

1 Organic composition and source apportionment of fine 2 aerosol at Monterrey, Mexico, based on organic markers

3
4 Y. Mancilla¹, A. Mendoza¹, M. P. Fraser² and P. Herckes³

5 [1]{School of Engineering and Sciences, Tecnológico de Monterrey, Monterrey, Mexico}

6 [2]{School of Sustainable Engineering and the Built Environment, Arizona State University,
7 Tempe, Arizona}

8 [3]{Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona}

9 Correspondence to: Y. Mancilla (y.mancilla@itesm.mx)

10 11 Abstract

12 Primary emissions from anthropogenic and biogenic sources as well as secondary formation
13 are responsible for the pollution levels of ambient air in major urban areas. These sources
14 release fine particles into the air that negatively impact human health and the environment.
15 Organic molecular markers, which are compounds that are unique to specific PM_{2.5} sources,
16 can be utilized to identify the major emission sources in urban areas. In this study, 43
17 representative PM_{2.5} samples, for both daytime and nighttime periods, were built from
18 individual samples collected in an urban site of the Monterrey Metropolitan Area (MMA)
19 during the spring and fall of 2011 and 2012. The samples were analyzed for organic carbon,
20 elemental carbon, and organic molecular markers. Several diagnostic tools were employed for
21 the preliminary identification of emission sources. Organic compounds for eight compound
22 classes were quantified. The *n*-alkanoic acids were the most abundant, followed by *n*-alkanes,
23 wood smoke markers, and levoglucosan/alkenoic acids. Polycyclic aromatic hydrocarbons
24 (PAHs) and hopanes were less abundant. The carbon preference index (0.7–2.6) for *n*-alkanes
25 indicate a major contribution of anthropogenic and mixed sources during the fall and the
26 spring, respectively. Hopanes levels confirmed the contribution from gasoline and diesel
27 engines. In addition, the contribution of gasoline and diesel vehicle exhaust was confirmed
28 and identified by the PAH concentrations in PM_{2.5}. Diagnostic ratios of PAH showed
29 emissions from burning coal, wood, biomass, and other fossil fuels. The total PAH and
30 elemental carbon were correlated ($r^2 = 0.39\text{--}0.70$) across the monitoring periods, reinforcing
31 that motor vehicles are the major contributors of PAH. Cholesterol levels remained constant

1 during the spring and fall, showing evidence of the contribution of meat cooking operations,
2 while the isolated concentrations of levoglucosan suggested occasional biomass burning
3 events. Finally, source attribution results obtained using the CMB model indicate that
4 emissions from motor vehicle exhausts are the most important, accounting for the 64% of the
5 $PM_{2.5}$, followed by meat cooking operations with 31%. The vegetative detritus and biomass
6 burning had the smallest contribution (2.2% of the $PM_{2.5}$). To our knowledge, this is the
7 second study to explore the organic composition and source apportionment of fine organic
8 aerosol based on molecular markers in Mexico and the first for the MMA. Particularly
9 molecular marker were quantified by solvent extraction with dichloromethane, derivatization,
10 and gas chromatography with mass spectrometry (GC/MS).

11

12 **1 Introduction**

13 Fine organic aerosol (OA) has a major role in environmental and human health impacts (Peng
14 et al., 2009). Some researchers have recently estimated that fine OA constitutes 23–38% of
15 the $PM_{2.5}$ mass in urban areas (Qin et al., 2006; Viana et al., 2006; Duan et al., 2007;
16 Upadhyay et al., 2011). In addition, OA along with elemental carbon (EC) can account for up
17 to 31–57% of the $PM_{2.5}$ mass (Duan et al., 2007; Upadhyay et al., 2011; Martínez et al.,
18 2012).

19 Atmospheric fine OA is a complex mixture of hundreds of organic compounds that are
20 directly emitted or are generated by atmospheric chemical processes. Many of these organic
21 compounds are toxic or carcinogenic (Spurny, 2000; Pope et al., 2002), but can be useful as
22 markers to identify the source of the aerosols being measured at a specific site. Organic
23 markers that have been used in the past include levoglucosan, cholesterol, nicotine, *n*-alkanes,
24 hopanes (pentacyclic triterpanes), and polycyclic aromatic hydrocarbons (PAHs).
25 Levoglucosan is a pyrolysis decomposition and combustion product of cellulose; therefore, it
26 can be used as a tracer for biomass burning sources (Fraser et al., 2000; Robinson et al.,
27 2006a; Alves et al., 2011; Gonçalves et al., 2011). Cholesterol and nicotine are good markers
28 for meat cooking operations (Rogge et al., 1991; Schauer et al., 2001b; Robinson et al.,
29 2006b) and cigarette smoke (Eatough et al., 1989; Hildemann et al., 1991; Rogge et al., 1994;
30 Kavouras et al., 1998), respectively. Hopanes are biomarkers of fuel oil combustion, coal
31 combustion and lubricants, and are useful to identify engine emissions (Rogge et al., 1993a;
32 Oros and Simoneit, 2000; Simoneit et al., 2004; Schnelle-Kreis et al., 2005). PAHs are semi-

1 volatile compounds formed from fossil fuel incomplete combustion processes (Rogge et al.,
2 1993a; Marr et al., 2004; Sklorz et al., 2007). Finally, *n*-alkanes are indicators of fossil fuel
3 utilization and biogenic emissions (Simoneit et al., 2004; Young and Wang, 2002). Additional
4 details about specific organic markers and their emission sources can be found elsewhere
5 (Simoneit et al., 1991; Simoneit, 1999; Lin et al., 2010; Blanchard et al., 2014).

