Chapter 9

Hot Asphalt Roofing Tar Pot Fumes

Introduction

Bituminous materials such as asphalt and coal tar are commonly used for road construction and roof sealing purposes. The bituminous products used in the United States are manufactured principally from crude oils (> 99%) and to a minor extent from coal. Nearly 30 million tons of asphalts were consumed in the United States during 1988, roughly one third of the world production (Tyler et al., 1990). About 15% of the bituminous type material produced is consumed by the building industry for roofing purposes (Kirk-Othmer, 1985) including asphalt roll and asphalt shingle roofing. During the construction of hot-process built-up roofs, hot asphalt tar or coal tar pitch is used as an adhesive. In order to fluidize the asphalt adhesives and sealant at construction sites, small portable heater units are used. These heaters, called roofing tar pots, produce a visible plume of particulate matter derived from the hot asphalt batch. Gray (1986) estimated that particulate emissions from roofing tar pots contributed roughly 920 kg/day of fine particulate matter ($d_p \leq 2.0\ \mu m$) to an 80 km × 80 km heavily urbanized area centered over Los Angeles during the year 1982.

Roofing tar fumes that are released during roof construction work, might be mutagenic and carcinogenic. For that reason, prior studies of roofing tar fumes have been concerned exclusively with the determination of the risk to roofing workers from exposure to such fumes (e.g., Bingham et al., 1980; Niemeier et al., 1988; Malaiyandi et al., 1982; Reed and Liss, 1984; Williams and Lewtas, 1985).

The purpose of the present study is different. A more complete characterization of the organic chemical composition of roofing tar pot aerosol is sought. These data on aerosol emissions from roofing tar pots will be combined with parallel studies on the other major urban organic aerosol sources (Rogge et al.,1991, 1993b-i). The complete set of data on all major organic aerosol sources can be used to support a comprehensive air quality modeling study of emissions and air quality relationships for urban organic aerosols.

Experimental Methods

Sampling

Petroleum-based build-up roofing asphalt (GAF brand) was heated in a typical roofing tar kettle to workable plasticity. The temperature of the tar pot was maintained between 250 – 300°C. Sample collection was performed using a specially designed dilution source sampling system (Hildemann et al., 1991a). Hot tar fumes (2 lpm) were sampled from above a vent opening at the top of the asphalt kettle and diluted 18-fold with precleaned air (activated carbon-filtered and HEPA-filtered). The cooled and diluted asphalt fumes were subsequently drawn through an AIHL-design cyclone separator that removed particles with an aerodynamic diameter > 2.0 μm. The cyclone separator was operated at a flow rate of 27.9±0.3L/min. Sampling time was 10 - 15 min for each test. Fine particulate matter was collected downstream of the cyclone separators on three parallel quartz fiber filters (Pallflex 2500QAO), and one Teflon filter (Gelman Teflo, 2.0 μm pore size). All quartz fiber filters were annealed at 750°C for 2-4h before use to ensure low contamination levels for organic substances.

Bulk Chemical Analysis

Trace elements, ionic species, organic carbon (OC), and elemental carbon (EC) have been previously quantified in the roofing tar pot samples. These data on the bulk chemical properties of roofing tar pot emissions are published elsewhere (Hildemann et al., 1991a).

Sample Extraction

An extraction scheme has been followed that originally was developed for ambient fine particulate matter by Mazurek et al. (1987) and subsequently has been used in several studies and companion papers (Mazurek et al., 1989, 1991; Hildemann et al., 1991b; Rogge et al., 1991, 1993a-d). The extraction protocol can be described as follows: Prior to sample extraction, perdeuterated tetracosane (n-$C_{24}D_{50}$) which served as an internal standard was spiked onto the filter composites. The internal standard should be in a concentration range comparable to the expected organic compound concentrations in the actual sample. To ensure that n-$C_{24}D_{50}$ is in a suitable concentration range, the amount to be added as internal standard was estimated using the OC-data acquired from EC/OC-combustion analysis of a sample taken in parallel with the samples that were to be extracted.

The quartz fiber filter samples were extracted together in a sequential procedure that included extraction with hexane (2 × 30 ml) followed by extraction with benzene/2-propanol (2:1 mixture, 3 × 30 ml). Each extraction sequence was conducted for 10-min and supported by mild ultrasonic agitation. Following each extraction step, the filter extracts were filtered and combined. 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 methoxy analogues. The sample extracts were stored in the dark at -21°C prior to GC/MS analysis.

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 supported 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 spectral data were acquired while operating the mass spectrometer in the electron impact mode (electron energy of 70eV). For supplemental studies a Varian 4600 high-resolution gas chromatograph (HRGC) with FID-detector was used that was operated with the same physical column and temperature program as used during GC/MS-analysis (Hildemann et al., 1991b). Additional information describing the analytical procedure can be found elsewhere (Mazurek et al., 1987, 1989; Rogge et al., 1991, 1993a,b).

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 for a large set of polar and nonpolar standard compounds, dilution air testing and more. For a more detailed discussion, the reader is refered to accompanying source and ambient fine organic particle studies published earlier (Mazurek et al., 1989; Rogge et al., 1991, 1993a,b).

Compound Identification and Quantification

Compound identification was conducted using the National Institute of Standards and Technology (NIST) mass spectral library accessed by the INCOS Data System, 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 conducted 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.

The compound quantification process was based on the application of n-$C_{24}D_{50}$ as internal standard and 1-phenyldodecane as coinjection 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 refered to Rogge et al. (1991, 1993a).

Standard Compounds

Confirmation and quantification of organic compounds was obtained through the use of more than 150 authentic standards, see Rogge et al. (1992b). The following standard mixtures were injected onto the GC/MS-systems: (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 8 aromatic and polycyclic aromatic N– and S–substituted compounds; (9) steroids including cholesterol and cholestane; (10) a set of 4 phytosterols; (11) several natural resins; (12) plasticizers; (13) a suite of 11 aliphatic dicarboxylic acids (C_3 – C_{10}); and (14) one suite made up of 7 aromatic di- and tri- carboxylic acids all as their methyl ester analogues; and (15) other compounds.

Results and Discussion

For hot-process built-up roofs, coal tar pitch and asphalt tar products are typically used as an adhesive (Niemeier et al., 1988; Malaiyandi et al., 1982). Coal tar pitches are a byproducts resulting from the pyrolysis of coal, often termed carbonization. Typically the carbonization process is conducted in the high temperature range of 900 - 1200°C (Kirk-Othmer, 1985). At those temperatures coal tars are distillated off of the bituminous coal leaving solid coke as a residue.

Asphalt, although also naturally occurring, is mainly obtained as byproduct from crude oil refining. Depending on the application and crude oil quality, asphalt is manufactured by straight reduction, air-blowing, propane deasphalting, and thermal cracking (Kirk-Othmer, 1985). During the refining process crude oil is injected into a fractionation column at temperatures ranging from 340 to 400°C. After removing the lighter crude oil fractions by distillation, the residuum is commonly termed straight-reduced asphalt. Straight-reduced asphalt is mainly used for road pavements. For roof surface coatings, an asphalt is desired that is more viscous and less resilient. To remove the more volatile organic fraction and to improve the quality of the asphalt by partial oxidation, straight-reduced asphalt is heat-treated by continously bubbling hot air through the asphalt at temperatures from 200 to 275°C. "Air-blown" asphalt is then used to produce asphalt impregnated paper rolls and asphalt shingles. For hot-process built-up roofs, asphalt tar is the adhesive of choice in oil producing countries.

Before application, asphalt tar (or alternatively coal tar pitch) is reheated to reach the desired workability. The recommended kettle temperature is 200 - 270°C (Niemeier et al., 1988). Commonly, the kettle temperature is poorly controlled and kettle temperatures above 600°C have been measured (Thomas and Mukai, 1975). At such high temperatures and in the absence of oxygen, pyrolysis of asphalt-containing precursor constituents leads to PAH-type compound synthesis resulting in increased mutagenic and carcinogenic activity of the hot tar fumes (Penalva et al., 1983; Niemeier et al., 1988).

Here, fine particulate roofing asphalt tar fumes are examined on a molecular level to provide a fine particulate source profile that can be used to estimate the contribution of organic matter released from hot-process built-up roofing to the urban atmosphere.

Mass Balance for Fine Particulate Organic Tar Pot Fumes

A material balance has been constructed for the extractable organic portion of fine particulate matter released from roofing tar pot operations and is shown schematically in Figure 9.1. Of the extractable and chromatographically elutable organic matter close to 16% is chromatographically resolved as single compound peaks. More than 50% of the chromatographically resolved compound mass could subsequently be identified. The overwhelming majority of the elutable organic mass that could be identified consists of *n*-alkanes (73%) and carboxylic acids such as *n*-alkanoic acids (17%) and to a minor extent benzoic acids. Of the identifiable mass 7.9% was made-up of polycyclic aromatic hydrocarbons (PAH) and thia-arenes (S-PAH). A quantitative assessment of individual compounds and compound classes is given in Table 9.1.

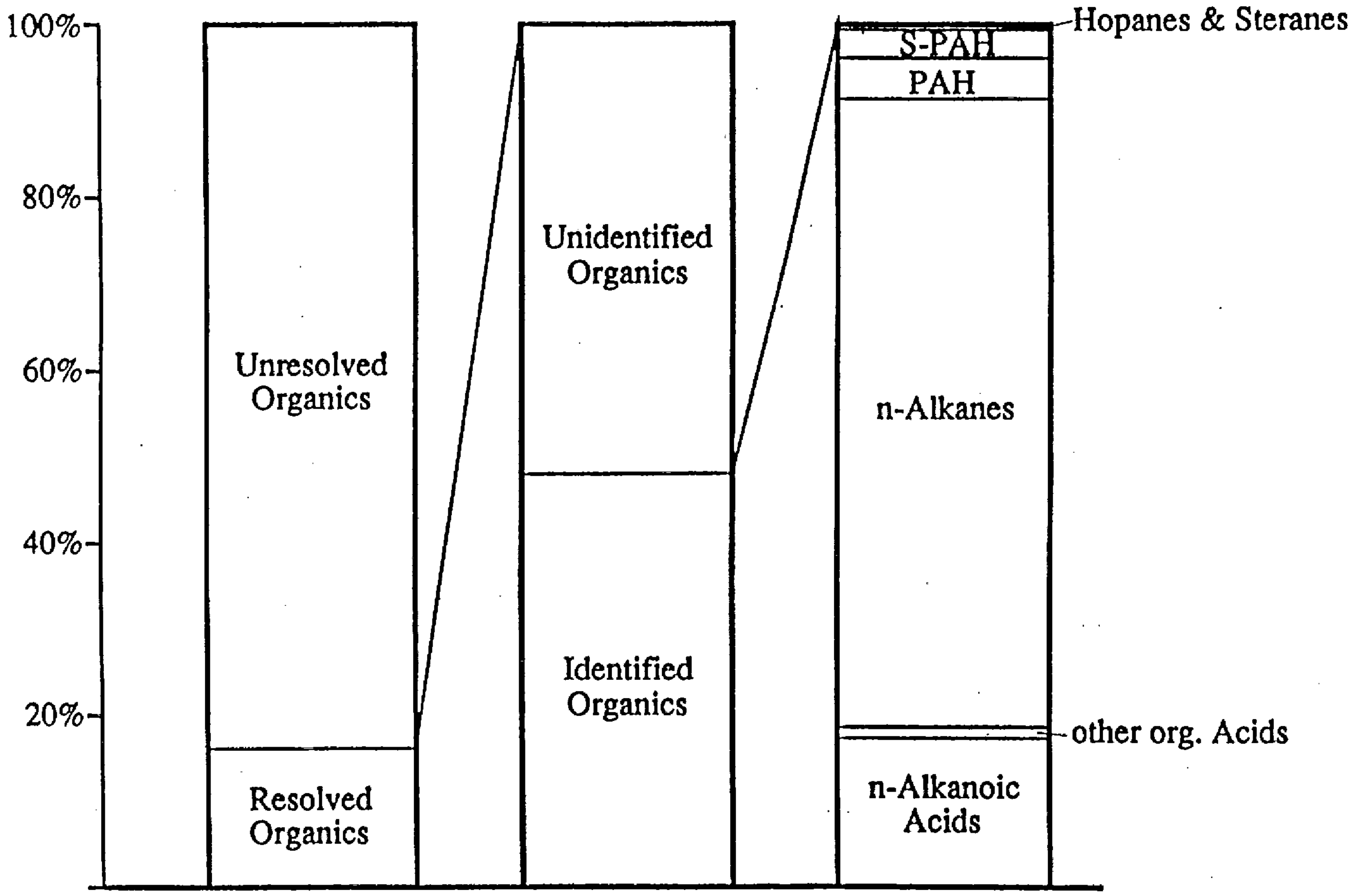

Fig. 9.1: Mass balance for elutable organic matter in the fine particle emissions of roofing tar pot fumes.

Alkanes

Figure 9.2a depicts the *n*-alkane concentration pattern found in the roofing asphalt fume particulate matter. *n*-Alkanes have been identified ranging from C_{14} to C_{32} with C_{17} as the most prominent member. At typical ambient concentrations and temperature, in the urban atmosphere, *n*-alkanes up to C_{18} are mainly found in the gas-phase (Cautreels and Van Cauwenberghe, 1978), while higher molecular weight *n*-alkanes are preferably found in the particle-phase (Cautreels and Van Cauwenberghe, 1978; Rogge et al., 1993a).

Adsorption of gas-phase organics onto the filter material is a known cause for the presence of some lower molecular weight organic compounds in aerosol samples. The increased low molecular weight particle-phase *n*-alkane concentrations ($< C_{18}$) found here is also caused in part by high *n*-alkane asphalt fume concentrations which favor formation of particle-phase material during the partitioning between the gas- and particle-phase that occurs as the tar pot vapors are cooled. Niemeier and coworkers (1988) pointed out that the carcinogenic activity of asphalt fumes cannot be explained solely on the basis of their PAH-content and hypothesized that co-carcinogenic effects of aliphatic hydrocarbons could be responsible for part of the carcinogenic activity, as was emphasized earlier by other researchers (Bingham and Nord, 1977; Horten et al., 1957; Bingham and Falk, 1969).

