



Secondary organic aerosol contributions to PM_{2.5} in Monterrey, Mexico: Temporal and seasonal variation



Yasmany Mancilla^{a,*}, Pierre Herckes^b, Matthew P. Fraser^c, Alberto Mendoza^a

^a Department of Chemical Engineering, Tecnológico de Monterrey, Av. Eugenio Garza Sada 2501, Monterrey NL 64849, Mexico

^b Department of Chemistry and Biochemistry, Arizona State University, 1711 S Rural Road, Tempe, AZ 85287, USA

^c School of Sustainable Engineering and the Built Environment, Arizona State University, 501 E Tyler Mall, Tempe, AZ 85287, USA

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ABSTRACT

Air pollution caused by fine particles is a problem of great concern in the Monterrey Metropolitan Area (MMA) which is the third largest city and the second most important industrial center in Mexico. In this study, samples of fine particulate matter emissions with an aerodynamic diameter of less than 2.5 μm (PM_{2.5}) were collected for 12-hour periods during the spring and fall of 2011 and 2012. Eighty-three samples were analyzed for organic carbon (OC) and elemental carbon (EC). The carbonaceous fraction (OC + EC) accounted for 28–55% of the PM_{2.5} mass. The average OC/EC ratios ranged from 7.4 to 12.6, and OC and EC concentrations were statistically significant correlated ($R^2 = 0.81$, $p < 0.01$). The secondary organic aerosol (SOA) contributions were determined using two approaches: the EC tracer method based on a primary OC/EC ratio derived from a tunnel study and the minimum observed OC/EC ratio. SOAs were determined to constitute, on average, 59–87% and 32–45% of the total OC and PM_{2.5}, respectively. The relationship between O₃ and wind speed indicated that pollutant levels were influenced by transport events during the spring, while stagnation events predominated during the fall campaigns. Statistically significant correlations were observed between OC and EC and gaseous species (CO, NO_x, and SO₂), indicating a contribution by combustion of fossil fuels to the carbonaceous material.

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1. Introduction

Carbonaceous material constitutes the major fraction of fine particulate matter emissions with an aerodynamic diameter of less than 2.5 μm (PM_{2.5}), accounting for 31–57% of the PM_{2.5} mass in urban areas (Na et al., 2004; Russell and Allen, 2004; Upadhyay et al., 2011; Martínez et al., 2012). Carbonaceous aerosols are composed of two main fractions: organic carbon (OC) and elemental carbon (EC). OC comprises a complex mixture of hundreds of organic compounds including a wide range of molecular forms and volatilities (Jacobson, 2000).

EC refers to light-absorbing refractory carbonaceous material that includes multiple types of graphitic structures. A low quantity of carbonates might also be found in some samples, but it is rarely comparable to the EC content (Watson et al., 2005). EC is a primary pollutant emitted during the incomplete combustion of fossil fuels and biomass burning (Chow et al., 2010) and plays a key role in radiative forcing by altering the radiative properties of the atmosphere (Jacobson, 2001; Bond et al., 2013). In contrast, OC can occur as a primary pollutant as well as a secondary pollutant. Secondary production comes from atmospheric reactions of organic precursor gases, gas-to-particle conversion of volatile organic compounds in the atmosphere, or the chemical adsorption of gaseous species onto other aerosol particle surfaces (Seinfeld and Pandis, 2006). OC chemical species have been associated with fine particles (Herckes et al., 2006; Duan et al., 2007) and cardiovascular and respiratory diseases (Peng et al., 2009).

* Corresponding author at: CO2 Solutions, Av. Lázaro Cárdenas 1007 Pte. 2.^o Piso, Residencial Santa Bárbara, San Pedro Garza García, NL 66266, Mexico. Tel.: +52 81 8220 9080; fax: +52 81 8220 9010.

E-mail addresses: ymancillam@gmail.com (Y. Mancilla), Pierre.Herckes@asu.edu (P. Herckes), Matthew.Fraser@asu.edu (M.P. Fraser), mendoza.alberto@itesm.mx (A. Mendoza).

Secondary organic aerosols (SOAs) are complex mixtures of organic compounds that vary according to the meteorology and predominant gas phase precursors of each region. SOAs contribute, on average, 45–90% to an organic aerosol (Na et al., 2004; Docherty et al., 2008; Fine et al., 2008). SOAs have a large biogenic contribution but near urban areas, the contribution is significantly less (Fine et al., 2008). However, in some urban locations, it has been estimated that up to 90% of the SOA is anthropogenic in origin (Hayes et al., 2013).

Quantification of the distribution of OC into primary and secondary pollutant fractions has been difficult to accomplish because no simple, direct analytical technique is available (Castro et al., 1999; Duan et al., 2007). Nevertheless, indirect methods such as the carbon isotopic composition (López-Veneroni, 2009); the OC/EC ratios (Turpin et al., 1991; Castro et al., 1999; Cabada et al., 2004); and, the use of chemical-transport models (Hildemann et al., 1994; Zeng and Wang, 2011), have been applied to estimate the secondary organic carbon (SOC) formation in ambient aerosols. EC and OC are good tracers for primary anthropogenic emissions that are formed by incomplete combustion (Bond et al., 2013). EC tends to be formed in larger amounts than OC when fossil fuels, such as oil, coal and diesel, are incompletely combusted. Conversely, when biomass fuels are incompletely combusted, OC is emitted in larger amounts than EC. Thus, the OC/EC ratio has become an important diagnostic ratio to estimate primary and secondary carbon pollution as well as the source type (biogenic or anthropogenic). As a result of SOA formation, ambient concentrations of OC, as well as the OC/EC ratios, increase. Therefore, OC/EC ratios that exceed the expected primary emission ratio indicate SOA formation (Cabada et al., 2004). OC/EC ratios were first studied in 1986 (Gray, 1986). Since then, an indirect method based on the minimum values of OC/EC has been developed to estimate the relative contribution of SOAs (Turpin et al., 1991; Turpin and Huntzicker, 1995). An extensive knowledge of OC/EC ratios is needed to apply this technique because OC/EC ratios vary considerably from source to source, from region to region, and among seasons (Chow et al., 2010; Ram and Sarin, 2011).

To support the explanations for the observed levels of OC/EC ratios and SOA formation, meteorological effects should be investigated. Using multiple meteorological indicators, transport and stagnation events in urban atmospheres can be identified, providing a better understanding of the origin of SOAs. These indicators include the wind speed (W_s) and its correlation with O_3 . The wind speed (W_s) is an important controlling factor for concentrations of air pollutants (Amador-Muñoz et al., 2011). Additionally, examination of a graph relating O_3 and W_s is useful for identifying whether the atmosphere is affected by transport or stagnation. If O_3 is dispersed by high levels of W_s , atmospheric transport will result in lower concentrations of O_3 ; whereas at low levels of W_s , the stagnation of the air mass will cause higher concentrations of O_3 . Interestingly, another indicator useful in identifying transport and stagnation conditions is the correlation between the OC/EC ratio and W_s . Better results can be obtained using the W_s from preceding periods rather than the W_s measured simultaneously with the OC/EC ratios (Salma et al., 2004).

The sources of primary and secondary carbonaceous materials must be determined to develop control strategies that address OC and EC airborne particle pollution. Therefore,

the goals of this study were (1) to monitor the temporal and seasonal differences in OC and EC mass concentrations in $PM_{2.5}$, (2) to estimate the correlations between carbonaceous species and gaseous pollutants, and (3) to quantify SOA formation and factors affecting carbonaceous fractions in the Monterrey Metropolitan Area (MMA).

