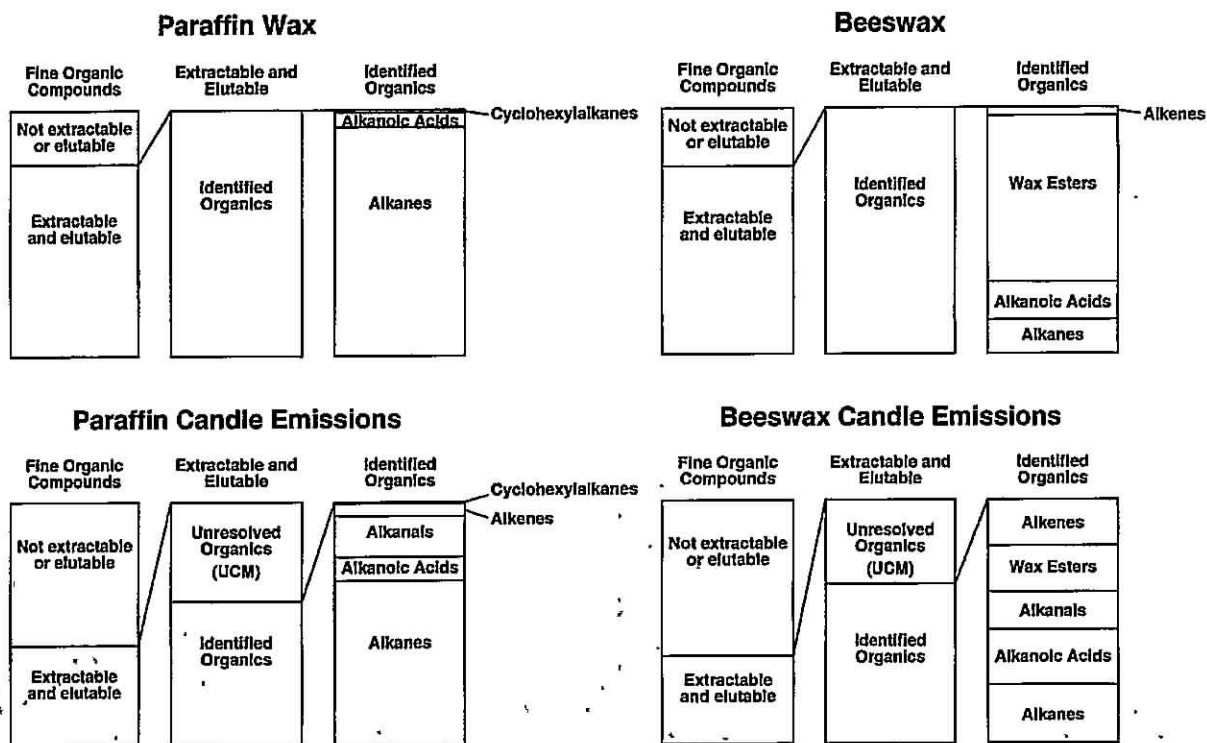

Beeswax Candle Emissions

FIGURE 3. Mass balance for total organic compounds in pure waxes and candle smoke.

neutral semivolatile compounds with carbon numbers less than about 21 and polar semivolatile compounds with carbon numbers less than about 14. Most of the compounds quantified in this study have molecular weights high enough to assume that they were originally present predominantly in the particle phase, but a fraction of the lowest molecular weight material may have been at least partially collected as vapors. Complete results of the GC/MS analysis are included in Table 2.

Alkanes. The distributions of the alkanes present in the unburned wax samples and in the smoke particles are given as histograms in Figure 4. The alkanes in the paraffin candle wax range from $C_{18}H_{38}$ to $C_{40}H_{82}$ with the peak in the distribution at $C_{29}H_{60}$. These results, showing no even or odd carbon number preference, are consistent with previous analyses of petroleum wax alkanes (28). The alkanes present in the paraffin candle smoke particles fall in a similar range with a maximum abundance at $C_{27}H_{56}$. The clear correspondence between the two distributions suggests that the alkane emissions occur due to direct volatilization and recondensation of wax material.