Carboxylic Acids

n-Alkanoic acids (C_8 - C_{24}) have been found in concentrations that are typically several times lower than for the *n*-alkanes. The *n*-alkanoic acids concentration profile in Figure 9.2b shows highest concentrations for hexadecanoic acid,

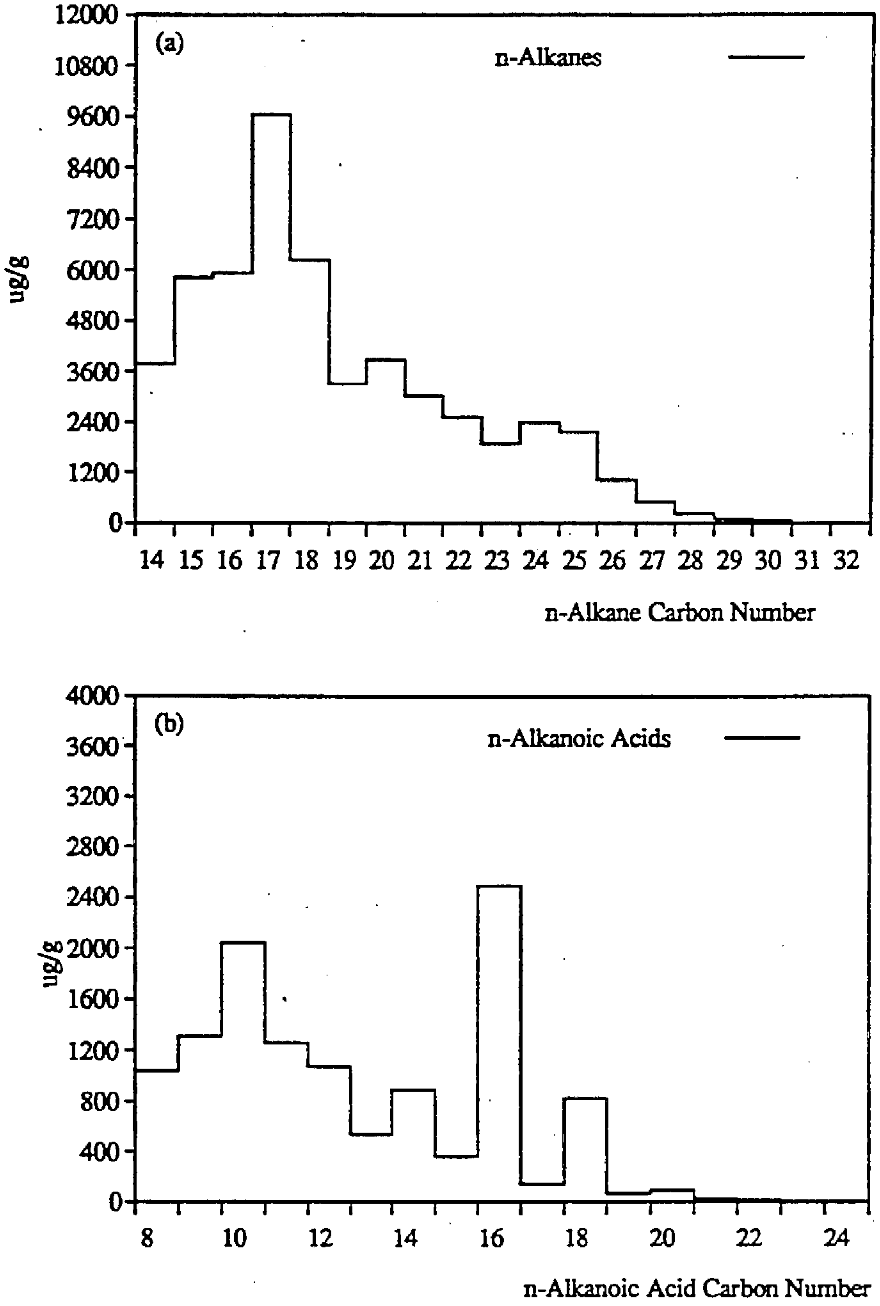

Fig. 9.2: Emission profiles for roofing tar pot fumes: (a) *n*-alkanes and (b) *n*-alkanoic acids.

which is commonly found in the emissions of fossil fuel burning sources (Rogge et al., 1993b). In addition, several methyl substituted benzoic acids and benzeneacetic acid have been identified. Of the benzoic acid-type compounds, 4-methylbenzoic acid is most abundant (see Table 9.1).

Polycyclic Aromatic Hydrocarbons

Because of their mutagenic and carcinogenic potential and the resulting health risk to roofing workers, the PAH content of asphalt and coal tar pitch fumes has been extensively investigated in the past. PAH concentrations have been measured in the raw material itself, in fume condensates, and as ambient samples in the breathing zone of roofing workers (Lijinsky et al., 1963; Niemeier et al., 1988; Malaiyandi et al., 1982; Wallcave et al., 1971). Roofing coal tar pitches have been found to contain PAH-levels several orders of magnitude higher than that of roofing asphalt tar. For example, benzo[a]pyrene concentrations have been determined in roofing asphalt ranging from 1 to 8 ppm, whereas roofing coal tar pitches revealed benzo[a]pyrene concentrations from 2,000 to 11,000 ppm (Lijinsky et al., 1963; Malaiyandi et al., 1981; Wallcave et al., 1971). Accordingly, ambient PAH-levels in the work environment of roofers differ drastically depending on the type of hot adhesive used (Malaiyandi et al., 1982).

During the course of the present study 17 individual PAH and alkyl-PAH have been identified in the roofing asphalt fumes. Phenanthrene and anthracene and their methyl- and dimethyl- alkylated analogues accounted for about 65% of the PAH-mass concentration identified. In contrast benzo[a]pyrene, a PAH typically monitored in roofing tar fumes (Niemeier et al., 1988; Malaiyandi et al., 1982; Williams et al., 1986), is found to contribute only 0.2% of the PAH-mass identified. Similar distribution patterns have been found in condensed asphalt tar fumes and in ambient air at roofing sites (Niemeier et al., 1988; Malaiyandi et al., 1981). In addition, heterocyclic aromatic hydrocarbons containing sulfur (S-PAH) such as dibenzothiophene and its methyl-substituted analogues have been identified at concentration levels similar to that of phenanthrene and its alkylated analogues. S-PAH show mutagenic potentials similar to other PAH, but due to their slightly increased polarity they are more soluble in water and more prone to aquatic bioaccumulation (Vassilaros et al., 1982; Willey et al., 1982).

Sterane and Triterpane Hydrocarbons

Fossil fuels such as coal and crude oil are the products of biogenic matter transformed by diagenesis and catagenesis over millions of years (Simoneit, 1984; Hunt, 1979; Tissot and Welte, 1984; Mackenzie et al., 1982). In geochemistry, steranes and triterpanes are commonly used as marker compounds to assess the maturity of crude oil and to trace its migration from the source rocks to the crude oil pockets (Hunt, 1979; Tissot and Welte, 1984). Steranes and triterpanoid hopanes have been identified in lubricating oils, vehicular exhaust, road dust, tire wear, and subsequently in airborne suspended particles (Simoneit, 1984, 1985; Simoneit et al., 1991; Rogge et al., 1993a-c). Among the spectrum of steranes and triterpanes present in petroleum, only those previously reported by Rogge et al. (1993b,c) have been quantified in the fine particulate asphalt tar fume samples. The results are summarized in Table 9.1. As shown by Rogge et al. (1993b) steranes and triterpanes can be used to trace the presence of motor vehicle exhaust in the urban atmosphere. The importance of the data on hopane and sterane emissions from roofing tar pots given in Table 9.1 is that these data help to quantify the magnitude of any possible interferences from roofing tar pot

Table 9.1 **Mass Concentration of Organic Compounds in the Fine Aerosol Emissions from Hot Asphalt Roofing Tar Pot Fumes.**

PART A	Emission Rates in $\mu g\ g^{-1}$	Compound[c] ID
	—*n*–Alkanes—	
n–tetradecane	3788.0	a
n–pentadecane	5827.0	a
n–hexadecane	5936.0	a
n–heptadecane	9659.0	a
n–octadecane	6231.0	a
n–nonadecane	3319.0	a
n–eicosane	3890.0	a
n–heneicosane	3042.0	a
n–docosane	2536.0	a
n–tricosane	1888.0	a
n–tetracosane	2396.0	a
n–pentacosane	2171.0	a
n–hexacosane	1040.0	a
n–heptacosane	496.5	a
n–octacosane	228.4	a
n–nonacosane	100.6	a
n–triacontane	64.6	a
n–hentriacontane	35.8	a
n–dotriacontane	17.9	a
Total class emission rate:	52666.8	
	—*n*–Alkanoic Acids[b]—	
n–heptanoic acid	87.1	a
n–octanoic acid	1043.0	a
n–nonanoic acid	1312.0	a
n–decanoic acid	2043.0	a
n–undecanoic acid	1263.0	a
n–dodecanoic acid	1081.0	a
n–tridecanoic acid	537.1	a
n–tetradecanoic acid (myristic acid)	894.9	a
n–pentadecanoic acid	362.4	a
n–hexadecanoic acid (palmitic acid)	2492.0	a
n–heptadecanoic acid	139.6	a
n–octadecanoic acid (stearic acid)	823.4	a
n–nonadecanoic acid	64.2	a
n–eicosanoic acid	89.8	a
n–heneicosanoic acid	28.5	a

Table 9.1 (continued)

PART B	Emission Rates in $\mu g\ g^{-1}$	Compound[a] ID
n–docosanoic acid	17.0	a
n–tricosanoic acid	7.3	a
n–tetracosanoic acid	8.3	a
Total class emission rate:	12293.6	
—*n*–Alkenoic Acid[b]—		
cis–9–octadecenoic acid (oleic acid)	338.8	a
Total class emission rate:	338.8	
— other Organic Acids[b]—		
3,5-dimethylbenzoic acid	97.2	b
2-methylbenzoic acid	38.9	b
3-methylbenzoic acid	124.6	b
4-methylbenzoic acid	477.7	a
benzeneactic acid	62.6	a
Total class emission rate:	801.0	
—Polycyclic Aromatic Hydrocarbons—		
dimethylnaphthalenes	604.6	a
phenanthrene	462.3	a
anthracene	130.3	a
methyl–(phenanthrenes, anthracenes)	844.5	b
dimethyl–(phenanthrenes, anthracenes)	751.8	b
fluoranthene	71.6	a
pyrene	136.9	a
benzacenaphthylene	11.4	b
2–phenylnaphthalene	46.2	b
methyl–(fluoranthenes, pyrenes)	124.9	b
benzo[a]fluorene/benzo[b]fluorene	61.2	a
benzo[ghi]flouranthene	4.3	b
benz[a]anthracene	24.8	a
chrysene/triphenylene	64.9	a
benzo[k]fluoranthene	11.7	a
benzo[b]fluoranthene	6.7	a
benzo[e]pyrene	6.0	a
benzo[a]pyrene	5.8	a
Total class emission rate:	3369.9	

Table 9.1 (continued)

PART C	Emission Rates in $\mu g\ g^{-1}$	Compound[a] ID
—Thia-Arenes—		
dimethylbenzo[b]thiophenes	244.6	a
dibenzothiophene	257.8	a
methyldibenzothiophene	629.9	b
dimethyldibenzothiophenes	1170.3	b
Total class emission rate:	2302.6	
—Regular Steranes—		
20S&R–5α(H),14β(H),17β(H)–cholestanes	113.9	b
20R–5α(H),14α(H),17α(H)–cholestane	101.4	a
20S&R–5α(H),14β(H),17β(H)–ergostanes	96.1	b
20S&R–5α(H),14β(H),17β(H)–sitostanes	34.0	b
Total class emission rate:	345.4	
—Pentacyclic Triterpanes—		
22,29,30–trisnorneohopane	34.1	b
17α(H),21β(H)-29-norhopane	54.8	b
17α(H),21β(H)-hopane	47.2	b
22S–17α(H),21β(H)-30-homohopane	21.7	b
22R–17α(H),21β(H)-30-homohopane	9.5	b
Total class emission rate:	167.3	

[a] for more details see text: a, positive; b, probable; c, possible; d, tentative.

[b] detected as methyl ester.

emissions when conducting a vehicular tracer analysis. For more details about fossil steranes and triterpanes the interested reader is refered to the literature cited above.

Estimated Roofing Tar Pot Emissions to the Los Angeles Atmosphere

Gray (1986) compiled an inventory for fine particulate organic carbon emissions within an 80 km x 80 km area centered over Los Angeles for the year 1982. A map of this study area is shown elsewhere; see Rogge et al. (1991). Roofing tar pot emissions are estimated to contribute on average 920 kg of fine particulate matter per day to the urban atmosphere within that study area. Because crude oil is the major fossil fuel processed and used in the Los Angeles area, it is a good assumption that asphalt-type roofing tars rather than coal tar pitches are used in Southern California.

Using Gray's overall emission estimate for roofing tar pot fumes along with the data of Table 9.1 of the present study and assuming that only asphalt-type roofing tars are used in the Los Angeles area, then the emissions of particular compound classes from roofing tar applications can be estimated for an average day during 1982; see Table 9.2. *n*-Alkanes constitute the dominant compound class released from roofing tar pot operations with daily emissions of 48.6 kg. In contrast PAH amount to 3.1 kg emitted daily. The daily PAH-emissions from built-up roofing would be appreciably higher if coal tar pitch instead of asphalt tar were used.

Recently, Rogge et al. (1993b) determined fine particle-associated vehicular PAH emissions within the 80 km x 80 km Los Angeles study area for 1982. Compared to the emissions from roofing tar use, the PAH emissions from catalyst-equipped vehicles (7.4 kg/day) are about threefold larger.

Table 9.2 **Estimated Fine Aerosol Emission Rates for Single Compound Classes Released from Hot Asphalt Roofing Tar Pot use within the Urbanized (80 km × 80 km) Los Angeles Study Area for 1982[a].**

Compound Class	Emission Rate (kg day^{-1})
n-Alkanes	48.6
n-Alkanoic Acids	11.3
n-Alkenoic Acids	0.031
Other Organic Acids	0.074
Polycyclic Aromatic Hydrocarbons (PAH)	3.1
Thia-Arenes (S-PAH)	2.1
Steranes	0.032
Pentacyclic Triterpanes	0.015
Total Identified	65.25

[a] Gray (1986) estimated that 920 kg/day of fine particulate matter is released within the study area from roofing tar pots where asphalt tar or coal tar pitch is used. Here, it is assumed that asphalt tar is used exclusively for construction of built-up roofs in the Los Angeles area, given that petroleum refineries provide a large local source of asphalt and coal is not used locally.

Instead, PAH-emissions from diesel automobiles plus heavy-duty diesel trucks (3.4 kg/day) are comparable to that from asphalt tar used to construct built-up roofs.

Conclusions

Fine organic aerosols are released with the hot fumes from asphalt tar that is commonly used as an adhesive for hot-process built-up roofs. The particulate organic compound emission rates from roofing tarpot use have been measured in the present study. Roughly 73% of the identifiable organic fine particulate mass consists of *n*-alkanes, which constitute the dominant compound class identified. Of the roofing asphalt tar fume aerosols collected 0.57% of the aerosol mass emitted consisted of PAH and S-PAH. When compared to the PAH content determined in fine particulate exhaust emitted from catalyst-equipped automobiles (~ 0.5%) and heavy-duty diesel trucks (~ 0.1%) (Rogge et al., 1993b), roofing tar pot aerosols show a PAH-content similar to that of vehicular exhaust.

If it is assumed that only asphalt tar is used for constructing built-up roofs in Southern California, then the daily PAH-emissions to the atmosphere of an 80 km × 80 km study area centered over Los Angeles area due to hot-process built-up roofing activities can be estimated at 3.1 kg/day. That is the same magnitude as the PAH emissions from all diesel vehicles in the same study area (3.4 kg/day). Because coal tar pitches are used as well for built-up roofs and show markedly increased PAH-contents, the daily PAH emission estimate provided here for asphalt use places a lower limit on PAH emitted from roofing operations to the Los Angeles atmosphere.