2. Methods

2.1. Sampling site

The MMA is composed of 12 municipalities (Fig. 1) with an area of 6680 km² (SEDESOL et al., 2007). The MMA has a vehicular fleet of 1.7 million vehicles (INEGI, 2010) and 4.2 million inhabitants (INEGI, 2011), and is considered the largest urban area in Northeastern Mexico and the third largest urban center in the country. The MMA has a network of air quality monitoring stations known locally as the *Sistema Integral de Monitoreo Ambiental* (SIMA). For this study, $PM_{2.5}$ samples were collected at only one sampling site (Fig. 2)—labeled the Downtown station (25°40' 32 N, 100°20' 18 W), at 556 m above sea level. From an anthropogenic standpoint, the sampling site is affected primarily by traffic and emissions from a wide range of industrial activities (e.g., steel and cement production). Winds in this area blow predominantly from the east. The sampling site was selected based on analysis of coefficients of divergence (COD). A detailed description of the statistical analysis based on COD appears in Table S1 of the supplemental materials.

2.2. Sampling periods and instruments

A time series analysis of the data obtained from the SIMA monitoring stations for 2006–2010 indicated that concentrations of $PM_{2.5}$ and O_3 were typically highest in the spring and fall months. Therefore, the sampling was designed to be representative of spring and fall conditions. The samples were collected during the spring and the fall of 2011 and 2012 (Table 1). Twelve-hour consecutive samples were collected for every sampling day to obtain information for daytime and nighttime periods. Daytime sampling was performed from 6:00 to 18:00 (local time), while nighttime samples were collected from 18:00, finishing at 6:00 the next day. For the spring and fall 2011 campaigns, sampling was performed on seven alternate days. The spring and fall 2012 campaigns were composed of 14 consecutive sampling days.

$PM_{2.5}$ samples were collected using either low-volume (MiniVol®, Airmetrics) or high-volume (Tisch Environmental) filter-based instruments, operated in situ at approximately 5.5 L min⁻¹ or 1.1 m³ min⁻¹, respectively. Flow rates for low-volume samplers were calibrated at the sampling site before and after each 12-hour sampling period, whereas for the high-volume samplers, calibration was performed at the beginning and end of each monitoring campaign. For each low- and high-volume sampler, the calibration was conducted using its corresponding calibration orifice (National Institute Standards and Technology (NIST) Traceable Calibration Certificate). The samplers were mounted on the rooftop of the Downtown SIMA monitoring station at 3 m above the ground. Fine particles were collected on 47 mm filters (Merck Millipore AQFA) or 8 in. × 10 in. (Whatman QMA) quartz microfiber filters depending on the sampling device available during each

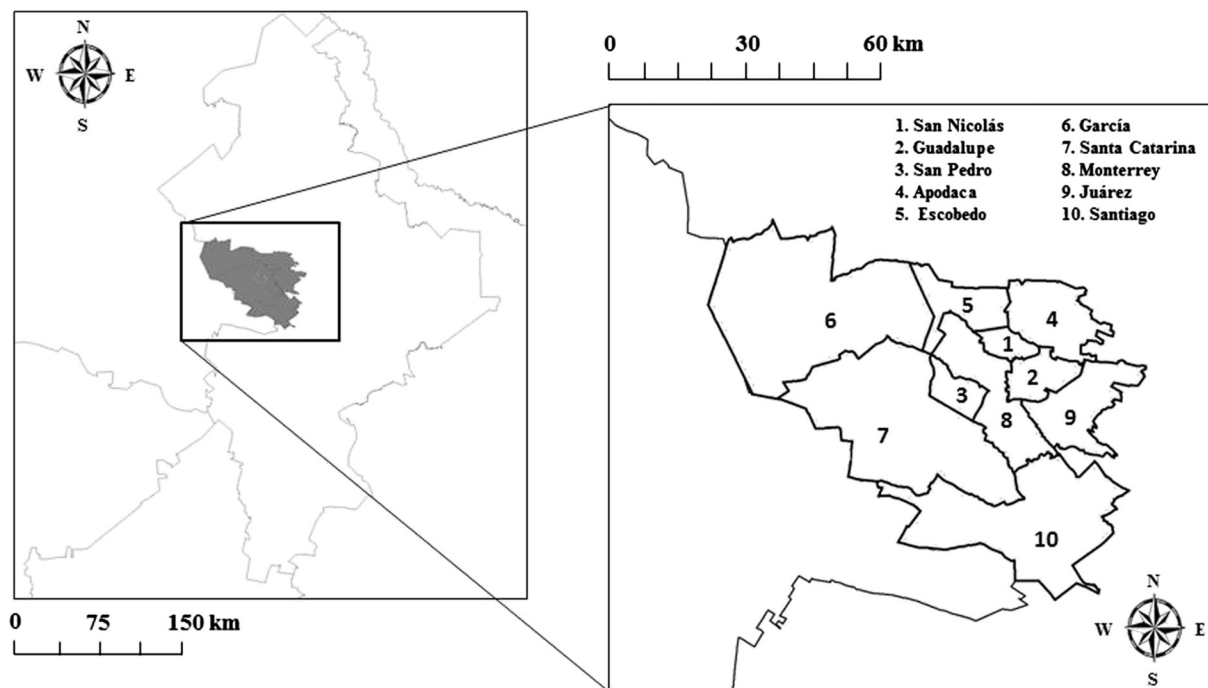


Fig. 1. Location and municipalities of the MMA.

period. Filters were previously baked for 8 h at 600 °C in a furnace to remove residual carbon and stored in baked aluminum foil within sealed plastic bags (Ziploc®) until they were used. After sampling, the 47 mm filters were stored in Petri dishes on a slide (Merck Millipore, PD1504700), while the 8 in. × 10 in. filters were stored in tall 8 oz glass jars (VWR, IR221-0250). All glass jars were previously rinsed with distilled water and isopropanol and baked for

8 h at 450 °C. The loaded filters were placed in a cooler with blue ice for immediate transport from the sampling site to the laboratory. All loaded filters were stored in a freezer at −20 °C to prevent the evaporation of volatile compounds until they were analyzed. A total of 83 samples and 8 field blanks were collected during the study. All concentrations of OC and EC were separately corrected for field blanks.

