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Primary and secondary carbonaceous species in the atmosphere of Western Riverside County, California

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Abstract

Elemental carbon (EC), organic carbon (OC) and $PM_{2.5}$ mass concentrations were measured from September 2001 through January 2002 in Mira Loma, CA. EC and OC were analyzed using the NIOSH (National Institute of Occupational Safety and Health) 5040 thermal/optical transmittance method. OC concentrations in Mira Loma were found to be higher than those of other urban sites in the South Coast Air Basin (SoCAB), while EC concentrations were comparable to or lower than those of other SoCAB sites. Overall, OC and EC concentrations accounted for 26% and 5% of the total $PM_{2.5}$, respectively. OC/EC ratios ranged from 1.6 to 12.8 with an average of 5.2. These values were higher than those observed at other urban sites in the United States by a factor of 2. A stronger correlation between suspended OC and EC concentrations was noted in months with lower photochemical activity (December and January, $r = 0.82$) than in months with greater photochemical activity (September and October, $r = 0.64$). The elevated levels of OC, OC/EC ratios, and the seasonal difference in correlation between OC and EC concentrations were attributed in part to significant secondary organic aerosol formation. The fraction of total organic carbon that was secondary organic carbon (SOC) was estimated using the OC/EC minimum ratio method and Chemical Mass Balance (CMB) modeling. Based on the OC/EC minimum ratio method, the contribution of SOC to the total organic carbon tended to be higher during the months with greater photochemical activity (63%) than those with lower photochemical activity (44%). Based on CMB modeling, SOC contributed to 14% of the total $PM_{2.5}$ mass and 57% of the total organic carbon during the study period. Overall, these findings suggest that photochemical activity can appreciably affect total $PM_{2.5}$ mass concentrations in Mira Loma, and that measures to control emissions of SOC precursors incorporated as part of a region-wide air quality management plan could lead to a perceptible drop in total $PM_{2.5}$ mass concentrations in this area.

Keywords: Organic carbon; Elemental carbon; $PM_{2.5}$; OC-to-EC ratio; Secondary organic carbon

1. Introduction

Studies conducted in southern California have shown that carbonaceous species are an important contributor to the mass concentration of particulate matter smaller than 2.5 μm in aerodynamic diameter ($PM_{2.5}$). It has been shown that carbonaceous species contribute between 26% and 39% of the total $PM_{2.5}$ mass in the South Coast Air Basin (SoCAB), a region encompassing Los Angeles and Orange counties, and part of Riverside and San Bernardino counties (Kim et al., 2000; ARB, 2000). The carbonaceous fraction of ambient $PM_{2.5}$ consists of elemental carbon (EC) and organic carbon (OC). A minor component of the fine fraction of the aerosol may also exist either as carbonates (e.g., $CaCO_3$) or carbon dioxide (CO_2)(Appel et al., 1989).

Elemental carbon (EC), also called "black carbon" or "graphitic carbon", has a chemical structure similar to impure graphite. EC is generated by the combustion of carbon-containing fuels. Even though EC is generally considered inert, the combustion process results in the EC being coated by organic matter such as polycyclic aromatic hydrocarbons (e.g., benzo[a]pyrene), which

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have been shown to have carcinogenic and mutagenic properties (Klaassen, 1996; Pitts, 1983). Carbon-containing components such as EC and OC contribute to visibility reduction. For example, Pratsinis et al. (1984) reported that the carbon-containing components were responsible for 27% and 44% of the incident light extinction at Lennox and Duarte, respectively, in the Los Angeles air basin.

Organic carbon (OC), a mixture of hydrocarbons and oxygenates, is formed by a variety of processes, including combustion and secondary organic aerosol (SOA) formation. Reactive organic gases (ROGs) such as toluene, xylenes and α-pinene react with photochemical oxidants to form SOA. The fractional conversion of ROGs to SOA is a function of vapor pressure of the oxidation products, the total concentration of organic aerosol, activity of solution, relative humidity (RH) and temperature. The conversion of ROGs to SOA has been previously investigated (Pankow, 1994; Odum et al., 1996; Griffin et al., 1999; Cocker et al., 2001). During air pollution episodes, SOA contributions as high as 75% on summer days and 50% on winter days have been observed in southern and central California (Strader et al., 1999; Turpin and Huntzicker, 1995). Therefore, in order to reduce the ambient OC mass concentration, it is very important to control both primary emissions of particulate OC and of ROGs that react to form SOA.

Mira Loma is located in Western Riverside County, California, approximately 81 km east of downtown Los Angeles. This area has a population of 17,617 and a total area of 16.9 km^2. As seen in Fig. 1, Mira Loma is situated at the intersection of two major freeways. On the western side of Mira Loma there is an agricultural area with a large number of dairy farms. Recently, Mira Loma has experienced significant growth in the number of warehouse and distribution centers, leading to an increase in heavy-duty diesel vehicular traffic in the area. Consequently, Mira Loma is situated in a region with potentially significant agricultural, upwind, and local sources for air quality degradation.