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Chapter 10

Boilers Burning No.2 Distillate Fuel Oil

Introduction

No.2 distillate fuel oil is commonly used for residential and commercial heating purposes and for steam and power generation in industrial utility boilers. The quality and composition of No.2 distillate fuel oil depends to a large degree on the type of crude oil refined. Although sulfur contents are typically kept low in No.2 fuel oil (0.1–0.4%) as a result of the desulfuration process, the content of aromatic compounds in the No.2 oil is typically directly proportional to the aromaticity found in the parent crude oils. Lee (1992) has shown that the particulate emission rate, when burning No.2 fuel oil, increases with the aromatics content and viscosity of the fuel oil. Goldstein and Siegmund (1976) as well as Hildemann et al. (1991a) have shown that there exists an optimal level of excess oxygen (as measured in the stack gas emissions) at which the particulate emission rate is at its minimum. In addition, it has been found that organic chlorine in the fuel burned promotes enhanced soot and PAH formation (e.g., Frenklach, 1990; Marr et al., 1992; McKinnon and Howard, 1990; Mulholland et al., 1993; Tsang, 1990). In contrast, organometallic additives, such as e.g., ferrocene derivatives, suppress soot formation (Mitchell, 1991; Somasundaram and Sunavala, 1989). Consequently, the chemical composition and particulate matter emission rate depends both on operating conditions and on the fuel batch burned.

In the present paper, an industrial-scale boiler burning No.2 fuel oil has been tested by dilution sampling, and the fine particulate matter collected from 2 out of 5 experiments has been analyzed to determine the organic compounds that are emitted. The purpose of this study is to provide detailed insight into the chemical nature of fine particulate organic matter emitted from oil-fired boilers that can be used along with the other studies in this series to provide quantitative input data needed by source-oriented models that relate organic aerosol emissions to ambient air quality.

Experimental Methods

Sampling

Fine particulate emissions were collected from an industrial boiler burning No.2 distillate fuel oil. The boiler was a Babcock & Wilcox Dual Fuel FM-type industrial-scale water tube boiler (steam production capacity of 53×10^{6} kJ/hr) equipped with a steam atomizer burner.

The oil-fired boiler tested was operated in steady state mode at about 60% of its capacity using a second boiler to adsorb the demand fluctuations. Sample collection was conducted using a dilution tunnel sampling system that was set up on the roof of the steam plant, as previously described in detail by Hildemann et al. (1989; 1991a). The stack was accessed from the roof via built-in sampling ports. The 1.1-m diameter stack was traversed twice during each experiment and samples taken from five equidistant points. The stack velocity was measured at each sampling point to allow isokinetic particle collection.

Five experiments were conducted with test durations ranging from 185 min to 375 min. The source testing program was executed over a period of three weeks with different batches of No.2 fuel oil. For more details see Hildemann et al. (1991a).

Hot emissions were withdrawn from the stack via a cyclone separator that removed particulate matter with an aerodynamic diameter of $> 10\ \mu$m. The remaining source effluent was drawn, using a heated inlet-line, into the sampling device dilution tunnel where the hot exhaust emissions were cooled and diluted with precleaned air (activated carbon filtered and HEPA-filtered). A portion of the diluted and cooled stack emissions were then diverted into a residence time chamber to allow gaseous organic compounds that would have condensed onto preexisting particulate matter in the atmospheric plume downwind of the source to equilibrate between gas- and particle-phase before sampling. Fine particulate matter was subsequently collected downstream of 8 AIHL-design cyclone separators operated in parallel, each connected to three 47-mm diameter filter holders which were used to sample particulate matter at a flow rate of 9.0 – 9.6 L/min per filter. Up to 18 filter holders were loaded with quartz fiber filters (Pallflex 2500 QAO) and the remaining filter holders contained Teflon filters (Gelman Teflo, 2.0-μm pore size). All quartz fiber filters were annealed at 750°C for 2-4h before use to ensure low organic contamination levels on the blank filter material.

Bulk Chemical Analysis

The emission rates of trace elements, ionic species, organic carbon (OC), and elemental carbon (EC) have been previously quantified are published elsewhere (Hildemann et al., 1991a).

Sample Extraction

An extraction scheme has been followed that originally was developed for the analysis of ambient fine organic particulate matter by Mazurek et al. (1987) and subsequently has been used in several studies (Mazurek et al., 1989, 1991;

Hildemann et al., 1991b; Rogge et al., 1991, 1993a-d). Briefly, the extraction protocol can be described as follows: Prior to sample extraction, perdeuterated tetracosane (n-$C_{24}D_{50}$) which served as an internal standard was spiked onto the filter composites. This internal standard should be applied in a quantity comparable to the organic compounds that are expected to be measured. In the present study, the amount of n-$C_{24}D_{50}$ added as an internal standard was estimated using the OC-data acquired from an EC/OC-combustion analysis of samples taken in parallel with those chosen for detailed organic chemical analysis.

The quartz fiber filter samples taken during each test were extracted together in a sequential procedure that included extraction twice with hexane (2 × 30 ml) followed by extraction three times with benzene/2-propanol (2:1 mixture, 3 × 30 ml). Each extraction sequence was conducted for 10-min and supported by mild ultrasonic agitation. Following each extraction step, the filter extracts were filtered and combined. 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 methoxy analogues. The sample extracts were stored in the dark at -21°C prior to GC/MS analysis.

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 supported 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 spectral data were acquired while operating the mass spectrometer in the electron impact mode (electron energy of 70eV). For supplemental studies a Varian 4600 high-resolution gas chromatograph (HRGC) with FID-detector was used that was operated with the same physical column and temperature program as used during GC/MS-analysis (Hildemann et al., 1991b). Additional information describing the analytical procedure can be found elsewhere (Mazurek et al., 1987, 1989; Rogge et al., 1991, 1993a,b).

Quality Assurance

A series of quality control and monitoring steps were followed. The major steps included field and laboratory blank testing, solvent testing to monitor for possible contaminants, recovery experiments for a large set of polar and nonpolar standard compounds, dilution air testing and more. For a detailed discussion, the reader is referred to accompanying source and ambient fine organic particle measurement studies published earlier (Mazurek et al., 1989; Rogge et al., 1991, 1993a,b).

Compound Identification and Quantification

Compound identification was conducted using the National Institute of Standards and Technology (NIST) mass spectral library accessed by the INCOS Data System, 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* — the sample mass spectrum, library 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.

The compound quantification process was based on the application of n-$C_{24}D_{50}$ as internal standard and 1-phenyldodecane as coinjection 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. (1991, 1993a).

Standard Compounds

Confirmation and quantification of organic compounds was obtained through the use of more than 150 authentic standards, see Rogge et al. (1993b). The following standard mixtures were injected onto the GC/MS-systems: (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 8 aromatic and polycyclic aromatic N– and S–substituted compounds; (9) steroids including cholesterol and cholestane; (10) a set of 4 phytosterols; (11) several natural resins; (12) plasticizers; (13) a suite of 11 aliphatic dicarboxylic acids ($C_3 - C_{10}$); and (14) one suite made up of 7 aromatic di- and tri- carboxylic acids all as their methyl ester analogues; and (15) other compounds.

Results and Discussion

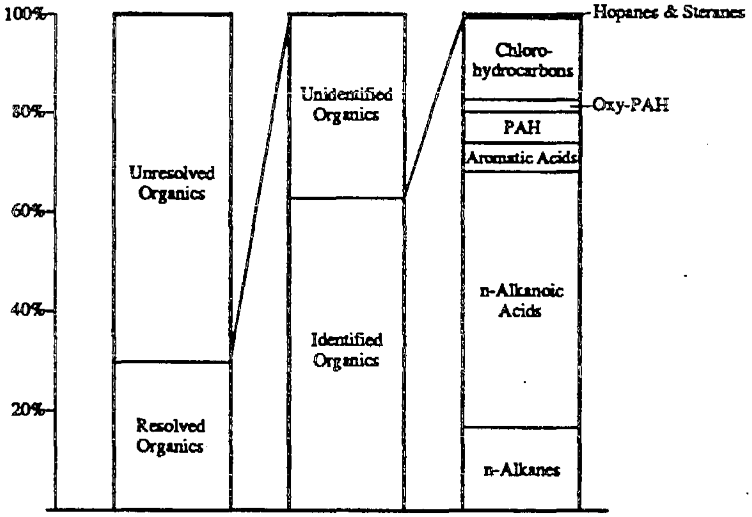
The industrial-scale boiler was tested burning different batches of No.2 fuel oil. To evaluate emission variations as a function of fuel batch, five consecutive tests were conducted over a 3 week time period. The fine particulate mass emission rates varied between the tests from 5 to 13 μg/kJ of fuel burned with an average fine particle emission rate of 9 (±3) μg/kJ. The fine particulate matter collected consisted on average of 32% sulfates, 29% elemental carbon (EC), 6% NH_4^+, 6% organic matter, and other materials (Hildemann et al., 1991). From prior studies it is known that the particulate emission rate and the composition of the fine particle organic matter depends on the excess oxygen in the stack gases, fuel batch used, and boiler operating conditions (Lee, 1992; Costa et al., 1991; Goldstein and Siegmund, 1976; Bennett et al., 1979; Barrett et al., 1973; Cato et al., 1976; Cato, 1976). In order to evaluate the range of fine particle organic compound mass emitted during typical boiler operation, 2 of the 5 test sample sets that revealed markedly different GC-traces were further subjected to a detailed investigation using GC/MS-techniques.

Mass Balance for Elutable Fine Particulate Organic Matter

For experiments No.2 and No.5 of this series, material balances have been constructed (Figure 10.1a,b) for the solvent extractable organic portion of the fine particulate matter collected during the boiler testing program. The organic matter that is both extractable and that will elute from the GC column used is comprised of resolved compounds (single chromatographically separated peaks) plus an unresolved complex mixture (UCM) that appears as a hump in the total reconstructed ion chromatogram (RIC). For both experiments, the portion of the organic matter that consists of resolved compounds is in the range 29.8 – 31.8%. For experiment No.2 (Figure 10.1a) the identifiable portion of the resolved organic matter is 62.8%, about twice as high as for experiment No.5 (Figure 10.1b).

The mass identified as particular organic compounds in both experiments is dominated by carboxylic acids (47.8–74.1%) of which *n*-alkanoic acids make up the biggest portion. Polycyclic aromatic hydrocarbons (PAH) and oxygenated polycyclic aromatic hydrocarbons (oxy-PAH) are more prominent in the particulate matter collected during experiment No.2 than during experiment No.5 (3.1 vs 8.6% of the identified compound mass), indicating that changes in fuel batch and operating conditions influence appreciably the amount of PAH and oxy-PAH formed (see also Table 10.1). Aside from typical hydrocarbons, fine particle associated chlorinated organic compounds have been identified in both experiments amounting to 5.8–16.4% of the identified organic compound mass emitted. In the following sections, the organic compound emission rates for both tests will be discussed and differences in concentrations between tests will be interpreted.

(a) GC/MS Elutable Organic Mass: Oil Boiler Experiment No. 2



(b) GC/MS Elutable Organic Mass: Oil Boiler Experiment No. 5

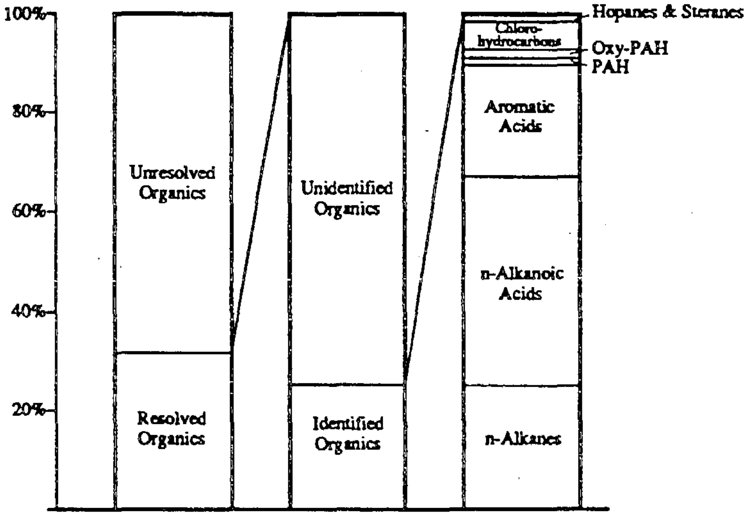


Fig. 10.1: Mass balance for elutable organic matter in the fine particle emissions from an industrial-scale boiler burning No.2 fuel oil: (a) experiment No.2, (b) experiment No.5.

Alkanes

Aliphatic hydrocarbons such as *n*-alkanes are common constituents in crude oils and are usually found up to C_{40+} with typically C_{22}–C_{25} as the most abundant homologues, followed by decreasing concentrations with further increases in weight (e.g., Bray and Evans, 1961; Kissin, 1987; Kvenvolden and Weiser, 1967; Simoneit, 1978; Tissot and Welte, 1984). The fine particulate organic matter emitted from the combustion of No.2 distillate oil contains *n*-alkanes ranging from C_{19}–C_{33} with C_{21} (experiment No.2) and C_{23} (experiment No.5) as the dominant *n*-alkanes. These *n*-alkanes either originated directly from fuel *n*-alkanes or indirectly from *n*-alkyl-substituted naphthenic and naphtho-aromatic fuel compounds that underwent mild thermo-cracking during oil combustion (Kissin, 1990). The total *n*-alkane emission rate during oil-fired boiler test No.2 was roughly 80% higher than was found for experiment No.5 (see Table 10.1) emphasizing the diversity in fuel oil composition.

Carboxylic Acids

Organic acids such as aliphatic *n*-alkanoic acids, aromatic acids and chlorine-substituted aromatic acids were identified in fine particulate matter emitted from the oil-fired boiler tested. *n*-Alkanoic acids, the most abundant compound class identified, showed a typical sawtooth pattern with even carbon numbered homologues predominating (see Table 10.1). The highest emission rates were for palmitic acid (C_{16}) and stearic acid (C_{18}). Only 2.2% of the *n*-alkanoic acids emitted showed carbon numbers $> C_{18}$; the main portion of the *n*-alkanoic acids mass identified has a molecular weight less than or equal to that of stearic acid. A similar *n*-alkanoic acid concentration pattern was found in emissions from other petroleum-based sources such as gasoline and diesel powered vehicles (Rogge et al., 1993b) and asphalt roofing tar pot fumes (Rogge et al., 1993f). Tire wear debris and road dust show a similar enrichment in lower molecular weight *n*-alkanoic acids (Rogge et al., 1993c). Consequently, ambient organic aerosol samples collected throughout Los Angeles reveal a similar concentration pattern (Rogge et al., 1993a).

Although the *n*-alkanoic acid concentration distributions for both oil-fired boiler experiments resemble each other, the emission rates for test No.2 were about three times higher than was found for test run No.5 (see Table 10.1). In contrast, aromatic acids such as benzoic acid and benzenedicarboxylic acids are more abundant in the emissions collected during experiment No.5. A different batch of No.2 distillate fuel oil and therefore modified combustion chemistry might provide a possible explanation for the observed differences in emissions.

Chlorinated Hydrocarbons

Chlorine-substituted aromatic compounds such as mono-, and dichlorohydroxybenzes, mono-, and dichlorobenzoic acids have been identified in the oil-fired boiler emissions (see Table 10.1). At this point, it is not clear if these chloro-organics are products from chlorinated organic precursor compounds or if they were simply synthesized from inorganic chlorine during combustion, or both. Oil desalting processes typically remove > 90% of the salts inherent in crude oils (Kirk-Othmer, 1988), so one expects that the chloride content of fuel oil will be quite low.

The inorganic chloride ion content of the oil-fired boiler aerosol was measured by ion chromatography (Hildemann et al., 1991a) and indicated that on average over all 5 experiments only 0.056% of the fine particulate mass emitted consisted of Cl^- (experiment No.2: 0.040% Cl^-; experiment No.5: 0.027% Cl^-). The total chloro-organic mass quantified in experiment No.5 amounted to only 12.7% of that found in experiment No.2; see Table 10.1.