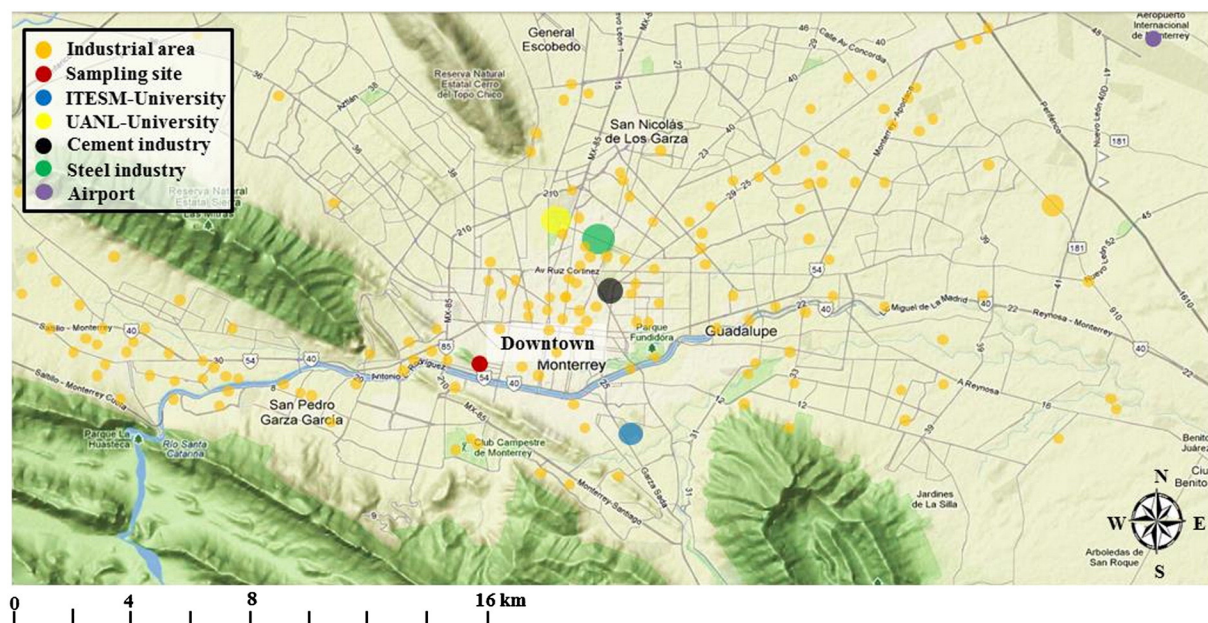


Fig. 2. Location of the sampling site in this study of the MMA.

Table 1

Monitoring experiments conducted for this study.

Campaign	Period	Sampler	Sampling days	Samples
Spring 2011	May 28 to June 11	Low-volume	7 ^a	14
Fall 2011	October 22 to November 3	High-volume	7 ^a	14
Spring 2012	June 6 to June 19	High-volume	14	27
Fall 2012	October 13 to October 26	High-volume	14	28

^a Non-consecutive days.

2.3. Meteorological and criteria pollutant data

Meteorological parameters for each sampling period were obtained from the Downtown station. The parameters included pressure, temperature, relative humidity, W_s , and wind direction. In addition, the concentrations of selected criteria pollutants (CO , SO_2 , O_3 , NO_x , and $\text{PM}_{2.5}$) were also obtained from the SIMA network. Correlations among meteorological data, criteria pollutants, and carbonaceous material are useful to identify the periods of time that are more likely to be impacted by primary or secondary organic aerosols. Among the meteorological parameters, the W_s plays a key role in identifying the stagnation and transport of airborne particles and other pollutants.

Each monitoring station in the SIMA network has rack-mounted instruments for measuring the criteria pollutants, meteorological sensors, and acquisition and data handling systems. The monitoring stations operate continuously and automatically. In particular, the $\text{PM}_{2.5}$ instruments are based on the Beta Attenuation method (GNL, 2009).

2.4. Chemical analysis

OC and EC concentrations in $\text{PM}_{2.5}$ were measured in bulk samples by thermal–optical transmittance (TOT) using a Sunset Laboratory Thermo-Optical Carbon Analyzer (Model 4L, USA). A 1 cm × 1.5 cm standard punch (1.5 cm²) was extracted from a loaded quartz microfiber filter and placed in the oven using a quartz boat. The transmittance of a diode laser light through the filter was monitored during the analysis. The oven was initially purged with helium (He). OC was then analyzed over varying time steps between 45 s and 300 s during the OC evolution at 310, 475, 615, and 870 °C in an inert atmosphere (pure He). The heating desorbs OC thermally. The evolved OC was catalytically oxidized to CO_2 in a manganese dioxide (MnO_2) oxidizing oven; subsequently the CO_2 was swept out of the oxidizing oven with the He stream and reduced to CH_4 in a (Ni/firebrick) Methanator and quantified as CH_4 by a flame ionization detector (FID). The EC analysis was conducted using temperature profiles of 550, 625, 700, 775, and 850 °C with hold time of 45 s and a final holding time of 120 s at 870 °C in an oxidizing atmosphere ($\text{He}:\text{O}_2$ 90:10 v/v). EC was oxidized from the filter into the oxidation oven, converted into CO_2 , reduced to CH_4 , and detected by FID as CH_4 . During this stage, a pyrolysis correction is made. To quantify the OC and EC, it is necessary to define a split point for these components. The split point is defined as the point at which the light transmittance of the sample returns to the initial value. The carbon that evolved before or after the split point was considered to be OC or EC, respectively. Additional

details of the technical aspects concerning OC and EC analysis can be found elsewhere (Birch and Cary, 1996).

The experimental procedure was conducted for each sample and field blank collected. The average OC and EC concentrations obtained from each sample were blank-corrected to eliminate possible contamination introduced during the transportation and field handling procedures. In all cases, the EC concentrations on these blank filters were below the detection limit. For OC, the blank-correction was approximately 2.7%, except for spring 2011 when it was up to 15%.

2.5. SOA estimation

The OC measured in ambient aerosol samples can be defined as the total OC (OC_{total}) concentration present in the atmosphere, and it can be expressed as follows:

$$\text{OC}_{\text{total}} = \text{OC}_{\text{prim}} + \text{OC}_{\text{sec}} \quad (1)$$

where OC_{prim} (or POC) and OC_{sec} (or SOC) are the concentrations ($\mu\text{g m}^{-3}$) of primary and secondary OC, respectively. Anthropogenic primary OC emissions are typically accompanied by EC emissions, whereas biogenic primary OC emissions are not. However, selected biogenic emissions (e.g., forest fires) can emit EC, but these emissions tend to be lower (OC/EC approximately 10) than anthropogenic EC emissions (OC/EC approximately 2) (Cao et al., 2006; Chow et al., 2010). In urban areas, the contributions from biogenic sources to primary OC levels are often negligible (Russell and Allen, 2004). Even though primary OC is emitted mainly by combustion sources (OC_{comb}), OC can be derived from non-combustion sources (OC_{nc}) (e.g., dust resuspension). Thus, OC_{prim} can be defined as follows:

$$\text{OC}_{\text{prim}} = \text{OC}_{\text{comb}} + \text{OC}_{\text{nc}} \quad (2)$$

where OC_{comb} can be expressed as follows:

$$\text{OC}_{\text{comb}} = (\text{OC}/\text{EC})_{\text{prim}} \times \text{EC} \quad (3)$$

where EC is the measured EC (e.g., $\mu\text{g m}^{-3}$) and $(\text{OC}/\text{EC})_{\text{prim}}$ is the estimated OC/EC ratio characteristic for combustion sources that predominate in urban areas. Finally, considering that the primary OC/EC ratio remains constant, the OC_{prim} and OC_{sec} can be calculated as follows:

$$\text{OC}_{\text{prim}} = (\text{OC}/\text{EC})_{\text{prim}} \times \text{EC} + \text{OC}_{\text{nc}} \quad (4)$$

and

$$\text{OC}_{\text{sec}} = \text{OC}_{\text{total}} - [(\text{OC}/\text{EC})_{\text{prim}} \times \text{EC} + \text{OC}_{\text{nc}}] \quad (5)$$

The approach described in Eqs. 1–5 is known as the EC tracer method (Cabada et al., 2004). In the absence of an analytical technique to quantify SOAs directly, this has become the most common approach to estimate the relative contribution of primary and secondary emission sources to the OC measured in airborne particles. However, results from this method must be evaluated with caution, because the OC/EC ratios can be affected by several factors, such as meteorology, temporal and seasonal fluctuations, local sources, and transport phenomena.

