Assessment of contribution of contemporary carbon sources to size-fractionated PM and time-resolved bulk PM using the measurement of radiocarbon

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

This study was motivated by a desire to improve understanding of the sources contributing to the carbon that is an important component of airborne particulate matter (PM). The ultimate goal of this project was to lay a ground work for future tools that might be easily implemented with archived or routinely collected samples. A key feature of this study was application of radiocarbon measurement that can be interpreted to indicate the relative contributions from fossil and non-fossil carbon sources of atmospheric PM. Size-resolved PM and time-resolved PM_{10} collected from a site in Sacramento, CA in November 2007 (Phase I) and March 2008 (Phase II) were analyzed for radiocarbon and source markers such as levoglucosan, cholesterol, and elemental carbon. Radiocarbon data indicates that the contributions of non-fossil carbon sources were much greater than that from fossil carbon sources in all samples. Radiocarbon and source marker measurements confirm that a greater contribution of non-fossil carbon sources in Phase I samples was highly likely due to residential wood combustion. The present study proves that measurement of radiocarbon and source markers can be readily applied to archived or routinely collected samples for better characterization of PM sources. More accurate source apportionment will support ARB in developing more efficient control strategies.

EXECUTIVE SUMMARY

Atmospheric particulate matter (PM) is of a great concern due to adverse impacts on public health, visibility degradation, and radiative forcing effects upon global climate. As source identification is a prerequisite for effective control of the levels of PM in the air, failure to definitively identify sources represents a major roadblock to improved air quality and the resulting decreases in mortality, cancer, respiratory disease, and hospital admissions. This study was motivated by a desire to improve understanding of the sources contributing to the carbon that is an important component of airborne ambient particles. More accurate source apportionment supports ARB in developing efficient control strategies. The ultimate goal of this project was to lay the ground work for future tools that might be easily implemented with archived or routinely collected samples so as to better identify sources of atmospheric particulate matter.

This study was designed to determine whether proposed sampling strategies could collect sufficient PM mass for reliable radiocarbon measurement and to evaluate whether analytical techniques could be applicable to routinely collected PM samples. A key feature of this study was application of radiocarbon measurement and source marker analyses on the same samples so that a combination of results might provide further resolution of source contributions than otherwise available. The primary distinctive feature of this study is the analysis of size-resolved and time-resolved PM samples for their radiocarbon content. The ratio of radiocarbon (^{14}C) to total carbon (^{12}C + ^{13}C + ^{14}C) in PM is used to estimate the percent of carbon originating from modern versus fossil sources with much greater accuracy. The carbon fraction is further differentiated by analysis for source-specific molecular markers such as alkanes and levoglucosan.

This project consisted of two phases that resulted in sample collection during two seasons, late fall (November 28-December 1; Phase I) 2007 and spring (March; Phase II) 2008. All samples were collected at a site (Del Paso Manor Elementary School) located in a residential neighborhood in Sacramento. The first phase was a pilot study intended to demonstrate and validate the proposed sample collection strategies for the differentiation of modern carbon from fossil carbon in size-fractionated PM and time-resolved bulk PM_{10} using radiocarbon measurement. PM samples were further analyzed for source-specific compounds. The sampling strategies that were validated in the first phase were duplicated for three sampling periods in the second phase. Particles resolved in 6 sizes ranging from 0.056 to 1.8 μm (aerodynamic diameter) were collected using micro-orifice uniform deposit impactor (MOUDI) samplers. To distinguish the contribution of different sources during different time periods of day (morning: 6am-11am; afternoon: 12pm-6pm; overnight: 7pm-5am), time-resolved PM_{10} samples were collected. Size-resolved PM samples were analyzed for radiocarbon and time-resolved PM_{10} samples were analyzed for radiocarbon and source-specific markers.

Carbon mass (organic carbon plus elemental carbon) of all samples (except one) collected for the present study was sufficient to measure radiocarbon content with high levels of confidence. One or two days of sampling is likely to be sufficient to collect the required amount (30 μg as carbon) of all size ranges of fine particles using two MOUDI samplers (30 mL/min) during the wintertime when ambient PM levels are high, while at least 3 or 4 days of collection was necessary during the spring and fall when ambient PM levels are low. In the case of bulk $PM_{1.8}$ (10 mL/min, 47 mm ID filter) and PM_{10} (1,130

mL/min, 8 in × 10 in filter), one day of sampling is probably sufficient to collect enough carbon during spring/fall and winter.

The radiocarbon data indicates that the contribution of non-fossil carbon sources was much greater than that of fossil carbon sources in all samples. Fossil carbon content in size-resolved PM collected in Phase I and Phase II varied from 14 to 25% and 17 to 37%, respectively, and smaller size particles had slightly greater fossil carbon fractions. Radiocarbon content indicates that the contribution of non-fossil carbon sources was higher in Phase I samples than in Phase II samples. A greater contribution of modern carbon in Phase I samples is highly likely due to residential wood combustion around the sampling site. The contribution of particles from modern carbon sources was always 7 to 16% greater in overnight samples than in morning and afternoon samples probably because of greater wood burning and lower traffic activity during the overnight period.

Among the quantified individual organic compounds, levoglucosan, which is a good chemical marker for wood burning, was the most abundant, ranging from 23.6 to 3,360 ng/m^3. Levoglucosan concentrations were also much higher in Phase I samples than in Phase II samples, indicating that residential wood burning was highly likely a cause of higher non-fossil carbon fraction. When fossil carbon fractions are plotted against levoglucosan to organic carbon (Levo/OC) ratios in all samples, they showed a good negative correlation. This plot generally indicates that when the levoglucosan contribution to OC increased by 10%, the fossil carbon fraction declined by 16%. This plot demonstrates that more robust and detailed source profile can be obtained when radiocarbon and conventional source marker results are combined together.

The EC/OC ratio of the MOUDI PM$_{1.8}$ sample collected during Phase I (0.35) was greater than those of Phase II samples (0.28 ± 0.03), indicating that the Phase I sample had a higher fraction of combustion originated particles, most likely from residential wood combustion as suggested by radiocarbon and levoglucosan data. Among the time-resolved PM$_{10}$ samples, the Phase I overnight sample had a much higher EC/OC ratio (0.28) than other samples (0.18 ± 0.04). This high EC/OC ratio indicates that wood combustion is likely a significant source of EC and it may not be reasonable to use EC as a diesel emission tracer in areas where wood combustion could be a confounding source of EC.

Alkane patterns in all samples, except the Phase I overnight sample, were very similar to each other. All samples showed a strong biogenic signal having carbon maximum (C_{max}) at C_{29} and C_{31} and a less significant input of gasoline vehicle emission. Wood combustion most significantly increased the levels of more carcinogenic PAHs such as benzo[a]pyrene. Cholesterol was not detected or was present at very low concentrations in all samples probably because particles generated from meat cooking were not significant contributors at this site or collection duration was not enough to collect measurable amounts of cholesterol.

Sample collection strategies and analytical techniques used in this study can be successfully applicable to archived and routinely collected samples if they are stored frozen (-20 °C). The results of this study also demonstrate that more robust and detailed source contribution can be obtained when radiocarbon and conventional source marker data are combined together. It is desirable to compare the source contribution results of this study with source attribution of PM samples collected at the Del Paso Manor monitoring site by the Sacramento Metropolitan Air Quality Management District.

INTRODUCTION

Atmospheric particulate matter (PM) is a complex mixture of small particles and liquid droplets in the air. These particles are of great concern due to adverse impacts on public health, visibility degradation, and radiative forcing effects upon global climate. Exposure to particulate matter in ambient air has been linked to increased aggravated asthma, premature death in people with heart and lung disease, and hospital admission for cardiovascular and respiratory diseases in many urban areas (Pope and Dockery, 2006).

To protect public health and welfare, USEPA promulgated national ambient air quality standards (NAAQS) for PM_{10} (150 $\mu g/m^3$, 24-h average; 50 $\mu g/m^3$, annual average) in 1987 and for $PM_{2.5}$ (65 $\mu g/m^3$, 24-h average; 15 $\mu g/m^3$, annual average) in 1997. USEPA revised PM standard in 2006 (USEPA, 2006) and tightened the 24-h average $PM_{2.5}$ standard from 65 to 35 $\mu g/m^3$ and retained existing annual average $PM_{2.5}$ standard of 15 $\mu g/m^3$ and 24-h average PM_{10} standard of 150 $\mu g/m^3$. The state of California has set a $PM_{2.5}$ standard of 12 $\mu g/m^3$ (annual average). The USEPA is currently reviewing the relevant health effects literature as the first step in revision of the national standards for PM. Based on the science review and a policy review that will follow, USEPA is expected to issue either a revised standard or a continuation of the current standard.

As source identification is a prerequisite for effective control of the levels of PM in the air, failure to definitively identify sources represents a major roadblock to improved air quality and the resulting decreases in mortality, cancer, respiratory disease, and hospital admissions. To identify sources of atmospheric PM, many approaches, including source inventory and chemical mass balance modeling, have been applied (Schauer and Cass, 2000). Despite significant past and ongoing research, the sources of particulate matter in ambient air often remain elusive.

This study was motivated by a desire to improve understanding of the sources contributing to the carbon that is an important component of airborne ambient particles. More accurate source apportionment supports ARB in developing efficient control strategies. The ultimate goal of this project was to lay the ground work for future tools that might be easily implemented with archived or routinely collected samples so as to better identify sources of atmospheric particulate matter. This study was designed to determine whether sampling strategies could collect sufficient PM mass for reliable radiocarbon measurement and source-specific marker analyses and to evaluate whether the analytical techniques were applicable to routinely collected PM samples. For example, the first phase investigated the length of sample collection period required to obtain sufficient PM mass for radiocarbon measurement.

Multiple analytical approaches have been used or proposed to assist in identifying the sources contributing to the measured PM at a site (Chow et al., 2008; Rogge et al., 1993a; 1998, Schauet and Cass, 2000; Simoneit, 1989). A traditional characterization of carbonaceous material has been an operationally defined split between organic and elemental carbon based on a particular analytical method of which several are in common use (Kleeman et al., 1999). In addition, certain organic compounds have proved useful for source identification and that approach was utilized in this study. Individual organic marker compounds may be source-specific or a distribution pattern of several compounds may indicate a likely source type. However, one uncertainty in using molecular markers for source apportionment is that emission rates of molecular markers are different even for the same types of material. As an example, emission rates of wood combustion markers such as levoglucosan and retene from different tree species are highly variable. Emission rates of levoglucosan and retene were higher up to 90 times and 400 times, respectively, in soft wood (e.g., Douglas fir loblolly pine) combustion than in hard wood (e.g., white oak, red maple, sugar maple) combustion (McDonald et al., 2000; Fine et al., 2004). Combustion conditions and emission collection methods also significantly affect the emission rates of tracers (Hildemann et al., 1991; McDonald et al., 2000). This type of bias is much less in the case of radiocarbon measurements, making them a good complementary technique to accompany chemical marker measurements.

A key feature of this study was application of radiocarbon measurement and source marker analyses on the same samples so that a combination of results might provide further resolution of source contributions than otherwise available. The primary distinctive feature of this study is addition of the analysis of the radiocarbon content, which is a fraction of radiocarbon (^{14}C) out of the total carbon (^{12}C + ^{13}C + ^{14}C) in PM. Isotopic analysis of the carbon allowed estimation of the percent of carbon originating from modern versus fossil sources with much greater accuracy. In fossil fuel originated particles, the radiocarbon fraction is nearly zero because, with a decay half-life of 5774 years, almost all has decayed into stable nitrogen (^{14}N). The radiocarbon fraction in modern carbon sources such as wood burning is similar to atmospheric contemporary ratios (around 1.05 in the winter of 2007). Radiocarbon content, therefore, can be interpreted to indicate the relative contributions from fossil and non-fossil carbon sources. For example, if biogenic carbon content of a PM sample is 50% of the total carbon, the contribution of fossil carbon sources is 50%. Analysis of the PM samples for source-specific markers such as levoglucosan and cholesterol provides further information on the likely emission sources. For example, the modern carbon fraction can be further divided into different sources (e.g., wood burning, meat cooking) using the chemical analysis of marker compounds such as levoglucosan and cholesterol. Combining a new approach such as radiocarbon (^{14}C) measurement with conventional source-specific marker measurement is highly desirable to validate and refine source apportionment modeling. Results of the measurement of radiocarbon and source-specific markers can then be used to confirm source apportionment modeling. This comparison can help ARB validate source profile selection practice and eventually perform source apportionment more accurately.

One hypothesis of this project was that smaller particles would contain a greater fossil carbon fraction. To test it, size-resolved PM samples were collected in six size bins (from 0.056 to 1.8 microns) using modified micro-orifice uniform deposit impactor (MOUDI) samplers for radiocarbon measurement. Another hypothesis was that fossil carbon fraction would be greater in daytime samples than in overnight samples due to differences in local emission sources with time of day (e.g., for traffic volume and residential wood combustion). Thus, the sampling strategy included sample collection for three daily periods (morning, 6 - 11am; afternoon, 12 pm - 6 pm; and overnight, 7pm – 5 am) for radiocarbon and source marker analyses.

This project took a phased approach that resulted in sample collection during two seasons; late fall 2007 and spring 2008. Each phase had two components, radiocarbon measurement and complementary source-specific marker analysis. During Phase I, one set of samples was collected (November 28-December 1, 2007) to test the sample collection strategy and determine whether sufficient PM mass could be collected to support radiocarbon analysis for both size-fractionated and time-resolved airborne PM samples. The sampling strategies that were validated during Phase I were duplicated for collection of samples during three periods of Phase II. All PM samples were collected at a single site near the Sacramento Metropolitan Air Quality Management District (AQMD) Del Paso Manor monitoring site, located at Del Paso Manor Elementary School in a residential neighborhood, northeast of the Sacramento downtown and commercial areas.

MATERIALS AND METHODS

Sampling site

The sampling site for this study was the rooftop of a gymnasium (Figure 1), at Del Paso Manor Elementary School (2700 Maryal Drive, Sacramento, CA). The rooftop is about 30 ft above the ground surface and about 150 m from a Sacramento Metropolitan Air Quality Management District (AQMD) Del Paso Manor monitoring site (Figure 2). This site is surrounded by residential houses. The closest local arterial roadways (El Camino Avenue; 2 lanes each way) and an interstate freeway (I-80) are approximately 250 m and 2,600 m distant, respectively (Figures 3 & 4).

Samplers were installed here.

Figure 1. The building that was used for PM collection.