6 Another feature used to identify the origin of fine OA are the diagnostic ratios between
7 homologues in series of biomolecules. For *n*-alkanes and alkanolic acids, the odd- and even-
8 carbon preferences are indicators of biogenic sources (Tsapakis et al., 2002). A lack of carbon
9 preference is indicative of fossil sources.. For the case of PAHs, some ratios can be used to
10 identify emissions from fossil fuel combustion (Zhang et al., 2005).

11 Source apportionment studies based on organic molecular markers have accomplished a better
12 understanding of the emission sources in urban areas. This approach considers two main
13 principles: (1) that organic molecular markers are present in relatively high concentrations in
14 emissions from a specific source and in lower concentrations in the remaining sources, and (2)
15 that they react slowly enough in the atmosphere to be conserved during transport from the
16 source to the observation/receptor site (Schauer et al., 1996; Lin et al., 2010). The use of
17 organic molecular markers in the last decade has proven to be a powerful method to identify
18 and attribute emission sources in urban areas (Alves et al., 2001; Fraser et al., 2003; Abas et
19 al., 2004; Kalaitzoglou et al., 2004; Zheng et al., 2005; Feng et al., 2006; Huang et al., 2006;
20 Li et al., 2006; Park et al., 2006; Alves et al., 2007; Chow et al., 2007; Ke et al., 2007; Stone
21 et al., 2008; Amador-Muñoz et al., 2010; Yin et al., 2010; Pietrogrande et al., 2011; Perrone et
22 al., 2012; Giri et al., 2013; Villalobos et al., 2015; Watson et al., 2015; Zheng et al., 2015).
23 In spite of recent research interest on organic molecular markers for source apportionment, the
24 application of this approach started in the 80s (Simoneit, 1985; Simoneit, 1986; Eatough et al.,
25 1989; Simoneit and Mazurek, 1989) and continued in the 90s (Simoneit et al., 1990; Simoneit
26 et al., 1991; Schauer et al., 1996; Simoneit, 1999; Schauer and Cass, 2000), especially, with
27 the development of organic source profiles for primary emission sources (Rogge et al., 1991;
28 Rogge et al., 1993a; Rogge et al., 1993b; Rogge et al., 1993c; Rogge et al., 1994; Rogge et al.,
29 1997; Fraser et al., 1999; Schauer et al., 1999) and alternative receptor models (Paatero 1997;
30 Wold et al., 2001). Furthermore, improved source apportionment methods have been
31 developed (Chen et al., 2011; Kelly et al., 2013; Watson et al., 2015) while other methods
32 have been suggested to be dropped as a receptor model (Hopke 2015). More detailed

1 information about source apportionment methods can be found elsewhere (Reff et al., 2007;
2 Viana et al., 2008; Lin et al., 2010; Nozière et al., 2015).

3 For the Monterrey Metropolitan Area (MMA), the third largest urban center of Mexico, there
4 is a growing concern to determine the emission sources of fine OA. It was recently
5 determined that fine OA accounts for 36–71% of PM_{2.5} mass in this urban center (Mancilla et
6 al., 2015). Previously, Martínez et al. (2012) estimated an OA fraction of ~40% of the PM_{2.5}
7 for the MMA. According to a recent tunnel study, PM_{2.5} emissions from gasoline-powered
8 vehicles (one of the major emission sources in the MMA) contain as much as 55% of
9 carbonaceous material (Mancilla and Mendoza, 2012). To date, only one study has addressed
10 the chemical characterization of fine OA in the MMA, but it focused exclusively on the levels
11 of PAHs (González-Santiago, 2009). More importantly, the present study would be the second
12 of this kind in Mexico and the first one for the MMA; previously, Stone et al. (2008) reported
13 an evaluation of molecular organic markers for source apportionment at the Mexico City. This
14 city has a temperate and wet climate while the MMA has a dry and extreme climate with
15 scarce rains. It is well-known that climate conditions can affect the air quality in urban areas.
16 Extreme climates, including high temperatures, could increase the concentrations of air
17 pollutants. For example, warm and dry climates promote photochemical reactions in the
18 atmosphere producing secondary OA. The unique geography and the changeable climate as
19 well as its typical industries of the region make of the MMA unique and different from other
20 Mexican cities.

21

22 **2 Methodology**

23 **2.1 Sampling site**

24 The MMA has a population of 4.2 million inhabitants (INEGI, 2011) and it is considered the
25 largest urban area in Northeastern Mexico and the third-largest urban center in the country.
26 The MMA is composed of 12 municipalities that overall cover an area of 6,680 km²
27 (SEDESOL et al., 2007), as shown in Fig. 1. The MMA has a vehicular fleet of 1.7 million
28 vehicles (INEGI, 2010) with a composition of approximately 73% gasoline-powered vehicles
29 (car passengers), 25% diesel-powered vehicles (buses and trucks) and 3% motorcycles. In
30 addition, the MMA has an industrial activity dominated by manufacturing industries,
31 construction and electricity, transport, restaurants and other local services. The MMA has a

1 network of air quality monitoring stations (*Sistema Integral de Monitoreo Ambiental, SIMA*).
2 For this study, PM_{2.5} samples were collected at only one site placed in the facilities of the
3 downtown monitoring station of the SIMA network (25° 40' 32" N, 100° 20' 18" W), 556
4 meters above sea level. The sampling site is affected mainly by traffic and emissions from a
5 wide range of industrial activities (e.g., steel and cement production). The vegetation around
6 the sampling site includes dispersed and scarce grass, shrubs, and street tree systems in the
7 immediate vicinity as well as in the periphery. The sampling site selection was based on
8 coefficients of divergence (COD) analysis using the 24-hour average PM_{2.5} concentrations
9 recorded in 2009 by the SIMA network. Details about this analysis can be found elsewhere
10 (Mancilla et al., 2015).