The EC tracer method relies mainly on the determination of the slope $(OC/EC)_{prim}$ and the intercept (OC_{nc}) in Eq. 4, which are commonly obtained by linear regression analysis of EC and OC concentrations measured during periods not affected by OC_{sec} (Turpin and Huntzicker, 1995; Cabada et al., 2004; Docherty et al., 2008). Because both EC and OC are measured, they have associated uncertainties; therefore, the Deming least squares solution is traditionally used to obtain the best estimates of the slope $(OC/EC)_{prim}$ and the intercept (OC_{nc}) (Turpin and Huntzicker, 1995). Some studies have ignored the OC_{nc} component, because it makes a small contribution to the primary OC in urban areas (Russell and Allen, 2004).

Other methods for the estimation of $(OC/EC)_{prim}$ include averaging the lowest OC/EC ratios (Cao et al., 2003; Na et al., 2004; Duan et al., 2007) or using the OC/EC ratios obtained from tunnel studies (Docherty et al., 2008; Pio et al., 2011). The average of the minimum OC/EC ratios can be valid if the meteorology impact on ambient OC and EC concentrations is minor (Castro et al., 1999; Rodríguez et al., 2003; Duan et al., 2007). However, tunnel studies are more representative when vehicle exhaust is the major contributor of airborne particles in urban areas (Cheng et al., 2010). OC/EC values obtained from this approach were derived exclusively from primary sources under actual conditions.

The EC tracer method estimates the SOAs in terms of SOC; therefore, a complicating factor is the estimation of organic matter concentrations from OC concentrations. To compensate for the non-carbon mass associated with OC (e.g., hydrogen, oxygen, and nitrogen) a multiplicative factor, k , can be used to convert OC to organic matter. This factor varies from 1.2 to 2.1 (Turpin and Lim, 2001; Fine et al., 2008; Aiken et al., 2008; El-Zanan et al., 2009). Therefore, the primary organic aerosol (POA), the SOA, and the total carbonaceous aerosol (TCA) concentrations can be estimated by Eqs. 6–8:

$$POA = k \times OC_{prim} \quad (6)$$

$$SOA = k \times OC_{sec} \quad (7)$$

$$POA = k \times OC_{total} \quad (8)$$

For this study, OC_{total} and EC concentrations were obtained from bulk samples collected during the four monitoring campaigns. The $(OC/EC)_{prim}$ ratio was estimated by two main approaches. The first approach was the use of the $(OC/EC)_{prim}$ ratio from a recent tunnel study conducted in the MMA (Mancilla and Mendoza, 2012). Tunnel studies have proven to be a reliable option; however, the $(OC/EC)_{prim}$ values derived from tunnel studies do not account for contributors

with elevated OC/EC ratios to primary OC, such as vegetative detritus, road dust, biomass burning, and cooking operations. The second approach was the use of the minimum OC/EC ratio observed during each monitoring campaign. Finally, several studies have suggested k values of 1.4 and 1.6 for urban areas (Turpin and Lim, 2001; Vega et al., 2004; El-Zanan et al., 2009; Mendoza et al., 2010; Amador-Muñoz et al., 2011). For this study, we used the most commonly accepted k value for urban areas, i.e., 1.4, to convert OC to organic matter.

3. Results and discussion

3.1. OC and EC concentrations in $PM_{2.5}$

The average ambient concentrations of $PM_{2.5}$, OC, EC, and total carbon (TC) as well as the OC/EC and TC/ $PM_{2.5}$ ratios for the four sampling periods are summarized in Table 2. Uncertainties (measurement errors) presented with the average ratios were estimated following uncertainty propagation methods—fractional uncertainties were added in quadrature (Taylor, 1997). As detailed in Table 2, $PM_{2.5}$ daytime mass concentrations were on average 20% higher than nighttime concentrations, except in the spring of 2011, when the opposite behavior was exhibited. The concentrations of carbonaceous species were on average 32% higher during the daytime than the nighttime. The individual results for each sample are shown in the supplemental material in Table S2 and Table S3. These results showed that carbonaceous species exhibited distinct daytime and nighttime variations. Higher nighttime concentrations of carbonaceous species can be attributed to an increase of primary emissions in the nighttime, especially those from diesel-powered vehicles and biomass burning; whereas sources responsible for higher daytime concentrations of carbonaceous species can include SOA formation and traffic emissions from gasoline-powered vehicles. In addition, a rather constant contribution from meat cooking operations could be important, because these sources are abundant and occur during the daytime and the nighttime in the MMA.

A one-way analysis of variance (ANOVA) was used to test for temporal and seasonal differences using the OC/EC ratios reported in Table 2. Significant temporal and seasonal differences were not found across the daytime/nighttime and the spring/fall sampling periods ($p > 0.05$ and $F < F_{crit}$), except in the spring of 2012 at night, when EC concentrations were not detected (not included in the ANOVA). The daytime mass concentrations of OC, EC, and TC were higher than the nighttime concentrations for the entire data set. The TC/ $PM_{2.5}$ ratios indicated that the carbonaceous fraction accounted for 28–49% and 46–55% of the $PM_{2.5}$ for spring and fall, respectively. Seasonally, variation existed between the daytime and the nighttime carbonaceous fractions. In the spring, the daytime carbonaceous fraction was 1.6–1.8 times higher than the corresponding nighttime fraction, whereas during the fall, it was 1.1–1.2 times higher. In other words, more variability was observed for spring days than for fall days. In spite of the pattern exhibited for individual carbonaceous species, as was mentioned previously, no significant differences existed for the daily or the seasonal average OC/EC ratios.

OC/EC ratios in urban areas that exceed a value of 3 suggest high SOA formation in addition to the contributions from primary emissions (Satsangi et al., 2012). The average OC/EC

Table 2Average ambient concentrations of PM_{2.5}, OC, EC, OC/EC ratios, and TC/PM_{2.5} ratios.

Year	Season	Period	PM _{2.5} (μg m ⁻³)	OC (μg m ⁻³)	EC (μg m ⁻³)	TC (μg m ⁻³)	OC/EC ^a	TC/PM _{2.5} ^b
2011	Spring	Day	21.3 ± 3.4	9.2 ± 0.8	1.3 ± 0.4	10.5 ± 1.1	7.4 ± 2.8	0.49 ± 0.10
		Night	27.9 ± 3.3	7.3 ± 0.7	0.6 ± 0.3	7.9 ± 1.0	12.6 ± 8.4	0.28 ± 0.05
	Fall	Day	19.4 ± 2.8	8.8 ± 0.5	0.9 ± 0.1	9.8 ± 0.6	9.3 ± 1.5	0.50 ± 0.08
		Night	14.0 ± 1.4	5.8 ± 0.3	0.7 ± 0.1	6.4 ± 0.4	8.8 ± 1.7	0.46 ± 0.05
2012	Spring	Day	15.8 ± 2.2	6.7 ± 0.4	0.5 ± 0.1	7.3 ± 0.5	12.4 ± 2.6	0.46 ± 0.07
		Night	13.7 ± 1.8	4.0 ± 0.3	0.01 ± 0.1	4.0 ± 0.3	^c	0.29 ± 0.04
	Fall	Day	20.1 ± 3.0	10.2 ± 0.6	0.9 ± 0.1	11.1 ± 0.6	11.6 ± 1.7	0.55 ± 0.09
		Night	16.0 ± 1.8	7.1 ± 0.4	0.7 ± 0.1	7.7 ± 0.4	10.6 ± 1.5	0.48 ± 0.06