The alkanes present in unburned beeswax exhibit a strong odd carbon number preference indicative of natural materials such as plant waxes (10, 32, 33). The excellent correlation between the unburned beeswax and the beeswax smoke particles confirms that the alkanes emitted in the smoke particles are the volatilization and recondensation products of unburned candle wax.

Wax Esters. Wax esters were only detected in the unburned beeswax and beeswax candle smoke emissions, and all correspond to hexadecanoic (palmitic) acid with the acid hydrogen replaced by an additional long alkyl chain. The distribution of the wax esters is given in Figure 5. The naturally occurring even carbon number preference is observed in the terminal alkyl chains (alkanol moiety), containing between 24 and 34 carbon atoms, with the peak occurring at triacontyl hexadecanoate ($C_{15}H_{31}COOC_{30}H_{61}$). These results are consistent with previous spectrographic

analyses of beeswax (34, 35). A similar wax ester distribution is seen in the beeswax candle smoke but at lower relative concentrations. The wax esters identified in the smoke particles are likely due to direct volatilization from the candle wax. However, the lower relative concentrations suggest that other compounds are being emitted as pyrolysis products of the wax esters in the beeswax.

Alkanoic and Alkenoic Acids. The predominant alkanoic acids found in the unburned paraffin wax were identified as the fatty acids palmitic acid (C_{16}) and stearic acid (C_{18}). These acids are added to candle wax during production in order to improve hardening properties (26, 27). Figure 6 shows that the relative concentrations of alkanoic acids in the paraffin candle smoke particles correspond to their distribution in the pure paraffin wax. Thus, the acid emissions from the paraffin candle are a result of unburned wax volatilization.

Figure 6 also shows that the unburned beeswax contains higher molecular weight alkanoic acids than the paraffin wax. The higher molecular weight acids range from C_{24} to C_{34} and exhibit the well-known even carbon number preference for acids found in natural materials such as plant epicuticular waxes (10, 33). This carbon number range and preference for even carbon number homologues follow the same pattern as the alkanol groups found in the wax esters described above. The unburned beeswax contains a significant quantity of palmitic acid (C_{16}). Since beeswax is composed of leaf wax emulsions collected by bees, the carbon number distributions of the alkanes, wax esters, and alkanoic acids arise from the preferred carbon numbers present in the natural wax products of the plants in the region of the hive (33). The fine particle smoke emissions from the beeswax candle also contain alkanoic acids in the range from C_{24} to C_{34}. However, a much larger relative concentration of palmitic acid is observed in the smoke emissions than in the unburned wax. The extra palmitic acid is probably a thermal alteration product from the wax esters that all contain the palmitic acid group.

TABLE 2. Organic Compounds Present in Candle Smoke Particles and in Unburned Candle Wax