11 **2.2 Sampling periods and instruments**

12 The samples were collected during the spring and fall of 2011 and 2012 (Table 1). For every
13 sampling day two consecutive twelve-hour samples were taken to obtain information for
14 daytime and nighttime periods. The daytime sampling was performed from 06:00 a.m. to
15 06:00 p.m. (local time), while nighttime samples were collected from 06:00 p.m. to 06:00 a.m.
16 the next day. For the spring and fall 2011 campaigns, sampling periods were performed on
17 alternate days. For example, for the spring of 2011, the first sampling day was on May 28, the
18 second on May 30, and so on. For the campaigns of 2012, both were conducted for 14
19 consecutive sampling days.

20 Carbonaceous aerosol samples were collected using high-volume filter-based instruments with
21 PM_{2.5} inlet (TE-6001-2.5, Tisch Environmental Inc), operating at a flow of 1.13 m³/min. The
22 flow rates for the high-volume samplers were calibrated at the start and end of each
23 monitoring campaign. For each high-volume sampler, the calibration was carried out using a
24 calibration orifice (NIST Traceable Calibration Certificate). The samplers were mounted on
25 the rooftop of the monitoring station three meters above the ground. One high-volume
26 sampler was used for each campaign, except for the campaign of fall 2012, in which two high-
27 volume samplers were deployed and operated simultaneously to collect pairs of samples for
28 each diurnal and nighttime sampling period. Fine particles were collected on 8"×10" quartz
29 microfiber filters (Whatman QMA). Filters were previously pre-fired for 8 hrs at 600°C in a
30 furnace to remove residual carbon and stored in baked aluminum foil within sealed plastic
31 bags (Ziploc®) until they were used. After sampling, loaded 8"×10" filters were stored in tall

1 8 oz. glass jars (VWR, IR221-0250). Loaded filters were placed in a cooler with blue ice for
2 immediate transport from the sampling site to the laboratory. All loaded filters were stored in
3 a freezer at -20°C to prevent the evaporation of volatile compounds until they were analyzed.
4 A total of 111 samples and 10 field blanks were collected throughout the study.

5 **2.3 Ambient measurements**

6 For spring 2011, analyses for each 12-hour sample were carried out as discussed by Mancilla
7 et al. (2015). Even though the samples collected for spring 2011 exhibited high levels of OC,
8 some concentrations for different organic compounds of interest were low (0.03 to 0.16 ng
9 m^{-3}). In addition, the OC concentrations for the last three campaigns (fall 2011, spring 2012,
10 and fall 2012) were on average up to 35% lower than OC concentrations of spring 2011.
11 Based on these findings, composites were formed for the last three campaigns to ensure higher
12 levels of collected mass used to identify the organic molecular markers. Weekday/weekend
13 and daytime/nighttime differences of fine OC levels were investigated and considered to pool
14 sample filters into weekday and weekend composites for the last three campaigns (Mancilla et
15 al., 2015). Each composite included only daytime or nighttime samples collected during
16 weekdays (Mon-Thu) or weekend (Fri-Sun). Sample groups for composites varied from two
17 to six sample filters. Thereafter, the number of individual samples (or filters) was reduced
18 from 111 to 43 representative samples. The composites made for this study are described in
19 Table 2.

20 Solvent-extractable molecular markers were quantified using gas chromatography mass
21 spectrometry (GC/MS) using dichloromethane (DCM), and methanol (MeOH) (high purity
22 99.9%, Fisher Scientific). Filters were spiked with 50 μL of the following deuterated internal
23 standards (Sigma Aldrich): *n*-hexadecane- d_{34} , *n*-hexatriacontane- d_{74} , *n*-eicosane- d_{42} , *n*-
24 triacontane- d_{62} , vanillin- d_3 , benzophenone- d_5 , chrysene- d_{12} , dibenz(a,h)anthracene- d_{14} ,
25 naphthalene- d_8 , pyrene- d_{10} , benzo(e)pyrene- d_{12} , coronene- d_{12} , decanoic acid- d_{19} , palmitic
26 acid- d_{31} , stearic acid- d_{35} , levoglucosan- d_{13} , and cholesterol- d_6 . Each individual filter or
27 sample composite was extracted three times with DCM. During each extraction, enough DCM
28 was added and then ultrasonic agitation was applied for 20 min using a sonicator
29 (Branson®[®], model 5510R-DTH). The extracts were combined and then concentrated by
30 evaporation under a gentle flow of ultra-high purity nitrogen until the extract reached a
31 volume of ~ 5 mL. The extracts were filtered through a pre-fired quartz filter, subsequently

1 reduced in volume to 250 μL , and then separated into three fractions. One fraction was a
2 direct portion of the 250 μL extract for direct analysis by GC/MS, and the other two fractions
3 were used for chemical derivatizations. One fraction was methylated using diazomethane
4 (CH_2N_2) to convert carboxylic acids to their respective methyl esters. Another fraction was
5 silylated using a combination of BSTFA (N, O-bis(trimethylsilyl)trifluoroacetamide) and
6 TMCS (trimethylchlorosilane) to convert sterols and sugars to their respective trimethylsilyl
7 esters. For methylation, 50 μL of a CH_2N_2 solution was combined in a vial with 50 μL of
8 extract. For the silylation, 50 μL of BSTFA+TMCS (molar ratio 99:1) was combined with 50
9 μL sample extract. Then, the mixture was allowed to react for 3 h at 65°C. The quantification
10 and identification of organic compounds was based on comparisons with authentic standards,
11 retention times, literature mass spectra, and fragmentation patterns using HP chemstation. A
12 detailed description of the extraction and analysis procedures as well as the chromatograph
13 and column used can be found in Brown et al. (2002).