Sample collection

All PM samples were collected at the gymnasium rooftop location shown in Figure 5. The periods of sample collection, the types of samplers, and the duration of sample collections are summarized in Table 1. Sampling spanned multiple days to acquire a sufficient mass of carbon for radiocarbon analysis. Before sample collection, all samplers were cleaned using tap water, methanol, and hexane in the laboratory to avoid any

Figure 2. Google Earth image showing the sampling site and the Sacramento Metropolitan Air Quality Management District Del Paso Manor monitoring site

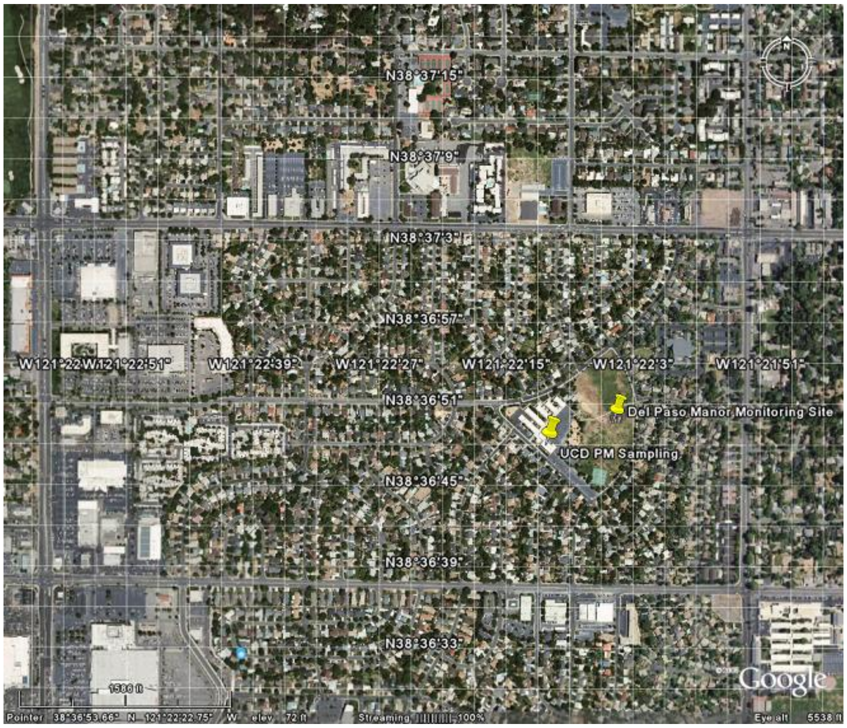


Figure 3. Google Earth image showing the sampling site and local area.

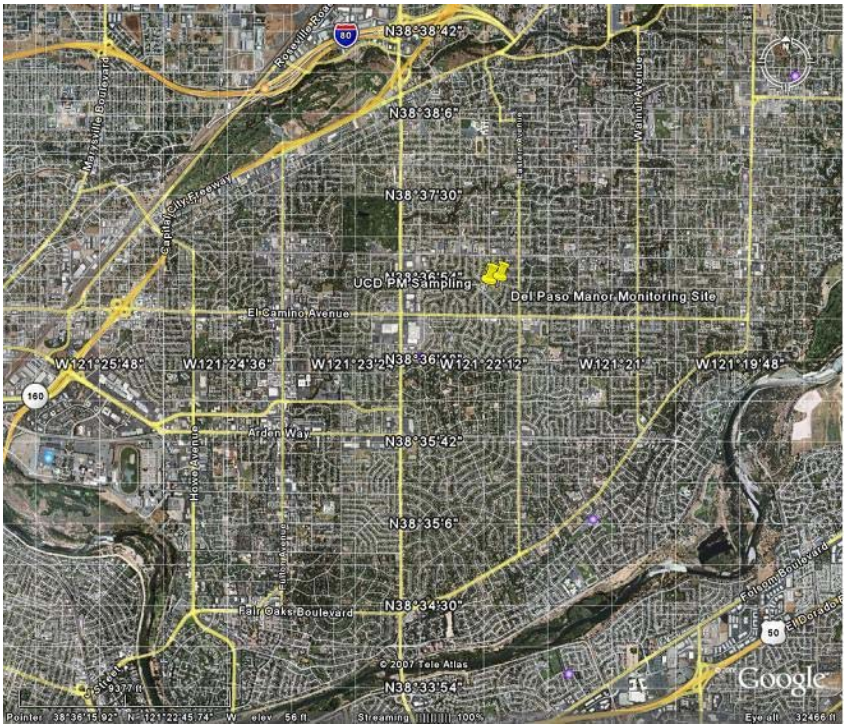


Figure 4. Google Earth image showing the sampling site and northern Sacramento area

Figure 5. MOUDI and PM_{10} samplers installed on the rooftop of a school gymnasium.

possible contamination. Aluminum foil substrates for the modified micro-orifice uniform deposit impactor (MOUDI) samplers were pre-combusted at 450 °C for 4 hours and weighed using a microbalance. Pre-weighed aluminum substrates were installed on each MOUDI plate in the laboratory.

Time-resolved PM_{10} samples were collected on quartz fiber filters (8 in × 10 in) using high volume PM_{10} samplers for 3 different segments of day; morning (6-11am), afternoon (noon-6pm), and overnight (7pm-5am). For each time segment, different quartz fiber filters were used and they were reused for the same time segments of the following days to increase PM_{10} mass on each filter. While they were not in use, the filters were placed on metal trays sealed with airtight plastic bags and stored in a cold room (4 °C) during sampling periods. Air pumping rate of the high volume PM_{10} samplers was 1,130 L/min. Size-resolved samples were collected with modified micro-orifice uniform deposit impactor (MOUDI) samplers. The MOUDI samplers that were used for this study were designed to collect atmospheric PM ranging from 0.056 to 18 μm on 11 size ranges. For the present study, however, they were modified to remove PM bigger than 1.8 μm using cyclones attached to inlets of each MOUDI sampler, so they collected PM ranging from 0.056 to 1.8 μm in 6 different ranges. For each sampling event, the MOUDI samplers were operated without replacing aluminum foil substrates to collect sufficient mass of PM on each substrate. Air pumping rate of MOUDI samplers was 30 L/min. Low-volume $PM_{1.8}$ samplers were originally planned for both phases, but due to safety concerns their installation was delayed until the first of the Phase II sampling periods. Low-volume $PM_{1.8}$ samplers were also operated without changing quartz fiber filters (47 mm ID) to collect sufficient PM mass for radiocarbon measurement. Air pumping rate of $PM_{1.8}$ samplers was 10 L/min.

After the sample collection was completed, PM_{10} quartz filters were individually placed in metal trays on site. Metal trays were covered with pre-combusted aluminum foil and were placed in plastic bags. PM_{10} samples were stored in a cold room (4 °C) until sample weight measurement and then stored in a freezer (-20 °C) until chemical marker analysis. $PM_{1.8}$ quartz filters were removed from the samplers on site and placed individually in Petri dishes. Aluminum foil substrates were transported to the laboratory installed in the MOUDI samplers and removed from each plate and individually placed in

Petri dishes lined with aluminum foil. All Petri dishes were sealed with Teflon tape and stored in a freezer (-20 °C).

Measurement of PM mass

Before weighing, the sample filters were removed from the cold room and the freezer and placed on a laboratory bench for 4 hours without opening sealing bags to equilibrate them with room temperature. Mass of size-resolved PM and bulk $PM_{1.8}$ samples were measured using a microbalance (Cahn C-30) that is able to measure masses as low as 1 μg precisely. In the case of time-resolved PM_{10} samples, a less sensitive analytical balance (Mettler Toledo AB265-S) was used. No pretreatment such as drying was performed.

Measurement of elemental carbon (EC) and organic carbon (OC)

For the measurement of the mass of organic carbon and elemental carbon, a small fraction (1.5 cm × 1 cm) of each quartz filter and aluminum substrate was analyzed using a Sunset carbon aerosol analyzer in the Department of Civil and Environmental Engineering, UCD. EC and OC were determined using thermal destruction and oxidization of carbonaceous matter with optical charring correction. EC and OC were converted to carbon dioxide and reduced to methane for the measurement using flame ionization detector. The analytical procedure was identical to the method used in Kleeman et al. (1999). Because inorganic carbon typically presents in minor concentrations in ambient aerosols, the sum of EC and OC is defined as total carbon (TC) for the present study.

Measurement of radiocarbon ratio ($^{14}C/C$)

The radiocarbon ratio of a sample (R_u) is defined as the total number of moles of radiocarbon ^{14}C divided by the total number of moles of all carbon isotopes ($C = {}^{12}C + {}^{13}C + {}^{14}C$). Radiocarbon ratios of samples are normalized to measurements of National

Institute of Standards and Technology (NIST) standard reference material (Oxalic Acid I 4990b) of known isotope concentration. To measure $^{14}C/C$ ratios, size-fractionated PM samples and time-resolved bulk PM samples were sent to the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory and analyzed on the high-precision HVEE FN system. All samples were prepared in the LLNL natural carbon preparation laboratory using established methods (Vogel et al., 1987, Santos et al, 2004). An overview of the AMS technique is described here. The AMS sample preparation method accommodates samples containing between 0.05 and 10 mg carbon. Samples containing 0.1-2 mg carbon are preferred for obtaining higher measurement precision and lower systematic backgrounds. Non-combustible quartz filters cut into strips are placed in 4 mm or 7 mm ID quartz tubes with copper oxide (CuO) as an oxygen source. The quartz tubes are evacuated, sealed with a H_2/O_2 torch, and heated to 900 °C for 3.5 hours to oxidize all carbon to CO_2. After each quartz sample tube cools to room temperature, it is placed in a flexible, evacuated chamber. The tube is broken and the gaseous species are transferred for analysis. Any filter remnants, reduced Cu, excess CuO, and AgS are left behind because they are in a solid phase. Water vapor, SO_2, and NO_2 are removed from the gaseous sample by passing the sample through an isopropanol/dry-ice cold trap. Passing the remaining gas mixture through a liquid-nitrogen cold trap condenses CO_2, and any non-condensing gases (e.g., N_2, NO, CO) are pumped off and discarded. The pure CO_2 sample is allowed to sublimate in a small fixed volume, after which its partial pressure is measured to determine the total mass of carbon in the sample. Then the purified CO_2 is cryogenically transferred to individual reactors where it is reduced with hydrogen gas in the presence of an iron catalyst to produce graphitic carbon. The mixture of solid carbon and iron powder is poured into an aluminum sample holder and placed in the ion source of the accelerator to measure $^{14}C/C$ ratios. Operation of the accelerator has been described in detail (Vogel at al., 1995).

The AMS instrument separates ^{14}C ions from the ^{13}C and ^{12}C ions produced by the ion source and counts them individually by measuring charge pulses deposited by a ^{14}C-ion beam. At the same time, the current carried by a ^{13}C-ion beam is measured. It is known that

Table 1. Sample collection periods and collection durations.

	Sample type		Start time	End time	Duration
Phase I	MOUDI		6:00PM, November 28, 2007	12:00PM, December 1, 2007	62 hr
	$PM_{1.8}$		Not Collected		0
	PM_{10}	Morning	6:00PM, November 28, 2007	1:00PM, December 1, 2007	12 hr
		Afternoon			10 hr
		Overnight			24 hr
Phase II-1	MOUDI		10:00PM, March 8, 2008	5:00PM, March 11, 2008	91 hr
	$PM_{1.8}$				91 hr
	PM_{10}	Morning	10:00PM, March 8, 2008	5:00PM, March 11, 2008	20 hr
		Afternoon			23 hr
		Overnight			42 hr 50 min
Phase II-2	MOUDI		5:40PM, March 16, 2008	5:40PM, March 19, 2008	72 hr
	$PM_{1.8}$				72 hr
	PM_{10}	Morning	7:00PM, March 16, 2008	6:00PM, March 19, 2008	15 hr
		Afternoon			15 hr
		Overnight			33 hr
Phase II-3	MOUDI		6:00PM, March 20, 2008	4:30PM, March 24, 2008	94 hr 50 min
	$PM_{1.8}$				94 hr 50 min
	PM_{10}	Morning	7:00PM, March 20, 2008	4:30PM, March 24, 2008	20 hr
		Afternoon			18 hr 50 min
		Overnight			44 hr

$$S_u = k\left(\frac{^{14}\text{C}}{^{13}\text{C}}\right)_u \qquad (1)$$

where S_u is the signal (^{14}C-ion charge divided by ^{13}C-ion current) from the sample, k is a proportionality constant, and $(^{14}\text{C}/^{13}\text{C})_u$ is the ^{14}C to ^{13}C isotope ratio of the unknown sample. The signal from a standard reference material with a known isotope ratio also can be measured:

$$S_s = k\left(\frac{^{14}\text{C}}{^{13}\text{C}}\right)_s \qquad (2)$$

Equations 1 and 2 can be used to show

$$\left(\frac{^{14}\text{C}}{^{13}\text{C}}\right)_u = \frac{S_u}{S_s}\left(\frac{^{14}\text{C}}{^{13}\text{C}}\right)_s \qquad (3)$$

However, the parameter we wish to know is

$$R_u \equiv \left(\frac{^{14}\text{C}}{\text{C}}\right)_u \equiv \left(\frac{^{14}\text{C}}{^{12}\text{C}+^{13}\text{C}+^{14}\text{C}}\right)_u \qquad (4)$$

Information about the relative concentrations of ^{14}C, ^{13}C, and ^{12}C in the sample and the standard must be known to obtain R_u. Stable isotope ratio mass spectrometry (IRMS, which is conducted using a different instrument than AMS) is used to measure $(^{13}\text{C/C})_u$ and $(^{13}\text{C/C})_s$, where

$$\left(\frac{\text{C}}{^{13}\text{C}}\right)_u = \left(1+\delta^{13}\text{C}\right)\left(\frac{\text{C}}{^{13}\text{C}}\right)_s \qquad (5)$$

Carbon sources may have slightly different ^{13}C/C ratios due to the chemical processes that produced them. In previous studies, the value of δ^{13}C for fuels (carbon sources) and emissions (PM) were the same, indicating no isotope effect. Equations 1 through 5 can be used to write

$$R_u = \left(\frac{^{14}\mathrm{C}}{^{13}\mathrm{C}}\right)_u \left(\frac{^{13}\mathrm{C}}{\mathrm{C}}\right)_u = \frac{R_s S_u}{S_s\left(1+\delta^{13}\mathrm{C}\right)} \qquad (6)$$

The isotope ratio of the standard, $R_s = (^{14}C/C)_s$, is known. S_u and S_s are measured using AMS, and $\delta^{13}C$ is measured using IRMS; therefore, R_u is easily calculated.

There are two major confounding factors that cause uncertainties in using the radiocarbon ratio as a marker of PM sources. One is the pulse of anthropogenic radiocarbon embedded in biomass. The radiocarbon ratio of atmospheric carbon was around 0.98 before atmospheric atomic bomb tests were conducted actively and contemporary ratios are around 1.03. The ratio at the time when the samples were collected for the present study was about 1.05. Radiocarbon ratios of atmospheric carbon dramatically increased to 1.9 in the early 1970s when atmospheric nuclear testing peaked. Atomic bomb tests conducted extensively in the late 1950s and early 1960s produced large amounts of anthropogenic radiocarbon in the air and its levels in the atmosphere were significantly elevated during this period. After adoption of the Limited Test Ban Treaty in 1963 prohibiting above-ground nuclear testing, its level has declined exponentially due to mixing of CO_2 with marine and terrestrial reservoirs and current carbon 14 levels in the atmosphere are only slightly higher than those of the pre-bomb period. Plants that have grown during this period have elevated radiocarbon signatures embedded in their structural carbon and hence particles released during the combustion of this biomass have slightly elevated radiocarbon ratios compared to contemporary ratios. The other factor is isotopic fractionation during the assimilation of atmospheric carbon into plant biomass and assimilation of plants into animal biomass. When carbon isotopes enter living organisms, heavier isotopes have a tendency to be less used for physiological processes so radiocarbon ratios in living organisms are slightly lower than contemporary atmospheric ratios.