This study is part of the Mira Loma air quality study (Sawant et al., 2004) and focuses on the organic and elemental carbon components in $PM_{2.5}$. The purpose of this study is to examine the concentration and characteristics of elemental carbon and organic carbon in the Mira Loma atmosphere and to estimate secondary organic carbon (SOC) formation in order to understand the contribution of SOC to the total organic carbon.

2. Experimental methods

2.1. Sample collection

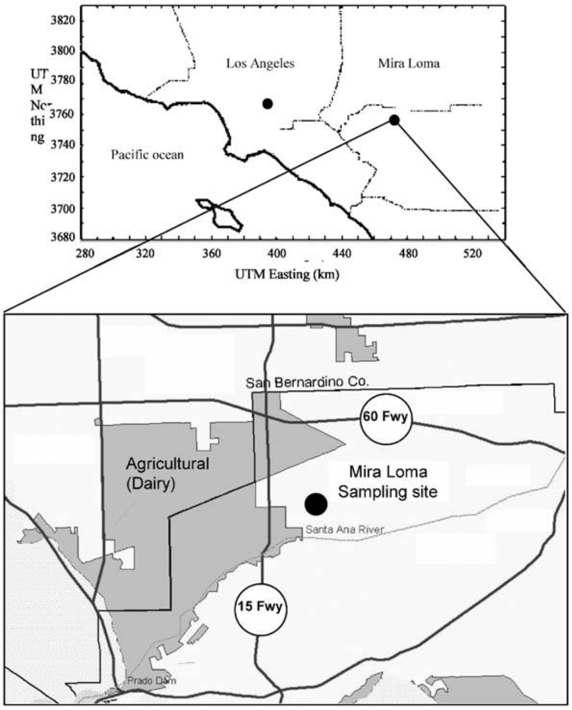

Fig. 1. Map of sampling location.

OC, EC and $PM_{2.5}$ samples were collected at an outdoor sampling site in southwestern Mira Loma (Fig. 1) from September 18, 2001 through January 26, 2002. The sampling systems used in this study employed the principle for $PM_{2.5}$ impactor design described by Biswas and Flagan (1988). The impactor was connected to a manifold with multiple sampling lines for measurement of total $PM_{2.5}$ mass by gravimetric analysis, organic and elemental carbon (OC/EC) by thermal/optical transmittance, ionic nitrate and sulfate by ion chromatography, and trace elements by X-ray fluorescence (XRF). Additional sampling lines were used for measurement of gas-phase ammonia, nitric acid and carbonyl compounds, and were not connected to the $PM_{2.5}$ impactor. Critical orifices (O'Keefe Controls, Trumbull, CT, USA) were used to control flow rates on all lines; these were calibrated every 12 days using a Gilibrator 2 bubble flow meter (Sensidyne, Clearwater, FL, USA). Critical orifices were connected by means of polyethylene piping to a 0.19 kW oil-less GAST 0523 vacuum pump (GAST, Benton Harbor, MI, USA). The pump was housed in a sound-insulated weatherproof container. $PM_{2.5}$ samples for mass determination were collected on 47 mm diameter PTFE Teflo™ filters (Pall-Gelman, Ann Arbor, MI, USA) with pore size of 2 μm. EC and OC samples were collected in parallel on precleaned QAT Tissuquartz™ quartz-fiber filters (Pall-Gelman, Ann Arbor, MI, USA). A quartz-fiber filter behind the front PTFE filter was used to estimate the sampling artifact due to the adsorption of organic gases in the absence of particles. Sample collection occurred from 8 p.m. to 8 p.m. (24 h) every other day. Samples for EC, OC and $PM_{2.5}$ measurement were collected approximately 1.5 m above ground level at flow rates of $5\,L\,min^{-1}$ through each sampling line.

2.2. Substrate preparation

Quartz fiber filters were pre-cleaned to remove carbonaceous contaminants by firing for 4 h at 600°C. Several such fired filters were analyzed as blanks for OC and EC. In all cases, the OC and EC concentrations on these filters were below the instrument detection limit.

These filters were stored in dark sealed petri dishes at 0°C until use. Teflo filters measured were conditioned for a minimum of 24 h in a controlled temperature/RH chamber at 25°C and 40% RH, both before and after sampling, to minimize the effects of water artifact (if any). Filter weights were obtained on an ATI-Cahn C-35 microbalance (Thermo Orion, Beverly, MA, USA). Weights were considered valid if duplicate weights on different days were within 3 μg of each other. The average of these two weights for each case (initial and final) were taken to be the initial and final weights, respectively.