^a The average OC/EC was calculated using the average OC and the average EC.^b The average TC/PM_{2.5} was calculated using the average TC and the average PM_{2.5}.^c EC was not detected.

ratios ranged from 7.4 to 12.6 during this study. SOA formation can be enhanced by stagnation conditions during cold seasons (Duan et al., 2007) or high photochemical activity during warm seasons (Jimenez et al., 2009). However, several other factors can also explain the high OC/EC ratios obtained (Hoyle et al., 2011). For example, higher contributions from biomass burning may exist during the cold season (fall). Some studies have reported high OC/EC ratios of 17 to 40 for wood combustion (Feng et al., 2009), ratios of approximately 8 for general biomass burning (Schauer et al., 2001), and ratios of 33 to 82 for kitchen emissions (He et al., 2004). This is further explored later in this manuscript. In addition, according to Stone et al. (2008), the contribution of vegetative detritus to the OC was 30% greater at night than during the daytime in Mexico City. This observation may imply that high biogenic emissions and low anthropogenic activity caused the high OC/EC ratios exhibited at night in the MMA.

The OC/EC ratios obtained in this study were consistent with those summarized by Zhang et al. (2011) for several locations around the world, whereas in comparison with Mexican studies, they were 2–10 times higher (Mendoza et al., 2010; Stone et al., 2008; Herrera-Murillo et al., 2012; Martinez et al., 2012). For example, in a prior study conducted in the MMA, Martínez et al. (2012) estimated average OC/EC ratios to be approximately 60% lower than those in the present study. The results obtained by Martínez et al. (2012) were statistically ($p < 0.05$ and $F > F_{crit}$) lower, because the study collected fresh aerosol samples downwind of industrial sources. In addition, during that study the samples were collected closer to the winter than in the present study, which resulted in a lower concentration of airborne particles according to the time series data for the MMA. In this study, the sampling site was chosen to sample fresh and aged aerosols downwind of a mixture of mobile and industrial sources. In comparison with the Mexico City studies, the OC/EC ratios of 1–10 estimated by Yu et al. (2009) were similar to those in this study, but the average OC/EC ratio of 2.3 obtained by Stone et al. (2008) was 70% to 80% lower.

The relationship between OC and EC mass concentrations may reflect the origin of a carbonaceous aerosol. If major fractions of OC and EC are emitted from a primary source, a correlation between OC and EC mass concentrations should exist, because the emission rates of OC and EC would be proportional to each other (Na et al., 2004). The correlations of OC with EC in all samples are described in Fig. 3. The meteorological conditions during the two consecutive years examined in this research were similar; therefore, the data

for 2011 and 2012 were combined for analyses according to season and time-of-day (Fig. 3). Statistically significant correlations for the spring seasons in the daytime ($R^2 = 0.81$, $p < 0.01$) or nighttime ($R^2 = 0.80$, $p < 0.01$) were observed; by contrast, the OC and EC values were not correlated for the fall seasons in the daytime ($R^2 = 0.06$, $p > 0.10$) or nighttime ($R^2 = 0.003$, $p > 0.10$). The determination of statistically significant correlations for the spring seasons in the daytime or nighttime suggested that the OC and the EC concentrations came from similar emission sources. By contrast, no correlation between the OC and the EC concentrations and high OC/EC ratios indicated the presence of mixed emission sources and a contribution of SOAs by photochemistry and/or local- or long-range transport (i.e., the presence of aged aerosols).

3.2. SOA formation

The primary OC/EC ratio derived from a tunnel study and the minimum OC/EC ratio (OC/EC_{min}) observed were compared and used to evaluate SOA formation using the EC tracer method. An average OC/EC ratio of 2.0 ± 0.7 obtained from a tunnel study conducted in the MMA in 2009 was used (Mancilla and Mendoza, 2012) in one approach, and the minimum OC/EC ratio observed during each monitoring campaign in this study was applied in a second approach. Here, the OC_{nc} term was neglected. The estimated levels of SOAs obtained are summarized in Tables 3 and Table 4.

For the tunnel data, the average SOA concentrations in the MMA were determined as follows: spring, $7.9\text{--}9.4 \mu\text{g m}^{-3}$ and $5.5\text{--}8.6 \mu\text{g m}^{-3}$, accounting for 73–84% and 84–100% of the measured OA during the day and the night, respectively; fall, $9.7\text{--}11.8 \mu\text{g m}^{-3}$ and $6.2\text{--}8.1 \mu\text{g m}^{-3}$, accounting for 78–83% and 77–81% during the day and the night, respectively. Thus, for this approach, more than 70% of the ambient OA in the MMA would appear to be secondary in origin. These results align with those reported for Riverside, CA (Docherty et al., 2008), Pasadena, CA (Hayes et al., 2013), and in other urban regions (Jimenez et al., 2009). However, in comparison with several studies conducted in Mexico (Mendoza et al., 2010; Stone et al., 2008; Herrera-Murillo et al., 2012; Martinez et al., 2012), the SOA contribution was 1.3 to 5.8 times higher in this study. For example, in Mexico City, average SOA contributions of 60% and 75% were determined by Stone et al. (2008) and Paredes-Miranda et al. (2009), respectively, which were lower than the results obtained in this study. In those studies, a primary OC/EC ratio derived from a Deming regression of the lowest OC and EC ambient concentrations was used. Thus, differences between

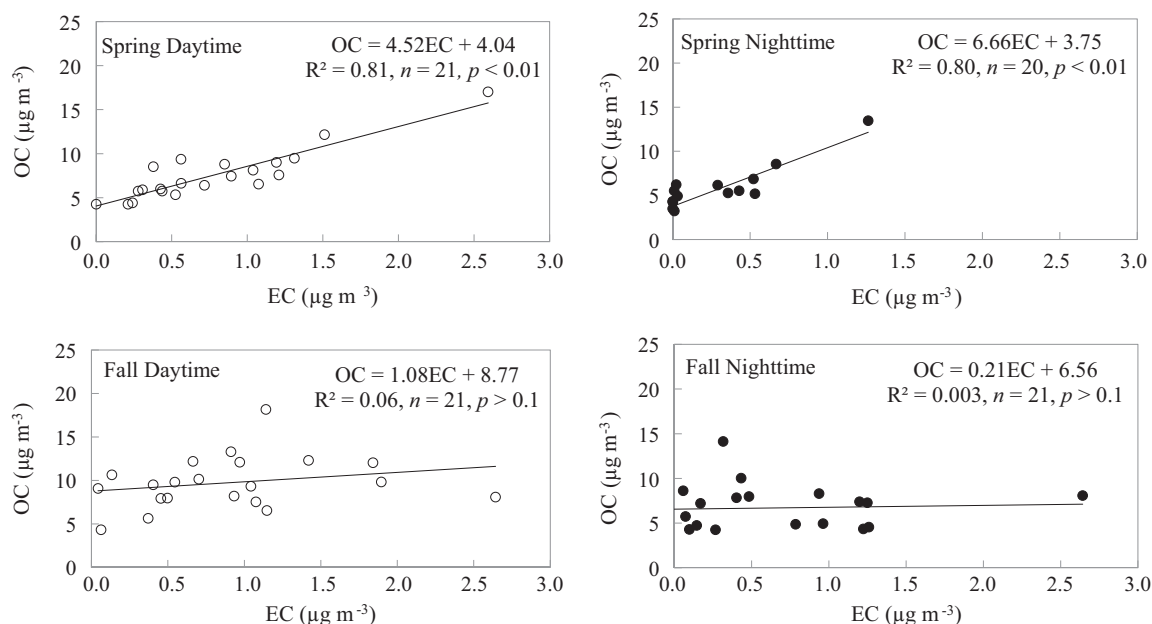


Fig. 3. Correlations between OC and EC in $PM_{2.5}$ during the spring and fall seasons in the MMA.