14 **2.4 Molecular diagnostic ratios**

15 To investigate the origin of fine organic aerosols, the following diagnostic ratios were used:

16 **2.4.1 Carbon Preference Index (CPI)**

17 The CPI is an indicator of the measure of odd or even carbon homologues series of organic
18 compounds within a sample. Based on several studies (Abas and Simoneit, 1996; Tsapakis et
19 al., 2002; Harrad et al., 2003), the CPI for *n*-alkanes (odd to even ratio) was calculated as
20 follows:

$$21 \quad \text{CPI} = \frac{\sum(\text{C}_{17} \text{ to } \text{C}_{33})}{\sum(\text{C}_{16} \text{ to } \text{C}_{32})} \quad (1)$$

22 and for *n*-alkanoic acids (even to odd ratio), as:

$$23 \quad \text{CPI} = \frac{\sum(\text{C}_{10} \text{ to } \text{C}_{32})}{\sum(\text{C}_{11} \text{ to } \text{C}_{31})} \quad (2)$$

24 The CPI is an important indicator that is used to determine whether emissions come from
25 natural or anthropogenic sources. For both *n*-alkanes and *n*-alkanoic acids, values of $\text{CPI} > 1$
26 indicate that hydrocarbons and carboxylic acids are emitted from natural sources. In contrast,

1 values of $CPI \leq 1$ (or close to one) indicate that they are emitted from anthropogenic sources
 2 (Gogou et al., 1996; Alves et al., 2001; Gelencsér, 2004).

3 Another useful indicator that is used to specify the origin of the emissions is the carbon
 4 number with maximum concentration (C_{max}). Hydrocarbons and carboxylic acids of high
 5 molecular weight ($> C_{25}$) are emitted from biogenic sources, while those with lower molecular
 6 weight ($\leq C_{25}$) are mainly emitted from fossil fuel combustion processes (Alves et al., 2001;
 7 Young and Wang, 2002; Gelencsér, 2004).

8 **2.4.2 Diagnostic ratios of PAHs**

9 Other indicators that have been used as markers of different source emissions of OA are the
 10 PAHs diagnostic ratios (DRs) (Dvorská et al., 2011; Katsoyiannis et al, 2011). The DRs
 11 calculated in this study are shown in Table 3. The values listed in this table can be found
 12 elsewhere (Ravindra et al., 2008; Tobiszewski and Namieśnik, 2012).

13 **2.5 Chemical Mass Balance model**

14 The CMB is a single-sample receptor model that can be stated in terms of the contribution
 15 from p independent sources to all chemical species as follows:

$$16 \quad x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \quad (1)$$

17 where x_{ij} is the measured concentration of species j in sample i , f_{kj} is the concentration of
 18 species j in the emissions of source k , g_{ik} is the contribution of source k to sample i , and e_{ij} is
 19 the model error. This model considers a prior knowledge of the source profiles and that the
 20 components of the source emissions do not undergo changes during their transport from the
 21 source to the receptor. CMB provides an effective variance-weighted least-squares solution to
 22 the overdetermined set of mass balance equations (Eq. 1). CMB takes into account the known
 23 uncertainties in the ambient measurements and the source emission data to minimize the chi-
 24 square (χ^2) goodness-of-fit parameter for each sample i :

$$25 \quad \chi^2 = \sum_{j=1}^m \left[\frac{x_j - \sum_{k=1}^p g_{jk} f_k}{\sigma_{x_j}^2 + \sum_{k=1}^p \sigma_{g_{jk}}^2 f_k} \right]^2 \quad (2)$$

1 where σ_{xj} is the standard deviation of the concentration of species j , σ_{gjk} is the standard
2 deviation of the g_{jk} , and m the total number of species. The U.S. EPA-CMB8.2 software has
3 been successfully used to apportion source contributions to ambient PM_{2.5} (Ke et al., 2007;
4 Stone et al., 2008; Watson et al., 2008; Kleeman et al., 2009; Schneidemesser et al., 2009; Yin
5 et al., 2010; Perrone et al., 2012; Villalobos et al., 2015) and was also used in the current
6 study. More details about CMB can be found elsewhere (e.g., Henry et al., 1984; Watson et
7 al., 2008).

8 **2.6 Source profiles**

9 The source profiles used in this work were taken from the most comprehensive studies
10 available. The selection of the source profiles was based on previous source apportionment
11 studies carried out for Mexican urban areas. Firstly, Stone et al. (2008) used CMB with
12 organic molecular markers profiles to estimate contributions from gasoline- and diesel-
13 powered vehicles, vegetative detritus and biomass burning in Mexico City. Secondly,
14 Martinez et al. (2012) based their factor analysis on trace elements identified primary sources
15 such as industrial sources, motor vehicle exhaust and biomass burning in the MMA. Finally,
16 from these studies, seven primary source profiles were selected.