2.3. Organic and elemental carbon analysis

A Thermal/Optical Carbon Aerosol Analyzer (Sunset Laboratory, Forest Grove, OR) operating on the NIOSH (National Institute of Occupational Safety and Health) Method 5040 was used to analyze for OC and EC. The analysis proceeds in two stages. In the first stage, organic and carbonate carbon (if present) are volatilized from the sample in a pure helium atmosphere as the temperature is stepped to about 820°C. Evolved carbon is catalytically oxidized to CO_2 in a bed of granular MnO_2, reduced to CH_4 in a nickel-firebrick methanator and quantified as CH_4 by a flame ionization detector (FID). During the second stage of the analysis, pyrolysis of OC correction and EC measurement are made. The oven temperature is lowered to 60°C, a 1:9 oxygen–helium mix is introduced and the oven temperature is then raised to about 860°C. As oxygen enters the oven, pyrolytically generated EC from OC is oxidized and a concurrent increase in filter transmittance occurs. Correction for the char contribution to EC is accomplished by measuring the amount of char oxidation required to return the filter to its initial transmittance value. More details on the analysis can be found elsewhere (Birch and Cary, 1996). The detection limit is 0.2 μg C.

2.4. Filter artifact correction of organic carbon

Ambient OC coexists in both the gas and particulate phases. Gas-phase OC may be adsorbed to the filter media or PM already collected during sampling, leading to a positive sampling artifact. Negative sampling artifacts may arise from the volatilization of organic compounds that are adsorbed to the PM. The combined effect of positive and negative OC artifacts can be estimated by measuring OC concentrations on a "back-up" quartz filter located behind a Teflon filter (Kim et al., 2001). Turpin et al. (1994) and Fitz (1990) concluded that positive sampling artifacts comprise the major sampling artifacts for OC. Fitz (1990) showed that OC on the back filter is primarily an artifact due to irreversible adsorption of gas-phase organics and suggested that the subtraction of weight of OC on the back filter from that on the front filter gave a reasonable correction to the sampling artifact. Consequently, in this study, final OC concentrations are estimated by subtracting the OC measured on backup filters from the OC measured on front filters. $48 \pm 15\%$ of the OC concentration collected on a front quartz filter was positive artifact.

However, it is still difficult to estimate the exact amount of positive and negative artifact with this tandem filter method. One reason is that the OC captured on the backup filter includes both positive and negative artifact. Another reason is that the gas/particle partitioning of semi-volatile organic compounds is a strong function of ambient temperature. Thus, higher temperatures can reduce the positive artifact and increase the negative artifact. In a tandem filter system, volatilization of OC adsorbed on the PM and the front filter substrate can increase with ambient temperature, leading to higher loading of OC on the backup filter. The correlation between the ratio (OC on backup filter/OC on front filter) and ambient temperature was studied to investigate this effect. For clarity, the data sets were grouped by season: fall (September and October) and winter (December and January), and the correlation coefficients estimated for the two groups. The temperature difference between the two seasons was approximately 10°C (see Section 3.4 for details on seasonal grouping). Very weak correlations were found for both groups (fall: $\text{slope} = -0.87$, $r = 0.22$; winter: $\text{slope} = -0.45$, $r = 0.1$). It appears plausible that the temperature difference between the two seasons is not sufficiently large to significantly affect artifact formation.

3. Results and discussion

3.1. Organic carbon and elemental carbon concentrations in $PM_{2.5}$

Table 1 lists monthly mean mass concentrations of $PM_{2.5}$, organic carbon (OC), and elemental carbon (EC) from this study and other studies at various sites. The organic carbon concentrations given throughout this

Table 1
Literature values for organic carbon (OC), elemental carbon (EC) and total carbon (TC) in $PM_{2.5}$ ($\mu g\,m^{-3}$)

Study	Time span	$PM_{2.5}$	OC	EC	OC/EC	% of TC in $PM_{2.5}$
This study	September	64.7 ± 8.7	15.1 ± 3.7	2.5 ± 0.7	6.1 ± 1.3	27.1 ± 4.4
	October	57.9 ± 22.1	11.9 ± 5.7	1.5 ± 0.6	8.1 ± 2.9	23.4 ± 5.4
	November	41.6 ± 23.2	10.0 ± 5.1	2.0 ± 1.1	6.0 ± 3.1	33.8 ± 16.1
	December	27.6 ± 14.3	9.7 ± 3.8	2.4 ± 1.0	4.2 ± 1.0	47.3 ± 12.9
	January	33.5 ± 11.3	9.8 ± 4.6	2.2 ± 0.9	4.8 ± 1.9	37.6 ± 12.3
	Average	41.8 ± 6.4	10.8 ± 4.9	2.1 ± 1.0	5.2 ± 2.7	30.5 ± 14.4
Diamond Bar, USA[a]	10/31–11/2/1997	89.6	17.1	3.2	5.3	29.5
Mira Loma, USA[a]		68.4	20.8	2.6	8.1	36.6
Riverside, USA[a]		77.8	15.2	2.3	6.7	30.5
Rubidoux, USA[b]	1–2/1999	26.7	5.7	3.3	1.7	33.7
Phoenix, USA[b]		14.9	7.6	3.3	2.3	73.2
Philadelphia, USA[b]		17.4	4.3	1.5	2.9	33.3
Los Angeles, USA[c]	1/1995–2/1996	31.32	7.74	3.81	2.03	36.9
San Nicolas Island, USA[c]		6.82	1.49	0.19	7.84	24.6
Beijing, China[d]	7/1999–9/2000	115	21.5	8.7	2.5	30.2
Abbotsford, Canada[e]	5/1994–2/1995	6.3	2.1	0.9	2.3	48.0
Kaohsiung, Taiwan[f]	11/1998–4/1999	68	10.4	4.0	2.6	21.3
São Paulo, Brazil[g]	7/11–9/10/1997	30.2	15.8	7.6	2.1	77.5
Seoul, South Korea[h]	11/27–12/9/1999	N.R.	15.2	7.3	2.1	—