compound	unburned wax (mg/g of wax)		candle smoke (mg/g of org compd)		notes
	paraffin	beeswax	paraffin	beeswax	
n-Alkanes					
n-octadecane	0.04	0.01	0.14	nd[e]	a
n-nonadecane	0.15	0.04	0.31	0.10	b
n-eicosane	0.91	0.02	0.54	0.20	a
n-heneicosane	3.77	0.29	1.68	0.68	b
n-docosane	10.31	0.11	4.52	0.61	a
n-tricosane	21.35	3.73	8.91	2.86	b
n-tetracosane	35.24	0.35	13.56	0.63	a
n-pentacosane	44.39	9.43	15.56	5.81	b
n-hexacosane	53.09	1.19	17.21	1.21	b
n-heptacosane	57.05	36.90	16.97	18.93	b
n-octacosane	61.20	1.28	16.43	0.93	a
n-nonacosane	62.41	26.16	15.08	12.97	b
n-triacontane	58.97	0.98	13.38	0.82	b
n-hentriacontane	52.37	21.62	10.71	9.49	b
n-dotriacontane	42.54	0.50	7.89	0.38	a
n-tritriacontane	38.82	2.74	6.41	1.19	b
n-tetratriacontane	32.59	0.16	4.89	0.16	b
n-pentatriacontane	25.88	0.21	3.34	nd	b
n-hexatriacontane	19.16	nd	2.11	nd	a
n-heptatriacontane	18.21	nd	1.60	nd	b
n-octatriacontane	12.95	nd	0.75	nd	b
n-nonatriacontane	19.01	nd	0.32	nd	b
n-tetracontane	3.70	nd	nd	nd	b
Branched Alkanes					
isotricosane	0.06	nd	nd	nd	c
isotetracosane	0.22	nd	nd	nd	c
isopentacosane	0.69	nd	nd	nd	c
isohexacosane	1.71	nd	0.51	nd	c
isoheptacosane	2.64	nd	0.56	nd	c
isooctacosane	3.83	nd	0.59	nd	c
isononacosane	4.01	0.09	0.31	nd	c
isotriacontane	4.46	nd	nd	nd	c
isohentriacontane	3.30	nd	nd	nd	c
isodotriacontane	3.59	nd	nd	nd	c
isotritriacontane	2.85	nd	nd	nd	c
isotetratriacontane	2.87	nd	nd	nd	c
isopentatriacontane	1.57	nd	nd	nd	c
isohexatriacontane	1.17	nd	nd	nd	c
anteisotricosane	0.01	nd	nd	nd	c
anteisotetracosane	0.05	nd	nd	nd	c
anteisopentacosane	0.21	nd	nd	nd	c
anteisohexacosane	0.65	nd	0.20	nd	c
anteisoheptacosane	1.47	nd	0.38	nd	c
anteisooctacosane	2.07	nd	nd	nd	c
anteisononacosane	2.65	nd	0.35	nd	c
anteisotriacontane	2.44	nd	nd	nd	c
anteisohentriacontane	2.34	nd	nd	nd	c
anteisodotriacontane	1.86	nd	nd	nd	c
anteisotritriacontane	1.95	nd	nd	nd	c
anteisotetratriacontane	1.39	nd	nd	nd	c
anteisopentatriacontane	1.09	nd	nd	nd	c
anteisohexatriacontane	0.58	nd	nd	nd	c
4-methylhexacosane	0.06	nd	nd	nd	c
4-methylheptacosane	0.15	nd	nd	nd	c
4-methyloctacosane	0.39	nd	nd	nd	c
4-methylnonacosane	0.40	nd	nd	nd	c
5-methylhentriacontane	nd	0.09	nd	0.07	c
5-methylnonacosane	nd	0.17	nd	0.16	c
5-methylheptacosane	nd	0.20	nd	nd	c
5-methylpentacosane	nd	0.03	nd	nd	c
Cyclohexylalkanes					
1-cyclohexyleicosane	0.09	nd	nd	nd	b
1-cyclohexylheneicosane	0.25	nd	0.08	nd	b
1-cyclohexyldocosane	0.53	nd	0.16	nd	b
1-cyclohexyltricosane	0.96	nd	0.22	nd	b
1-cyclohexyltetracosane	0.98	nd	0.25	nd	b
1-cyclohexylpentacosane	1.12	nd	0.21	nd	b
1-cyclohexylhexacosane	1.02	nd	0.19	nd	b
1-cyclohexylheptacosane	1.05	nd	0.17	nd	b
1-cyclohexyloctacosane	0.67	nd	0.13	nd	b
1-cyclohexylnonacosane	0.78	nd	0.12	nd	b
1-cyclohexyltriacontane	0.34	nd	0.04	nd	b