Recently, Mulholland et al. (1993) pointed out that the pyrolysis of chlorinated organics during oil combustion leads to increased soot production and PAH formation. The PAH synthesis is promoted by initial chlorine-catalyzed organic compound degradation resulting in enhanced aryl radical formation that leads to increased aromatic condensation and subsequently PAH formation (Frenklach, 1990). PAH formation increases with a greater Cl/H-ratio in the fuel combusted. It was found that at low fuel Cl/H-ratios organic chlorine is mainly removed from the combustion process by HCl formation, at intermediate Cl/H-ratios of 0.3–0.6 mono- and dichlorinated aromatics are formed, and at high fuel Cl/H-ratios of 3 perchloroaromatics were synthesized (Mulholland et al., 1993). Consequently, with increased fuel chlorine content, not only are higher PAH emission levels observed but also possibly hazardous chlorinated compounds are generated.

Polycyclic Aromatic Hydrocarbons

Because No.2 distillate fuel oil (sulfur $< 0.4\%$) is commonly used for residential and commercial heating as well as commercial steam and power generation, one would like to know the emission rates of potentially mutagenic and carcinogenic compounds.

In the present study, individual PAH and alkyl-PAH have been identified in the exhaust emissions from both boiler experiments and are summarized in Table 10.1. The highest single PAH emission rate for experiment No.2 was found for chrysene and or triphenylene. Because the two PAH show a very similar mass fragmentation pattern and elute together from the column used, they can not be distinguished and therefore are mentioned together. Experiment No.5 in contrast to experiment No.2 revealed much lower PAH emission rates. Bennett et al. (1979) reported similar inter-experimental variations in PAH emissions from an oil-fired power plant burning different batches of residual fuel oil with a sulfur content of 2.5%. Further, comparing the emission ratio of PAH to that of chloro-organics between the two boiler tests conducted shows that changes in PAH and chloro-organics emissions track each other more closely than is the case for all other compound classes (PAH-test5/test2 = 1:12.7; chloro-organics–test5/test2: = 1:7.9).

Several factors could be responsible for the different PAH emission rates encountered between tests in the present study: (1) differences in fuel oil composition (e.g., aromaticity) and fuel oil properties (e.g., ***API***-Gravity) (Bennett et al., 1979; Lee, 1992); (2) boiler operating conditions (e.g., combustion air temperature, degree of flue gas recirculation, excess oxygen) (Cato, 1976; Goldstein and Siegmund, 1976; Hildemann et al., 1991a); and (3) the content of chlorinated compounds as discussed above (e.g., Frenklach, 1990; Marr et al., 1992; McKinnon and Howard, 1990; Mulholland et al., 1993; Tsang, 1990).

Polycyclic Aromatic Ketones and Quinones

Oxygenated polycyclic aromatic hydrocarbons (oxy-PAH) have been quantified in the oil-fired boiler aerosol. Emission rates are comparable to single PAH; see Table 10.1. Anthraquinone and 2-methylfluoren-9-one are predominant and roughly 2 to 5 times more abundant in the fine particulate matter collected during experiment No.2 than was found during experiment No.5. The relative change in oxy-PAH emissions from one test to the other is less pronounced than that of the normal PAH.

Hopanes and Steranes

Fossil fuels such as coal and crude oil are the products of biogenic matter transformed by diagenesis and catagenesis over millions of years (Simoneit, 1984; Hunt, 1979; Tissot and Welte, 1984; Mackenzie et al., 1982). In geochemistry, steranes and triterpanes are commonly used as marker compounds to assess the maturity of crude oil and to trace its migration from the source rocks to the crude oil pockets (Hunt, 1979; Tissot and Welte, 1984). Sterane and triterpanoid hopanes have been identified in lubricating oils, vehicular exhaust, road dust, tire wear, roofing tar pot fumes, and subsequently in airborne suspended particles (Simoneit, 1984, 1985; Rogge et al., 1993a-c,f). Among the large spectrum of steranes and triterpanes present in petroleum, only the major compounds previously reported by Rogge et al. (1993b) have been quantified in the fine particulate samples. The results are summarized in Table 10.1. For more details about fossil steranes and triterpanes the interested reader is referred to the literature cited above.

Table 10.1 Fine Aerosol Emission Rates for Single Organic Compounds from an Industrial-Scale Boiler Burning No.2 Distillate Fuel Oil.

PART A	Emission Rates[a] in pg kJ^{-1}		
	Experiment		Compound
	No. 2	No. 5	ID[b]
	— *n*–Alkanes —		
n–nonadecane	416.8	62.5	a
n–eicosane	654.6	112.3	a
n–heneicosane	718.6	170.6	a
n–docosane	567.7	266.8	a
n–tricosane	428.2	358.0	a
n–tetracosane	318.4	322.0	a
n–pentacosane	226.0	234.2	a
n–hexacosane	114.8	119.0	a
n–heptacosane	86.9	98.2	a
n–octacosane	49.9	45.1	a
n–nonacosane	65.1	92.2	a
n–triacontane	50.8	78.3	a
n–hentriacontane	19.3	47.0	a
n–dotriacontane	9.7	13.3	a
n–tritriacontane	7.1	4.0	a
Total class emission rate:	3733.9	2023.5	
	— *n*–Alkanoic Acids[c] —		
n–nonanoic acid	184.8	n.d.	a
n–decanoic acid	337.3	58.4	a
n–undecanoic acid	195.5	n.d.	a
n–dodecanoic acid	1349.4	157.2	a
n–tridecanoic acid	83.4	n.d.	a
n–tetradecanoic acid (myristic acid)	879.8	283.8	a
n–pentadecanoic acid	264.9	78.2	a
n–hexadecanoic acid (palmitic acid)	5717.3	1956.2	a
n–heptadecanoic acid	146.6	75.7	a
n–octadecanoic acid (stearic acid)	2104.4	715.3	a
n–nonadecanoic acid	71.2	n.d.	a
n–eicosanoic acid	66.3	41.0	a
n–heneicosanoic acid	16.0	n.d.	a
n–docosanoic acid	33.4	15.1	a
n–tricosanoic acid	9.0	n.d.	a
n–tetracosanoic acid	35.2	18.1	a
n–pentacosanoic acid	6.8	n.d.	a
n–hexacosanoic acid	10.8	n.d.	a
Total class emission rate:	11512.1	3399.0	

Table 10.1 (continued)

PART B	Emission Rates[a] in pg kJ^{-1}		
	Experiment		Compound
	No. 2	No. 5	ID[b]
— Aromatic Acids[c] —			
benzoic acid	898.7	1443.7	b
1,3-benzenedicarboxylic acid	217.4	243.4	a
1,4-benzenedicarboxylic acid	180.4	143.7	a
Total class emission rate:	1296.5	1830.8	
— Chloro–Hydrocarbons —			
1-chloro-4-hydroxybenzene	1035.7	58.1	b
1,3-dichloro-2-hydroxybenzene	163.2	179.4	b
3-chlorobenzoic acid[c]	2124.7	172.2	b
2,5-dichlorobenzoic acid[c]	349.8	55.9	b
Total class emission rate:	3673.4	465.6	
— Polycyclic Aromatic Hydrocarbons (PAH) —			
phenanthrene	75.9	19.1	a
anthracene	4.9	1.2	a
methyl–(phenanthrenes, anthracenes)	105.0	26.7	b
dimethyl–(phenanthrenes, anthracenes)	84.3	29.6	b
fluoranthene	119.4	9.0	a
pyrene	133.2	7.3	a
benzo[ghi]flouranthene	88.4	5.0	b
benz[a]anthracene	118.7	1.5	a
chrysene/triphenylene	414.6	11.0	a
benzo[k]fluoranthene	105.3	n.d.	a
benzo[b]fluoranthene	99.4	n.d.	a
benzo[e]pyrene	47.8	n.d.	a
benzo[a]pyrene	3.3	n.d.	a
Total class emission rate:	1400.2	110.4	

Table 10.1 (continued)

PART C	Emission Rates[a] in pg kJ^{-1}		
	Experiment		Compound
	No. 2	No. 5	ID[b]
— Polycyclic Aromatic Ketones (PAK) and Quinones (PAQ) —			
9H–fluoren-9-one (fluorenone)	32.3	25.0	a
2–methylfluoren-9-one	174.7	59.8	b
9,10–anthracenedione (anthraquinone)	297.9	48.5	a
1–H–benz[de]anthracen-1-one	8.8	3.5	b
7–H–benz[de]anthracen-7-one	24.1	4.0	b
Total class emission rate:	537.8	140.8	
— Regular Steranes —			
20R–5α(H),14α(H),17α(H)–cholestane	22.1	16.1	a
20S&R–5α(H),14β(H),17β(H)–ergostanes	50.4	34.8	b
20S&R–5α(H),14β(H),17β(H)–sitostanes	23.1	13.6	b
Total class emission rate:	95.6	64.5	
— Pentacyclic Triterpanes —			
22,29,30–trisnorneohopane	20.7	9.5	b
17α(H),21β(H)-29-norhopane	28.8	12.9	b
17α(H),21β(H)-hopane	42.1	24.2	b
22S–17α(H),21β(H)-30-homohopane	13.5	5.7	b
22R–17α(H),21β(H)-30-homohopane	7.2	4.8	b
22S–17α(H),21β(H)-30-bishomohopane	5.5	n.d.	b
22R–17α(H),21β(H)-30-bishomohopane	3.8	n.d.	b
Total class emission rate:	121.6	57.1	

[a] n.d. = not detected; accuracy determinations were performed for both polar and nonpolar standard compounds, showing that the relative standard deviations were between 4 to 8% depending on the amount of the standard compounds injected.

[b] for more details see text: a, positive; b, probable; c, possible; d, tentative.

[c] detected as methyl ester.

Conclusions

Organic compounds present in the fine particulate emissions from an industrial oil-fired boiler burning different batches of No.2 distillate fuel oil have been quantified by GC/MS techniques. Organic compounds including *n*-alkanes, *n*-alkanoic acids, aromatic acids, chlorinated hydrocarbons, PAH, oxy-PAH, and fossil petroleum compounds such as hopanes and steranes have been identified. Although the compound emission rates varies appreciably between the two boiler tests discussed here, the relative magnitude of the identified compound classes vary less dramatically. Carboxylic acids constitute the largest part (47.8–74.1%) of the total compound mass identified. PAH and oxy-PAH (3.1–8.6%) together with chlorinated hydrocarbons (5.8–16.4%) show the largest variations in emission rates between the two experiments reported here. The relative increase in chlorinated hydrocarbon emissions between tests is similar to the increase observed for PAH which may follow the results of laboratory experiments that suggest that the presence of chlorinated compounds can enhance PAH formation.

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Chapter 11

Pine, Oak, and Synthetic Log Combustion in Residential Fireplaces

Introduction

Wood combustion has been identified in earlier studies as a non-fossil fuel source (biofuel) that can contribute appreciably to the deterioration of ambient air-quality (Core et al., 1984; Hawthorne et al., 1992; Ramdahl et al., 1984; Sexton et al., 1984; Standley and Simoneit, 1987). Due to their mutagenic and carcinogenic potential, previous studies characterizing wood smoke emissions have focused on the identification of PAH-type compounds in wood smoke. (Claessens and Lammerts van Bueren, 1987; Freeman and Cattell, 1990; Guenther et al., 1988; Kleindienst et al, 1986; Kamens et al., 1984, 1985; Ramdahl, 1983; Ramdahl and Becher, 1982). In the present work, we seek a more complete description of the organic compounds found in wood smoke emissions, with particular emphasis on the detection of compounds that may serve as nearly unique tracers for the presence of woodsmoke in ambient aerosol samples.

To identify the contribution of wood smoke aerosols to ambient particle concentrations several different organic tracer compounds have been proposed including resin acids, retene, and methoxylated phenols (Edye and Richards, 1991; Ramdahl, 1983; Hawthorne et al., 1988, 1989; Standley and Simoneit, 1990; Simoneit et al., 1993; Simoneit and Mazurek, 1982). In addition to the potential wood smoke tracer compounds already mentioned, lignans (dimers of substituted phenols) recently have been suggested as wood smoke tracers that aid in distinguishing between coniferous versus deciduous wood fires (Simoneit et al., 1993).

In this study, combustion aerosols from pine and oak wood, as well as from synthetic logs have been characterized on a molecular level. That analysis provides source profiles that can be used to test whether or not certain organic compounds can be used to trace wood smoke aerosols in the urban atmosphere.

Experimental Methods

The wood combustion experiments were conducted in a single-family house using a traditional undampered brick fireplace that is typical of those found in Southern California. Each wood type (seasoned pine and oak wood) or synthetic log (Pine Mountain brand, 5lb) was burned in separate combustion experiments, typically over the course of about 3h for each experiment. To start the fire, a few pieces of newspaper were used. Kindling was exclusively made of the type of wood tested.

For the pine and oak wood fires, wood logs having weights from 1 kg to 6 kg were used. To mimic traditional undampered fires in residential fireplaces, wood logs were added to the fire at intervals and the fire was periodically stirred (wood burned per test: 12.5 kg to 20 kg). In contrast, the synthetic log was left burning undisturbed during testing according to the manufacturer's guidelines. For more details on the sampling procedure see Hildemann et al., 1991.

Smoke aerosols were withdrawn from the chimney at four different horizontal sampling points along the axis of the chimney and collected using the dilution sampling system described in the previous chapters. Fine particulate emission rates averaged over the course of each experiment ranged from 6.2 ± 0.3 g/kg of oak wood, 13.0 ± 4.1 g/kg of pine wood, and 12.0 g/kg of synthetic log burned.

Fine organic particulate emissions from the fireplace combustion of pine, oak, and synthetic logs have been analyzed on a compound by compound basis using GC/MS-techniques identical to those described in the previous chapters. Compounds either have been identified by comparison to authentic standards or by comparison to library mass spectra. Lignans have been identified by comparison to published mass spectra (Duffield, 1967; Pelter, 1967, 1968; Pelter et al., 1966). In general, lignans show strong molecular ions, facilitating the identification process (Simoneit et al., 1993).

Results and Discussion

Emissions from the combustion of any type of fuel depends directly on the chemical composition of the fuel and the combustion conditions. Upon their genesis, different species of trees show markedly different lignin constitutions. In temperate regions conifers are prolific resin acid producers, while deciduous trees, for example oak, are not. Synthetic logs are typically proprietary products manufactured using sawdust and petroleum waxes. Such differences in fuel composition will be seen to be directly reflected in the compounds emitted during the different source tests.

The results of the organic analyses of this study are summarized in Table 11.1. The total compound mass identified and quantified in this study resembles closely the trend observed for the fine particulate emission rates. Fireplace combustion of oak wood produces the lowest emission rates with 620 mg of total identified compound mass released per kg of oak wood burned. In comparison, pine wood combustion shows for the same compound classes an emission rate roughly 40% higher (912 mg/kg). Synthetic logs release identifiable organic matter at emission rates higher (1300 mg/kg) than was found for pine or oak.

On a detailed molecular level, the emissions of *n*-alkanes, *n*-alkenes, cyclohexylalkyls, *n*-alkanals, PAH, and oxy-PAH are highest for the synthetic log combustion. Per kg of material burned, synthetic logs produce PAH emission rates that are somewhat higher than was found for pine wood and roughly two times higher than for oak wood. Even though synthetic logs show the highest PAH emission rates per kg of wood burned, it is possible that the emission rate per unit time that such fires burn is lower than for oak or pine. That is because one synthetic log of 2.3 kg is burned typically over a 3-hour period. In contrast, a natural wood fire could easily consume 12 to 20 kg of wood over the same 3-hour period.