Note: N.R. = not reported.
[a] Allen et al. (2000).
[b] Tolocka et al. (2001).
[c] Kim et al. (2000).
[d] He et al. (2001).
[e] Brook and Dann (1999).
[f] Lin and Tai (2001).
[g] Castanho and Artaxo (2001).
[h] Park et al. (2002).

study are estimated to be 1.9 times the measured OC. This is to account for oxygen, nitrogen and hydrogen associated with organic matter. The use of a factor of 1.9 was based on previous recommendations of 1.6 ± 0.2 for urban organic carbon, and 2.1 ± 0.2 for non-urban organic carbon (Turpin and Lim, 2001). Since Mira Loma is a semi-rural area downwind of a major urban area, the 1.9 factor was deemed to be appropriate, being the lower limit for the rural aerosol in the above paper. Within the same paper, the researchers cited their estimations of the factor based on the data of Rogge et al. (1993) and calculated an OC factor of 1.77 for the Rubidoux area, which is ~7 km due east of our outdoor sampling site. Russell (2003) estimated a factor of 1.6 for this same area. However, Russell stated that OC factors based on limited GC-MS data (which can account for only about 10% or so of total organic aerosol mass) gives the OC factor a range from 1.1 to 2.8, depending upon the degree of unsaturation or oxygenation of the organic aerosol mass. Further, when the factor of 1.9 was applied to the recalculated data, the final value came very close to the total measurement of PM (accounting for 92.5% of the mass). Percent differences between reconstituted $PM_{2.5}$ masses calculated using the factors of 1.9 and 1.4 were 10 ± 5%, showing that the use of different factors did not lead to significant differences in the reconstituted $PM_{2.5}$ mass.

In this study, 24-h average $PM_{2.5}$ mass concentrations ranged from 7.0 to 97.3 $g\,m^{-3}$, with an average of 41.8 $\mu g\,m^{-3}$. Current federal standards require the annual average and daily $PM_{2.5}$ mass concentration to be <15 and 65 $\mu g\,m^{-3}$, respectively. Our average $PM_{2.5}$ value of 41.8 $\mu g\,m^{-3}$ is comparable to the annual average values obtained at the nearby SCAQMD monitoring site in Rubidoux in 1995 (39.75 $\mu g\,m^{-3}$) (Kim et al., 2000).

In this study, OC concentrations in the total $PM_{2.5}$ mass ranged from 2.8 to 26.1 $\mu g\,m^{-3}$ with an average of 10.8 $\mu g\,m^{-3}$, contributing, on average, 25.5% to the total $PM_{2.5}$. EC concentrations varied from 0.7 to

4.6 μg m^{-3} with an average of 2.1 μg m^{-3}, contributing, on average, 4.9% to the total $PM_{2.5}$. This indicates that total carbon is a significant contributor to the total $PM_{2.5}$ mass concentration. OC was the predominant contributor to the total carbon, contributing on average 83.7% of the measured total carbon. In addition, OC was the second-highest contributor (after inorganic nitrate, which contributed 26%) to total $PM_{2.5}$ mass (Sawant et al., 2004).