SOA levels estimated in Mexican studies as well as in other locations around the world can be attributed to the selection of the expected primary OC/EC ratio.

For the second approach in which the minimum OC/EC ratio observed during each monitoring campaign in this study was applied, average SOA concentrations were determined as follows: spring, $2.3\text{--}3.9\ \mu\text{g m}^{-3}$ and $5.3\text{--}5.6\ \mu\text{g m}^{-3}$, accounting for 18–41% and 52–100% of the measured OA during the day and the night, respectively; fall, $7.5\text{--}10.5\ \mu\text{g m}^{-3}$ and $4.8\text{--}6.7\ \mu\text{g m}^{-3}$, accounting for 61–74% and 59–66% during the day and the night, respectively. In comparison with the first approach, the SOA contributions for the spring decreased 62% and 17% on average during the day and the night, respectively; whereas in the fall, the SOA contributions decreased 16% and 20% on average during the day and the night, respectively. The lower values obtained for the spring can be explained by the elevated primary OC/EC ratios used for the second approach. These ratios were higher than those for the fall (Table 4). The persistence of higher primary OC/EC ratios during the spring can be explained by the fact that the atmosphere in Northeastern Mexico is highly influenced by forest wild fires and prescribed agricultural burning during the spring (Mendoza et al., 2005). The wildfires and prescribed burns exhibit high OC/EC ratios, which contribute significantly to the primary OC concentration.

Both approaches demonstrated the overall dominance of SOAs over fine organic aerosols. The two approaches exhibited distinct results that relied on the primary OC/EC ratio used by the EC tracer method. The first approach considered only the primary contribution from fossil fuel combustion sources; whereas the second approach also took into account the primary contribution from biogenic sources and biomass burning. The latter source is one of the largest sources of primary fine carbonaceous particles in Mexico (Yokelson et al., 2011). Therefore, the second approach can be viewed as a more realistic estimate of the SOA formation in the MMA.

Photochemical activity and transport are clearly the main factors responsible for the high levels of SOAs in the spring. In contrast, the vertical recirculation of stagnated air masses and decreasing temperatures—conditions that promote the condensation of aged aerosols—are responsible for the SOA concentrations in the fall. In addition, a hypothesis exists that a fraction of the SOAs can be formed from biomass burning emissions (Aiken et al., 2009; Hoyle et al., 2011). Based on the results from the second approach, the small changes exhibited in the SOA contributions during the nighttime in the spring, and the daytime and the nighttime in the fall, may be explained by local emissions from the main contributors to the primary OC, while the marked reduction

Table 3

Average contributions of SOA concentrations in the MMA based on the tunnel approach.

Year	Season	Period	SOC ($\mu\text{g m}^{-3}$)	SOA ($\mu\text{g m}^{-3}$)	SOA/OA	SOC/ $PM_{2.5}$	SOA/ $PM_{2.5}$	TCA/ $PM_{2.5}$
2011	Spring	Daytime	6.7 ± 2.4	9.4 ± 3.3	0.73 ± 0.32	0.32 ± 0.12	0.44 ± 0.17	0.67 ± 0.21
		Nighttime	6.1 ± 1.8	8.6 ± 2.5	0.84 ± 0.32	0.22 ± 0.07	0.31 ± 0.10	0.39 ± 0.11
	Fall	Daytime	6.9 ± 1.4	9.7 ± 1.9	0.78 ± 0.20	0.36 ± 0.09	0.50 ± 0.12	0.69 ± 0.14
		Nighttime	4.4 ± 1.0	6.2 ± 1.4	0.77 ± 0.22	0.32 ± 0.08	0.44 ± 0.11	0.62 ± 0.13
2012	Spring	Daytime	5.6 ± 0.9	7.9 ± 1.3	0.84 ± 0.19	0.35 ± 0.08	0.50 ± 0.11	0.63 ± 0.12
		Nighttime	4.0 ± 0.4	5.5 ± 0.5	1.00 ± 0.16	0.29 ± 0.05	0.41 ± 0.07	0.41 ± 0.07
	Fall	Daytime	8.4 ± 1.3	11.8 ± 1.9	0.83 ± 0.18	0.42 ± 0.09	0.59 ± 0.13	0.75 ± 0.14
		Nighttime	5.8 ± 1.0	8.1 ± 1.4	0.81 ± 0.18	0.36 ± 0.07	0.51 ± 0.10	0.67 ± 0.12

Table 4

Average contributions of SOA concentrations in the MMA based on the minimum OC/EC ratio observed.

Year	Season	Period	(OC/EC) _{min}	SOC ($\mu\text{g m}^{-3}$)	SOA ($\mu\text{g m}^{-3}$)	SOA/OA	SOC/PM _{2.5}	SOA/PM _{2.5}	TCA/PM _{2.5}
2011	Spring	Daytime	6.1 ± 2.6	1.7 ± 6.1	2.3 ± 8.6	0.18 ± 0.68	0.08 ± 0.29	0.11 ± 0.40	0.67 ± 0.21
		Nighttime		3.8 ± 4.2	5.3 ± 5.9	0.52 ± 0.62	0.13 ± 0.15	0.19 ± 0.21	0.39 ± 0.11
	Fall	Daytime	3.6 ± 0.6	5.4 ± 1.4	7.5 ± 2.0	0.61 ± 0.19	0.28 ± 0.08	0.39 ± 0.12	0.69 ± 0.14
		Nighttime		3.4 ± 1.0	4.8 ± 1.4	0.59 ± 0.21	0.24 ± 0.08	0.34 ± 0.11	0.62 ± 0.13
2012	Spring	Daytime	7.2 ± 1.1	2.8 ± 1.6	3.9 ± 2.2	0.41 ± 0.26	0.18 ± 0.10	0.25 ± 0.14	0.63 ± 0.12
		Nighttime		4.0 ± 0.3	5.6 ± 0.4	1.00 ± 0.14	0.29 ± 0.05	0.41 ± 0.06	0.41 ± 0.07
	Fall	Daytime	3.1 ± 0.4	7.5 ± 1.1	10.5 ± 1.6	0.74 ± 0.15	0.37 ± 0.08	0.52 ± 0.11	0.75 ± 0.14
		Nighttime		4.8 ± 0.9	6.7 ± 1.3	0.66 ± 0.17	0.30 ± 0.07	0.42 ± 0.09	0.67 ± 0.12

exhibited during the daytime in the spring can be explained by regional and long-range transported SOAs given the high value for the $(OC/EC)_{\min}$ used to estimate the relative contribution of SOAs for that sampling period (Pio et al., 2011).

The average SOA/PM_{2.5} ratios obtained during the entire sampling period are listed in Tables 3 and 4. The results show that SOAs represent a major fraction of the PM_{2.5} in the MMA, accounting for 31–59% using the first approach versus 11–52% using the second approach. Additionally, the temporal pattern followed by the SOAs (as SOC) in the MMA is illustrated (Fig. 4).