17 The source profiles for gasoline- and diesel-powered vehicles were taken from Schauer et al.
18 (2002) and Fraser et al. (2002), respectively. In the MMA, the gasoline vehicle fleet seems to
19 be rather well maintained and of a recent model year, while the diesel vehicle fleet is
20 composed of heavy duty vehicle trucks and buses. Therefore, the profiles reported for
21 catalyst-equipped gasoline-powered motor vehicles emissions and heavy duty trucks from
22 dynamometer tests were used.

23 From evidence of industrial sources in Mexican urban atmospheres, source profiles for natural
24 gas combustion and fuel oil combustion were taken from Rogge et al. (1993c) and Rogge et
25 al. (1997), respectively.

26 Finally, source profiles for meat cooking operations, vegetative detritus, and biomass burning
27 were taken from Schauer et al. (1999), Rogge et al. (1993b) and Schauer et al. (2001a),
28 respectively. Most traditional restaurants activities of the region of study include meat
29 charbroiling operations. For biomass burning, given the existence of softwood and hardwood
30 sources in the region (Zurita, 2009), the softwood pine and hardwood oak profiles were used
31 in this study. These last profiles were used separately because they are highly collinear.

1 Regarding vegetative detritus, a source profile was included based on the contributions
2 determined by Stone et al. (2008) in Mexico City along with the fact that the MMA is
3 surrounded by rural areas with vast green covers. Therefore, it is possible to have an impact
4 from transport of biogenic emissions.

5 For individual organic compound quantification, an uncertainty of $\pm 20\%$ of the measured
6 concentration was used for all ambient samples and source profiles (Schauer et al., 2000;
7 SRM 1649a, 2007; SRM 1649b, 2009; Fraser et al., 2003; Schantz et al., 2005). A detailed
8 description of the source profiles and settings used to perform the CMB in this study can be
9 found in Fraser et al. (2003). For the current application, the fitting species for CMB included
10 20 organic compounds along with EC and overall OC. The molecular markers included seven
11 *n*-alkanes (C27-C33), four petroleum biomarkers (17a(H),21b(H)-29-norhopane,
12 17a(H),21b(H)-hopane, 22R+S 17a(H),21b(H)-30-homohopane, and 22R+S 17a(H),21b(H)-
13 30-bishomohopane), five polycyclic aromatic hydrocarbons (benzo[a]anthracene,
14 benzofluoranthenes, benzo[a]pyrene, indeno[123-cd]pyrene and benzo[ghi]perylene), two
15 saturated fatty acids (C16:0 and C18:0), cholesterol and levoglucosan.

16 **3 Results and discussion**

17 **3.1 Resolved organic aerosols**

18 The results for the chemical characterization of the fine organic aerosol for the MMA are
19 summarized in Table S1. In this and other sections, averaged values for concentrations and
20 other parameters are given \pm one standard deviation. Most of the PM_{2.5} daytime
21 concentrations were 20% higher than nighttime concentrations. The concentrations of OC and
22 EC were on average 32% higher during the daytime than the nighttime. In addition, the OC
23 and EC accounted together for 28–49% and 46–55% of the PM_{2.5} for spring and fall,
24 respectively. In the spring, the daytime carbonaceous fraction was 1.6–1.8 times higher than
25 the corresponding nighttime fraction, whereas during the fall, it was 1.1–1.2 times higher. The
26 average OC/EC ratios ranged from 7.4 to 12.6 during this study. Detailed information and
27 analysis of the carbonaceous aerosol for this study can be found in Mancilla et al. (2015).

28 All samples collected during this study were analyzed for seven organic compound classes
29 except those samples collected in the spring of the 2011 campaign, for which carboxylic
30 acids, wood smoke markers, and nitro-PAH compounds were not included for the chemical
31 analysis. Therefore, the overall contribution of the resolved organic compounds to OC in the

1 spring of 2011 is not directly comparable to that of the last three campaigns. For the seven
2 resolved compound classes in the last three campaigns (Fig. 2), the *n*-alkanoic acids were the
3 most abundant, followed by *n*-alkanes, wood smoke markers, and levoglucosan/alkenoic
4 acids. The PAHs and triterpanes hydrocarbons were less abundant. The same tendency was
5 observed in the spring of 2011, except that the *n*-alkanes were the most abundant. The
6 concentrations of nitro-PAH were neglected because their levels were below the detection
7 limit of the method.

8 The daytime and nighttime concentrations of the resolved organics for the spring 2011
9 accounted for $0.49\pm 0.52\%$ and $0.46\pm 0.41\%$ of the ambient OC, respectively. These
10 contributions were much lower than the following three campaigns due to the fact that some
11 compounds classes were not included. For spring 2012 and all fall campaigns, the total
12 daytime concentrations of the resolved organics accounted for $7.58\pm 4.89\%$ and $2.64\pm 1.82\%$ to
13 $4.67\pm 1.76\%$, respectively, while the total nighttime concentrations accounted for $11.0\pm 6.3\%$
14 and $3.2\pm 2.4\%$ to $8.0\pm 4.0\%$, respectively. These observations are consistent with the findings
15 that typically, around 84% of the fine OC is either non-extractable or will not elute from the
16 GC column (Schauer and Cass, 2000). In the following sections the organic composition of
17 the fine organic aerosols will be analyzed using several diagnostic ratios to identify the
18 primary emission sources. Then the relative contribution of each primary source to the $PM_{2.5}$
19 will be calculated by using the CMB receptor model.