Historical nuclear testing may have increased radiocarbon ratios in trees by about 5 to 10% compared with historical pre-bomb atmospheric levels, while biological isotopic fractionation decreases radiocarbon ratios by about 5 to 10%. Considering these confounding factors together, it is reasonable not to adjust the ratios measured in atmospheric particle samples. The modern carbon fraction of contemporary carbon in the atmosphere was about 1.05 during the sample collection campaigns of this study. So, if modern carbon fraction of PM samples is around 1.05, the contribution of fossil fuel combustion to atmospheric PM is negligible, while if it is zero, then all PM originated from the combustion of fossil fuels. The percentage of modern carbon in carbonaceous particles can be calculated using the following relationship:

$$\text{Modern carbon percentage} = 100 \times (\text{modern carbon fraction}/1.05) \quad (7)$$

It should be noted that these two major confounding factors might cause about ± 5% of variability in differentiating between the contributions of fossil and modern carbon sources.

Measurement of molecular markers

Size-resolved PM and $PM_{1.8}$ samples were not analyzed for molecular markers due to insufficient carbon mass. Only time-resolved PM_{10} samples were analyzed for levoglucosan, alkanes, hopanes, PAHs, and cholesterol. Quartz filters were extracted with dichloromethane using a Soxhlet extraction apparatus for 8 hours. Surrogate compounds were added before extraction. Sample extracts were concentrated to 1 mL and analyzed with GC-MS for compounds that do not require derivatization. To analyze levoglucosan and cholesterol, sample extracts were mixed with 300 μL of BSTFA [bis(trimethylsilyl)trifluoroacetamide] and placed in a water bath (70 °C) for 3 hours. The derivatized target compounds were identified and quantified using GC-MS. For the quantification of target compounds, calibration curves were produced using pure genuine chemicals purchased from Accustandard and Aldrich.

RESULTS AND DISCUSSION

Atmospheric concentrations (μg/m^3) of particles, organic carbon, and elemental carbon and content (%) of modern and fossil carbon are presented in Tables 2-5. Examples of size-resolved particles deposited on aluminum substrates are shown in Figure 6. After three days of collection during Phase I, the PM_{10} overnight sample (Figure 7 C) was a dark gray color that was clearly different from that of the morning (Figure 7 A) and afternoon (Figure 7 B) samples, implying that the overnight sample was likely to be dominated by particles from different sources, probably residential wood burning. The color of the overnight period PM_{10} samples collected during Phase II differed only slightly from that of morning and afternoon samples. Pictures were not taken for the Phase II samples. A strong odor of wood smoke was noted by sampling crews upon arrival around 6am in November (Phase I), but not in March (Phase II).

Radiocarbon

Carbon mass (organic carbon plus elemental carbon) of all size-resolved PM, bulk $PM_{1.8}$, and time-resolved bulk PM_{10} samples (except one size-resolved sample) collected for the present study exceeded minimum amounts (~30 μg) required for radiocarbon measurement. **When two MOUDI samplers (30 mL/min) are used, 1 or 2 days of sampling is likely to be sufficient to collect the required amount of all size ranges of fine particles during the wintertime when ambient PM levels are high, while at least 3 or 4 days of collection is necessary during the spring and fall when ambient PM levels are low. In the case of bulk $PM_{1.8}$ (10 mL/min, 47 mm filter) and time-resolved bulk PM_{10} (1,130 mL/min, 8 in × 10 in filter) samples, one day of sampling is sufficient to collect enough carbon mass during spring/fall and winter.**

The results of the present study indicate that the approach used in this study is applicable to archived and routinely collected samples if they have been stored frozen (-20 °C). When this approach is applied to current ARB's archived $PM_{2.5}$ and PM_{10} samples, considerable amount of uncertainty is expected because of the loss of volatile organic compounds during sample storage periods. Currently ARB stores $PM_{2.5}$

samples in refrigerators (4 °C). In the case of PM_{10} samples collected on quartz filters, ARB places them in manila folders that are stored at the room temperature. Unless collected PM samples are kept frozen (-20 °C), loss of volatile organic compounds is inevitable as the samples age under the current ARB's storage conditions for archived samples. **If ARB changes storage conditions for both $PM_{2.5}$ and PM_{10} samples, the technique validated in this study can be successfully applied to archived and routinely collected samples in the future.**

The contribution of carbonaceous PM originating from non-fossil carbon sources consistently exceeded contributions from fossil carbon sources. The fossil carbon fraction in Phase I size-resolved PM ranged from 14 to 25%, with a mass-weighted content of 16%. In Phase II-2 and Phase II-3 size-resolved PM samples, fossil carbon content varied from 17 to 37% with mass- weighted contents of 29% (Phase II-2) and 21% (Phase II-3). In size-resolved PM samples, smaller size PM had slightly greater fossil carbon fractions. In time-resolved PM_{10} samples, fossil carbon accounted for 15 to 40% of the total carbon. The least and greatest fossil carbon fractions were found in the Phase I overnight sample and in the Phase II-1 morning sample, respectively. Modern carbon fractions in the Phase I overnight sample were 7 to 14% higher than Phase II overnight samples, likely due to much more extensive local residential wood combustion during Phase I. Synthetic logs containing both wood chips and petroleum wax are commonly burned in home fireplaces, and the fine particles from their combustion have modern carbon contents of about 20% (McDonald et al., 2000). Thus, although the fossil carbon content of fine particles in November was 16% (Table 2), some of this carbon was likely contributed by combustion of synthetic logs rather than from typical (exclusively) fossil fuel sources such as vehicle exhaust and natural gas burning. The contribution of PM from modern sources was consistently greater in overnight samples probably due to more wood burning and less traffic activity during this time of day. Fossil carbon accounted for 25 to 34% of the total carbon in bulk $PM_{1.8}$ samples and these fractions are similar to time-weighted average fossil carbon content in PM_{10} samples.

Table 2. Concentrations of total and carbonaceous particle and content of modern and fossil carbon in samples collected for Phase I.

	PM Concentration	Total Carbon	Organic Carbon	Elemental Carbon	Modern Carbon	Fossil Carbon
MOUDI	μg/m^3				(%)	
1.0-1.8	2.84	0.68	0.53	0.16	80	20
0.56-1.0	4.40	3.40	2.47	0.93	85	15
0.32-0.56	4.65	3.86	2.94	0.92	86	14
0.18-0.32	6.15	4.42	3.38	1.04	86	14
0.10-0.18	2.82	2.34	1.62	0.72	81	19
0.056-0.10	1.26	0.97	0.65	0.32	75	25
Total	22.1	15.7	11.6	4.09	84	16
PM_{10} (bulk)						
Morning	22.0	6.30	5.40	0.90	69	31
Afternoon	45.3	7.75	6.72	1.03	71	29
Overnight	40.5	18.0	14.0	4.00	85	15
Average*	37.1	12.5	10.0	2.48	81	19

* Time-weighted average

Table 3. Concentrations of total and carbonaceous particle and content of modern and fossil carbon in samples collected for Phase II-1.

	PM Concentration	Total Carbon	Organic Carbon	Elemental Carbon	Modern Carbon	Fossil Carbon
MOUDI	µg/m^3				(%)	
1.0-1.8	0.66	0.22	0.21	0.02		
0.56-1.0	1.07	0.49	0.33	0.16	91	9
0.32-0.56	1.23	0.48	0.37	0.11	87	13
0.18-0.32	1.45	0.58	0.39	0.19	85	15
0.10-0.18	0.91	0.50	0.44	0.06	72	28
0.056-0.10	0.45	0.21	0.17	0.04	NA	NA
Total	5.77	2.48	1.91	0.57		
$PM_{1.8}$ (bulk)	7.54	3.24	2.61	0.63	66	34
PM_{10} (bulk)						
Morning	31.6	5.32	4.21	1.11	60	40
Afternoon	22.1	3.63	3.12	0.51	61	39
Overnight	19.1	4.21	3.51	0.70	71	29
Average*	22.96	4.34	3.59	0.75	66	34

* Time-weighted average

Table 4. Concentrations of total and carbonaceous particle and content of modern and fossil carbon in samples collected for Phase II-2.

	PM Concentration	Total Carbon	Organic Carbon	Elemental Carbon	Modern Carbon	Fossil Carbon
MOUDI	μg/m^3				(%)	
1.0-1.8	0.39	0.21	0.19	0.02	80	20
0.56-1.0	0.78	0.22	0.15	0.07	68	32
0.32-0.56	0.91	0.30	0.25	0.05	81	19
0.18-0.32	0.80	0.31	0.24	0.07	63	37
0.10-0.18	0.54	0.26	0.22	0.04	64	36
0.056-0.10	0.41	0.14	0.11	0.03	70	30
Total	3.81	1.44	1.16	0.28	71	29
$PM_{1.8}$ (bulk)	6.51	2.46	2.05	0.41	67	33
PM_{10} (bulk)						
Morning	28.2	3.52	2.94	0.58	64	36
Afternoon	21.2	2.74	2.44	0.30	66	34
Overnight	16.6	3.09	2.59	0.50	73	27
Average*	20.64	3.11	2.64	0.47	69	31

* Time-weighted average

Table 5. Concentrations of total and carbonaceous particle and content of modern and fossil carbon in samples collected for Phase II-3.

	PM Concentration	Total Carbon	Organic Carbon	Elemental Carbon	Modern Carbon	Fossil Carbon
MOUDI	μg/m^3				(%)	
1.0-1.8	0.73	0.22	0.19	0.03	83	17
0.56-1.0	1.10	0.44	0.32	0.11	81	19
0.32-0.56	1.31	0.47	0.34	0.13	78	22
0.18-0.32	1.94	0.84	0.60	0.23	79	21
0.10-0.18	1.01	0.53	0.45	0.08	75	25
0.056-0.10	0.48	0.22	0.19	0.03	77	23
Total	6.57	2.71	2.10	0.61	79	21
$PM_{1.8}$ (bulk)	8.34	3.44	2.85	0.59	75	25
PM_{10} (bulk)						
Morning	19.6	4.97	4.21	0.76	68	32
Afternoon	17.5	4.17	3.73	0.44	67	33
Overnight	17.4	4.84	4.11	0.73	78	22
Average*	17.97	4.71	4.04	0.67	73	27

* Time-weighted average

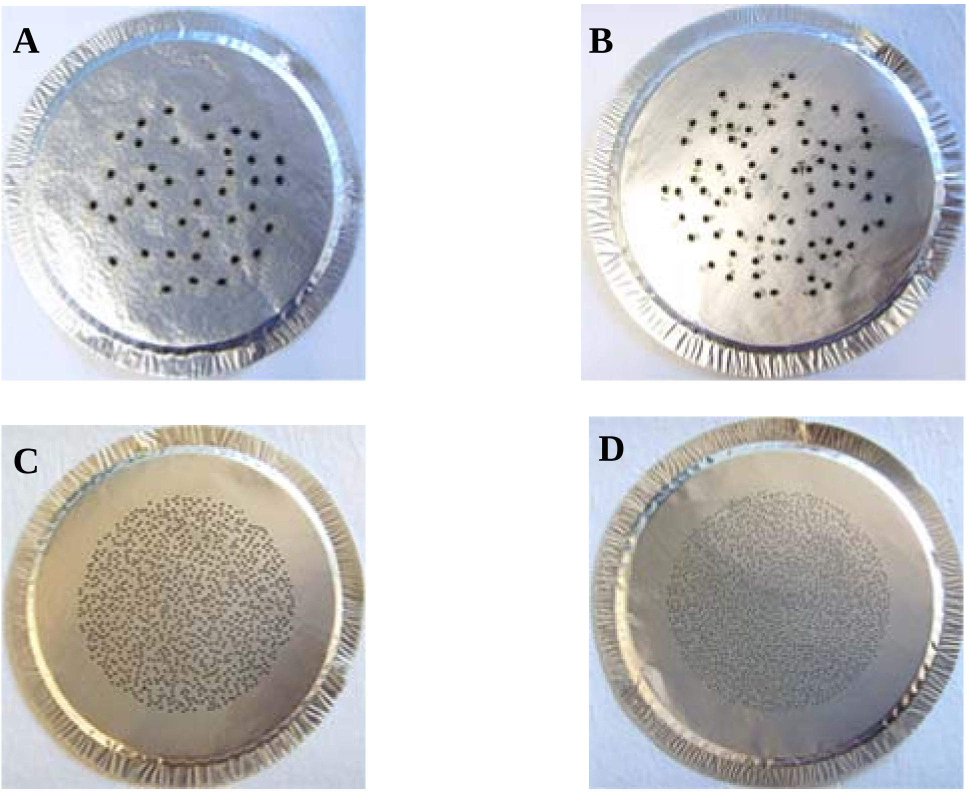


Figure 6. Size-resolved PM (A: 1.0-1.8 μm, B: 0.56-1.0 μm, C: 0.18-0.32 μm, D: 0.10-0.18 μm) deposited on aluminum foil substrates collected from the Del Paso Manor School site in Sacramento, CA in November (Phase I) 2007.

Figure 7. PM_{10} samples (A: morning, B: afternoon, C: overnight) collected from a Del Paso Manor School site in November (Phase I) 2007.

Ambient levels of size-resolved PM and time-resolved bulk PM_{10}

The levels of size-resolved PM varied from 1.26 to 6.15 μg/m^3 during Phase I and lower levels (0.39 to 1.94 μg/m^3) were observed during Phase II. The mass was greater for the 0.18-0.32 μm and 0.32-0.56 μm size bins (Figures 8-11). This pattern is similar to those typically found in atmospheric particles (Jimenez et al., 2003; Clarke et al., 2004; Chow et al., 2008). Higher concentrations of time-resolved PM_{10} were also observed in Phase I samples than in Phase II samples. Levels of PM_{10} in the Phase I morning, afternoon and overnight samples were 22.0, 45.3, and 40.5 μg/m^3, respectively, while levels of PM_{10} in Phase II samples ranged from 16.6 to 31.6 μg/m^3. Construction activity at a house near the sampling site possibly contributed to the high level of PM_{10} observed in the Phase I afternoon sample.

Concentrations of all size ranges of particles collected on MOUDI aluminum substrates were significantly higher in Phase I samples than in Phase II samples by factors of 2.6 to 7.7, while mass of PM_{10} in Phase I samples was higher by factors of 0.7 to 2.6. As described below, Phase I samples were highly affected by residential wood combustion and hence **residential wood combustion increased the levels of fine particles more significantly than coarse particles**.

Concentrations of bulk $PM_{1.8}$ samples collected during Phase II were 7.54 (Phase II-1), 6.51 (Phase II-2), and 8.34 (Phase II-3) μg/m^3. These concentrations were always greater than the mass of MOUDI $PM_{1.8}$, which is the sum of the PM on all 6 MOUDI stages. This discrepancy occurred because some particles were not deposited on these 6 stages. Some less sticky particles have a tendency not to be deposited on the aluminum substrates and they end up on quartz back-up filters. Particles smaller than the lowest cut (0.056 μm) of MOUDI stages are also collected on the back-up filters. Although they are not reported here, the mass of PM collected on backup filters was the equivalent of about 10% of the MOUDI $PM_{1.8}$ mass. Some particles were also deposited on upper stages for particles bigger than 1.8 μm. Those particles were also the equivalent of 5 to 10 % of the MOUDI $PM_{1.8}$ mass. Another uncertainty is the possible loss of particles during sample handling. Some less sticky particles may come off the aluminum substrates during the sample handling, potentially lowering the reported MOUDI $PM_{1.8}$ mass.