TABLE 2. (Continued)

compound	unburned wax (mg/g of wax)		candle smoke (mg/g of org compd)		notes
	paraffin	beeswax	paraffin	beeswax	
n-Alkanals					
undecanal	nd	nd	0.90	0.38	a
dodecanal	nd	nd	1.63	0.66	a
tridecanal	nd	nd	2.32	1.07	a
tetradecanal	nd	nd	3.12	1.31	a
pentadecanal	nd	nd	nq	nq	b
hexadecanal	nd	nd	2.15	1.62	b
heptadecanal	nd	nd	2.40	0.91	b
octadecanal	nd	nd	2.89	1.76	b
nonadecanal	nd	nd	3.42	2.22	b
eicosanal	nd	nd	3.63	2.44	b
heneicosanal	nd	nd	3.56	2.85	b
docosanal	nd	nd	3.16	2.42	b
tricosanal	nd	nd	2.87	3.78	b
tetracosanal	nd	nd	2.60	3.51	b
pentacosanal	nd	nd	1.90	1.81	b
hexacosanal	nd	nd	0.95	2.22	b
heptacosanal	nd	nd	1.34	1.48	b
octacosanal	nd	nd	1.16	2.03	b
nonacosanal	nd	nd	0.83	1.15	b
triacontanal	nd	nd	0.52	2.91	b
n-Alkanoic Acids					
nonanoic acid	0.33	0.30	0.25	0.31	b
decanoic acid	nd	nd	0.16	0.32	a
undecanoic acid	nd	nd	0.02	0.02	b
dodecanoic acid	nd	nd	0.37	0.49	a
tridecanoic acid	0.04	nd	0.11	0.34	b
tetradecanoic acid	0.60	nd	0.61	0.59	a
pentadecanoic acid	0.04	nd	0.20	0.35	b
hexadecanoic acid	18.09	8.29	9.94	28.34	a
heptadecanoic acid	0.26	0.04	0.30	0.28	b
octadecanoic acid	25.56	0.75	10.66	1.85	a
nonadecanoic acid	0.06	0.08	0.13	0.14	b
eicosanoic acid	0.36	0.13	0.25	0.30	a
heneicosanoic acid	nd	nd	0.11	0.17	b
docosanoic acid	0.15	3.34	0.15	1.21	a
tricosanoic acid	nd	0.05	0.10	0.19	b
tetracosanoic acid	0.62	47.55	0.25	9.12	b
pentacosanoic acid	nd	nd	nd	nd	b
hexacosanoic acid	0.10	14.00	0.08	2.27	b
heptacosanoic acid	nd	nd	nd	nd	b
octacosanoic acid	0.07	14.83	0.03	1.96	b
nonacosanoic acid	nd	nd	nd	nd	b
triacontanoic acid	nd	10.87	nd	1.06	b
hentriacontanoic acid	nd	nd	nd	nd	b
dotriacontanoic acid	nd	7.44	nd	0.43	b
tritriacontanoic acid	nd	nd	nd	nd	b
tetratriacontanoic acid	nd	8.73	nd	0.23	b
n-Alkenoic Acids					
9-hexadecenoic acid	nd	nd	nd	0.65	b
9-octadecenoic acid	nd	1.15	nd	2.70	a
Wax Esters					
tetracosyl hexadecanoate	nd	46.68	nd	9.71	b
hexacosyl hexadecanoate	nd	39.27	nd	5.03	b
octacosyl hexadecanoate	nd	57.44	nd	5.19	b
triacontyl hexadecanoate	nd	188.68	nd	13.46	b
dotriacontyl hexadecanoate	nd	160.31	nd	9.62	b
tetratriacontyl hexadecanoate	nd	22.70	nd	1.76	b
Alkenes					
1-heptadecene	nd	nd	0.22	0.24	a
1-octadecene	nd	nd	nq	1.01	a
1-nonadecene	nd	nd	0.68	0.72	a
1-eicosene	nd	nd	1.27	1.53	a
1-heneicosene	nd	nd	1.31	1.89	b
1-docosene	nd	nd	1.41	2.25	b
1-tricosene	nd	0.08	1.41	2.31	b
1-tetracosene	nd	nd	1.20	4.94	b
1-pentacosene	nd	0.25	1.21	1.78	b
1-hexacosene	nd	nd	1.01	3.51	b
1-heptacosene	nd	0.16	0.77	1.22	b
1-octacosene	nd	nd	0.54	3.35	b
1-nonacosene	nd	0.22	0.74	0.83	b