Carboxylic acids such as *n*-alkanoic acids, and *n*-alkenoic acids show emission rates per kg of fuel burned that are comparable for all three fireplace fuels. Unaltered natural resin acids (e.g., abietic, pimaric, and *iso*-pimaric acids) and their partially altered combustion products (e.g., dehydroabietic acid) instead show highest concentrations when burning pine wood. Small amounts of dehydroabietic acid also have been found during the oak wood burning experiments conducted here. Because oak wood typically does not contain resinous compounds, there might have been some carry over of compounds evolved from soot deposits on the chimney walls due to previous fires burning pine wood in the same fireplace.

The synthetic logs burned during the present experiments show no traces of resin acids. On the contrary retene (1-methyl-7-isopropylphenanthrene), a pyrolysis product of resin diterpenoids that have an abietane skeleton (including resin acids such as abietic, dehydroabietic, pimaric acid, and others; Ramdahl, 1983; Simoneit and Mazurek, 1982), is substantially more abundant in the synthetic log smoke than in pine or oak smoke aerosol emissions. This indicates that the slow combustion process inherent with synthetic logs produces an enhanced tendency to pyrolyze log constituents, which is also expressed in the form of the increased PAH-emissions from such logs.

Lignin, a biopolymer and major part of woody tissue is typically made up of aromatic phenol/alcohols such as *p*-coumaryl, coniferyl, and sinapyl alcohols (e.g., Simoneit et al., 1993).. The lignin of gymnosperms (e.g., pine) is primarily derived from coniferyl-alcohol type compounds, whereas the lignin of angiosperms (e.g., oak) is enriched in products from sinapyl alcohols. Upon combustion of wood, lignin breakdown products include hydroxylated and methoxylated phenols that often preserve the original substituents on the phenyl ring. From Table 11.1 it can be seen that phenolic compounds with two substituents are typically favored in pine smoke (coniferyl type), whereas phenolic compounds with three substituents are mainly found in oak wood smoke (sinapyl type).

In addition to combustion products derived from lignins, lignans that are a part of woody plants also were identified. Lignans are basically dimers of coniferyl and sinapyl alcohols and are found mainly in pine wood smoke including compounds such as divanillyl, tetrahydro-3,4-divanillylfuran, matairesinol, and others, see Table 11.1. Dimers related to sinapyl type compounds are bisguaiacylsyringyl and disyringyl and are exclusively found in the smoke from oak wood.

Likely Woodsmoke Markers

Of the wood smoke compounds identified in the present study, all resin acids, except abietic acid, have been identified in the ambient aerosol samples characterized in Chapter 2. Atmospheric fine particulate resin acid concentrations are dominated by dehydroabietic acid, and show a sesonal pattern that follows closely the seasonal use of wood for space heating. Such diterpenoid acids, especially dehydroabietic acid, *iso*-pimaric acid, and pimaric acid have been used in the past to evaluate the impact on ambient air quality of wood use for heating purposes (Hawthorne et al., 1988; Standley and Simoneit, 1987, 1990; Ramdahl, 1983).

Although retene is expected to be an endproduct of the aromatization and decarboxylation process ongoing during combustion, it has been detected only in trace amounts in the Los Angeles atmosphere. This is in good agreement with the low retene emission rates found in this study for the fireplace combustion of pine and oak wood.

Conclusions

The fine particulate emissions from combustion of wood fuels typically used in the Los Angeles area have been examined on a molecular level. Together, more than 100 organic compounds have been identified ranging from aliphatic compounds (e.g., *n*-alkanes) to aromatic compounds (e.g., PAH). The data set provided can be used to determine the compound by compound contributions of wood combustion to the urban atmosphere, provided that it is known how much wood is burned in a given time in the area of interest. Ambient fine aerosol data have been presented in Chapter 2 that include wood smoke related compounds such as resin acids. Those data can be used to calculate the contribution of wood smoked to the urban atmosphere via molecular tracer techniques.

Table 11.1 Emission Rates for Organic Compounds released from Burning Pine Wood, Oak Wood, and Synthetic Logs in Residential Fireplaces.

Emission Rates[a] in mg kg^{-1} of Logs Burned

PART A	Pine Wood	Oak Wood	Synthetic Logs	Compound ID[b]
	— *n*-Alkanes—			
nonadecane	n.d.	n.d.	8.80	a
eicosane	n.d.	n.d.	21.74	a
heneicosane	0.44	0.32	15.98	a
docosane	0.45	0.28	16.41	a
tricosane	0.41	0.41	19.94	a
tetracosane	0.29	0.26	20.24	a
pentacosane	0.28	0.25	18.03	a
hexacosane	0.36	0.20	17.74	a
heptacosane	0.47	0.094	18.18	a
octacosane	0.41	0.13	17.58	a
nonacosane	0.61	0.15	17.62	a
triacontane	0.42	0.089	17.19	a
hentriacontane	0.48	0.077	18.84	a
dotriacontane	0.19	n.d.	18.97	a
tritriacontane	0.13	0.027	23.63	a
tetratriacontane	0.12	0.023	29.45	a
pentatriacontane	n.d.	n.d.	37.53	a
hexatriacontane	n.d.	n.d.	39.22	a
heptatriacontane	n.d.	n.d.	44.15	b
octatriacontane	n.d.	n.d.	45.36	b
nonatriacontane	n.d.	n.d.	42.87	b
tetracontane	n.d.	n.d.	38.01	b
Total class emission rate:	5.06	2.31	547.48	
	— *n*-Alkenes—			
nonadecene	n.d.	n.d.	12.48	b
eicosene	n.d.	n.d.	18.11	b
heneicosene	n.d.	n.d.	24.40	b
docosene	n.d.	n.d.	19.98	b
tricosene	n.d.	n.d.	20.67	b
tetracosene	n.d.	n.d.	22.96	b
pentacosene	n.d.	n.d.	23.99	b
hexacosene	n.d.	n.d.	21.92	b
heptacosene	n.d.	n.d.	19.13	b
octacosene	n.d.	n.d.	14.81	b
nonacosene	n.d.	n.d.	10.88	b
triacontene	n.d.	n.d.	14.55	b
hentriacontene	n.d.	n.d.	10.32	b

Table 11.1 (continued)

Emission Rates[a] in mg kg^{-1} of Logs Burned

PART B	Pine Wood	Oak Wood	Synthetic Logs	Compound ID[b]
dotriacontene	n.d.	n.d.	8.29	b
tritriacontene	n.d.	n.d.	5.70	b
tetratriacontene	n.d.	n.d.	5.34	b
pentatriacontene	n.d.	n.d.	5.19	b
hexatriacontene	n.d.	n.d.	5.97	b
heptatriacontene	n.d.	n.d.	4.40	b
octatriacontene	n.d.	n.d.	4.38	b
nonatriacontene	n.d.	n.d.	4.31	b
tetracontene	n.d.	n.d.	3.82	b
Total class emission rate:			281.60	
— Cyclohexylalkanes —				
cyclohexylpentacosane	n.d.	n.d.	0.77	b
cyclohexylhexacosane	n.d.	n.d.	0.71	b
cyclohexylheptacosane	n.d.	n.d.	0.75	b
cyclohexyloctacosane	n.d.	n.d.	1.77	b
cyclohexylnonacosane	n.d.	n.d.	3.13	b
cyclohexyltriacontane	n.d.	n.d.	4.17	b
cyclohexylhentriacontane	n.d.	n.d.	3.99	b
cyclohexyldotriacontane	n.d.	n.d.	2.59	b
cyclohexyltritriacontane	n.d.	n.d.	2.18	b
cyclohexyltetratriacontane	n.d.	n.d.	1.17	b
Total class emission rate:			21.23	
—*n*-Alkanals —				
nonanal	n.d.	n.d.	2.97	a
decanal	n.d.	n.d.	1.13	b
undecanal	n.d.	n.d.	0.94	b
dodecanal	n.d.	n.d.	2.25	b
tridecanal	n.d.	n.d.	n.d.	b
tetradecanal	n.d.	n.d.	4.12	b
pentadecanal	n.d.	n.d.	8.02	b
hexadecanal	n.d.	n.d.	6.15	b
heptadecanal	n.d.	n.d.	9.19	b
octadecanal	n.d.	n.d.	13.48	b
nonadecanal	n.d.	n.d.	8.82	b
eicosanal	n.d.	n.d.	12.54	b
heneicosanal	n.d.	n.d.	14.64	b
docosanal	n.d.	n.d.	20.21	b
tricosanal	n.d.	n.d.	17.21	b

Table 11.1 (continued)

Emission Rates[a] in mg kg^{-1} of Logs Burned

PART C	Pine Wood	Oak Wood	Synthetic Logs	Compound ID[b]
tetracosanal	n.d.	n.d.	16.27	b
pentacosanal	n.d.	n.d.	14.56	b
hexacosanal	n.d.	n.d.	13.89	b
heptacosanal	n.d.	n.d.	16.28	b
octacosanal	n.d.	n.d.	20.59	b
nonacosanal	n.d.	n.d.	31.95	b
triacontanal	n.d.	n.d.	41.17	b
hentriacontanal	n.d.	n.d.	39.76	b
dotriacontanal	n.d.	n.d.	31.60	b
Total class emission rate:			347.74	
	—*n*-Alkanoic Acids[c]—			
nonanoic acid	n.d.	0.24	0.97	a
decanoic acid	0.095	0.39	0.70	a
undecanoic acid	n.d.	n.d.	0.82	a
dodecanoic acid	1.85	1.65	1.41	a
tridecanoic acid	n.d.	n.d.	1.26	a
tetradecanoic acid	1.74	4.89	2.27	a
pentadecanoic acid	0.85	1.55	2.64	a
hexadecanoic acid	13.91	21.46	10.11	a
heptadecanoic acid	1.62	2.55	1.79	a
octadecanoic acid	4.31	3.33	2.33	a
nonadecanoic acid	0.51	0.41	0.93	a
eicosanoic acid	6.46	2.59	1.46	a
heneicosanoic acid	5.15	1.50	0.92	a
docosanoic acid	7.98	4.65	0.99	a
tricosanoic acid	1.63	2.16	0.55	a
tetracosanoic acid	9.87	13.89	1.70	a
pentacosanoic acid	0.85	1.29	0.80	a
hexacosanoic acid	1.55	6.76	0.67	a
heptacosanoic acid	0.096	0.33	0.49	a
octacosanoic acid	0.15	0.64	0.49	a
nonacosanoic acid	n.d.	0.098	0.38	a
triacontanoic acid	n.d.	0.079	0.29	a
Total class emission rate:	58.621	70.457	33.97	

Table 11.1 (continued)

Emission Rates[a] in mg kg^{-1} of Logs Burned

PART D	Pine Wood	Oak Wood	Synthetic Logs	Compound ID[b]
—*n*-Alkenoic Acids[c]—				
cis-9–octadecenoic acid (oleic acid)	7.62	1.15	0.93	a
9,12-octadecadienoic acid (linoleic acid)	8.35	1.45	n.d.	a
Total class emission rate:	15.97	2.60	0.93	
— Dicarboxylic Acids[c]—				
propanedioic acid	38.35	n.d.	n.d.	a
butanedioic acid	0.89	11.68	n.d.	a
methylbutanedioic acid	n.d.	3.35	n.d.	a
pentanedioic acid	6.65	5.44	n.d.	a
hexanedioic acid	0.63	1.75	n.d.	a
Total class emission rate:	46.52	22.22		
— Resin Acids[c]—				
abietic acid	1.06	n.d.	n.d.	b
dehydroabietic acid	37.23	5.60	n.d.	a
13-isopropyl-5α-podocarpa-6,8,11,13--tetraen-16-oic acid	2.02	n.d.	n.d.	b
8,15-pimaradien-18-oic acid	4.02	n.d.	n.d.	b
pimaric acid	24.17	n.d.	n.d.	a
iso-pimaric acid	6.55	n.d.	n.d.	b
7-oxodehydroabietic acid	3.31	n.d.	n.d.	a
sandaracopimaric acid	47.03	n.d.	n.d.	b
Total class emission rate:	125.39	5.60		
—Other Acids[c] —				
2-furancarboxylic acid	3.02	1.77	n.d.	b
2-hydroxybenzoic acid[d]	4.28	7.53	n.d.	b
3,4-dimethoxybenzoic acid (veratric acid)[e]	65.04	18.68	0.69	a
3,4-dimethoxyphenylacetic acid (homoveratric acid)	5.72	n.d.	n.d.	a
4-hydroxy-3-methoxyphenylacetic acid (homovanillic acid)	82.82	15.02	n.d.	a
3,4,5-trimethoxybenzoic acid[f]	n.d.	22.57	n.d.	a
Total class emission rate:	160.88	66.57	0.69	

Table 11.1 (continued)

PART E	Emission Rates[a] in mg kg^{-1} of Logs Burned			
	Pine Wood	Oak Wood	Synthetic Logs	Compound ID[b]
—Hydroxylated/Methoxylated Phenols —				
1,4-benzenediol (hydroquinone)[g]	61.78	22.52	n.d.	b
1,3-benzenediol (resorcinol)[h]	3.33	3.54	n.d.	b
3-methyl-1,2-benzenediol (3-methylcatechol)[i]	34.94	13.27	n.d.	b
4-methyl-1,2-benzenediol (4-methylcatechol)[j]	19.53	3.33	n.d.	a
4-propyl-benzenediol[k]	18.75	n.d.	n.d.	b
2-methyl-5-(1-methylethyl)-2,5-cyclohexadien--1,4-dione (thymoquinone)	0.58	n.d.	n.d.	b
2-methoxy-4-(2-propenyl)phenol (eugenol)	1.54	n.d.	n.d.	b
2-methoxyphenol (guaiacol)	0.21	0.067	n.d.	b
2-methoxy-3-methylphenol (3-methylguaiacol)	0.78	0.042	n.d.	b
2-methoxy-4-propylphenol (1-guaiacylpropane)	19.53	3.37	n.d.	b
2-methoxy-5-(1-propenyl)phenol	8.04	0.16	n.d.	b
2,6-dimethoxyphenol (syringol)	1.13	10.81	n.d.	a
1-(4-methoxyphenyl)ethanone	5.19	3.78	n.d.	b
3,4-dimethoxyphenylacetone (veratrylacetone)	10.41	6.34	n.d.	b
1-(2,4-dimethoxyphenyl)propan-2-one	8.98	2.37	n.d.	b
1-(4-hydroxy-3-methoxyphenyl)ethan-2-one (guaiacylacetone)	36.27	3.63	0.78	b
1-(4-hydroxy-3-methoxyphenyl)propan-2-one	39.32	10.73	0.79	b
1-(3,5-dimethoxy-4-hydroxyphenyl)ethan-2-one	n.d.	55.52	15.79	a
1-(3,5-dimethoxy-4-hydroxyphenyl)propan-2-one (1-syringylpropanone)	n.d.	20.82	5.93	b
2,6-dimethoxy-4-(2-propenyl)phenol	n.d.	1.98	n.d.	b
1-(3,4,5-trimethoxyphenyl)ethan-2-one	n.d.	35.61	5.55	b
1-(3,4,5-trimethoxyphenyl)propan-2-one	n.d.	80.27	n.d.	b
dimers				
bis(3,4-dimethoxyphenyl)methane	6.34	0.81	n.d.	b
divanillyl	22.25	2.38	n.d.	b
tetrahydro-3,4-divanillylfuran	22.87	0.60	n.d.	b
tetrahydro-3-vanillyl-4-veratrylfuran	8.93	0.35	n.d.	b
matairesinol	2.78	n.d.	n.d.	b
dihydro-3,4-diveratryl-2(3H)-furanone	2.24	n.d.	n.d.	b
tetrahydro-3,4-diveratrylfuran	3.84	0.13	n.d.	b
dihydrovanillylsyringol-2(3H)-furanone	4.93	n.d.	n.d.	b
bisguaiacylsyringyl	n.d.	3.08	n.d.	b
disyringyl	n.d.	7.10	n.d.	b
bis(3,4,5-trimethoxyphenyl)ethane	n.d.	0.77	n.d.	b
Total class emission rate:	344.49	293.379	28.84	