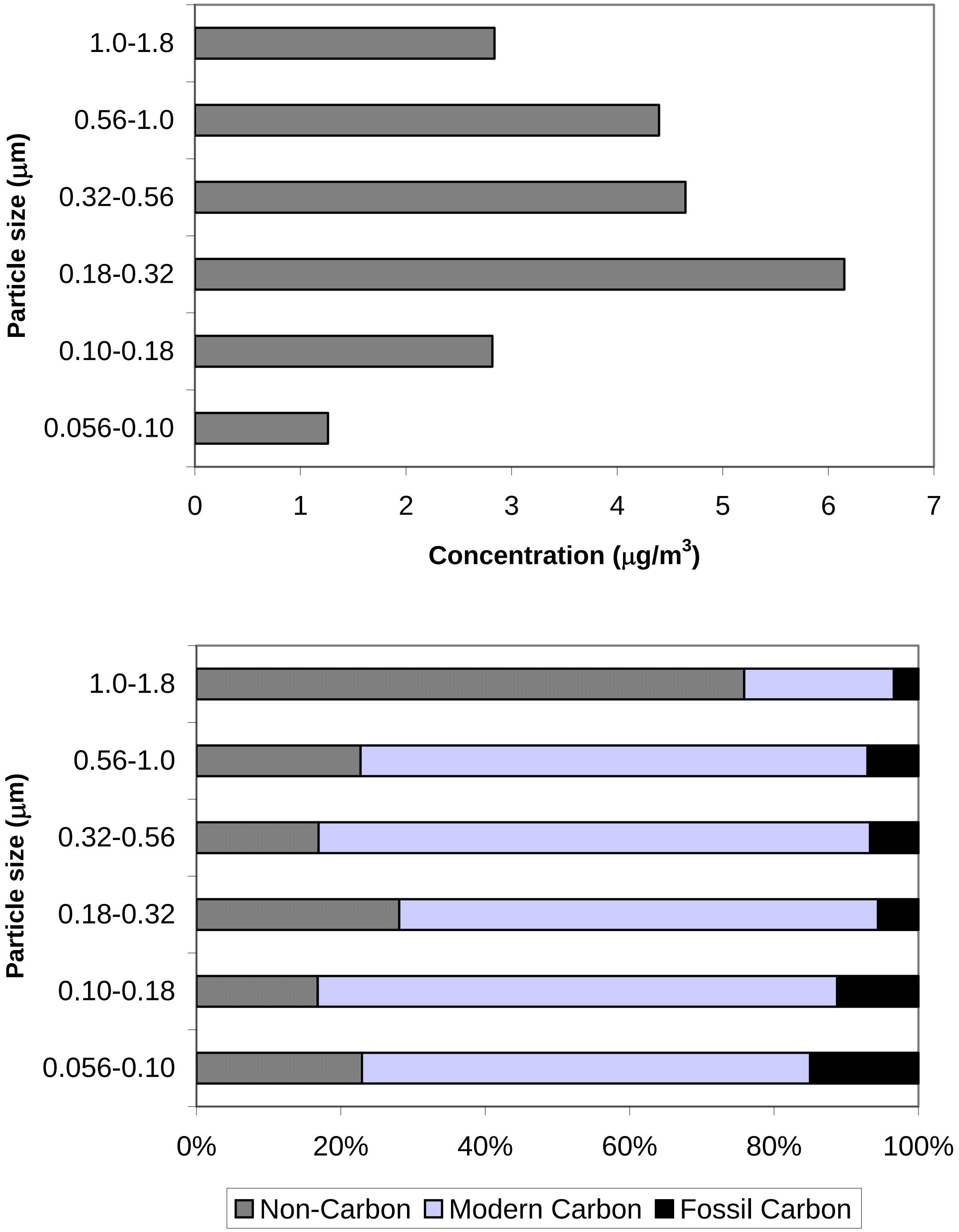


Figure 8. Concentrations (top) and composition (bottom) of size-resolved PM collected during Phase I.

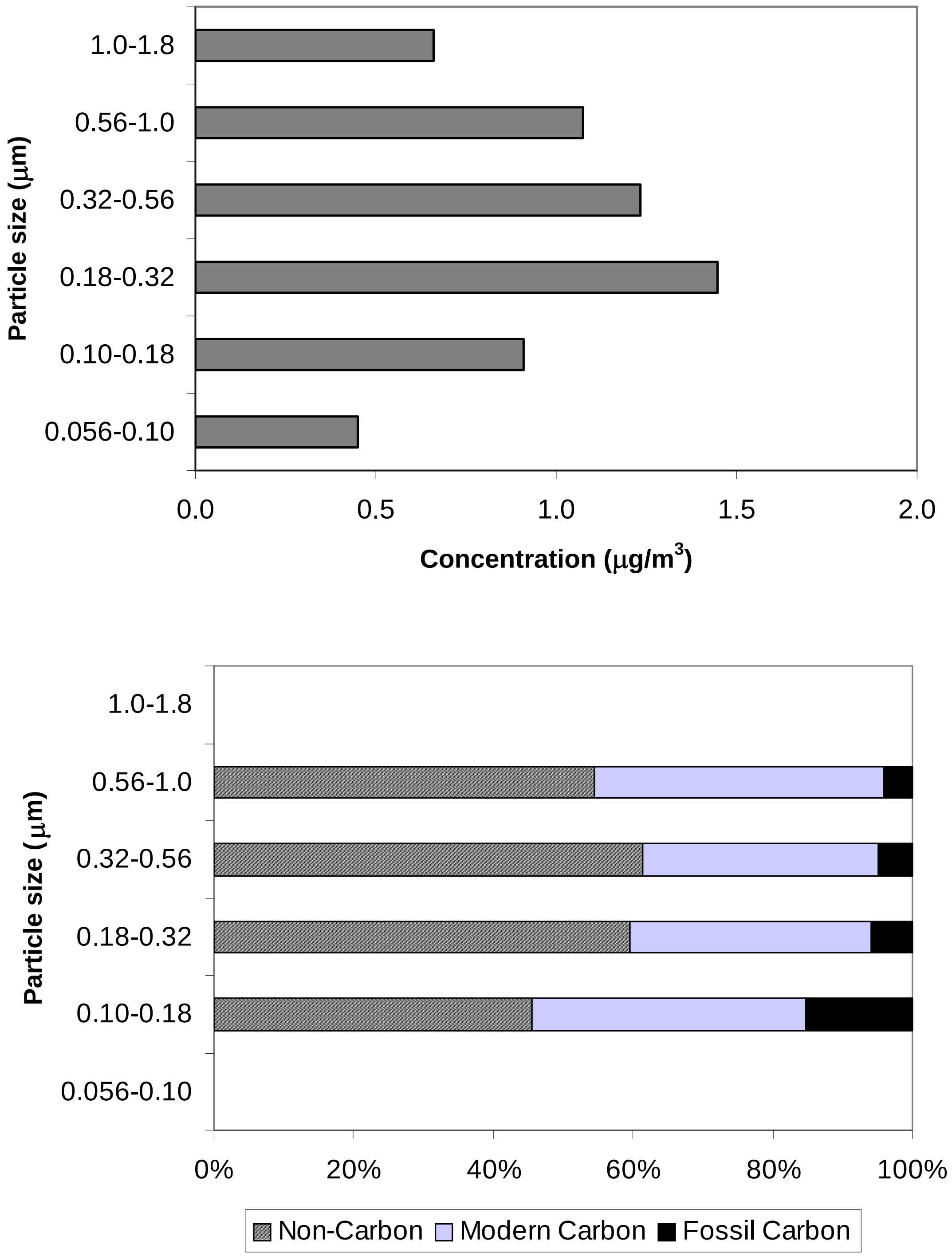
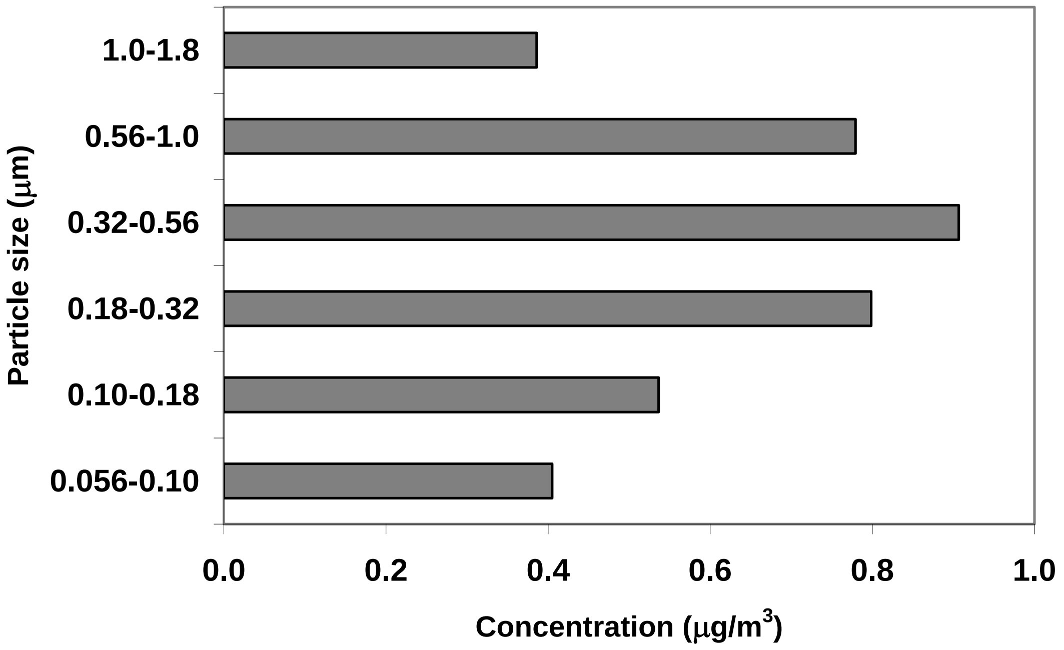


Figure 9. Concentrations (top) and composition (bottom) of size-resolved PM collected during Phase II-1.



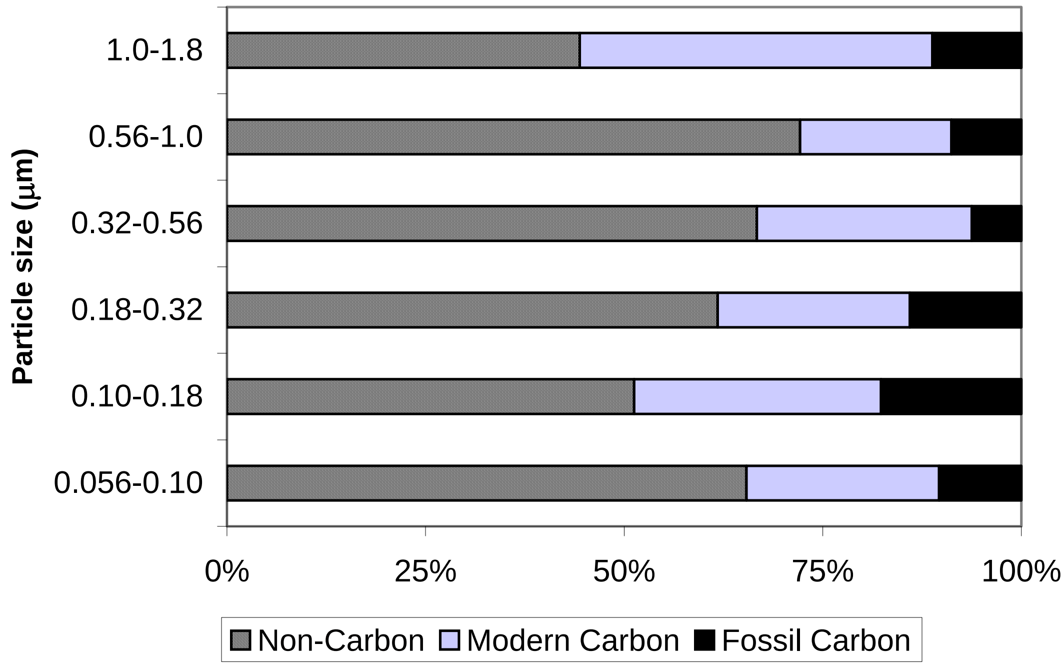
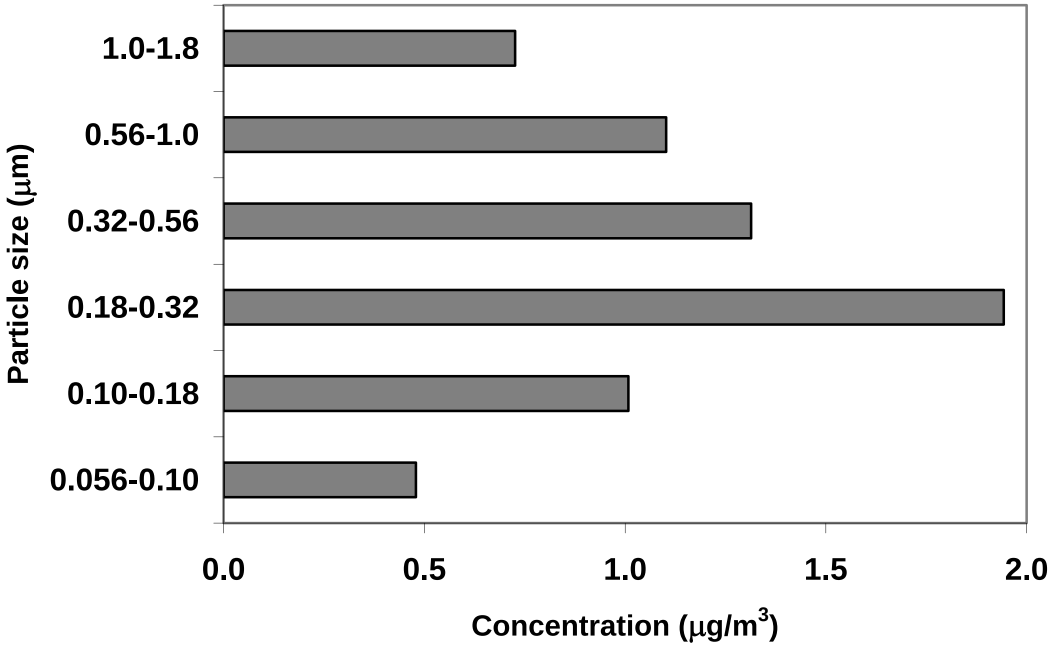


Figure 10. Concentrations (top) and composition (bottom) of size-resolved PM collected during Phase II-2.