20 **3.2 *n*-Alkanes and Hopanes**

21 The *n*-alkanes have two main sources: petroleum product utilization and natural vegetation
22 waxes. The latter source consists of the longer chain plant lipids ($>C_{20}$) as *n*-alkanes (Simoneit
23 and Mazurek, 1982). In this study, the *n*-alkanes in the range of C_{17} – C_{33} were detected. For
24 the samples collected for spring 2011 and fall 2011, the average daytime and nighttime
25 concentrations of *n*-alkanes were 1.6 and 2.3 times higher for the fall than the spring,
26 respectively. This is consistent with the high contribution of the OC to $PM_{2.5}$ and the lowest
27 OC/EC ratios exhibited during the fall (Mancilla et al., 2015). In addition, the average
28 temperature in the fall was 18.7 – $22.1^\circ C$ versus 27.8 – $29.4^\circ C$ in the spring. Low temperatures
29 typically promote the utilization of petroleum products. In Mexico, the government sets the
30 tariff-rates for the electric energy consumption with regard to the temperature; during the cold
31 seasons the government removes the subsidy to the domestic electric energy due to the

1 demand on fossil fuels in those seasons, and the sampling years of this study were not the
2 exception (SENER, 2013). The average CPI values of *n*-alkanes in the spring were 1.5 ± 0.3
3 (range: 1.1–1.9) in the daytime and 1.7 ± 0.5 (range: 1.1–2.6) in the nighttime, while the CPI
4 values in the fall were 1.0 ± 0.3 (range: 0.7–1.2) in the daytime and 0.9 ± 0.1 (range: 0.7–1.0) in
5 the nighttime. The CPI values in the spring suggest the mixed contribution of anthropogenic
6 and biogenic emission sources, whereas those values in the fall indicated a dominance of
7 anthropogenic emissions. In addition, the contribution of anthropogenic emission sources is
8 confirmed by the presence of petroleum biomarkers (hopanes: range of 0.06 to 2.36 ng m^{-3})
9 and *n*-alkanes $\leq C_{25}$ (Fig. 3). For the fall, the average daytime and nighttime concentrations of
10 hopanes were 2.3 and 4.2 times higher than in the spring, respectively. Similarly, the presence
11 of biogenic emissions due to C_{max} was found at C_{27} , C_{29} , or C_{31} (Fig. 3). These carbons'
12 number dominance and trace levels of hopanes are characteristics of plant wax emissions and
13 urban traffic emissions, respectively (Standley and Simoneit, 1987; Cass, 1998; Simoneit et
14 al., 2004).

15 For the spring 2012 and fall 2012, the behavior of *n*-alkanes was the opposite of 2011. The
16 average daytime and nighttime concentrations of *n*-alkanes were 1.5 and 2.0 times higher in
17 the spring than in the fall, respectively. The EC levels remained similar to those of 2011, but
18 the OC levels were higher during the fall 2012 increasing the OC/EC ratios. Some of these
19 ratios exhibited high peaks suggesting a contribution from primary emission sources with
20 elevated OC/EC ratios like biomass burning (Mancilla et al., 2015). The average temperature
21 in the fall was $23.5\text{--}26.4^\circ\text{C}$ versus $28.0\text{--}30.7^\circ\text{C}$ in the spring. The average fall temperatures
22 were not consistent with the average of 2011. In the fall of 2012, the warmer temperatures
23 might have promoted less utilization of some fuels compared to the 2011 in which lower
24 temperatures could have promoted their utilization, increasing the *n*-alkanes' concentrations in
25 fall 2011. The average CPI values of *n*-alkanes in the spring 2012 were 0.9 ± 0.1 (range: 0.8–
26 1.1) in the daytime and 1.2 ± 0.1 (range: 1.2–1.3) in the nighttime, while the CPI values in the
27 fall 2012 were 1.3 ± 0.1 (range: 1.0–1.4) in the daytime and 1.5 ± 0.2 (range: 1.3–1.6) in the
28 nighttime. From these CPI values, it appears that biogenic emissions are relevant in all
29 sampling periods. For spring 2012 daytime, the emissions appear to be heavily dominated by
30 anthropogenic emissions due to the low CPI value exhibited. The presence of petroleum
31 biomarkers supports the relative contribution of anthropogenic emissions. However, in 2012
32 the hopanes levels were ~35% lower at daytime and ~43% lower at nighttime than those in

1 the previous year. The low hopane levels (range of 0.10 to 1.49 ng m⁻³) highlight the possible
2 presence of biogenic emissions (Fig. 2).

3 **3.3 PAHs**

4 Twelve PAH compounds, fluoranthene (FLT), acephenanthrylene (ACE), pyrene (PYR),
5 benzo(a)anthracene (BAA), chrysene (CRY), benzo(k)fluoranthene + benzo(b)fluoranthene
6 (BFA), benzo(a)pyrene + benzo(e)pyrene (BaP+BeP), perylene (PER), indeno(123cd)pyrene
7 (IP), benzo(ghi)perylene (BgP), dibenz(ah)anthracene (DaA), and coronene (Cor), were
8 identified in the MMA fine samples. For both sampling years, the average daytime and
9 nighttime concentrations of PAHs were 1.4–5.9 and 1.4–2.4 times higher in the fall than in the
10 spring, respectively. This is consistent with the high contribution of the OC to the PM_{2.5}
11 during the falls. Independently of the season, the daytime concentrations were 1.3–1.6 times
12 higher than nighttime concentrations. These seasonal differences are consistent with the
13 results of Guo et al. (2003) and Li et al. (2006), where PAH levels were 2–4 and 14.4 times
14 higher in the cold seasons than in the warm seasons, respectively.