Table 11.1 (continued)

Emission Rates[a] in mg kg^{-1} of Logs Burned

PART F

	Pine Wood	Oak Wood	Synthetic Logs	Compound ID[b]
— Substituted Benzenes/Benzaldehydes —				
1,2-dimethoxybenzene (veratrole)	2.96	1.89	n.d.	a
1,3-dimethoxybenzene	1.02	1.84	n.d.	b
1,4-dimethoxybenzene	n.d.	1.52	n.d.	b
1,4-dimethoxy-2-methylbenzene	28.12	n.d.	n.d.	b
3-methoxy-4-hydroxybenzaldehyde (vanillin)	29.27	2.05	n.d.	a
3-methoxybenzaldehyde	0.74	n.d.	n.d.	b
3,4-dimethoxybenzaldehyde (veratraldehyde)	22.62	4.60	n.d.	a
4-hydroxy-3,5-dimethoxybenzaldehyde (syringaldehyde)	n.d.	66.61	15.86	a
3,4,5-trimethoxybenzaldehyde	n.d.	62.42	5.28	a
Total class emission rate:	84.73	140.93	21.14	
— Phytosterols —				
β-sitosterol	45.50	9.94	n.d.	a
stigmast-4-en-3-one	2.87	1.29	n.d.	b
Total class emission rate:	48.37	11.23		
—Polycyclic Aromatic Hydrocarbons (PAH)—				
phenanthrene	0.47	0.30	0.46	a
anthracene	0.051	0.057	0.07	a
methyl–(phenanthrenes, anthracenes)	n.d.	n.d.	0.75	b
dimethyl–(phenanthrenes, anthracenes)	n.d.	n.d.	0.79	b
1-methyl-7-isopropylphenanthrene (retene)	0.68	0.11	2.72	a
fluoranthene	1.24	0.40	0.70	a
pyrene	1.59	0.53	0.94	a
benzacenaphthylene	0.57	0.16	0.24	b
2–phenylnaphthalene	n.d.	n.d.	0.21	b
methyl–(fluoranthenes, pyrenes)	1.19	0.33	0.99	b
benzo[a]fluorene/benzo[b]fluorene	0.056	0.11	0.56	a
benzo[ghi]fluoranthene	0.27	0.11	0.24	a
cyclopenta[cd]pyrene	0.72	0.23	n.d.	a
benzo[c]phenanthrene	0.15	0.033	n.d.	a
benz[a]anthracene	0.63	0.21	0.38	a
chrysene/triphenylene	0.98	2.83	0.75	a
methyl–(benz[a]anthracenes, chrysenes, triphenylenes)	n.d.	n.d.	0.56	b
dimethyl–(fluoranthenes, pyrenes)	n.d.	n.d.	0.78	b
benzo[k]fluoranthene	0.51	0.26	0.51	a
benzo[b]fluoranthene	0.53	0.21	0.42	a

Table 11.1 (continued)

Emission Rates[a] in mg kg^{-1} of Logs Burned

PART G	Pine Wood	Oak Wood	Synthetic Logs	Compound ID[b]
benzo[j]fluoranthene	0.28	0.11	0.14	a
benzo[e]pyrene	0.30	0.13	0.44	a
benzo[a]pyrene	0.62	0.23	0.40	a
perylene	0.12	0.038	0.043	a
indeno[1,2,3-cd]pyrene	0.087	0.047	0.10	a
indeno[1,2,3-cd]fluoranthene	0.35	0.15	0.26	a
benzo[ghi]perylene	0.32	0.13	0.52	a
anthanthrene	0.12	0.039	n.d.	a
dibenz[a,h]anthracene	0.079	0.012	0.045	a
benzo[b]triphenylene	n.d.	n.d.	0.19	b
coronene	n.d.	n.d.	0.10	a
Total class emission rate:	11.913	6.766	14.318	
—Polycyclic Aromatic Ketones (PAK) and Quinones (PAQ)—				
1H-phenalen-1-one	1.87	0.81	0.75	b
9,10-phenanthrenedione (phenanthrenequinone)	n.d.	n.d.	0.38	a
1H-benz[de]anthracen-1-one	0.13	0.076	n.d.	a
7H-benz[de]anthracen-7-one	0.50	0.19	0.30	a
6H-benzo[cd]pyren-6-one (benzo[cd]pyrenone)	n.d.	n.d.	0.11	b
Total class emission rate:	2.50	1.076	1.54	

[a] n.d. = not detected.

[b] for more details see text. a, positive: authentic std. verification; b, probable: library spectrum verification;c, possible; d, tentative.

[c] detected as methyl ester.

[d] determined as 2-methoxybenzoic acid (o-Anisic acid).

[e] could also have been originally 4-hydroxy-3-methoxybenzoic acid (vanillic acid) or both due to the methylation step.

[f] could also have been originally 4-hydroxy-3,5-dimethoxybenzoic acid (syringic acid) or both due to the methylation step.

[g] determined as 2-methoxyphenol in the methylated fraction only.

[h] determined as 3-methoxyphenol in the methylated fraction only.

[i] determined as 2-methoxy-3-methylphenol in the methylated fraction only.

[j] determined as 2-methoxy-4-methylphenol in the methylated fraction only.

[k] determined as 2-methoxy-4-propylphenol in the methylated fraction only.

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Chapter 12

Comparison of Fine Particulate Organic Compound Emissions to Atmospheric Concentrations for the Los Angeles Study Area

Introduction

In the present research, unique data sets on the organic chemical composition of both source effluents and atmospheric fine particulate matter have been developed. These data sets provide new opportunities to test our current understanding of the relationships between emissions and air quality for organic aerosols.

In the present chapter, a comprehensive emission inventory for more than 400 organic compounds that are present in primary organic aerosol emissions first will be assembled for an 80 km × 80 km study area centered over Los Angeles, CA. That study area is mapped in Figure 3.5 of Chapter 3 of this work. The combined emissions from the major primary organic aerosol sources acting together first will be compared to measured pollutant concentrations. It will be seen that there is an obvious and close correspondence between these two data sets for the case of the least chemically reactive compounds studied. Evidence for the production of secondary organic aerosols and for the degradation of primary organic species by volatilization and/or chemical reaction will be sought through examination of the source and ambient data sets.

Prior Emission Inventory Development

An air quality model has been applied by Gray (1986) to predict monthly average concentrations of fine particulate elemental carbon (EC) and total carbon (TC) at seven urban monitoring sites within the Los Angeles study area for the year 1982.

As part of the input data prepared for that model simulation, an inventory of fine carbon particle emissions was compiled for mobile as well as stationary sources that are located within the 80 km by 80 km modeling domain shown in Figure 3.5. The spatial and temporal distribution of emissions was estimated for over 70 different source types. Emissions from major point sources were assigned to the actual locations of those sources. Residential source emissions were distributed throughout the grid system in proportion to population density. Vehicular exhaust emissions were allocated to the grid system in proportion to traffic densities observed on surface streets and freeways. For all other source classes the source locations and emissions strengths were extracted from a spatially distributed emission inventory forecast provided by the California Air Resources Board (see Gray, 1986).

Recently, Hildemann (1990) used the same model and meteorological data to predict primary organic aerosol characteristics from measured source emissions. To complement the ambient sampling program conducted by Gray in 1982, the major urban source types were tested that together represent close to 80% of the primary organic carbon emissions to the Los Angeles atmosphere. These source test results were used to modify the OC-emission inventory complied originally by Gray (1986). That revised emission inventory is shown in Table 12.1. The organic aerosol characteristics of both source samples and ambient samples were

Table 12.1 Estimate of Fine Aerosol Organic Carbon (OC) Emissions within the 80 × 80 km Study Area Centered over Los Angeles for 1982.

Source Type	OC emitted kg/day	Profile No. of Source tested in this study	Source Profile used to represent source within the inventory[a]
(1) Meat-cooking operations			
Charbroiling	4938	1,2[b]	1
Frying	1393	3	3
(2) Paved road dust	4728	4	4
(3) Fireplaces			
Pine wood	3332	5	5
Oak wood	840	6	6
Synthetic logs	n.k.	7	7
(4) Noncatalyst gasoline vehicles			
Automobiles	2088	8	8
Other vehicles[c]	1372		8
(5) Diesel vehicles			
Heavy-duty trucks	1242	9	9
Other vehicles[d]	617		9
(6) Surface Coating	1433		
(7) Forest Fires	877		
(8) Cigarettes	802	10	10
(9) Catalyst-equipped gasoline vehicles			
Automobiles	780	11	11
Other vehicles[e]	79		11
(10) Organic chemical processes	692		
(11) Brake lining	690	12	12
(12) Roofing tar pots	556	13	13
(13) Tire wear	414	14	14
(14) Misc industrial point sources	393		
(15) Natural gas combustion			
Residential/commercial	30	15	15
Other sources[f]	262		15
(16) Misc petroleum industry processes	278		
(17) Primary metallurgical processes	228		
(18) Railroad (diesel oil)	211		9
(19) Residual oil stationary sources[g]	206		16
(20) Refinery gas combustion	195		15
(21) Secondary metallurgical processes	167		
(22) Mineral industrial processes	158		
(23) Other organic solvent use	106		
(24) Jet aircraft	92		
(25) Asphalt roofing manufacturing	81		13
(26) Coal burning	76		
(27) Wood processing	74		

Source Type	OC emitted kg/day	Profile No. of Source tested in this study	Source Profile used to represent source within the inventory[a]
(28) Residual oil-fired ships	66		
(29) Structural fires[h]	63		5
(30) Distillate oil stationary sources			
Industrial[i]	13	16	16
Other[j]	23		16
(31) Vegetative detritus			
Green leaf abrasion products[k]	n.k.	17	17
Dead leaf abrasion products	n.k.	18	
(32) Other sources[l]	226		8,9,15,16
Total	29822		

n.k. = not known

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

[b] profile No. 1: charbroiling regular hamburger meat with a fat content of 21%; profile No. 2: charbroiling extra-lean meat with a fat content of 10%.

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

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

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

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

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

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

[i] the average compound emission rates from two single source tests are used (see Rogge et al, 1993h).

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

[k] for model calculations only the source profile derived from green leaf abrasion products is used (see Rogge et al., 1993).

[l] other sources include: Diesel powered ships, electric utilities burning distillate oil, refinery processes, industrial boilers burning LPG, industrial internal combustion engines using gasoline (for more details see Gray, 1986).

defined through measurements of elutable organic matter as detected by a high resolution gas chromatograph (GC) equipped with a flame ionization detector system (Hildemann, 1990). A 52–parameter "fingerprint" was constructed to characterize the emissions from each source type by measuring the quantity of the organic compounds in both the non-polar and polar fractions of each source sample that elutes from the GC column between the successive elution points of the C_{12} to C_{36} n-alkanes. The data on the mass emissions from each source type within each GC elution zone defined above were entered into the air quality model. The model then was used to predict the characteristic distribution of organic aerosol mass as a function of polarity and elution time that would be found in ambient air if these source effluents were transported without chemical reaction. Model results were compared against high resolution GC measurements of ambient samples taken at West Los Angeles, downtown Los Angeles, and Pasadena. More details regarding the source "fingerprinting" technique and modeling results can be found in the work by Hildemann (1990).

Present Application

In the present study, ambient concentrations of individual organic compounds are compared to the relative abundance of single compounds present in the emissions from all fine particle sources acting together. The OC-emission inventory originally compiled for Los Angeles by Gray (1986) and updated by Hildemann et al. (1991) is combined with the chemical characterization of the emissions from each source that was presented in Chapters 3 – 11 of this work. The relative abundance of organic compounds present in that emissions inventory then is compared to the measured ambient organic compound concentrations reported in Chapter 2.

Organic Compound Aerosol Source Profiles

The fine particle samples collected during the source testing campaign by Hildemann et al. (1991) were analyzed using GC/MS-techniques (Rogge et al., 1991, 1993b-i). Organic chemical composition profiles for eighteen source types were generated that together include roughly 400 different organic compounds.

Ambient samples used in this study were collected by Gray et al. (1986) at West Los Angeles, downtown Los Angeles, Pasadena, and Rubidoux (outside the modeling region to the east) during the year 1982. The filter samples were composited month by month prior to analysis. All fine particle samples, including the source and ambient samples were collected using comparable equipment and materials and were processed by the same analytical extraction technique that was originally developed by Mazurek et al. (1987, 1989). All source and ambient samples were characterized and quantified by the same GC/MS-techniques as described in full detail by Rogge et al. (1991, 1993a-i).

Of the 18 organic compound source profiles generated (see Table 12.1), 15 profiles were used as input data for these calculations. The other three profiles were bypassed for the following reasons. The organic aerosol released as meat is charbroiled was assumed to be best characterized by charbroiling regular meat (21% fat content; profile 1) and not by charbroiling extra-lean meat (10% fat content; profile 2). Combustion of synthetic logs in fireplaces has not been included in the calculations due to a lack of data on synthetic log consumption. The relative magnitude of the emissions of particles shed from the surfaces of green vegetation, as distinct from dead vegetation, is not yet known. Because the waxy leaf surface abrasion products from green and dead leaves do not differ significantly, only the source profile for green vegetative detritus will be used in this study.

Individual Emission Sources Considered

A multitude of different urban sources contribute fine particulate matter to the urban atmosphere. Of the more than 70 source types included in the inventory compiled by Gray (1986), 43 sources were chosen that are either directly represented by the authentic source profiles available (Rogge et al., 1991, 1993b-i) or that are closely related to the sources tested. For example, the source profile obtained for the noncatalyst gasoline-powered vehicles tested is also applied to noncatalyst light-duty trucks, medium-duty gasoline-powered trucks, heavy-duty gasoline-powered trucks, off-road gasoline-powered vehicles, and motorcycles. Table 12.1 lists the source profiles that are used for each of the 43 sources considered. That table also shows that the sources included in the study account for 83.4% of the primary OC emissions within the Los Angeles area. In order to organize the discussion of the results, the 43 sources studied are further grouped into 12 source categories that are described in Table 12.2.

The overall daily emission rates of organic compound mass based on the OC-emission inventory first will be discussed. Next, the total daily single compound emission rates (kg/day) summed over all source categories will be compared to the measured monthly ambient organic compound concentrations, determined as the mean of the monthly concentrations measured at West Los Angeles, downtown Los Angeles, and Pasadena.