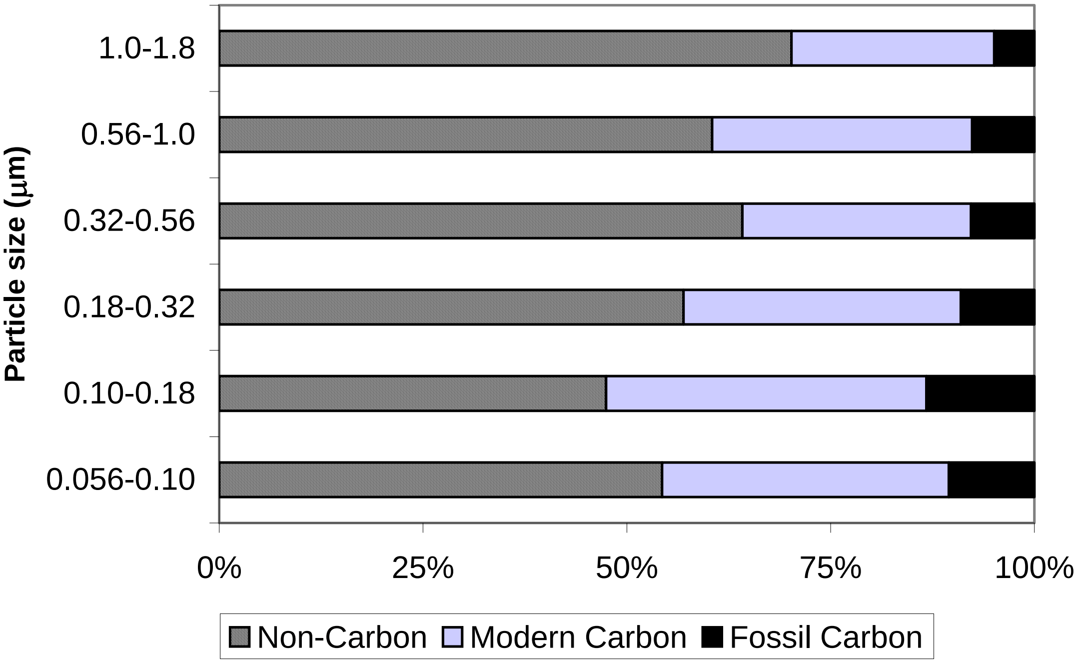


Figure 11. Concentrations (top) and composition (bottom) of size-resolved PM collected during Phase II-3.

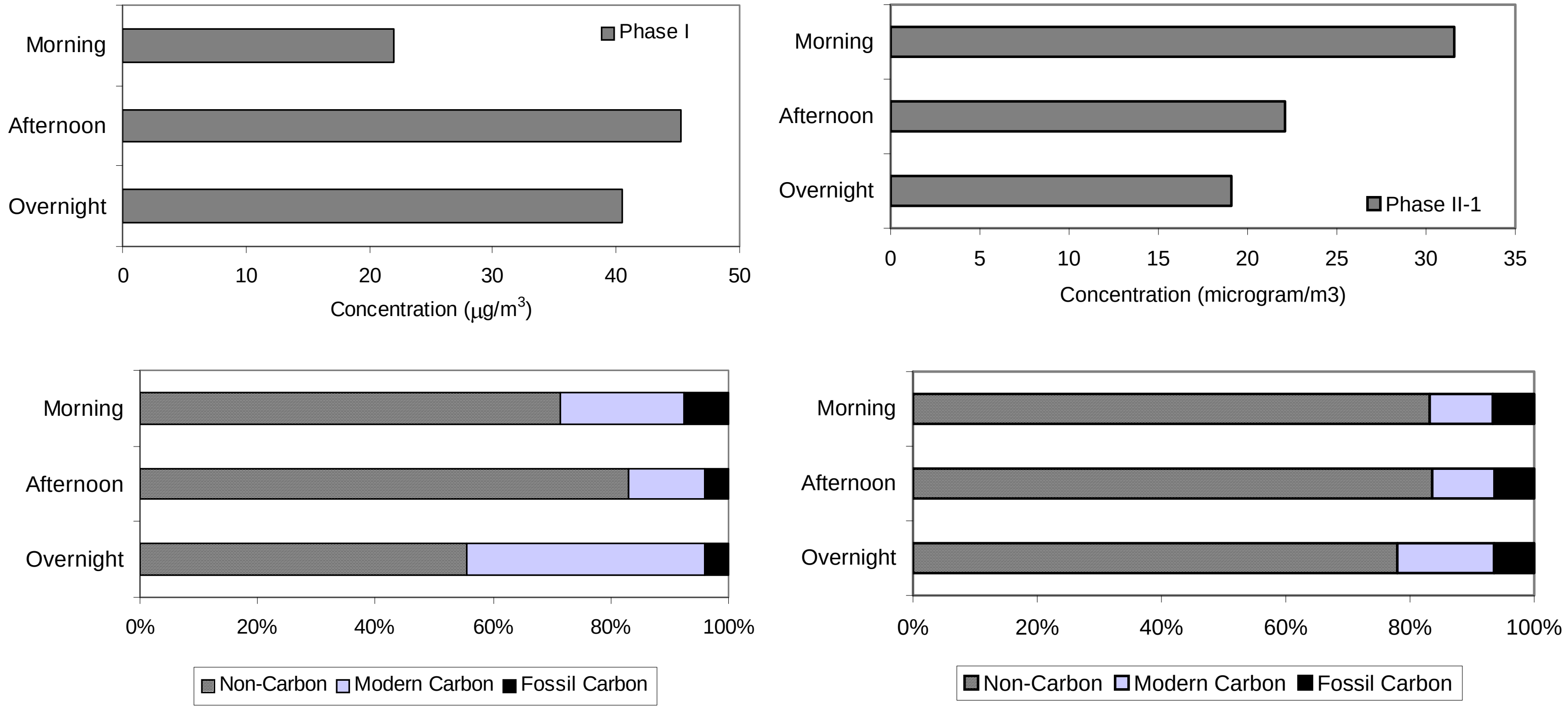


Figure 12. Concentrations (top) and composition (bottom) of time-resolved PM_{10} samples collected during Phases I and II-1.

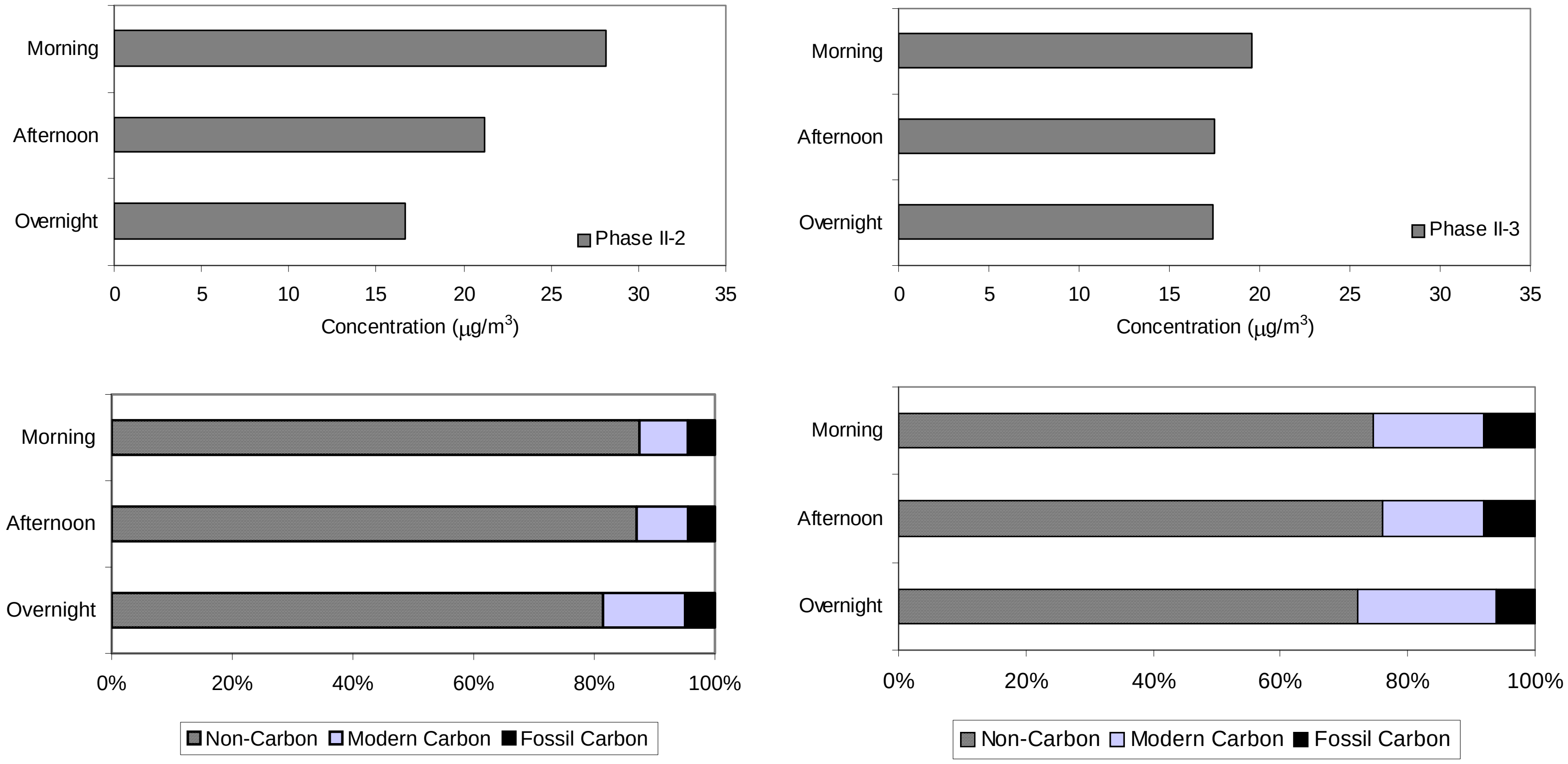


Figure 13. Concentrations (top) and composition (bottom) of time-resolved PM_{10} samples collected during Phases II-2 and II-3.

Carbon content and EC/OC ratios

In comparison with coarse particles, fine particles were more enriched with carbonaceous matter (organic carbon plus elemental carbon), as typically observed in atmospheric samples (Kim et al., 2000). The carbon content of PM_{10} samples was always 20 to 30% lower than MOUDI $PM_{1.8}$ samples. In the overnight PM_{10} sample collected during Phase I, the contribution of carbonaceous matter was about 45%, which was much greater than those of morning (29%) and afternoon (17%) samples. Carbon content of PM_{10} samples collected during Phase II varied from 13 to 28% of the total PM_{10} mass (Figures 12 and 13). During Phase I, the mass of size-resolved PM smaller than 1.8 μm was substantially dominated by carbonaceous matter that accounted for about 80% of the total mass (Figure 8). During Phase II, non- carbonaceous matter was more abundant, accounting for 50 to 70% (Figures 9, 10, 11). As described below, the Phase I samples were highly influenced by residential wood combustion, therefore, significantly higher levels of OC and EC found in the Phase I samples can be ascribed to active wood burning.

EC to OC (EC/OC) ratios in atmospheric particles can tell the relative contribution of combustion and non-combustion sources. EC is generated during the incomplete combustion of organic carbonaceous matter such as fossil fuels and biomass and thus can be used as a tracer for combustion sources. In urban areas, diesel powered vehicles are typically the predominant sources of elemental carbon (Kleeman et al., 2000). Contrary to EC, OC can originate from both combustion and non-combustion sources (e.g., emission from plants, abrasion of fallen leaves, photochemical reactions).

Concentrations of EC and OC in size-resolved PM and time-resolved bulk PM_{10} samples are presented in Figures 14 and 15, respectively. The EC/OC ratio of the MOUDI $PM_{1.8}$ sample collected during Phase I (0.35) was greater than those of Phase II samples (0.28 ± 0.03), indicating that the Phase I sample had a higher fraction of combustion originated particles, most likely from residential wood combustion as suggested by radiocarbon ratios and levoglucosan concentrations reported below. EC/OC ratios of the MOUDI samples were higher than those of corresponding time-resolved PM_{10} samples (except for the Phase I overnight sample) consistent with greater contribution of combustion originated particles to the smaller particle fraction. Among the time-resolved PM_{10} samples, the Phase I overnight sample had a much higher EC/OC ratio (0.28) than other samples (0.18 ± 0.04) (Figure 15). **This high EC/OC ratio indicates that wood combustion is likely a significant source of EC and it may not be reasonable to use EC as a diesel emission tracer in areas with extensive wood or other biomass combustion.** McDonald et al. (2000) and Fine et al. (2004) reported that EC accounted for up to 22.3% of the total mass of fine particles emitted from residential wood combustion. EC is non-volatile in the atmosphere while some OC compounds may be transferred between solid and gas forms depending on ambient air temperature (Turpin et al., 2000). This means that even though the same amounts of EC and OC are emitted from the same sets of sources, EC/OC ratios of atmospheric particles may be different depending on the ambient air temperature. Considering this ambient temperature effect, the EC/OC ratios of Phase II samples may overestimate the contribution of combustion sources.

Levoglucosan

Among the quantified individual organic compounds, levoglucosan, which is a good chemical marker for wood burning (Simoneit et al., 1999), was the most abundant ranging from 23.6 to 3,360 ng/m^3. Fine et al. (2004) reported that levoglucosan accounted for 10 to 40% of the organic carbon emitted from hard wood or soft wood combustion. Levoglucosan concentrations were much higher in Phase I samples than in Phase II samples (Figure 16). Levoglucosan in the Phase I overnight sample was up to 18-fold higher than the Phase II overnight samples. Comparing levoglucosan concentrations between morning, afternoon, and overnight periods, overnight samples were always highest and afternoon samples lowest. Timing of local residential wood burning is an obvious factor because it typically occurs during evening hours.

Ambient atmospheric temperature patterns may also affect the reported concentrations. During periods of relatively higher wind speeds or deeper mixing (as are typical during afternoon) the dilution of emissions into a larger atmospheric volume

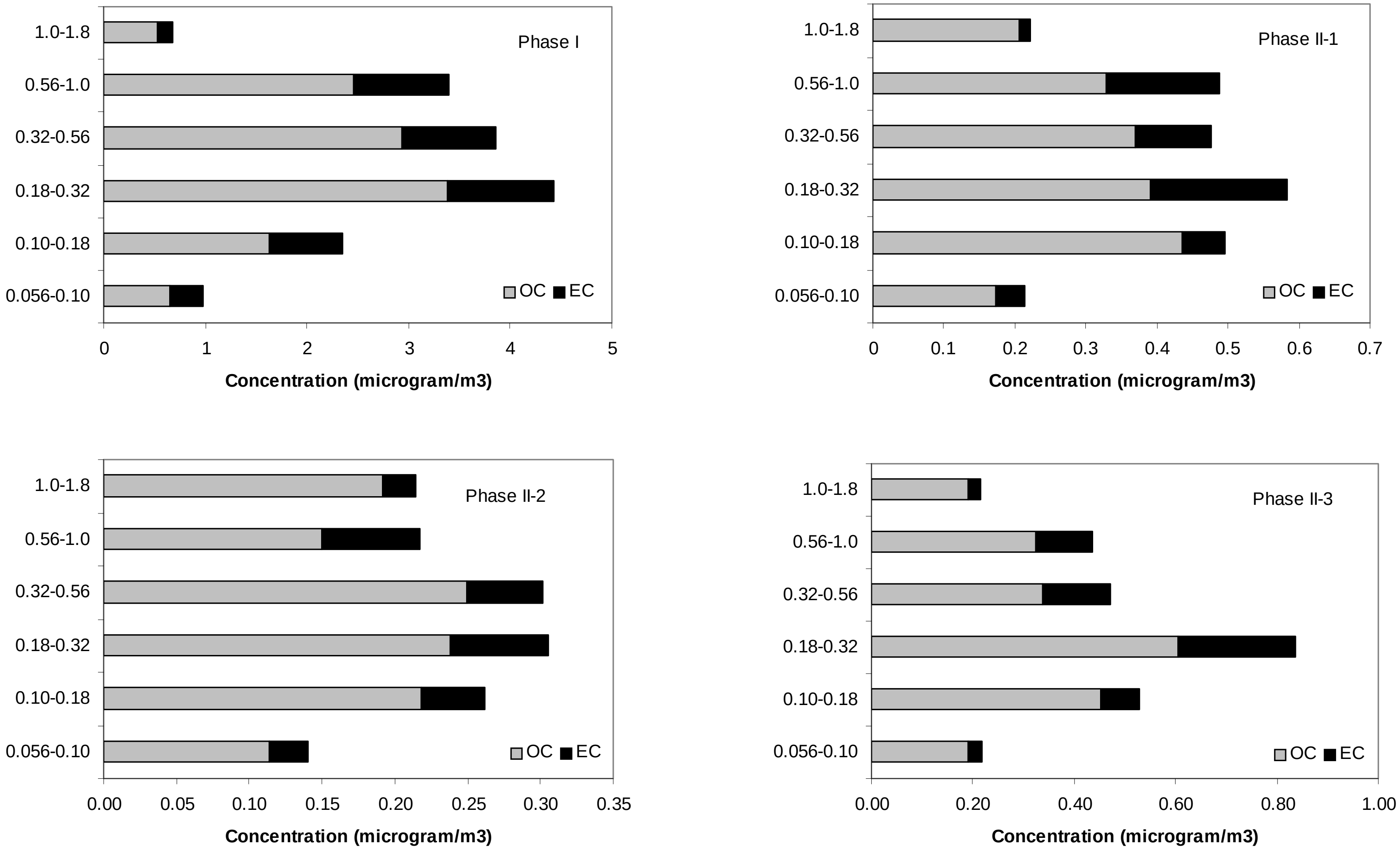


Figure 14. Concentrations (μg/m^3) of organic carbon (OC) and elemental carbon (EC) in size-resolved PM samples.