15 As illustrated in Fig. 4, the high molecular weight (HMW) PAHs were the most abundant for
16 the MMA. The presence of HMW PAHs such as BaP+BeP, IP, and BgP is an indication of
17 gasoline-powered vehicle emissions (Katsoyiannis et al, 2011; Tobiszewski and Namieśnik,
18 2012). In addition, a possible contribution of diesel-powered vehicles is indicated by the low
19 concentrations of the low molecular weight (LMW) PAHs such as FLT, PYR, and CRY. To
20 identify the emission sources of PAH, diagnostic ratios were calculated (Table 4). These ratios
21 should be used with caution because PAHs are emitted from a variety of emission sources,
22 particularly combustion sources, and their profiles can be modified due to their reactivity
23 (Tsapakis et al., 2002). From these ratios, the source could be determined (e.g., pyrogenic and
24 petrogenic sources). Then, these qualitative conclusions will be considered for the source
25 apportionment to estimate the relative contribution of primary emission sources. The average
26 ratios of IP/(IP+BgP) indicate that ambient PAHs in the MMA originated from gasoline and
27 diesel combustion, whereas the ratios of BAA/(BAA+CRY) show the presence of petrogenic
28 sources as well as vehicle emissions. To complement these results, the ratios of
29 (BaP+BeP)/BgP identified a marked contribution of non-traffic sources for the spring of 2011,
30 traffic sources for the fall 2011 and the spring 2012, and mixed-sources for the fall 2012. of
31 the presence of gas-phase PAHs was not evaluated and thus no information on gas/particle

1 partitioning of these semivolatile species is available. Thus, only diagnostic ratios for HMW
2 PAHs were calculated for this study because those PAHs exhibit low volatility (Kavouras et
3 al, 1999).

4 In this study, the average total concentrations of the quantified PAHs (TPAHs) were
5 $2.42 \pm 2.45 \text{ ng m}^{-3}$ (range: $0.65\text{--}8.31 \text{ ng m}^{-3}$) and $4.11 \pm 2.62 \text{ ng m}^{-3}$ (range: $1.42\text{--}11.97 \text{ ng m}^{-3}$)
6 during 2011 and 2012, respectively, whilst those quantified by González-Santiago (2009) at
7 two different sites in the MMA were $1.30 \pm 1.64 \text{ ng m}^{-3}$ (range: $0.05\text{--}6.93 \text{ ng m}^{-3}$) and
8 $1.70 \pm 1.88 \text{ ng m}^{-3}$ (range: $0.07\text{--}9.14 \text{ ng m}^{-3}$). The lowest concentrations were obtained during
9 the spring because its average temperature was statistically higher than during the fall seasons
10 ($p < 0.05$). The volatility of PAH increases with temperature; as a result low concentrations are
11 obtained in comparison with fall and winter seasons. For this study the concentrations of PAH
12 were lower during the spring than concentrations during fall; this pattern was exhibited during
13 the two sampling years. González-Santiago (2009) identified only six PAHs, while in this
14 study were identified twelve. In the current study, the total concentrations calculated for the
15 six common PAHs were from 3 to 8 times higher than those estimated by González-Santiago
16 (2009). Similar concentrations (between 0.04 ng/m^3 and 1.78 ng/m^3) were also reported for
17 six individual PAHs in urban samples collected in Mexico City (Stone et al., 2008). Of the
18 same PAHs identified among these studies, their levels were in the same concentration range.
19 However, the TPAH levels in the MMA compared to those calculated by Marr et al. (2006)
20 ($20\text{--}100 \text{ ng m}^{-3}$) in Mexico City were found at appreciably lower concentrations. In addition,
21 Marr et al. (2006) suggest that vehicles are the major source of PAHs. They demonstrated that
22 PAHs and carbon monoxide (CO) concentrations are well correlated in Mexico City and,
23 given that 99% of CO emissions are emitted by motor vehicles, this source is a major
24 contribution of PAH emissions. For the current study, daytime correlations (r) of $+0.76$ ($p >$
25 0.05) were found between TPAH and CO, reinforcing the conclusion that motor vehicles are
26 one major source of PAH emissions for the MMA. The concentrations of CO during this
27 study were obtained from the SIMA network.

28 The total PAH (TPAH) concentrations were compared with the EC and OC levels. TPAH
29 concentrations measured in the MMA exhibited fair daytime correlations with EC ($r = +0.79$;
30 $p > 0.05$), but low correlations with OC ($r = +0.57$; $p > 0.05$). According to Marr et al. (2004), the
31 strong correlation between TPAH and EC indicated the relative contribution of diesel-
32 powered vehicle exhaust, while weak correlations may be due to the low concentrations of EC

1 determined during this study (Mancilla et al., 2015). Furthermore, the weak correlation
2 between TPAH and EC suggests the presence of emission sources with an elevated OC/EC.