TABLE 2. (Continued)

compound	unburned wax (mg/g of wax)		candle smoke (mg/g of org compd)		notes
	paraffin	beeswax	paraffin	beeswax	
		Alkenes (continued)			
1-triacontene	nd	nd	0.78	6.08	b
?-hentriacontene (peak a)	nd	3.04	nd	1.36	b
?-hentriacontene (peak b)	nd	2.66	nd	1.09	b
1-dotriacontene	nd	nd	nd	4.18	b
1-tritriacontene	nd	18.56	nd	6.17	b
1-tetratriacontene	nd	nd	nd	0.46	b
		PAH			
naphthalene	<0.003	<0.001	<0.03	<0.02	d
acenaphthylene	<0.002	<0.0006	<0.004	<0.01	d
acenaphthene	<0.001	<0.001	<0.02	<0.005	d
fluorene	<0.002	<0.0005	<0.03	<0.006	d
benzophenone	<0.01	<0.004	<0.05	<0.03	d
phenanthrene	<0.08	<0.08	<0.3	<0.2	d
anthracene	<0.12	<0.1	<0.07	<0.07	d
anthracenedione	<0.09	<0.07	<0.04	<0.05	d
fluoranthene	<0.002	<0.001	<0.04	<0.006	d
pyrene	<0.002	<0.001	<0.02	<0.02	d
chrysene	<0.0006	<0.0003	<0.006	<0.004	d
benz[a]anthracene	<0.0007	<0.0004	<0.007	<0.003	d
benz[a]anthracene-7,12-dione	<0.002	<0.002	<0.007	<0.02	d
benzo[a]pyrene	<0.009	<0.01	<0.004	<0.002	d
benzo[k]fluoranthene	<0.01	<0.02	<0.005	<0.003	d
indeno[1,2,3-cd]pyrene	<0.0005	<0.0004	<0.001	<0.0007	d
dibenz[a,h]anthracene	<0.05	<0.03	<0.02	<0.02	d
benzo[ghi]perylene	<0.0004	<0.0004	<0.001	<0.001	d
unresolved complex mixture (UCM)	nd	nd	168.52	124.80	
total extractable and elutable	780.91	763.87	412.90	361.52	

[a] Authentic quantitative standard. [b] Identification and quantification estimated from authentic standards for compounds in same homologous series. [c] Identification based on relative retention times and mass spectra, quantification based on authentic standards for similar compounds. [d] No PAH were detected; detection limits are given. [e] nd, not detected; nq, detected but unable to quantify due to coelution with other compounds.
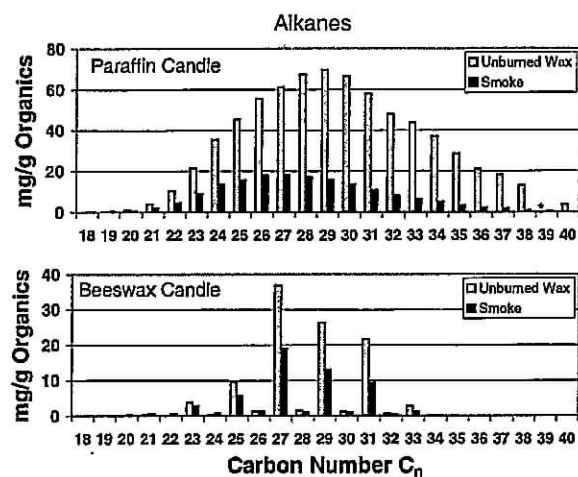

FIGURE 4. Alkane distributions by carbon number. All straight chain and branched alkanes (i.e., iso-, anteiso-) are grouped by carbon number. An asterisk (*) indicates not quantifiable due to coelution with other compounds.
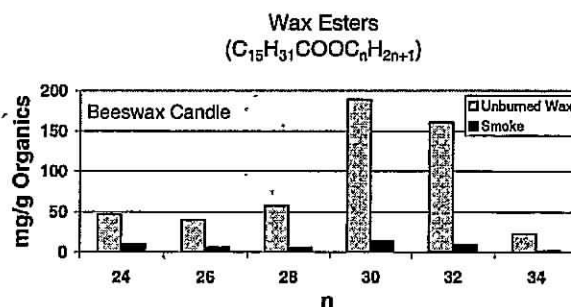

FIGURE 5. Wax ester distribution in unburned beeswax and in beeswax candle smoke, organized according to the carbon number (n) of the longest alkyl (alkanol) carbon chain in the ester. All wax esters contained a C_{16} alkanoate group. No wax esters were detected in the paraffin wax or paraffin candle smoke.