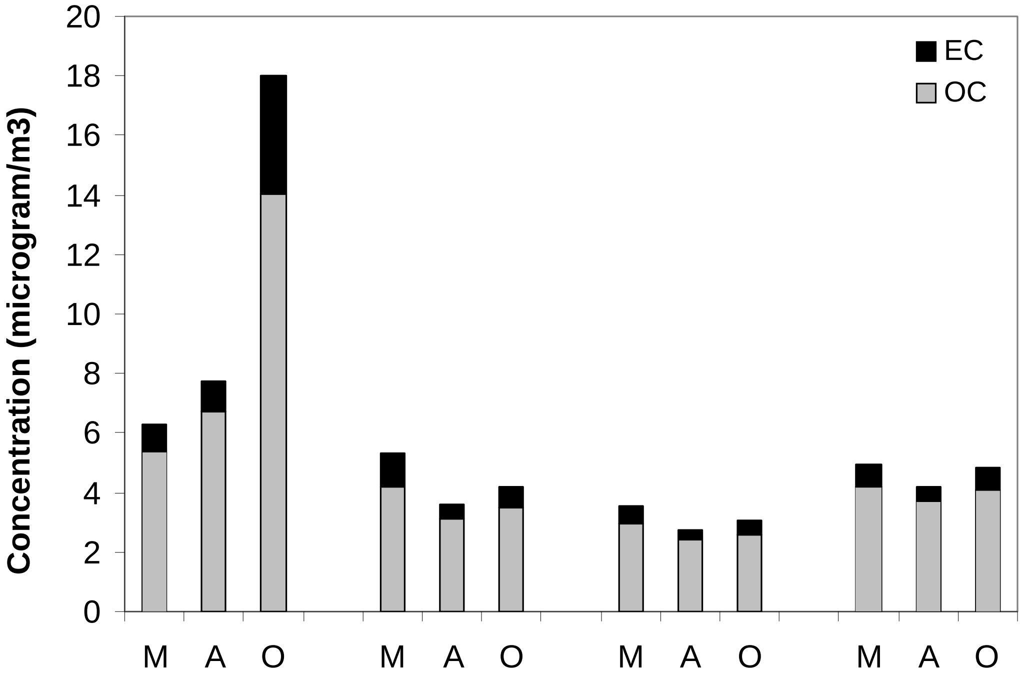


Figure 15. Concentrations (μg/m^3) of organic carbon (OC) and elemental carbon (EC) in time-resolved PM$_{10}$. (M: morning, A: afternoon, O: overnight).

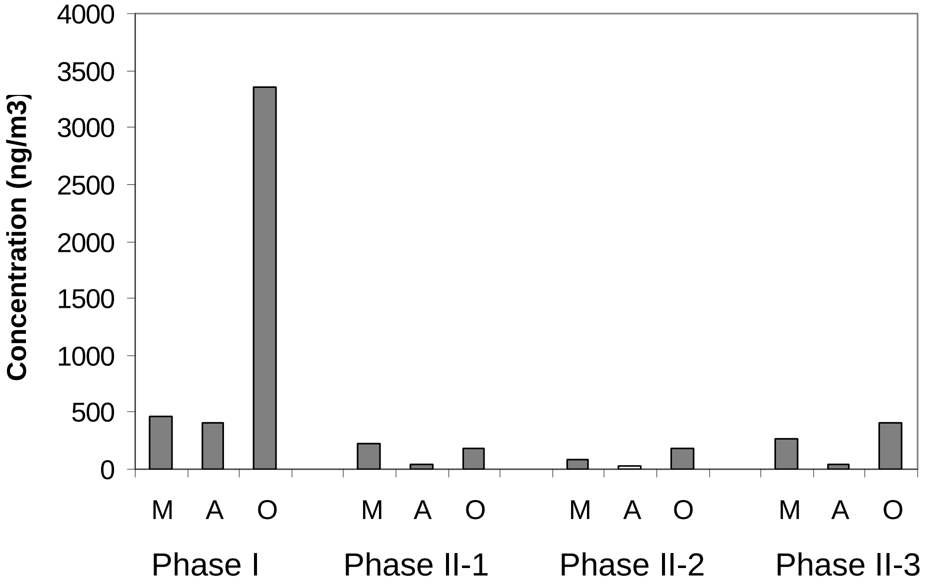


Figure 16. Atmospheric concentrations of levoglucosan in time-resolved PM$_{10}$ samples. (M: morning, A: afternoon, O: overnight).

would lower concentrations for all locally emitted pollutants and may be a factor in non-detects for levoglucosan. Typically mixing height is much higher in daytime than overnight. An increase in mixing height decreases the atmospheric concentration for a given mass of pollutant emitted to the air. Levoglucosan is one of the most commonly used source markers for source-receptor models. The basic assumption of these models is that source markers are essentially conserved and not subject to phase changes or other transformations between the times of emission and collection. However, almost no studies have systematically investigated the fate of levoglucosan in the ambient air.

Emissions of PM_{10} from some major sources such as vehicles, road dust, and meat cooking are likely to be relatively constant contributors to aerosol organic carbon throughout the year. However, wood combustion is more variable and occurs more frequently during the winter and at night in this area. **Increases in the contribution of PM from wood burning to the total PM load are expected to increase the observed ratio of levoglucosan to organic carbon (Levo/OC) and we suggest variation in Levo/OC as an indicator for the relative contribution of wood burning to the levels of PM_{10}.** Levo/OC ratios in the Phase I PM_{10} samples were 0.07 (afternoon), 0.09 (morning), and 0.19 (overnight), while those in the Phase II PM_{10} samples were much lower (0.01 to 0.10) confirming that wood burning was a more significant source during Phase I. In all 4 events, the Levo/OC ratios were much higher in samples collected overnight, followed by morning samples and afternoon samples. **When fossil carbon fractions are plotted against Levo/OC ratios in all samples (Figure 17) they showed a significant negative correlation (R^2=0.75). This plot indicates when the levoglucosan contribution to OC increased by 10%, the fossil carbon fraction declined by 16%. This result demonstrates the value of combining radiocarbon and conventional source marker results for more robust and detailed source attributions for ambient PM.**

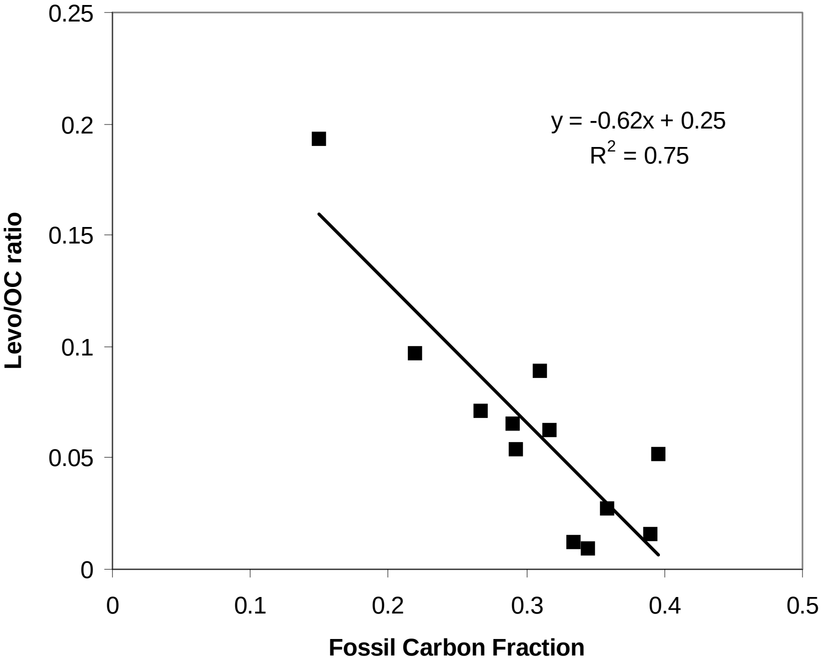


Figure 17. Comparison of fossil fuel fractions and levoglucosan to organic carbon (Levo/OC) ratios in time-resolved PM_{10} samples.

Alkanes

The distribution patterns of n-alkanes in PM_{10} collected during Phases I and II are shown in Figures 18-21. Alkane patterns were similar in all samples, except the Phase I overnight sample, which differed significantly. The carbon maximum (C_{max}) observed at C_{29} and C_{31} indicates a strong contribution from plant materials (Simoneit, 1989; Rogge et al., 1993b). Alkane distribution patterns observed in these samples suggest a less significant input of gasoline vehicle emissions as they do not reflect the alkane patterns for vehicle emissions (Figure 22) reported by Rogge et al. (1993a). The clearly different alkane pattern for the Phase I overnight sample, indicates significantly different PM source contributions during this sampling period. The Phase I overnight sample had a lower CPI (carbon preference index; odd-to-even ratio) of alkanes (C_{21} to C_{36}) of 1.18 compared to the other samples which all had CPIs around 2. Generally, lower CPI values have been used as an indicator of significant input from petroleum related sources such as gasoline and diesel combustion (Simoneit, 1986; Rogge et al., 1993a). However, particles from biomass burning have a wide range of CPIs depending on the types and species of biomass (Oros and Simoneit, 2001a, 2001b) and hence CPI alone may not indicate the sources of particles clearly. Particles from fossil fuel related sources are typically enriched with more volatile alkanes ($< C_{25}$) and their C_{max} is around 25 (Figure 22). The alkane distribution pattern in the Phase I overnight sample is not similar to any of those in vehicle emissions presented in Figure 22 and hence it does not represent fossil fuel dominated PM.

PAHs (polycyclic aromatic hydrocarbons)

Total PAH concentrations in time-resolved PM_{10} samples varied from 0.741 to 25.5 ng/m^3 (Table 6). The lowest and highest levels of PAHs were found in Phase II-2 afternoon and Phase I overnight samples, respectively. Volatile PAHs (2- and 3-ring PAHs) were not detected or were present at very low concentrations in all PM_{10} samples as typically observed in atmospheric PM samples. Wood combustion substantially increased the atmospheric concentrations of PAHs in the Phase I overnight sample. The concentration of total PAHs in the Phase I overnight sample was 7 to 13 times higher than those in the Phase II overnight samples. Similarly, higher levels of more carcinogenic PAHs such as benzo[a]pyrene, benzo[b]fluoranthene, benzo[g,h,i]perylene, indeno[1,2,3-cd]pyrene, and chrysene were observed during Phase I. All samples collected during Phase II had lower levels of PAH in afternoon samples than in morning and overnight samples by factors of 2 to 5. This finding is probably related to higher ambient atmospheric temperature during afternoon that enhanced volatilization. Volatilization loss of particle associated PAHs during air sampling is commonly known and 24-h sampling cycle is recommended to start early in the morning to minimize sampling artifact (Coutant et al., 1988; Peltonen and Kuljukka, 1995). Volatilization loss of low and medium molecular weight PAHs varies from 10 to 90% of particle Phase concentrations depending on ambient temperature (Coutant et al., 1988).

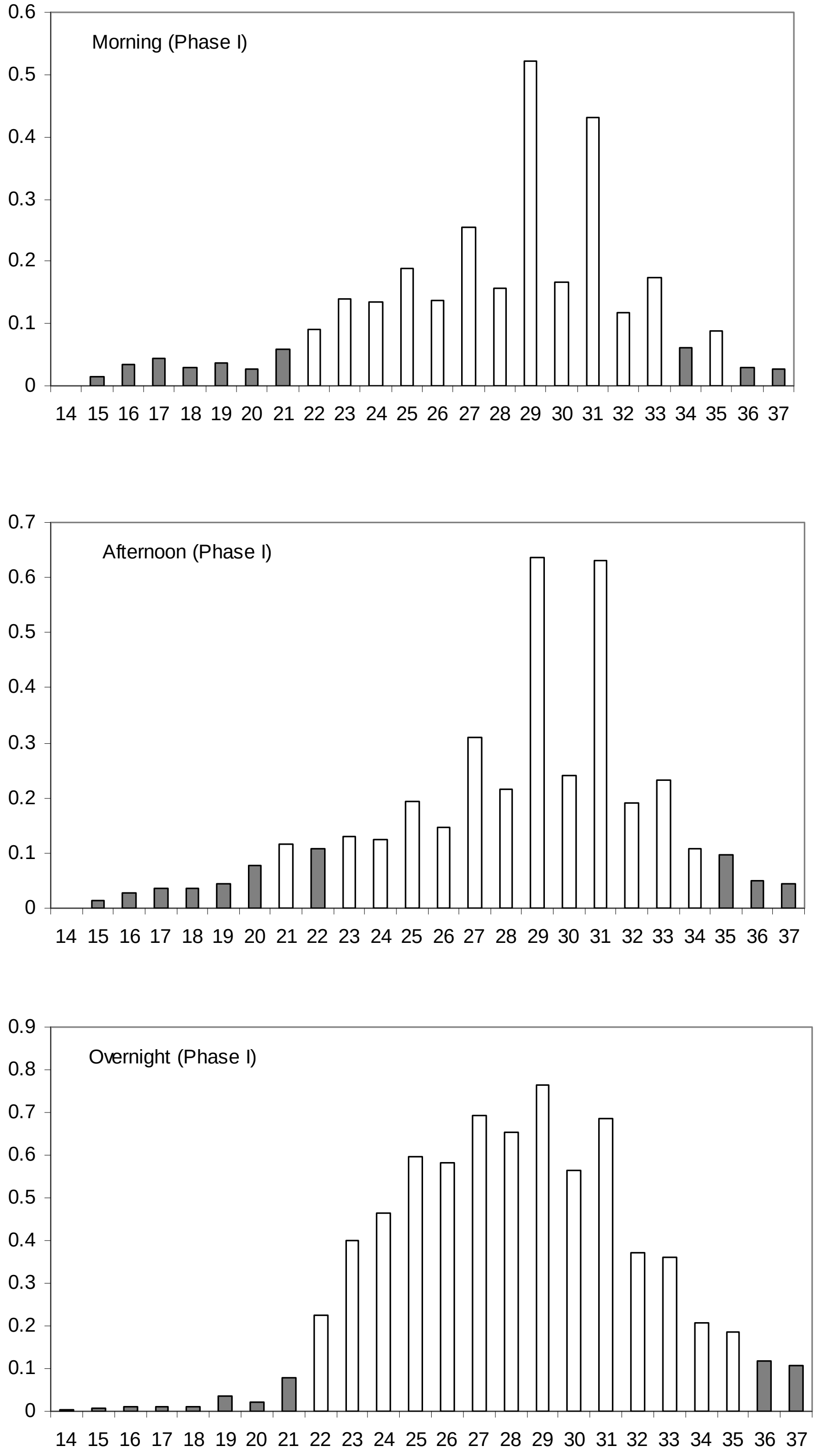


Figure 18. Distribution patterns of *n*-alkanes in time-resolved PM_{10} samples collected during Phase I.