O'Kelly (2001) reported that the elemental carbon fraction of PM_{10} in Mira Loma (3.7 μg m^{-3}), located downwind of Los Angeles (LA), was less than the level measured in Central LA (4.0 μg m^{-3}), but the overall OC concentrations were higher in Mira Loma (10.8 μg m^{-3}) than those in Central Los Angeles (9.0 μg m^{-3}). As presented in Table 1, Allen et al. (2000) reported that the highest average OC concentrations were in Mira Loma (20.78 μg m^{-3}), followed by Diamond Bar (17.05 μg m^{-3}) and Riverside (15.21 μg m^{-3}), while average EC concentrations were the highest in Diamond Bar (3.24 μg m^{-3}), followed by Mira Loma (2.56 μg m^{-3}) and Riverside (2.27 μg m^{-3}). The data of O'Kelly and Allen were based on a limited number of days. According to the study results conducted in the South Coast Air Basin (SoCAB) (Kim et al., 2000), higher secondary OC, NH_4^+, NO_3^- and SO_4^{2-} were observed at inland sites such as Rubidoux compared with coastal sites such as downtown Los Angeles. Elevated secondary aerosol concentrations are expected as transported precursor emissions have more time to react to form secondary OC, NH_4NO_3 and $(NH_4)_2SO_4$. In contrast, the level of EC concentrations in Mira Loma is comparable to or lower than other urban sites in the SoCAB.

In summary, total carbon (i.e., OC + EC) was a significant contributor to the observed $PM_{2.5}$ mass in Mira Loma during the study period, accounting for over 30% of the total $PM_{2.5}$ mass concentration. OC was the major contributor to total carbon. On average, OC accounted for almost 84% of the total carbon, and almost 26% of the total $PM_{2.5}$ mass observed in Mira Loma during the study duration.

3.2. OC/EC concentration ratios

OC/EC ratios in this study ranged from 1.6 to 12.8 with an average of 5.2. As shown in Table 1, the average OC/EC ratios in Los Angeles and San Nicolas Island between January 1995 and February 1996 were 2.03 and 7.84, respectively. In general, OC/EC ratios are in the range of 2.0–3.0 for the urban sites listed in Table 1. In contrast with San Nicolas Island, the high OC/EC ratio in $PM_{2.5}$ in Mira Loma is due to high OC mass concentration rather than low EC mass concentrations. Kim et al. (2000) reported that the high OC concentration in inland areas such as Rubidoux was due to the formation of secondary OC, while the high OC levels in downtown Los Angeles were due to primary OC. Additionally, based on CMB results, Kim et al. (2000) showed that 40% of the total OC concentration is attributed to secondary and 60% to primary sources.

However, it is difficult to conclude the presence of secondary OC from the absolute values of OC/EC alone. For example, as shown in Table 1, San Nicolas Island has 50% higher OC/EC ratio than measured in Mira Loma despite the much lower overall OC and EC concentrations observed at San Nicolas Island. This is not necessarily due to the existence of secondary organic carbon derived from photochemical reactions. In a clean environment, emissions of EC are limited; thus the OC/EC ratio tends to be high. If EC exists at a much lower level relative to OC and if significant local sources (e.g., wood combustion, meat cooking) with higher OC and lower EC emission rates exist, higher values of OC/EC may be observed. Consequently, qualitative estimation of secondary organic carbon using OC/EC ratios should be applied only after careful inspection of local sources of OC and EC.

In summary, the OC/EC ratios observed in this study were on average higher than those observed in other urban areas in the South Coast Air Basin, and consistent with observations made for other inland sites in this region.

3.3. Relationship between OC and EC concentrations

As seen in Table 1, the highest monthly concentration of OC of 15.1 μg m^{-3} was observed in September and the lowest concentration of 9.7 μg m^{-3} was observed in December. The monthly mean OC concentration decreases from September to December. In contrast, no apparent monthly trend was observed for EC concentration. This trend in OC concentration is consistent with the findings of Kim et al. (2000). Their study showed that monthly total carbon concentrations measured at five stations (Anaheim, downtown LA, Diamond Bar, Fontana and Rubidoux) gradually increased from January to September, reaching a maximum during the fall season.

The origin of carbonaceous particles can be qualitatively estimated by looking into the relationship between OC and EC concentrations (Turpin and Huntzicker, 1995). If major fractions of OC and EC are emitted by a dominant primary source (e.g., vehicle emissions, meat cooking), the correlation between the OC and EC concentrations should be high because the relative rates of EC and OC emission would be proportional to each other.

In the present study, a weak correlation coefficient ($r = 0.50$) was found between organic and elemental carbon if the data are considered without sorting of any type. This suggests that OC and EC fractions in Mira

Loma may not be released from a single, dominant primary source. This result is similar to the weak correlation between OC and EC reported by Kim et al. (2002). Their investigation showed that OC concentrations in Downey (near central LA) were strongly correlated ($r = 0.94$) with concentrations of EC, while a rather weak association ($r = 0.52$) between OC and EC was observed in Riverside (downwind of Downey), which is located near Mira Loma. The reason for this difference was explained by the impact of sources unrelated to local vehicular emissions (i.e., secondary organic carbon).