Small quantities of n-alkenoic acids were also detected in the unburned beeswax and in the beeswax candle smoke. The results for 9-hexadecenoic acid and 9-octadecenoic acid are given in the Table 2.

Alkenes. The paraffin wax did not contain any identifiable alkenes, but small quantities were detected in the paraffin candle smoke particles as shown in Figure 7. The observed distribution is possibly the result of alkane combustion in the candle flame (36). The unburned beeswax contained some alkenes with the expected odd carbon number preference and a very strong predominance of C_{31} and C_{33}. These two predominant alkenes are seen in the same relative concentrations in the unburned beeswax as in the beeswax candle smoke, suggesting that these alkenes are emitted by direct volatilization. Setting these two compounds aside, we see that the emissions also contain alkenes with an even carbon number preference between C_{24} and C_{34}. The relative abundance of these compounds roughly resembles the distribution of the long chain wax ester alkyl groups seen in Figure 5. We have already observed an abundance of the thermal alteration product, palmitic acid, derived from the other half of the wax esters in the beeswax candle emissions. The even numbered alkenes $>C_{24}$ represent the other major fragment produced by pyrolysis of the alkanol moiety in the wax esters. The remaining alkenes observed between C_{17} and C_{29} are most likely derived from alkanes that are thermally altered in the same manner as those observed in the paraffin candle emissions. Almost all alkenes present were identifiable
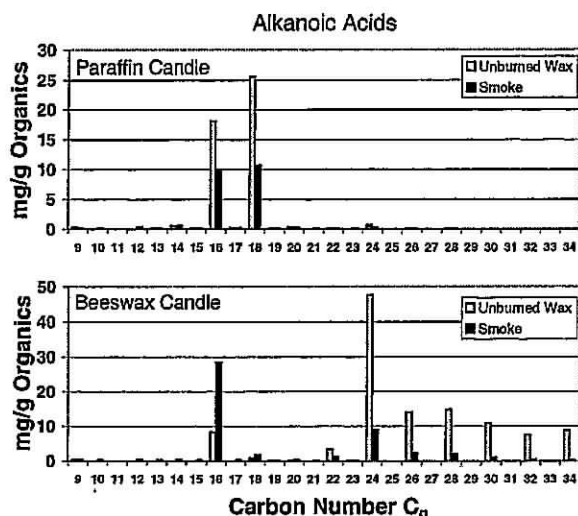
FIGURE 6. Alkanoic acid distributions by carbon number.
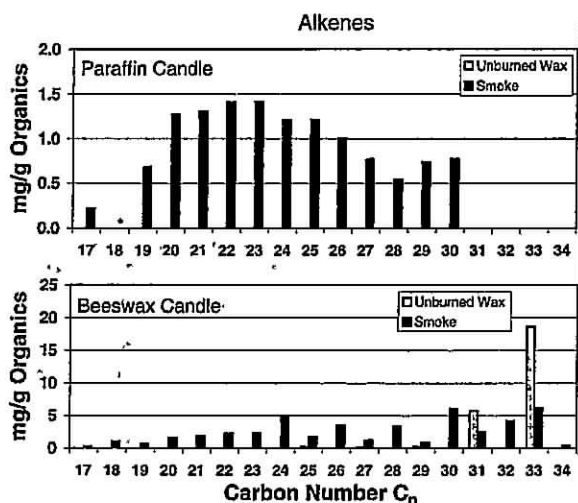