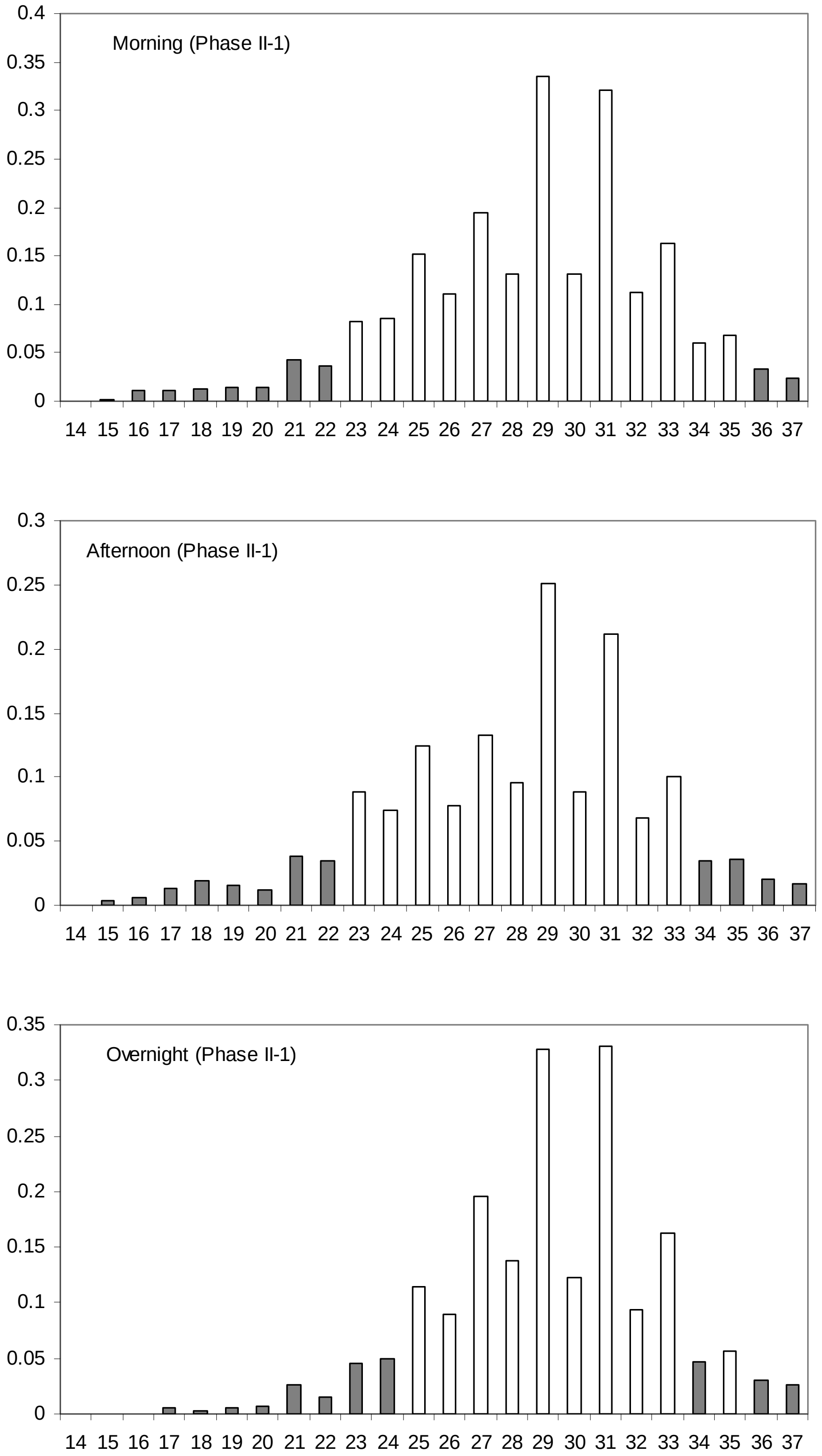


Figure 19. Distribution patterns of *n*-alkanes in time-resolved PM_{10} samples collected during Phase II-1.

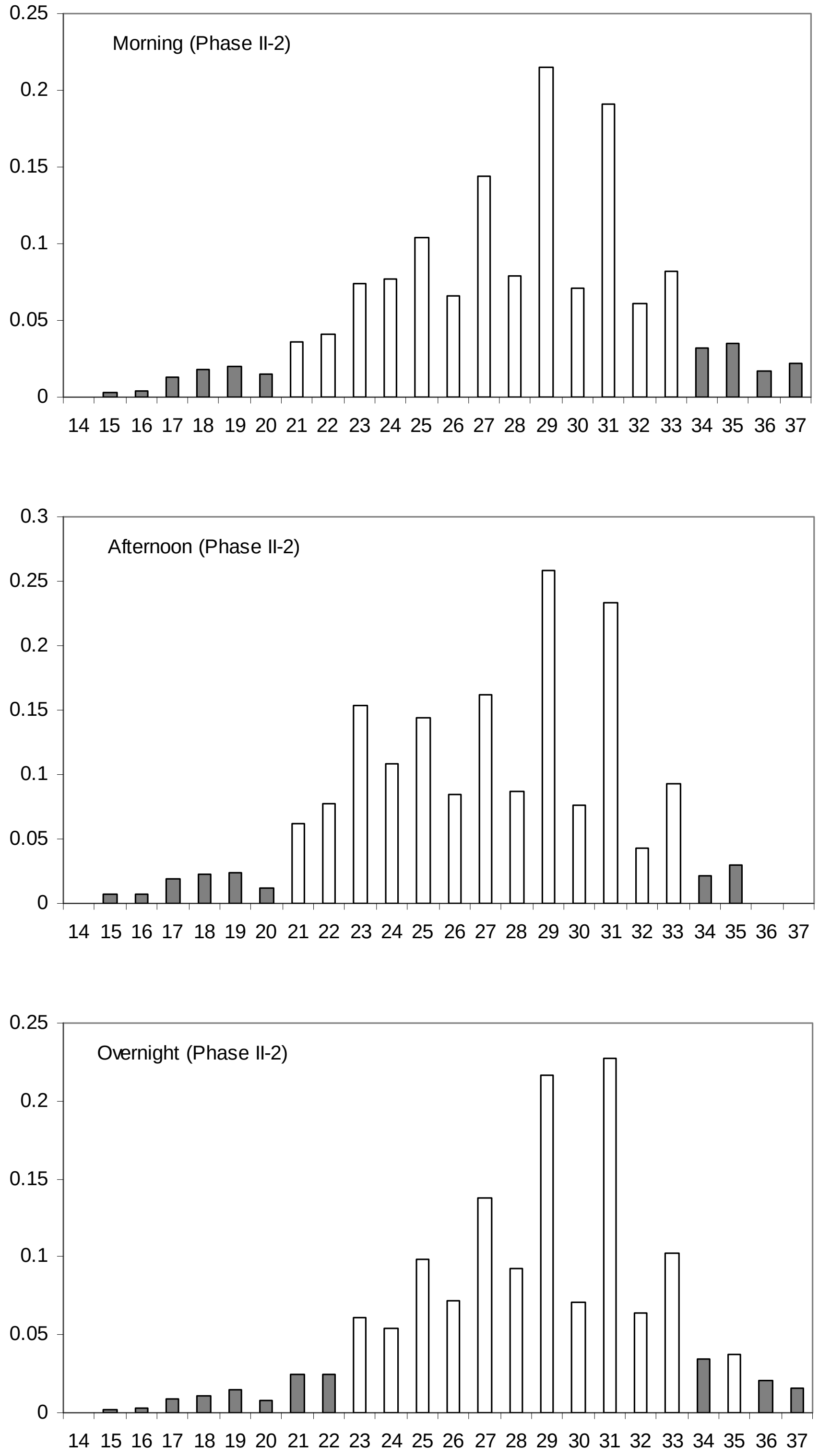


Figure 20. Distribution patterns of n-alkanes in time-resolved PM_{10} samples collected during Phase II-2.

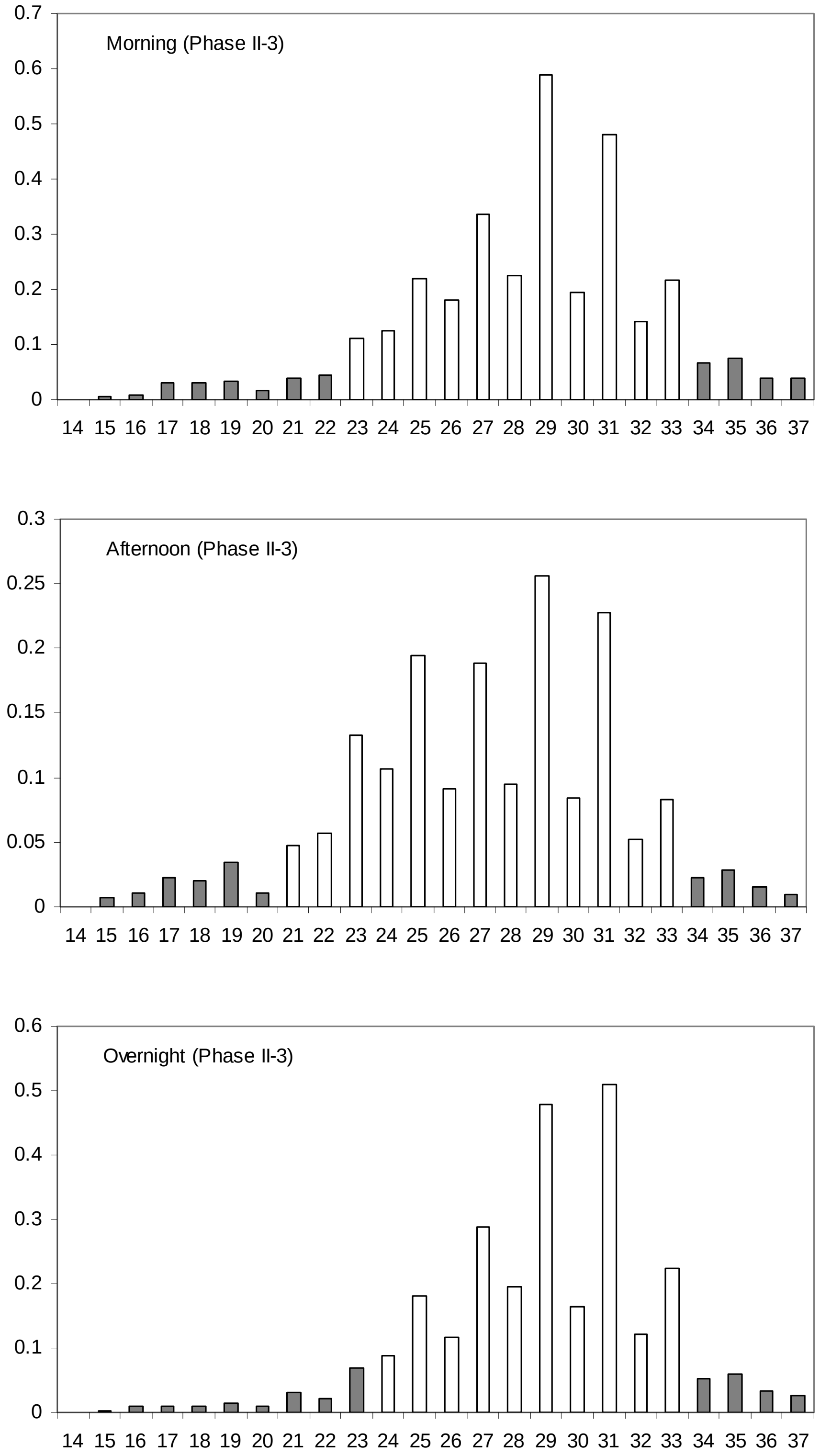


Figure 21. Distribution patterns of n-alkanes in time-resolved PM_{10} samples collected during Phase II-3.

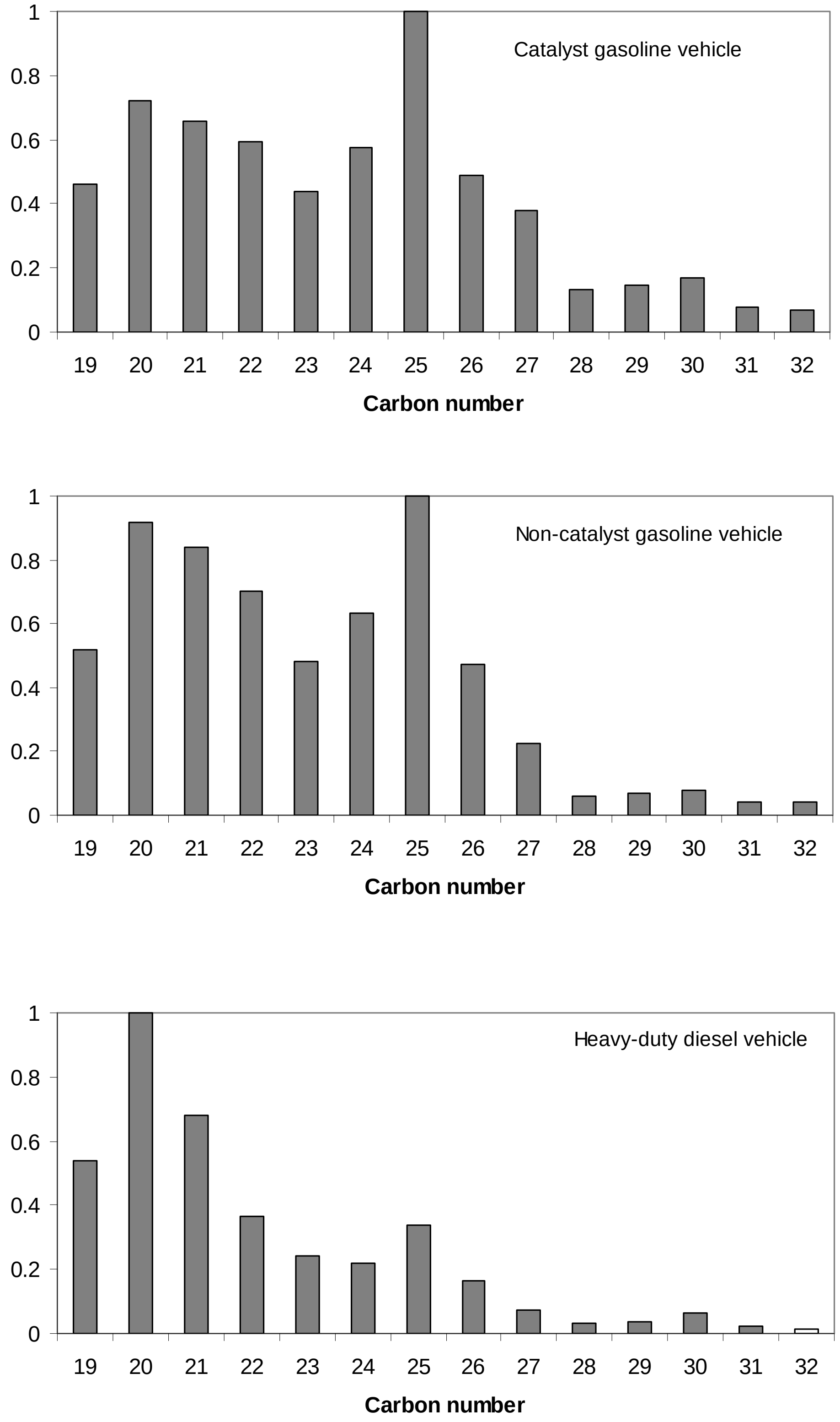


Figure 22. Distribution patterns of n-alkanes in $PM_{2.5}$ from vehicle emissions (Rogge et al., 1993).