If the data are sorted by month, it can be seen that there are two distinct populations. Fig. 2 shows correlations between OC and EC concentration measured during September and October (higher photochemical activity) and December and January (lower photochemical activity). The correlation is better during December and January ($r = 0.82$) than that during September and October ($r = 0.64$). The slope (i.e., OC/EC ratio) is higher during the September and October period. This weak correlation and high OC/EC ratio during September and October may be due to the influence of SOC formation or other significant primary organic sources. This is consistent with a study conducted by Offenberg and Baker (2000) who observed that summer particulate matter samples collected in the Chicago and Lake Michigan areas contained a greater fraction of organic matter than the winter samples. In the present case, however, primary OC sources are not believed to be strong functions of time of year during the study duration.

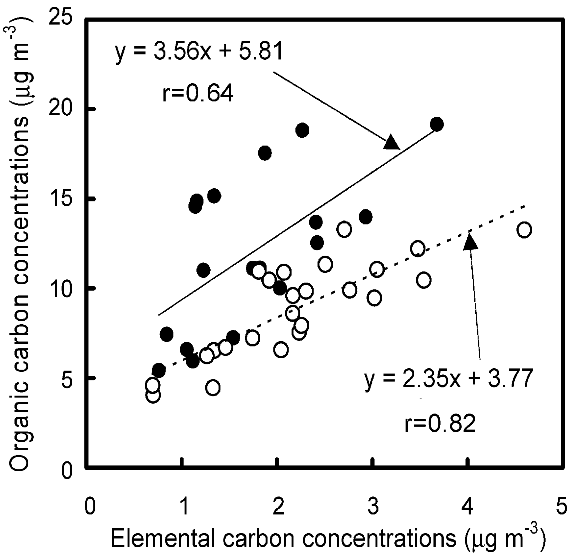

Fig. 2. Correlation between OC and EC concentrations for the two different cases (●: September and October 2001; ○: December 2001 and January 2002).

3.4. Estimation of secondary organic carbon and observed seasonal trends

Castro et al. (1999) reported that the consistent presence of a clear minimum ratio for OC/EC in urban and rural areas, in winter and summer, suggests that samples having the lowest OC/EC ratios contain almost exclusively primary carbonaceous compounds. The minimum ratios can be affected by various factors such as meteorology, diurnal and seasonal fluctuations in emissions, local sources and long-range aerosol transport. Table 2 shows the ratios of OC to EC in emissions from different sources as reported in the literature. These different OC/EC ratios indicate that OC/EC ratios vary considerably from source to source due to different source emission strengths of OC and EC.

For this study, we used an OC/EC ratio of 3.7, the average of the three lowest OC/EC ratios in this study, to estimate the secondary organic carbon (SOC) content of Mira Loma $PM_{2.5}$. Although carbonaceous samples with minimum OC/EC ratios are expected to contain exclusively primary OC, small proportions of secondary OC may still exist. Therefore, the results of this OC/EC method provide a lower limit for SOC content. The concentration of secondary organic carbon (OC_{sec}) can be estimated from:

$$OC_{sec} = OC_{tot} - EC \times (OC/EC)_{primary},$$

where $(OC/EC)_{primary}$ is the average value of the three lowest OC/EC ratios. Monthly average concentrations of secondary organic carbon of $PM_{2.5}$ calculated from the primary OC/EC ratio, ozone concentration and meteorological data measured in the vicinity of Mira Loma during this study period are summarized in Table 3. In addition, the effective actinic flux for 12:00 noon at Mira Loma for $290 < \lambda < 400$ nm was also calculated (Finlayson-Pitts and Pitts, 2000; NOAA, 2003). Ozone concentration data (ARB, 2003) were used as an indicator of photochemical activity, and correlated well with the calculated effective actinic flux ($r = 0.99$). Thus, there are significant differences in observed conditions from month to month.

During the study period, the SOC concentrations varied significantly from month to month. For illustration purposes, the data is grouped as follows: September and October ("Sep.–Oct.", having higher temperature and photochemical activity) and December and January ("Dec.–Jan.", having lower temperature and photochemical activity). It is observed that there is a 43% difference in SOC concentrations between Sep.–Oct. and Dec.–Jan. For comparison, the differences in ozone levels and effective actinic flux between Sep.–Oct. and Dec.–Jan. are 59% and 33%, respectively. Thus, the amount of SOC is significantly higher during periods with meteorological conditions favorable to the occurrence of photochemical activity. In addition, SOC

Table 2
Ratios of OC to EC in this study and in emissions by different sources

Emission source	EC	OC	OC/EC ratio	References
Ambient $PM_{2.5}$ (this study)	2.1±1.0	10.8±4.9	5.2±2.7	—
Light-duty gasoline vehicles[a]	22.6	50.1	2.2	Hildemann et al. (1991)
Light-duty gasoline vehicles[b]	13.5±8.02	30.1±12.3	2.2	Watson et al. (1994)
Heavy-duty diesel vehicles[a]	40.5	32.6	0.8	Hildemann et al. (1991)
Tunnel[c]	25.50±4.98	19.27±8.46	0.76	Gillies et al. (2001)
Paved road dust[b]	1.12±0.30	14.7±2.0	13.1	Watson et al. (1994)
Residential wood combustion[b]	12.39±4.20	51.37±11.72	4.15	Watson et al. (2001)
Meat charbroiling[a]	0.0±0.5	33.8±2.0	N.A.	Schauer et al. (1999)
Natural gas home appliances[a]	6.7	84.9	12.7	Hildemann et al. (1991)
Forest fire[a]	3.23±1.80	46.88±15.67	14.51	Watson et al. (2001)