3.3. Meteorological impacts on carbonaceous species

The averaged meteorological parameters measured in the MMA are listed in Table 5. The solar radiation was observed to be 1.4–1.9 times higher in the spring than in the fall, suggesting high levels of carbonaceous species would be present during the daytime due to photochemical activity, which promotes the aging of organic aerosols. During the nighttime, the high levels

of organic aerosols may be explained by the low height of the mixing layer in the atmosphere and inversions due to low ambient temperatures (Feng et al., 2006; Upadhyay et al., 2011). Here, the fall temperatures were lower than the spring temperatures.

Furthermore, meteorological scenarios inducing the transport of fine particulate matter from other regions to the MMA were associated with moderate and intense winds. The spring was dominated by higher W_s than the fall. High W_s during the spring accompanied by high levels of carbonaceous species indicated a contribution of local-range transport to local fine particulate matter. Lower W_s was measured in the fall compared with the spring, but not too low as to indicate a lack of air movement. Therefore, during the fall in the MMA, the high levels of carbonaceous fractions were influenced by a combination of local-range transport and stagnation events. Wind rose plots prepared during the sampling periods (Figure S1) showed a predominant pattern of high and low W_s coming from the northeast during the spring and the fall, respectively. In

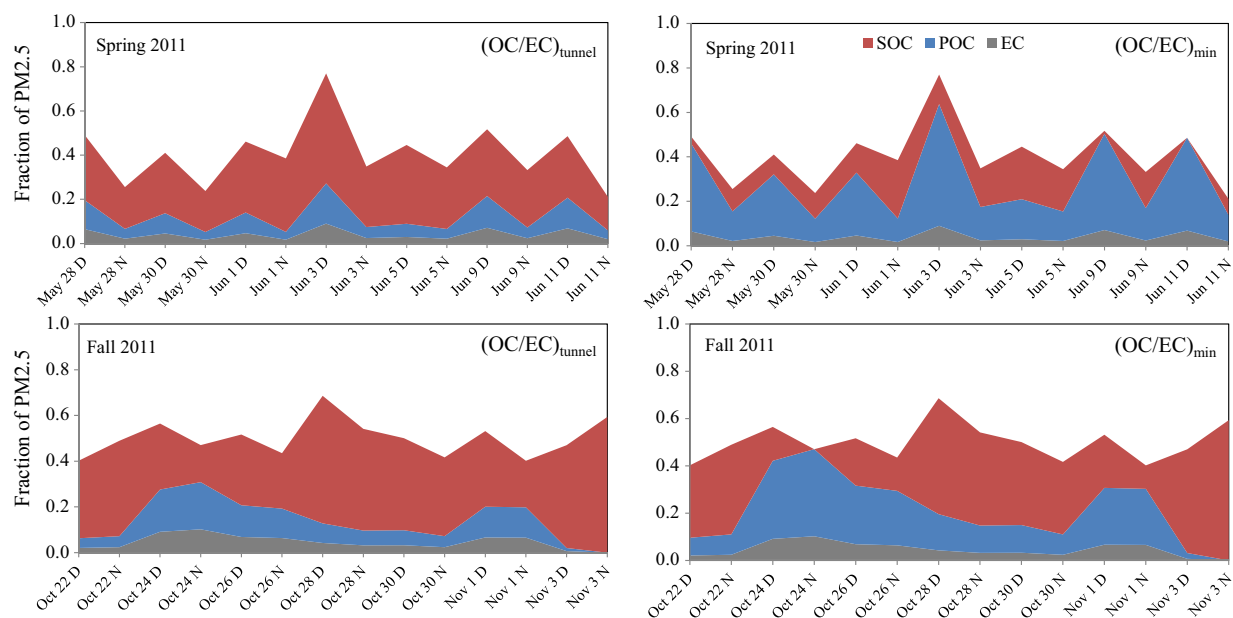


Fig. 4. Temporal behavior of the carbonaceous species in the MMA during 2011 and comparison between $(OC/EC)_{\text{tunnel}}$ and $(OC/EC)_{\min}$ approaches; D = daytime, N = nighttime.

Table 5

The meteorological data during the sampling periods in the MMA.

Year	Season	Period	T (°C)	RH (%)	W _s (m s ⁻¹)	Wd (°)	SR (W m ⁻²)
2011	Spring	Daytime	29.4 ± 1.3	60 ± 5	2.6 ± 0.3	89 ± 12	560 ± 100
		Nighttime	27.8 ± 1.1	62 ± 5	2.7 ± 0.3	83 ± 6	N.A. ^a
	Fall	Daytime	22.1 ± 1.1	55 ± 3	1.8 ± 0.2	105 ± 27	390 ± 90
		Nighttime	18.7 ± 0.8	63 ± 4	1.4 ± 0.2	146 ± 29	N.A. ^a
2012	Spring	Daytime	30.7 ± 1.2	54 ± 6	2.3 ± 0.3	69 ± 11	600 ± 100
		Nighttime	28.0 ± 1.0	65 ± 5	2.4 ± 0.3	89 ± 11	N.A. ^a
	Fall	Daytime	26.4 ± 0.9	69 ± 3	1.6 ± 0.2	120 ± 25	310 ± 80
		Nighttime	23.5 ± 0.5	75 ± 2	1.4 ± 0.2	127 ± 24	N.A. ^a

T = temperature; RH = relative humidity; W_s = wind speed; Wd = wind direction; SR = solar radiation.^a Not applicable.

addition, backward trajectories reinforced the possible transport from the northeast, showing long-range transport from the northeast and the southeast in the MMA. The pattern observed supports the potential for the contribution of biomass burning to the OC given that [Mendoza et al. \(2005\)](#) reported an influence in the Northeastern region of Mexico from forest wild fires and prescribed agricultural burning.

From scatter plots ([Fig. 5](#)) relating O₃ concentrations and W_s in the MMA, a dominance of local-range transport in the spring and stagnation in the fall can be observed. The ranges of W_s by which the O₃ concentrations were scattered were 1–5 m s⁻¹ and 0.3–3 m s⁻¹ in the spring and the fall, respectively. Additionally, correlations between the OC/EC ratios and the W_s of the previous daytime or the previous nighttime were obtained for the MMA ([Table 6](#)). Local-range transport events were observed in the first monitoring year in the spring (high correlation with preceding periods) and stagnation events in the fall (poor correlation with preceding periods). For the second monitoring year, a mixed influence of local-range transport and stagnation appeared to exist. Relatively high correlations during the daytime may indicate contributions

due to transport; conversely, low correlations at night may indicate contributions due to stagnation.

3.4. Relationships among carbonaceous species and gaseous pollutants

The correlations between carbonaceous species and gaseous pollutants, such as CO, NO_x, and SO₂, can be useful in identifying possible sources of OC and EC. The correlation between CO and EC is associated with incomplete combustion processes. In the spring, statistically significant correlations between CO and EC ($R^2 = 0.4–0.7$, $p < 0.05$) were observed in the MMA during the daytime; by contrast, the CO and EC values were not correlated ($R^2 = 0.3$, $p > 0.1$) at nighttime. These results are an indicator of primary emission sources, such as traffic and industry, and they are consistent with the OC/EC ratios obtained in this study that were lower during the day than at night during the spring. In the fall, the CO and EC values were not correlated at daytime ($R^2 < 0.3$, $p > 0.1$) and nighttime ($R^2 < 0.2$, $p > 0.1$).