Table 12.2 **Source Categories used to Group the Individual Emission Sources that are used in the Air Quality Calculations.**

Source Categories	
(I) Catalyst-equipped Vehicles	
1	Catalyst-equipped autos
2	Catalyst-equipped light trucks
3	Catalyst-equipped medium trucks
(II) Noncatalyst Vehicles	
4	Noncatalyst autos
5	Noncatalyst light trucks
6	Noncatalyst medium trucks
7	Noncatalyst heavy-duty trucks
8	Motorcycles
9	Noncatalyst off-road vehicles
(III) Diesel Vehicles	
10	Diesel autos
11	Diesel light trucks
12	Diesel heavy-duty trucks
13	Diesel off-road vehicles
14	Railroad diesel locomotives
15	Diesel Ships
(IV) Brake and Tire Dust	
16	Tire wear dust
17	Brake lining attrition
(V) Paved Road Dust	
18	Paved Road Dust
(VI) Natural Gas Combustion	
19	Natural gas–residential/commercial
20	Natural gas–electric utility boilers
21	Natural gas–electric utility turbines
22	Natural gas–refineries
23	Refinery gas–refineries
24	Natural gas–industrial boilers
25	LPG–industrial boilers
26	LPG–residential/commercial

Table 12.2 continued

Source Categories
(VII) Stationary Source Fuel Oil Combustion
27 Residual oil–electrical utilities
28 Distillate oil–electric utilities
29 Residual oil–refineries
30 Residual oil–industrial boilers
31 Distillate oil–industrial boilers
32 Industrial internal combustion gasoline engines
33 Residual oil–residential/commercial
34 Distillate oil–residential/commercial
(VIII) Wood Combustion
35 Pine wood burning fireplaces
36 Oak wood burning fireplaces
37 Structural fires
(IX) Meat Cooking
38 Charbroiling meat
39 Frying meat
(X) Cigarette Smoking
40 Cigarettes
(XI) Roofing Tar Pots
41 Roofing tar pots
42 Asphalt roofing manufacturing
(XII) Vegetation
43 Green leaf abrasion products

Daily Mean Organic Compound Class Emissions

Using the organic compound source profiles (see Rogge et al., 1991, 1993b-i) together with the OC-emission inventory (Table 12.1), the mean daily emission rates of identified organic compounds from each source type can be estimated. Because the source strength for leaf surface abrasion products is not known a priori, emissions from that source category cannot be included in these calculations.

In Figure 12.1, the identified organic compounds associated with each of eleven major source profiles are grouped into 16 compound classes based on organic chemical structural similarities. The amount of identified compound mass associated with each source profile that is emitted to the 80 km × 80 km study area on average throughout 1982 also is listed in kg/day in Figure 12.1. The emissions of identified compounds from these sources total 2836 kg/day, or 9.5% of the total fine primary organic aerosol emitted in the study area as shown in Figure 12.1. The remaining primary organic aerosol emissions consist largely of compounds that are not solvent-extractable or are not elutable under the analytical conditions used here or are present as part of the large hump of unresolved compounds present in many source samples that cannot be identified as single compound peaks.

From Figure 12.1 it can be concluded that no two source categories possess a similar organic compound emissions profile. While the identified portion of the exhaust emissions from catalyst-equipped vehicles mainly consists of *n*-alkanoic acids, the identified fraction of the organic fine particulate emissions from non-catalyst vehicles is dominated by polycyclic aromatic hydrocarbons (PAH). In contrast diesel exhaust emissions show a strong preference for *n*-alkanes. The identified compounds present in particles from products such as brake linings

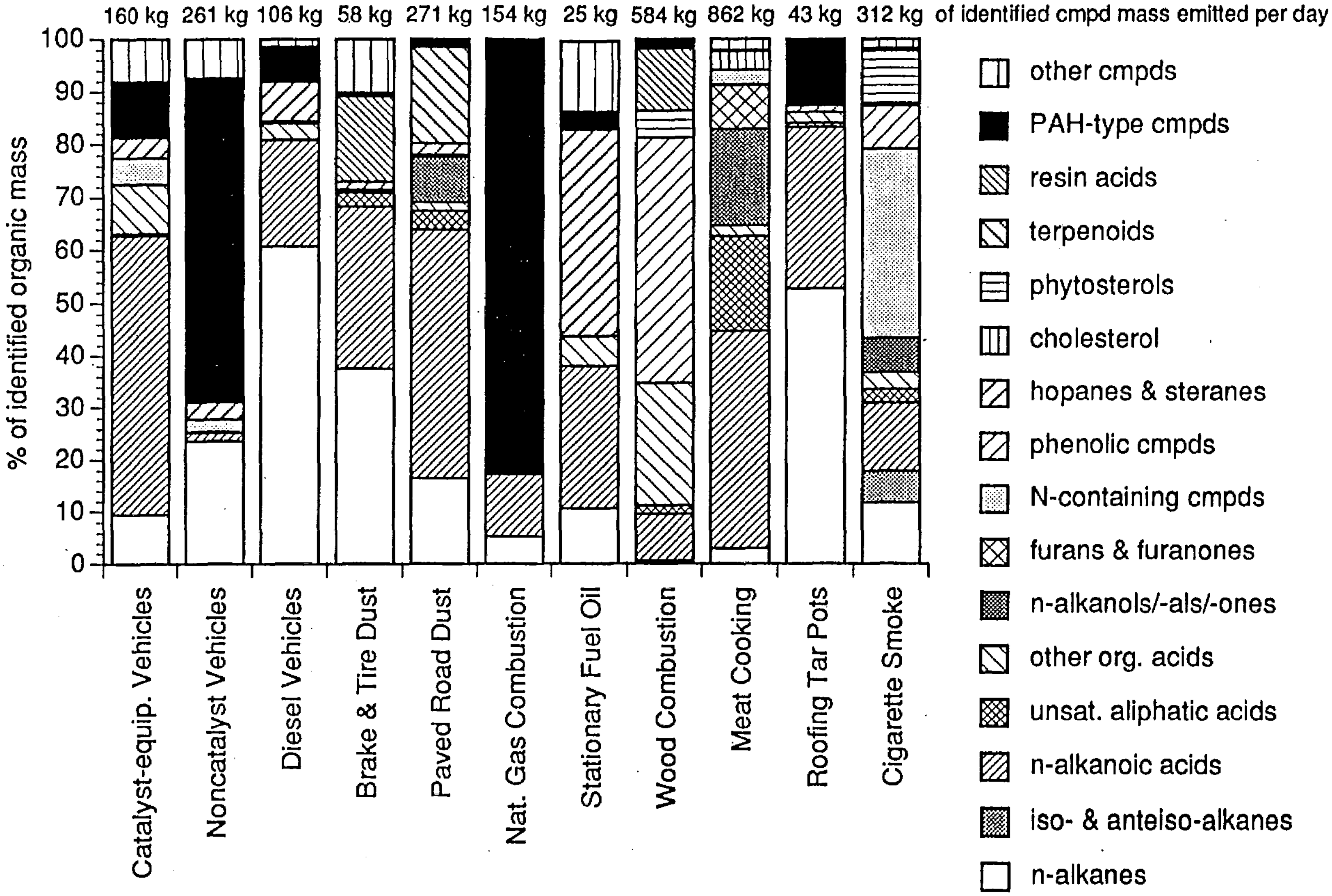

Figure 12.1: Compound class distributions of the organics that can be identifed as single compounds emitted from the 11 source categories

and car tires, together as a source category, are dominated by n-alkanes, n-alkanoic acids, and resin acids. Fine particulate paved road dust reveals an organic composition similar to ambient fine particle samples with n-alkanoic acids as the major identified compound class (Rogge et al., 1993c). Although very low in fine particulate emission rates, natural gas combustion aerosols consist to an appreciable fraction (22.5% of total fine particle mass; more than 80% of identified compound mass) of PAH, oxy-PAH, aza-arenes, and thia-arenes (Rogge et al., 1993e). Stationary sources burning fuel oil, such as electric utility boilers, industrial boilers, and others, show relatively low total OC-emissions (154.9 kg of fine particulate OC per day), and the identified compound mass emitted is low as well (25 kg/day). Most of the identified compound mass emitted from boilers consists of n-alkanoic acids and fossil petroleum markers such as hopanes and steranes. More than 85% of the hopanes and steranes emitted to the study area are released from vehicular exhaust emissions. The rest comes mainly from paved road dust and to a small extent from tire wear debris and asphalt roofing tar pots.

Burning wood in domestic fireplaces is the third largest source of fine particulate OC (see Table 12.1), and is the second largest source in terms of identified compound mass emitted per day (584 kg/day). The identified compounds consist mainly of phenolic type compounds that are breakdown products derived from wood lignin (see Rogge et al., 1993i). Resin acids are the next most prominent compound class in wood smoke emissions (Rogge et al., 1993i; Simoneit et al., 1993).

Meat cooking, the source category with the highest daily fine particulate OC-emission rates, also shows the largest amount of identifiable compound mass

(862 kg/day). *n*-Alkanoic acids and their unsaturated homologues such as oleic ($C_{18:1}$) and palmitoleic ($C_{16:1}$) acids are by far the dominant compound classes emitted, responsible for more than 60% of the identified compound mass.

The last two source categories in Figure 12.1 are asphalt roofing tar pots and cigarette smoke. Roofing tar pot emissions (Rogge et al., 1993g) are dominated by *n*-alkanes, *n*-alkanoic acids, and PAH-type compounds. N-containing heterocyclic compounds such as pyridine alkaloids (e.g., nicotine) make up the largest portion of the identified compounds in cigarette smoke, followed by several other compound classes including source specific *iso-* and *anteiso*-alkanes (Rogge et al., 1993f).

Ambient Concentrations vs. Daily Emission Rates for Single Aerosol Organic Compounds

In the study by Gray (1986), a known stable tracer, elemental carbon (EC), was used to confirm transport calculations. In the current study, single organic compounds are tracked that may be partitioned between the gas-phase and the aerosol-phase and whose chemical stability in the urban atmosphere often is unknown. Therefore, it is useful at the outset of the present work to examine the source and ambient data sets for evidence that the two data sets are or are not clearly related to one another.

One possible method to deduce qualitative information regarding single organic compound stability is to graphically compare the daily organic compound emission rates with ambient concentration data on a compound by compound basis. Discrepancies between these two data sets can occur due to the following reasons: (1) not all emissions sources are yet considered; (2) the most volatile compounds might partition to the gas-phase in the presence of diurnal temperature variations; (3) semi-volatile compounds might react preferentially in the gas-phase causing a net flux from the particle-phase to the gas-phase as concentrations re-equilibrate; and (4) heterogeneous chemical reactions might occur on the particle surface itself causing a loss of certain reactive compounds. Very limited knowledge presently exists concerning the atmospheric stability of semi-volatile and reactive non-volatile organic compounds. The current study will provide at least a qualitative examination of the likely stability of such compounds.

Figures 12.2a and 12.2b show the primary emissions of single organic compounds in kg/day released to the atmosphere of the Los Angeles study area. The annual mean ambient compound concentrations averaged over all measurements made at West Los Angeles, downtown Los Angeles, and Pasadena throughout the entire year 1982 are shown on the same graph. The alignment of the emissions and ambient concentration axes is arbitrary; no air quality modeling calculations are involved here. Included in these figures are most of the organic compounds identified in the year long study of ambient air quality detailed in Chapter 2 along with the respective compounds released from the source types investigated (Rogge et al.,1991, 1993a-i).

Figure 12.2a shows that organic compounds such as the *n*-alkanes, *iso*- and *anteiso*-alkanes, higher molecular weight *n*-alkanoic acids, and fossil petroleum compounds including hopanes and steranes, display changes in relative emission rates between compounds that are quite similar to the measured relative abundance of such compounds in ambient air. This indicates that such particle-bound compounds are relatively stable chemically at least for the time that it takes for

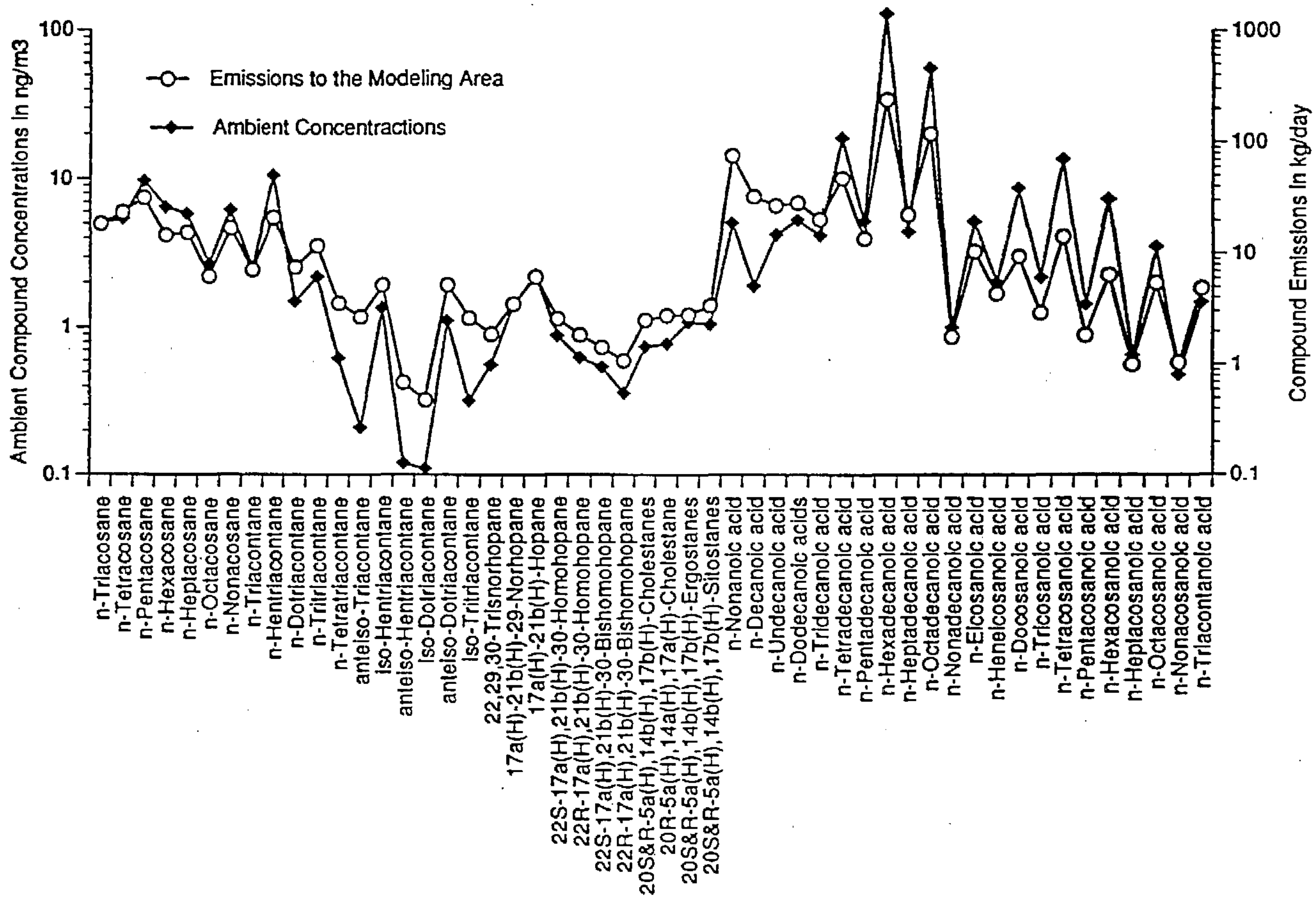

Figure 12.2a: Comparison between compound emission rates and ambient concentrations