Concentrations of retene, which is another marker for wood combustion (Ramdahl, 1983), in time-resolved bulk PM_{10} were much higher in Phase I samples than in Phase II samples. Interestingly, the highest level of retene was found not in the Phase I overnight sample but in the morning sample. Retene concentrations varied by a factor of more than 20 across three samples which had very similar levoglucosan concentrations. Retene concentrations plotted against levoglucosan concentrations with the Phase I morning sample excluded as an outlier (Figure 23, top) suggests positive correlation but the number of samples and their range of concentrations is limited. Comparing retene and levoglucosan as wood combustion markers, significantly lower concentrations of retene limit its use in atmospheric particle source apportionment. Retene concentrations were lower than levoglucosan concentrations by 3 orders of magnitude or more. Total PAHs and levoglucosan were also positively correlated (Figure 23, bottom), further supporting the idea that atmospheric concentrations of particle associated PAHs were highly influenced by residential wood combustion.

Cholesterol

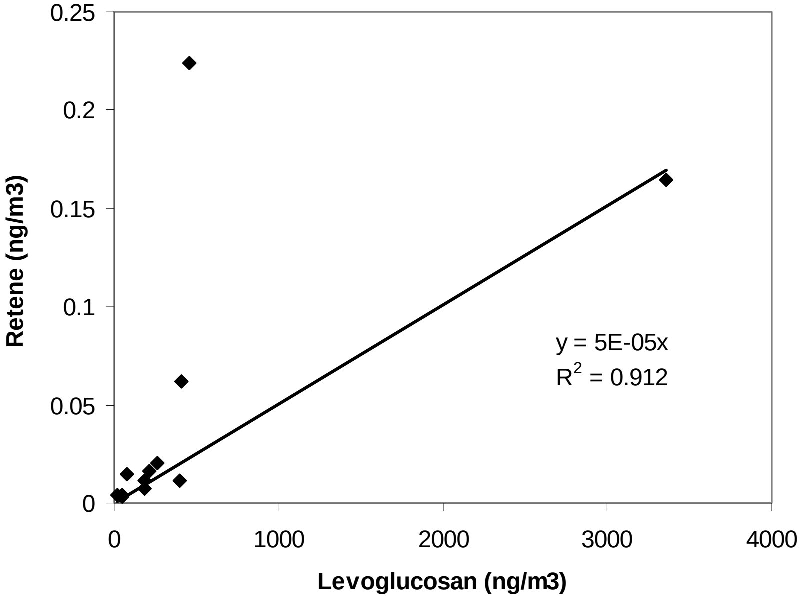
In all samples, cholesterol was either not detected or was present at very low concentrations, indicating that particles generated from meat cooking were not significant contributors to carbonaceous PM at this site or that collection duration was insufficient to collect measurable amounts of cholesterol. During the study period, particles filtered from water samples collected from a local creek were analyzed for cholesterol although this was not a part of the present study. Very high levels of cholesterol were found in those creek water samples (data are not reported here). Kanazawa and Teshima (1971) found high levels of cholesterol (2.3 to 20.5 μg/L) in sea water. Biosolids and animal manure also contain very high levels of cholesterol (Ibanez et al., 2000) so suspended soil particles from areas with biosolid or animal manure application may contribute to cholesterol content of PM. Thus, use of cholesterol as a marker for meat cooking might be erroneous in areas where sea aerosols or suspended biosolid particles could be confounding sources for cholesterol.

Table 6. Concentrations (ng/m^3) of PAHs in time-resolved PM$_{10}$ samples.

	Phase I			Phase II-1		
	Morning	Afternoon	Overnight	Morning	Afternoon	Overnight
Phenanthrene	0.062	0.122	0.102	0.048	0.021	0.056
Anthracene	0.005	0.018	0.036	0.010	0.005	0.016
Retene	0.224	0.062	0.164	0.016	0.003	0.007
C1-Dibenzothiophene	<MDL	0.096	0.143	0.042	0.052	0.038
C2-Dibenzothiophene	0.125	0.202	0.411	0.098	0.147	0.000
C3-Dibenzothiophene	0.141	0.217	0.296	0.105	0.164	0.100
Fluoranthene	0.150	0.276	0.487	0.113	0.044	0.144
Pyrene	0.154	0.300	0.575	0.130	0.044	0.162
C1-Flu/Pyr	0.124	0.185	0.753	0.077	<MDL	0.087
Benz[a]anthracene	0.126	0.214	2.398	0.098	0.024	0.153
Chrysene	0.226	0.297	5.293	0.147	0.040	0.164
C1-chrysene	0.115	0.122	1.784	0.096	0.020	0.079
Benzo[b]fluoranthene	0.553	0.676	1.903	0.511	0.102	0.642
Benzo[k]fluoranthene	0.134	0.149	1.159	0.107	0.020	0.157
Benzo[a]fluoranthene	0.028	0.044	0.532	0.025	0.005	0.050
Benzo[e]pyrene	0.260	0.321	1.746	0.261	0.050	0.327
Benzo[a]pyrene	0.099	0.183	1.768	0.106	0.017	0.140
Perylene	0.029	0.049	0.472	0.027	<MDL	0.049
Indeno[1,2,3-cd]pyrene	0.512	0.628	1.728	0.474	0.084	0.568
Dibenzo[a,h]anthracene	0.062	0.070	0.694	0.046	0.010	0.085
Benzo[g,h,i]perylene	0.506	0.678	2.253	0.504	0.087	0.498
Coronene	0.157	0.199	0.676	0.156	0.024	0.120
Total PAHs	3.792	5.106	25.536	3.197	0.966	3.642

Table 6. Continued.

	Phase II-2			Phase II-3		
	Morning	Afternoon	Overnight	Morning	Afternoon	Overnight
Phenanthrene	0.053	0.020	0.024	0.102	0.035	0.037
Anthracene	0.015	ND	0.004	0.018	0.006	0.007
Retene	0.015	0.004	0.011	0.020	0.004	0.011
C1-Dibenzothiophene	0.079	0.053	0.044	0.067	0.086	0.037
C2-Dibenzothiophene	0.181	0.141	0.106	0.103	0.204	0.096
C3-Dibenzothiophene	0.237	0.181	0.112	0.120	0.234	0.103
Fluoranthene	0.163	0.037	0.060	0.366	0.087	0.074
Pyrene	0.194	0.041	0.081	0.396	0.078	0.082
C1-Flu/Pyr	0.109	0.003	0.036	0.146	<MDL	0.039
Benz[a]anthracene	0.203	0.011	0.051	0.185	0.019	0.050
Chrysene	0.235	0.037	0.076	0.231	0.046	0.085
C1-chrysene	0.090	<MDL	0.044	0.051	<MDL	0.062
Benzo[b]fluoranthene	0.565	0.057	0.301	0.642	0.086	0.375
Benzo[k]fluoranthene	0.130	0.013	0.071	0.146	0.021	0.102
Benzo[a]fluoranthene	0.037	<MDL	0.012	0.042	<MDL	0.027
Benzo[e]pyrene	0.253	0.030	0.159	0.293	0.035	0.195
Benzo[a]pyrene	0.152	0.011	0.058	0.155	0.016	0.072
Perylene	0.037	<MDL	0.018	0.040	<MDL	0.033
Indeno[1,2,3-cd]pyrene	0.430	0.044	0.269	0.489	0.053	0.315
Dibenzo(a,h)anthracene	0.056	ND	0.029	0.052	ND	0.029
Benzo[ghi]perylene	0.372	0.045	0.259	0.413	0.053	0.288
Coronene	0.088	0.012	0.063	0.111	0.025	0.064
Total PAHs	3.696	0.741	1.888	4.188	1.091	2.183



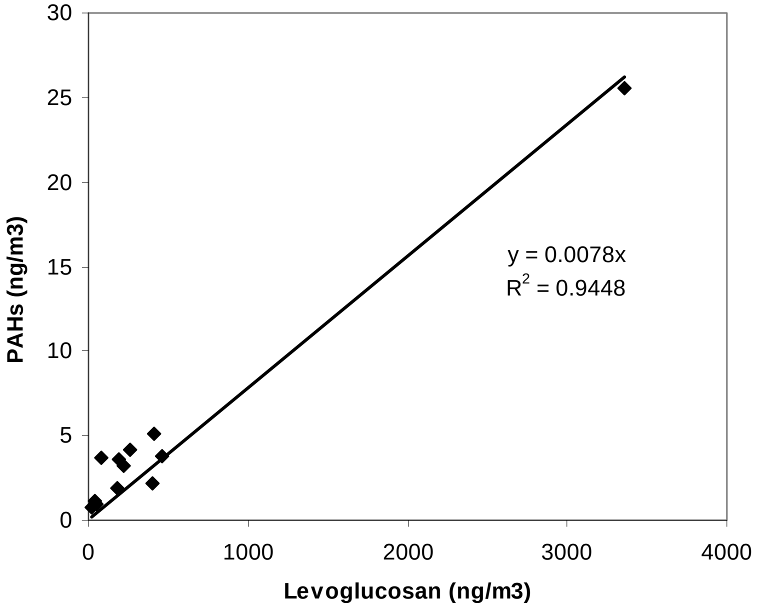


Figure 23. Comparison of levoglucosan with retene (top) and total PAHs (bottom).

SUMMARY AND CONCOLUSIONS

This project was conducted to improve understanding of the sources of carbonaceous component of atmospheric particulate matter. The ultimate goal of this project was to lay the ground work for future tools that might be easily implemented with archived or routinely collected samples. A key feature of this study was application of radiocarbon measurement that can be interpreted to indicate the relative contributions from fossil and non-fossil carbon sources of atmospheric PM. As a complementary tool, source-specific markers such as levoglucosan, cholesterol, and elemental carbon were also measured to provide further information on the likely emission sources.

This project consisted of two phases that were conducted in late November 2007 (Phase I) and in March 2008 (Phase II). The first phase was a pilot study intended to demonstrate the proposed strategies and methods of sample collection and measurement of radiocarbon and source markers to differentiate fossil carbon and non-fossil carbon sources. For the second phase, the same methods and strategies as of the pilot study were applied to collect three sets of samples.

For each phase, size-resolved particles (0.056 to 1.8 μm) and time-resolved PM_{10} (morning, afternoon, overnight) were collected using MOUDI samplers and high volume PM_{10} samplers, respectively, for the measurement of radiocarbon and source markers. All PM samples were collected near the Sacramento Metropolitan AQMD Del Paso Manor monitoring site, located at an elementary school in a residential neighborhood northeast of the Sacramento downtown and commercial areas.

Carbon mass (organic carbon plus elemental carbon) of all samples (except one) collected for the present study was sufficient to measure radiocarbon content with high levels of confidence. One or two days of sampling is likely to be sufficient to collect the required carbon mass (30 μg) for all size ranges of fine particles using MOUDI samplers (flow rate: 30 mL/min) during the wintertime when ambient PM levels are high, while at least 3 or 4 days of collection is necessary during the spring and fall when ambient PM levels are low. In the case of bulk $PM_{1.8}$ (10 mL/min, 47 mm ID filter) and PM_{10} (1,113 mL/min, 8 in × 10 in filter), one day of sampling is probably sufficient to collect enough carbon during spring/fall and winter.

Radiocarbon data indicates that the contribution of non-fossil carbon sources was much greater than that of fossil carbon sources in all samples. A greater contribution of modern carbon in Phase I samples is highly likely due to residential wood combustion around the sampling site.

Among the quantified individual organic compounds, levoglucosan was the most abundant. Levoglucosan concentrations were also much higher in Phase I samples than in Phase II samples, indicating that residential wood burning was highly likely a cause of higher non-fossil carbon fraction. The plot of fossil carbon fractions against levoglucosan to organic carbon content ratios indicates that when the levoglucosan contribution to OC increased by 10%, the fossil carbon fraction declined by 16%. This plot demonstrates that more robust and detailed source profile can be obtained when radiocarbon and conventional source marker results are combined together.

Much higher ambient EC/OC ratios found in Phase I samples indicate that wood combustion is likely a significant source of EC and demonstrate that EC is not a unique tracer for diesel emissions. In particular, use of EC as a diesel emission tracer may not be reasonable in areas where wood combustion could be a confounding source for EC.

The present study provides evidence that typical or slightly modified sample collection strategies (e.g., extending collection time to ensure sufficient TC mass for analysis) allow analytical techniques used in the present study to be successfully applied to archived or routinely collected samples.

The results of the present study demonstrate that more robust and detailed source attribution can be obtained when radiocarbon and conventional source marker data are combined together.

It is desirable to compare the results of the present study and source attribution of PM samples collected at the Sacramento Metropolitan Air Quality Management District (AQMD) Del Paso Manor monitoring site during the same period of the present study.

RECOMMENDATION

Apply the approach used in the present study to archived and routinely collected samples if they are stored frozen (-20 °C). If ARB changes storage conditions for both $PM_{2.5}$ and PM_{10} samples, analytical techniques used in this study can be directly applied to samples that will be archived and routinely collected in the future. This study provides evidence that additional sample collection activities, which need additional cost and labor, are not required for radiocarbon measurement and source marker analysis. The approach used in the present study has both economic and technical merits and can be adopted easily for more accurate PM source apportionment.

Compare the source contribution results of the present study with source attribution of PM samples collected at the Del Paso Manor monitoring site by the Sacramento Metropolitan Air Quality Management District during the same period of this study. This comparison will further help ARB evaluate and refine processes for PM source apportionment.

Systematically investigate the atmospheric fate and sources of some source-specific markers such as levoglucosan, cholesterol, and elemental carbon to minimize uncertainties in estimating contribution of sources represented by these markers. Volatilization of semi-volatile organic compounds from the filters during sample collection may result in underestimation of emission from certain sources. Much higher EC/OC ratios found in Phase I samples indicate that wood combustion is likely a significant source of EC and it may not be reasonable to use EC as a diesel emission tracer in areas wood combustion could be a confounding source for EC. PM from sea aerosols and resuspended soil particles may contain significant amounts of cholesterol and thus may cause significant uncertainties in estimating the contribution of meat cooking based on cholesterol.

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