Note: N.A. = not applicable.
[a] Mass % of fine particle mass.
[b] Mass concentration.
[c] mg per vehicle-kilometer.

concentrations are well correlated with effective actinic flux ($r = 0.95$), while primary OC concentrations are poorly correlated with effective actinic flux ($r = 0.13$).

An investigation of the effect of temperature on SOC formation is instructive. A modeling study by Strader et al. (1999) showed that an increase in temperature of 10°C results in an 18% decrease in SOC concentration. Similarly, Sheehan and Bowman (2001) found that high daytime temperatures tend to reduce SOC concentrations by 16–24%, while cooler nighttime temperatures lead to a 22–34% increase. Thus, an increase in temperature appears to reduce the SOC concentration, contrary to the observations in the present study.

It is well known that SOC is formed from reactive organic gases (ROGs) by two processes: production of condensable organic compounds through oxidation reaction and subsequent nucleation and condensation. Radicals such as OH, NO_3, and O_3 are required in order for oxidation to occur, and there is greater formation of these radicals in summer than in winter, in part due to higher actinic fluxes observed in summer. The ROG oxidation process is also enhanced by higher temperatures (Seinfeld and Pandis, 1998).

In summary, there is sufficient reason to believe that the observed differences in SOC concentrations between Sep.–Oct. and Dec.–Jan. are related to differences in photochemical activity, with greater SOC being formed during periods with greater photochemical activity (in this case, Sep.–Oct.).

3.5. Source contribution to organic carbon concentrations

In this study, OC is found to be the second largest contributor to the $PM_{2.5}$ mass accounting for 26% of total $PM_{2.5}$ by mass. Therefore, it is worth estimating which sources have the largest contribution to the ambient OC. It has been reported that atmospheric carbon particles are emitted from more than 70 different types of air pollution sources (Cass et al., 1982). Emission sources of OC include gasoline-powered vehicles, diesel-powered vehicles, wood burning, food cooking operations and soil-related emission sources such as paved road dust, tire dust and vehicular brake lining wear particles. In the present study, the following three emission sources were used: soil-related emission, gasoline-fueled vehicles and diesel-fueled vehicles for the estimation of the contribution of primary sources of organic carbon (Watson et al., 1994, 1998a). The observed OC cannot entirely be accounted for by primary emissions. Thus, pure organic carbon was used to apportion remaining OC that is not apportioned to the primary OC profiles. Therefore, total SOC obtained is a combination of actual secondary organic carbon and primary organic carbon from emission sources not considered in this CMB calculation. Fractional contribution of these sources to total organic carbon (TOC) was determined using the CMB8 receptor model (Watson et al., 1998b). 27 samples were chosen to meet the typical criteria for the CMB calculation (R^2: 0.8–1.0; χ^2: <4.0; percent mass: 80–120%). The results are illustrated in Fig. 3. Here, the length of the line represents the measured range. It is apparent that secondary organic carbon is the most significant portion of the TOC, ranging from 25% to 83% with an average of 57% of the total organic carbon. Gasoline-fueled vehicles are the second largest contributor accounting for 25% of the TOC. The contribution of SOC to TOC was found to be 52% using the OC/EC minimum ratio method. In conjunction with the contribution of OC to the total $PM_{2.5}$, this implies that SOC accounts for 14% of the total $PM_{2.5}$ mass concentration observed in Mira Loma during the study period.

In summary, these results highlight the similar SOC contributions obtained using two different methods.

Table 3

Monthly mean levels of primary and secondary organic carbon in Mira Loma from September 2001 through January 2002