FIGURE 7. Alkene distribution by carbon number. All alkenes are grouped together although almost all are identifiable as alk-1-enes. No alkenes were detected in the paraffin wax. An asterisk (*) indicates not quantifiable due to coelution with other compounds.
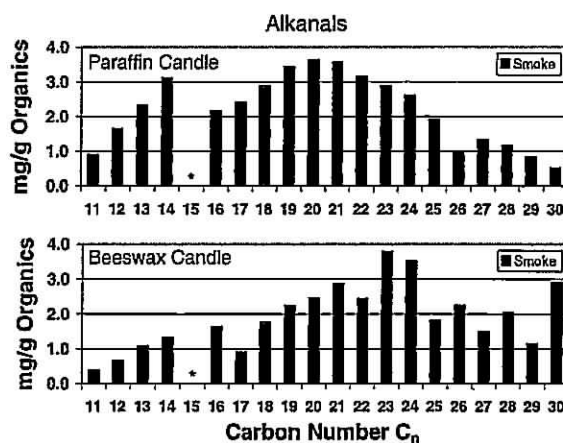

FIGURE 8. Alkanal distribution by carbon number. No alkanals were identified in the unburned beeswax or paraffin wax. An asterisk (*) indicates not quantifiable due to coelution with other compounds.
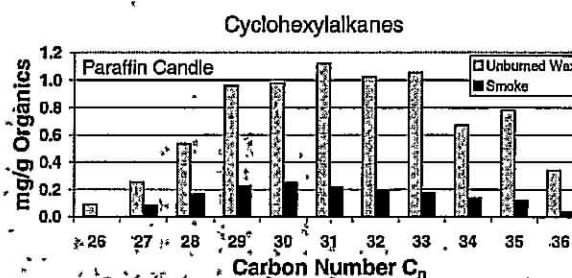

FIGURE 9. Cyclohexylalkane distributions by carbon number. No cyclohexylalkanes were detected in the unburned beeswax or beeswax candle emissions.

as alk-1-enes, although the location of the double bond could not be confirmed in a few of the alkenes present at low concentrations.

Aldehydes, Cyclohexylalkanes, and PAH. While no aldehydes were detected in the unburned waxes, Figure 8 shows that aldehydes are found in the fine particle emissions from combustion of each type of candle. All identified aldehydes, emitted as combustion products of the alkanes present in the unburned wax (36), were alkanals consisting of long, straight alkyl chains ranging from C_{11} to C_{30} with terminal aldehyde groups.

The cyclohexylalkane distributions in the paraffin wax and paraffin candle smoke emissions are compared in Figure 9. The similarity of the two distributions suggests that cyclohexylalkanes are emitted during candle combustion by volatilization of the unburned wax. No cyclohexylalkanes were detected in the beeswax or beeswax candle emissions.

Like other combustion phenomena, one might expect a burning candle to emit polycyclic aromatic hydrocarbons (PAH) that are present in the particle phase (8, 11, 12, 14, 15). Since certain PAH are carcinogens or mutagens (37, 38), prolonged exposure to high concentrations of candle smoke might be suspected to pose a potential health risk. A concerted

effort was made to identify PAH in the fine particle emissions from the combined normal burn and smoldering combustion of both candle types, and a search for PAH in the unburned wax was conducted as well. However, no PAH were positively identified. Table 2 presents the PAH detection limits for the compounds for which we had standards. Other studies have found very small amounts of PAH in fine particle candle smoke emissions but at levels below health exposure standards (19). The emissions from the heavily sooting candle could not be examined by GC/MS due to extreme overloading of the filter. The extremely large quantities of soot particles suspended in the solvent extract from this sample, despite the attempt to separate them from the extract, prevented the blow down of the sample to the proper concentration for GC/MS detection. Therefore, no conclusions can be drawn about the PAH emissions under sooting conditions.