In addition to examination of CO concentrations, correlations between carbonaceous species and NO_x and SO₂ suggest a

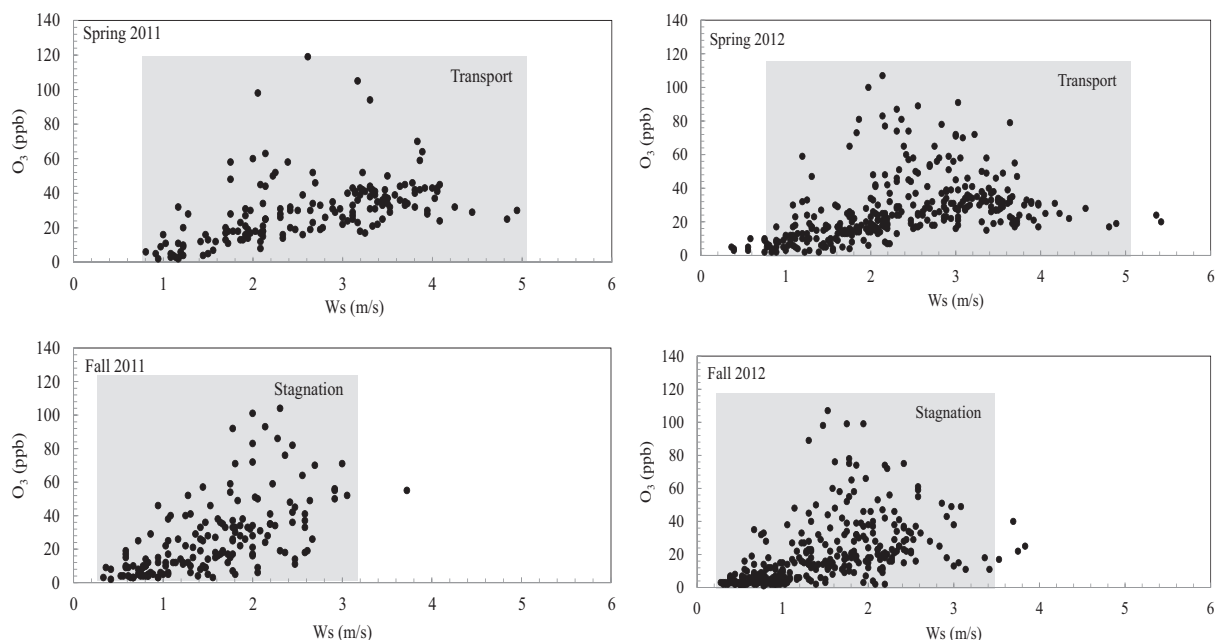
**Fig. 5.** Scatter plots relating O₃ concentrations and W_s during sampling in the MMA.

Table 6

Correlations between the OC/EC ratios and wind speed in the MMA.

	Spring 2011	Fall 2011	Spring 2012	Fall 2012
<i>Daytime</i>				
W _s	0.7	0.0	0.3	0.0
W _s (previous nighttime)	0.1	0.3	0.4	0.5
W _s (previous daytime)	0.8	0.0	0.1	0.4
<i>Nighttime</i>				
W _s	0.2	0.0	*	0.2
W _s (previous daytime)	0.7	0.0	*	0.1
W _s (previous nighttime)	0.4	0.2	*	0.2

The asterisks mean that the OC/EC values were not available due to EC was not detected, therefore the correlation against W_s could not be estimated.

primary origin for aerosols. No defined tendency was found for NO_x and SO₂ correlations. During the spring of 2012, correlations of carbonaceous species with NO_x occurred during the daytime (EC: $R^2 = 0.4$, $p < 0.05$; OC: $R^2 = 0.4$, $p < 0.05$) and at nighttime (EC: $R^2 = 0.2$, $p > 0.1$; OC: $R^2 = 0.6$, $p < 0.01$), but during the spring of 2011, these species were not correlated. During the fall, statistically significant correlations of NO_x with EC were found only in 2011 during the day ($R^2 = 0.9$, $p < 0.01$), whereas, statistically significant correlations for NO_x with OC were found in both sampling years during the daytime ($R^2 = 0.3$ – 0.4 , $p < 0.1$) and at nighttime ($R^2 = 0.6$ – 0.8 , $p < 0.05$), respectively. Correlations of carbonaceous species with SO₂ were found only in 2012. In that year, correlations of SO₂ with EC were found during the daytime ($R^2 = 0.4$ – 0.7 , $p < 0.01$) and at nighttime ($R^2 < 0.3$, $p < 0.1$). In addition, correlations were found with OC during the daytime ($R^2 < 0.3$, $p < 0.1$) and at nighttime ($R^2 = 0.4$ – 0.5 , $p < 0.05$). NO_x and SO₂ are influenced by regional meteorological conditions and photochemistry in contrast to the primary particulate nature of EC. NO_x is also emitted by the high temperature combustion of fossil fuels. The primary emission source of NO_x at the sampling site is postulated to be motor vehicle exhaust. In addition, in a tunnel study conducted in the MMA, a potential relationship between CO and NO_x was observed, indicating a high contribution by gasoline- and diesel-powered vehicles (Mancilla et al., 2012). Therefore, relatively high correlations of NO_x with EC indicated that EC emissions from vehicle exhaust may occur (Kim et al., 2011). In the same way, the strong correlations of EC with SO₂ during the day may be explained by the sulfur content emitted by diesel-powered vehicles. In addition, the moderate correlation of OC with SO₂ may indicate a possible contribution to the OC from emissions transported from a region located to the east of the sampling point, particularly from a large petroleum oil refinery located approximately 33 km to the east of the MMA. According to these results, anthropogenic emissions of NO_x and SO₂ can affect the emissions of carbonaceous species as well as the yields of SOAs, but the total effect depends on the organic species involved (Hoyle et al., 2011).

4. Conclusions

PM_{2.5} samples collected during the spring and the fall at one representative site in the MMA were analyzed for OC and EC. Ambient concentrations of PM_{2.5} demonstrated that the MMA experienced 20% higher concentrations during the daytime than the nighttime and 32% higher concentrations for the

carbonaceous species. No statistically significant temporal and seasonal differences between OC/EC ratios across the daytime/nighttime and the spring/fall sampling periods were observed. The TC/PM_{2.5} ratios demonstrated that OC and EC accounted for 28–49% and 46–55% of the PM_{2.5} for the spring and the fall, respectively. For the spring, the daytime carbonaceous fraction was 1.6–1.8 times higher than the nighttime fraction, whereas during the fall, it was 1.1–1.2 times higher. The results indicated more variability on spring days compared to fall days.

The average OC/EC ratios, ranging from 7.4 to 12.6, indicated a dominance of SOAs in the atmosphere of the MMA. The minimum OC/EC ratio approach showed that SOAs represented a major fraction of the PM_{2.5}, accounting for 11–52% in the MMA. In addition, statistically significant correlations between OC and EC were found. High correlations suggested that OC and EC concentrations originated from similar emission sources, while low correlations indicated mixed emission sources and a contribution of SOAs by photochemistry and/or local-range transport.

Meteorological parameters showed that transport phenomena during the spring were more important given that the OC/EC ratios were relatively high, while stagnation was more important during the fall when the OC/EC ratios were relatively low. This was consistent with the high and low levels of SOA formation during the spring and the fall, respectively. Finally, some statistically significant correlations between carbonaceous species and gaseous pollutants suggested a contribution by combustion of fossil fuels.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.atmosres.2014.09.009>.

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