Locations	Period	Organic carbon ($\mu g\,m^{-3}$)		% of secondary OC to the total OC	Ozone[a] (ppb)	Temp[b] (°C)	Relative Humidity[b] (%)	Wind Speed[b] ($km\,h^{-1}$)	Effective actinic flux ($\times 10^{-15}$ photons $cm^{-2}\,s^{-1}$)[c]
		Primary	Secondary						
This study ($PM_{2.5}$)	September	6.0±1.7	9.0±2.8	60.0±7.1	88.2±31.2	23.5±3.0	56.7±14.0	5.2±3.0	5.76
	October	3.6±1.5	8.3±4.9	66.7±11.9	59.2±18.5	20.9±3.6	63.9±11.0	6.9±3.5	4.81
	November	4.7±2.6	5.3±4.4	50.0±22.0	37.2±8.0	15.5±3.2	69.4±14.3	5.9±4.0	4.11
	December	5.9±2.5	3.8±2.4	40.0±13.7	27.7±10.5	9.8±1.8	70.4±12.7	5.5±2.4	3.46
	January	4.9±1.8	5.2±3.9	48.8±15.2	32.5±8.6	12.0±2.1	66.1±15.0	9.2±3.3	3.54
	Mean	5.0±2.2	6.0±4.2	52.0±17.9					
Kaohsiung City, Taiwan ($PM_{2.5}$)[d]	11/1998–4/1999	6.2	4.2	40.0					
Birmingham, UK (PM_{10})[e]	Winter	3.95	0.63	17					
	Summer (1993–1996)	1.65	3.10	65					
Claremont, US ($PM_{2.5}$)[f]	Summer, 1987	N.R.	N.R.	40–80					
Fresno, US[g] ($PM_{2.5}$)	Winter, 1995–1996	N.R.	1.2–6.8	5–26					

Note: N.R. = not reported.

Note that all data referred represent the calculations using a primary OC/EC value.

[a] Average values of daily maximum ozone concentration at Ontario Airport (ARB, 2003).

[b] Values calculated from daily average temperature in Riverside.

[c] Total actinic flux calculated from formula for solar zenith angle and table in Finlayson-Pitts and Pitts (2000). Criteria: $290 < \lambda < 400$ nm; local time: 12:00 noon; location: Mira Loma (33°59′N, 117°31′W). Effective actinic flux obtained by multiplication of total actinic flux by sunshine reaching the Earth's surface from sunrise to sunset under clear sky conditions, as a percentage of the maximum amount possible (NOAA, 2003).

[d] Lin and Tai (2001).

[e] Castro et al. (1999).

[f] Turpin and Huntzicker (1995).

[g] Strader et al. (1999).

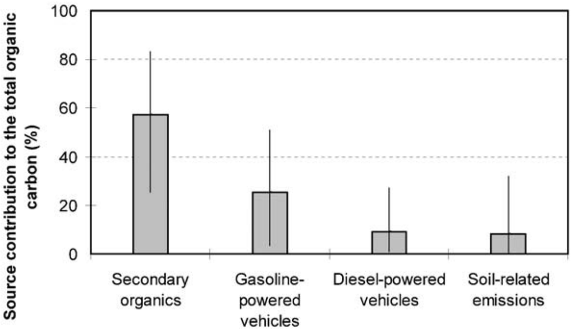

Fig. 3. Source contribution to the total organic carbon (%) (values of secondary organics in the bar graph include source contributions not considered in the Chemical Mass Balance calculation).

They also suggest a substantial contribution of secondary OC to the total OC for this area. Since TOC itself is a major contributor to total $PM_{2.5}$ in Mira Loma (see Section 3.1), this implies that the contribution of SOC to total $PM_{2.5}$ is not insignificant.

4. Summary and conclusions

A study on elemental carbon (EC), organic carbon (OC) and $PM_{2.5}$ mass concentrations was carried out in Mira Loma in Western Riverside County, California. During this study it was determined that OC concentrations in Mira Loma were higher than those of other urban sites in South Coast Air Basin (SoCAB), while EC concentrations are similar to other areas in SoCAB. Furthermore, total organic carbon (TOC) was a significant contributor to $PM_{2.5}$ accounting for 12.8% to 77.3% of total $PM_{2.5}$, with an average of 30.4%. OC alone accounted for nearly 84% of the total carbon. A stronger correlation between OC and EC was observed in December and January than September and October. OC/EC ratios observed in this study ranged from 1.6 to 12.8, averaging 5.2. These were higher than values observed for most urban sites in the South Coast Air Basin. Overall, poor correlation was observed between OC and EC, suggesting lack of a single dominant source. Based on OC/EC ratio method and CMB calculations, the calculated contributions of secondary organic carbon (SOC) to TOC were in good agreement: 52% and 57%, respectively. This indicated the substantial contribution of SOC to TOC and, in turn, to total $PM_{2.5}$ mass. The highest mean SOC of $9.0\,\mu g\,m^{-3}$ was observed in September, while the lowest mean SOC of $3.8\,\mu g\,m^{-3}$ was observed in December, indicating variations in SOC concentrations that were correlated with observed ozone concentrations and calculated effective actinic fluxes, both indicators of photochemical activity.

It is seen from these results that SOC contributed ~14% of total $PM_{2.5}$ mass concentration in the Mira Loma area, with a significant dependence of SOC concentrations on photochemical activity (represented by time of year). This suggests that photochemical activity can appreciably affect total $PM_{2.5}$ mass concentrations in Mira Loma, and that measures to control emissions of SOC precursors incorporated as part of a region-wide air quality management plan could lead to a perceptible drop in total $PM_{2.5}$ mass concentrations in this area.

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