Possible Tracers. The emissions of many of the compound classes found in candle smoke are very similar to the unburned wax material. An analysis of the candle wax from the candles burned in a particular situation will therefore provide an indication of molecular tracers that could be used to determine the contribution of candle smoke to ambient and indoor fine particle levels. Compounds that are nearly unique to beeswax candles and not found in many other fine particle sources, such as the wax esters, are ideal tracers. When the wax does not contain unique tracer compounds, as is the case with paraffin candles, the relative distributions of the organic compounds create a unique fingerprint for the candle smoke. Figure 10 compares the fine particle alkane distribution of paraffin candle smoke emissions to the alkane distribution found in two other important fine particle sources, diesel engine exhaust and cigarette smoke. The distributions differ significantly, and a chemical mass balance that uses organic compounds as tracers (16) should be able
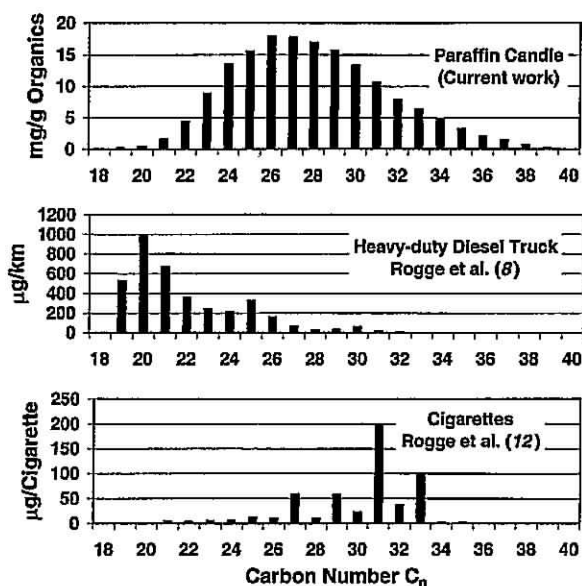
FIGURE 10. Alkane distributions in fine particle emissions from various sources.

·to resolve the relative contributions of each of these source ·types to·airborne or deposited particle samples.

·Discussion

Burning candles emit fine particles at different rates depending on combustion behavior. A sooting flame and a ·smoldering wick produce much higher fine particle mass emission rates than a quiet normal burning candle and are responsible for the vast majority of the fine particle emissions from this source. Fortunately, these two modes of smoke generation may be easily controlled. Sooting often is caused by wick position or by forced flow around the flame, and it may be reduced by better wick design arid control of indoor air flow conditions. The degree of smoldering is affected by the method used to extinguish the flame. An extinguishing method, such as cutting off the tip of the wick, which avoids the creation of an ember at the end of the wick, will reduce or eliminate smoldering emissions. Extinguishing a candle by oxygen deprivation with an inverted cup over the flame or by simply blowing out the candle will cause significant smoldering to occur.

A sooting flame emits fine black elemental carbon particles that will darken interior surfaces through airborne particle deposition. A smoldering wick produces fine particles that are mostly composed of organic compounds. The detailed chemical analysis of smoldering particle emissions reveals volatilized wax combined with thermally altered products that in many cases bear structural similarity to precursor compounds found in unburned candle wax. No significant levels of PAH were detected in the emissions from normal burning and smoldering candles; the PAH content of sooting candle smoke, however, was not examined.

The information provided in this study, combined with airborne or deposited particle samples, can be used in future receptor-based mass balance calculations to determine the contribution of candle smoke to indoor airborne and deposited fine particle levels. The elemental carbon content attributable to candle combustion will come from the sooting mode of combustion while the organic compounds present represent the contribution from the smoldering process. It appears that appropriate control measures can be taken to protect historic and cultural artifacts inside candle-burning churches through consideration of the air flow around the

candles, wick design, and choice of an appropriate method for extinguishing the candles. The candles used in this study are typical of many of the paraffin and beeswax candles in use throughout the world in private households as well as churches. Therefore, these results should be applicable to similar candles burned in any location. The wax from any particular candle can be easily analyzed by GC/MS to test for similarity to the candles used in this study. Our results suggest that even when the candle is of a different composition, the emissions may be very similar to the unburned wax material thus providing a basis for estimating the chemical composition of the organic compounds in the smoke without conducting an elaborate source test experiment.

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