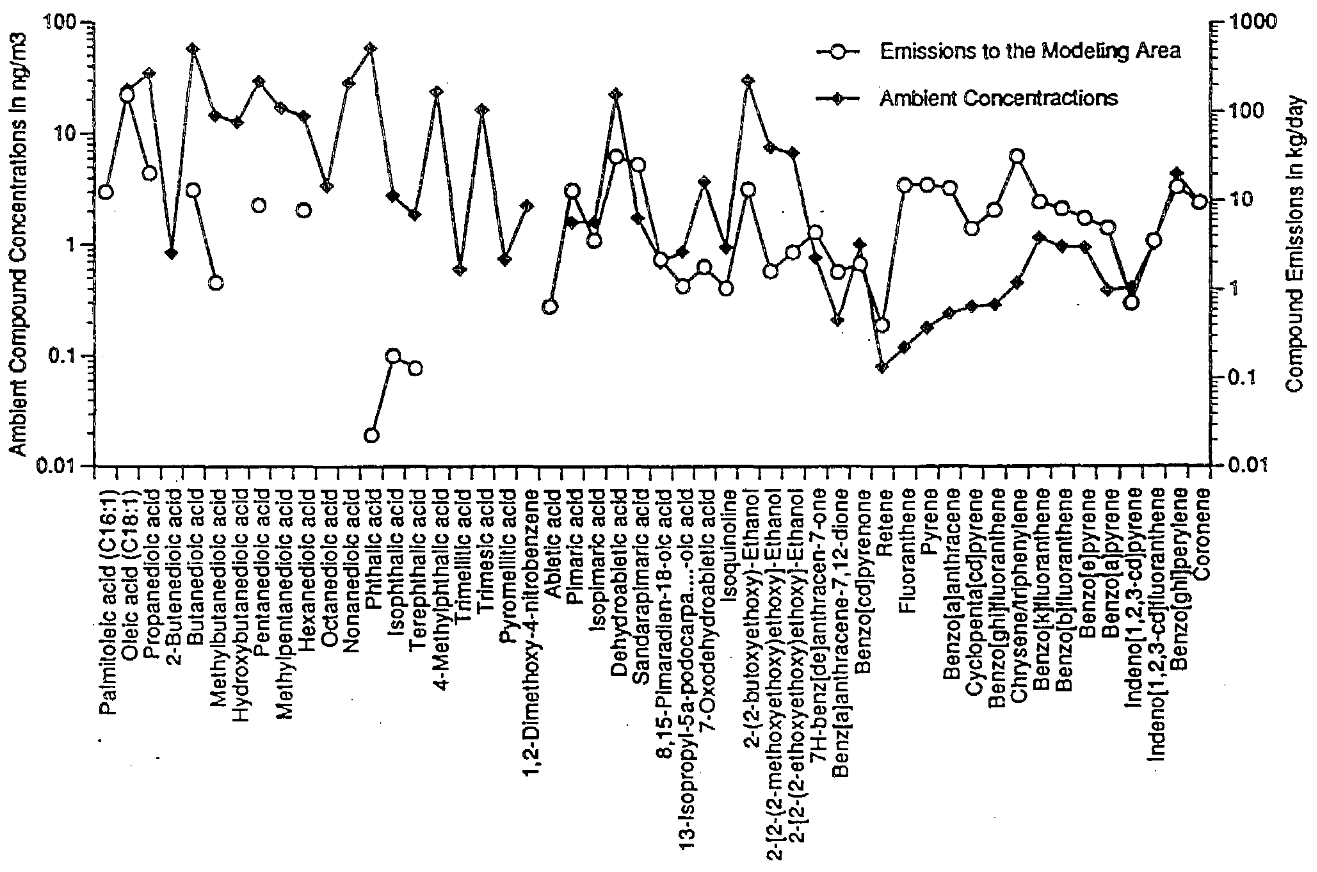

Figure 12.2b: Comparison between compound emission rates and ambient concentrations

the transport from the sources to the ambient monitoring sites. For lower molecular weight n-alkanoic acids ($C_9 - C_{14}$), the emission profile is somewhat elevated compared to the ambient concentration profile. Possibly, such low molecular weight n-alkanoic acids are lost from the fine aerosol-phase via volatilization or chemical reaction.

Palmitoleic acid ($C_{16:1}$) and oleic acid ($C_{18:1}$), are two unsaturated fatty acids that are mainly released from meat cooking operations within the current emission inventory. While oleic acid was identified in the atmospheric aerosol samples, palmitoleic acid was not found (see Figure 12.2b). This difficulty in measuring palmitoleic acid in the atmosphere could either be due to its low emission rate compared to oleic acid, or due to its higher volatility and possible degradation in the gas-phase, or due to heterogeneous attack on the double-bond by ozone or other radicals yielding in part aliphatic dicarboxylic acids as suggested by several researchers (e.g., Kawamura and Kaplan, 1987; Killops, 1986).

Aliphatic dicarboxylic acids and aromatic polycarboxylic acids have been quantified in the ambient aerosol characterization study conducted by Rogge et al. (1993a). Both compound classes are important due to their possible formation by chemical reactions in the atmosphere (Grosjean, 1977; Grosjean and Friedlander, 1980; Grosjean and Seinfeld, 1989; Hatakeyama et al., 1985, 1987; Rogge et al., 1993a; Tao and McMurry, 1989). During the source emission characterization campaign, aliphatic dicarboxylic and aromatic polycarboxylic acids have been found only in trace amounts in the emissions of some of the sources tested. Accordingly, the ambient compound concentration profile is not matched at all by the source emission profile as indicated in Figure 12.2b. This in turn suggests that such aliphatic and aromatic polycarboxylic acids are indeed of secondary origin, formed by atmospheric chemical processes.

Moving to the right in Figure 12.2b, the next group of compounds, resin acids, are mainly released during the combustion of pine wood in fireplaces in Southern California. Abietic acid is released only in small amounts and therefore is below detection in the ambient samples. Polyalkylene glycol ethers (e.g., 2-(2-butoxyethoxy)-ethanol), that are typically used as hydraulic fluids (e.g., in vehicle braking systems; Rogge et al., 1993c), show a pattern of relative concentrations that is similar between the sources and ambient data but the absolute magnitude of the ambient concentrations seems to exceed the known emission rates. This suggests that there are sources of these compounds other than brake dust.

While higher molecular weight PAH such as indeno[1,2,3-cd]pyrene, indeno-[1,2,3-cd]fluoranthene, benzo[ghi]perylene, and coronene show close agreement between ambient concentration and emission rate data, lower molecular weight PAH (e.g., fluoranthene, pyrene and others) show concentrations significantly lower than emission data would suggest. This suggests that such low moleculer weight PAH may preferably degrade in the gas-phase by photochemical processes and radical attack (Kamens et al., 1990; Pitts et al., 1969, 1978, 1980, 1985; Lane and Katz, 1977; Van Cauwenberghe, 1983) which leads in turn to further volatilization of such particle-phase associated PAH in the attempt to restore the gas-/particle-phase equilibrium. Alternatively, the low molecular weight PAH may be degraded by heterogeneous chemical reactions between gas-phase oxidants and particle-phase PAH.

Conclusions

The relative abundance of individual particle-phase organic compounds present in source emissions and in ambient air has been compared within an 80 km by 80 km study area centered over Los Angeles. Typically good agreement between measured concentration levels in outdoor air and the relative abundance of compounds in the emission inventory has been found for stable organic compounds that are exclusively present in the particle-phase such as *n*-alkanes, *iso*- and *anteiso*-alkanes, higher molecular weight PAH (e.g., coronene, benzo[ghi]perylene), and fossil petroleum compounds including hopanes and steranes.

Iso- and *anteiso*-alkanes, characteristic markers for cigarette smoke, show predicted concentrations that agree well with measured concentration levels. High molecular weight PAH such as benzo[ghi]perylene and coronene show measured ambient concentration levels that are in good agreement with their abundance in primary source emissions while low molecular weight PAH concentrations are clearly depleted in the atmosphere by further volatilization and/or atmospheric chemical reactions. *n*-Alkanoic acid concentrations are typically under represented by the emission data, suggesting that other sources, not yet considered, such as cooking with vegetable oils could contribute significant amounts of *n*-alkanoic acids. Aliphatic dicarboxylic acids and aromatic polycarboxylic acids are released only in small amounts to the urban atmosphere from primary aerosol sources indicating that such compounds are indeed mainly the result of atmospheric formation processes that occur in photochemical smog.

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Chapter 13

Summary and Conclusions

Fine organic aerosol samples collected systematically throughout a complete annual cycle at 4 urban sites in Southern California have been examined by gas chromatography/mass spectrometry. More than 100 organic compounds were quantified and their seasonal ambient concentration patterns were discussed. Primary organic aerosol constituents revealed an annual ambient concentration pattern with high winter and low summer concentrations. In contrast, aliphatic dicarboxylic acids and aromatic polycarboxylic acids of possible secondary origin showed a reverse pattern, with high concentrations in late spring/early summer. Molecular markers characteristic of several source types have been identified that would permit back calculation of the contribution of specific sources to the ambient aerosol if the concentration of these tracers in source emissions were known. In pursuit of such data on tracer concentrations in source emissions, fine organic aerosol emissions from 18 different source types were characterized using sampling and analytical techniques that were comparable to those employed during the ambient aerosol characterization campaign. The source samples investigated here were collected using a dilution sampler that simulates the cooling and dilution processes that occur in the atmosphere immediately downwind of a hot emission source, allowing condensible organic compounds emitted in the vapor-phase to condense onto particles prior to filter sampling.

Together, more than 400 different organic compounds have been identified and quantified in the source emissions studied here. It has been shown that meat cooking operations contribute substantial amounts of fine particle-bound organics to the ambient atmosphere. Cholesterol, a constituent in the fatty portion of meat, is proposed as a marker compound for the smoke from meat cooking operations and has also been identified in the urban atmosphere.

The emissions from 13 motor vehicles, including noncatalyst and catalyst-equipped automobiles, and heavy-duty diesel trucks, have been examined. It has been shown that the organic particulate exhaust emissions differ greatly from vehicle type to vehicle type. The identifiable portion of the organic aerosol emitted from gasoline-powered noncatalyst automobiles, for example, was dominated by polycyclic aromatic hydrocarbons (PAH), whereas the particle-phase organic compounds in the exhaust from catalyst-equipped automobiles included large amounts of organic acids dominated by *n*-alkanoic acids. The fine particulate matter emitted from diesel truck exhaust showed high concentrations of *n*-alkanes. More than 100 different organic compounds have been identified in the vehicular exhaust emissions, including fossil petroleum markers such as steranes and pentacyclic triterpanes (hopanes) that likewise have been found in ambient fine aerosol samples. It has been shown that the ambient concentrations of hopanes and steranes measured in the Los Angeles atmosphere are attributable mainly to vehicular exhaust emissions. Thus hopanes and steranes act as useful tracers for motor vehicle exhaust that can be used in future source/receptor reconciliation studies.

Fugitive dust sources, including tire dust, motor vehicle brake wear dust, and paved road dust have been examined. Tire dust was found to contain natural resins and thiazols used as vulcanization accelerators that might be useful as atmospheric tracers for that source. Brake lining wear particles were found to contain glycol ethers, probably from brake fluid contamination, that also were identified in ambient particulate matter samples. Contributions to the paved road dust deposits from vehicular exhaust emissions, tire wear, and vegetative detritus, coming from nearby plants and trees, have been estimated using authentic source profiles generated during the course of the present source characterization study.

In order to trace biogenic emissions, fine particles shed from leaf surfaces were investigated. Leaf composites were made up that represent green leaves (and separately; dead leaves) from 62 different plant species that are characteristic of vegetation in the Los Angeles area. It has been shown that fine particle leaf surface abrasion products exhibit a concentration pattern of higher molecular weight *n*-alkanes ($C_{27} - C_{33}$) with a pronounced odd/even carbon number predominance that is preserved in the urban atmosphere. This marker assemblage of higher molecular weight *n*-alkanes has been demonstrated in the air quality modeling part of this study as a means for tracing the contribution of vegetative detritus emissions to the urban atmosphere.

Cigarette smoke, a typical fugitive urban emission source, has been studied previously in indoor environments. In this study, molecular marker compounds such as *iso*- and *anteiso*-alkanes ($C_{29} - C_{34}$) have been identified that are enriched in cigarette smoke aerosol and that 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. When this finding is applied to the ambient aerosol, it has been shown that cigarette smoke contributes 0.57 to 0.72 $\mu g\ m^{-3}$ of the fine particulate matter measured in the outdoor Los Angeles area atmosphere on an average during 1982 (or 2.0 to 2.5% of the total fine ambient particle mass).

The combustion of natural gas in residential home appliances also has been investigated. Previous studies indicated that natural gas combustion shows fairly low fine particulate emission rates and consequently the chemical composition was not identified in the past. Here, it has been shown that at least 22.5% of the particle mass emitted from natural gas combustion in residential home appliances consists of PAH-type compounds. If the source test results obtained here are confirmed through testing of additional units, then natural gas combustion in residential homes and commercial establishments could emit amounts of PAH and oxy-PAH to the urban atmosphere that are comparable to that from all types of diesel vehicles or about half the amount emitted from catalyst-equipped automobiles on a daily basis.

The remaining source types examined include wood combustion in residential fireplaces, along with roofing tar pot effluent and the exhaust aerosol from industrial-scale distillate oil-fired boilers. The wood smokes were measured to contain resin acids that can be used to trace the quantity of wood smoke in the ambient aerosol. The roofing tar pot exhaust was found to consist largely of *n*-alkanes distilled from the melted tar, plus quantities of PAH similar to that found in motor vehicle exhaust. The oil-fired boiler effluent contains both burned and unburned petroleum compounds, including substantial quantities of organic acids.

The source emission data sets just described have have been used to construct an inventory for fine particulate organic compound emissions within an 80 km × 80 km study area centered over Los Angeles during the year 1982. The relative abundance of organic compounds in that inventory has been compared to the relative abundance of such compounds in the atmosphere. Typically, the emission inventory and measured ambient concentrations for stable particle-phase organic compounds such as higher molecular *n*-alkanes, PAH, hopanes, and steranes agree well. Aliphatic dicarboxylic acids and aromatic polycarboxylic acids, that have been suggested to be the products of atmospheric chemical reactions involving gaseous precursor compounds, show only small amounts of primary emissions from sources. The current study underlines that indeed such oxygenated organic compounds must be synthesized in the reactive urban atmosphere in the form of secondary aerosols because they are simply not present in primary source emissions in anywhere near the quantities needed to explain the observed ambient concentrations.

Volatile low molecular weight PAH show ambient concentrations that are depleted relative to their abundance in the emissions data base. In contrast, higher molecular weight PAH that do not partition between the gas- and particle-phase show measured ambient concentrations that agree quite well with their abundance in the emission inventory. It is concluded that particle-bound high molecular weight PAH indeed show life times at least as long as it takes for transport from the sources to the receptor air monitoring sites, while the lower molecular weight PAH are stripped from the particle-phase by volatilization and/or chemical reaction over the same time scale.

Many of the most important molecular markers identified in the present study, for example, hopanes and steranes that act as tracers for vehicular emissions, or *iso*- and *anteiso*-alkanes (C_{29} – C_{34}) that act as tracers for cigarette smoke, show good agreement between measured concentrations and their abundance in the emission inventory. This consistency between emissions data and observed molecular marker concentrations adds support to the notion that these compounds do indeed act as conserved tracers for the particular sources identified in the present study.