3 **3.4 *n*-Alkanoic acids**

4 The carboxylic acids or *n*-alkanoic acids are mainly derived from biogenic emissions (Rogge
5 et al., 1993b). However, these acids have also been identified in several primary sources such
6 as cooking operations (Rogge et al., 1991; Schauer et al., 2001b) and fossil fuel combustion
7 (Schauer et al., 2002). The *n*-alkanoic acids from C₁₀ to C₃₂ were quantified only for the three
8 last monitoring campaigns. The *n*-alkanoic acids were the most abundant, accounting for
9 69±16% at daytime and 78±11% of the total resolved organics at nighttime for both spring
10 and fall. The daytime and nighttime concentration levels were two times higher in the spring
11 than in the fall. As can be seen in Fig. 5, the *n*-alkanoic acids measured in the MMA were
12 dominated by hexadecanoic acid (palmitic acid) and octadecanoic acid (stearic acid). This
13 dominance is consistent with measurements in other locations (Fraser et al., 2002; Simoneit
14 2004; Li et al., 2006).

15 The average CPI values of *n*-alkanoic acids in the fall of 2011 were 4.3±1.0 (range: 3.3–5.3)
16 during the day and 5.0±0.4 (range: 4.6–5.4) at night. For the 2012 year the CPI values in the
17 spring were 3.6±0.6 (range: 2.9–4.5) during the day and 4.7±0.8 (range: 3.9–5.8) at night,
18 while the CPI values in the fall were 4.7±0.3 (range: 4.3–5.1) during the day and 5.3±1.1
19 (range: 4.0–6.8) at night. These elevated CPI values indicated the significant influence of
20 biogenic sources such as microbial and plant wax sources. The *n*-alkanoic acids <C₂₀ are
21 derived in part from microbial sources while those >C₂₀ are from vascular plant waxes (Guo
22 et al., 2003; Yue and Fraser, 2004; Simoneit et al., 2004). Fig. 5 clearly shows influence of
23 long chain (>C₂₀) plant wax particles for the MMA. The CPI values in this study were
24 consistent with those obtained by Wang and Kawamura (2005) (CPI: 5.3–10) and Yue and
25 Fraser (2004) (CPI: 3.2–11.2). Regardless of the elevated CPI values obtained for the MMA,
26 the values were not as high as those reported by the other mentioned studies due to a scarcity
27 of green vegetation covers in the MMA.

28 The *n*-alkenoic acids only included cis-9-octadecenoic acid (oleic acid) and trans-9-
29 octadecenoic acid (elaidic acid). The concentrations of cis-9-octadecenoic acid ranged from
30 0.96 ng m⁻³ to 15.38 ng m⁻³, while the concentrations of trans-9-octadecenoic acid ranged
31 from 2.11 ng m⁻³ to 13.35 ng m⁻³. The ratio of octadecanoic acid to cis-9-octadecenoic acid

1 has been used as an indicator of the atmospheric chemical processing (aging) of aerosols,
2 since the unsaturated acids are susceptible to atmospheric oxidation (Brown et al., 2002; Yue
3 and Fraser, 2004). In this study, the average ratios were 5.0 (range: 1.5–9.4) during the day
4 and 3.8 (range: 2.5–4.9) at night for the spring, versus 20.3 (range: 4.7–38.6) during the day
5 and 21.0 (range: 10.5–29.1) at night for the fall. The transport of aerosols from local and rural
6 sources can lead to the loss of cis-9-octadecenoic acid producing high octadecanoic acid to
7 cis-9-octadecenoic acid ratios. Similarly, the stagnation of aerosols may reflect the impact of
8 high oxidant concentrations in an urban atmosphere producing high ratios (Brown et al., 2002;
9 Yue and Fraser, 2004). Therefore, these ratios suggest that the ambient organic aerosols for
10 the MMA were aged and might be produced from transport and atmospheric oxidation. Air
11 circulation patterns (Hysplit backward trajectories) during these monitoring campaigns
12 suggested a long-range transport from the northeast and southeast (Mancilla et al., 2015). As
13 expected, the lowest and highest octadecanoic acid to cis-9-octadecenoic acid ratios obtained
14 for the MMA were consistent with the highest OC/EC ratios estimated for the MMA for the
15 same campaign; high OC/EC ratios identified transport and stagnation scenarios for the spring
16 and fall, respectively (Mancilla et al., 2015). In addition, these results are in line with those
17 reported by Brown et al. (2002) and Yue and Fraser (2004), who obtained ratios of 5–11 and
18 1.0–21.5, respectively.

19 In addition, a minor biogenic contribution can be identified by the presence of terpenoic acids
20 such as cis-pinonic acid and pinic acid. These acids are known to be a secondary, particle-
21 phase products of pinene, which is emitted from plants, particularly conifers (Plewka et al.,
22 2006; Sheesley et al., 2004). Both pinonic acid and pinic acid exhibited higher concentrations
23 in the spring than in the fall (Table S1), indicating biogenic emissions from softwood sources.

24

25 **3.5 Meat cooking and biomass burning tracers**

26 The major tracers for meat cooking particles are the steroids, while for biomass burning are
27 the anhydrosaccharides and methoxyphenols. All of these organic tracers were intermittent in
28 only 80% of the total OA samples/composites collected during this study.

29 There was not a clear trend between spring and fall samples during the two sampling years for
30 steroids (Table S1). However, the evidence of cooking operations' impact on the MMA was
31 confirmed by the presence of cholesterol and stigmaterol along with hexadecanoic acid,

1 octadecanoic acid, and oleic acid. Although cholesterol is considered a good marker for meat
2 cooking, studies have reported unexpectedly high levels of cholesterol from non-cooking
3 related sources such as soil and prescribed burns (Sheesley et al., 2004; Lee et al., 2005;
4 Robinson et al., 2006a).

5 Anhydrosaccharides are the tracers from burning cellulose and hemicelluloses, whereas the
6 methoxyphenols the tracer from burning of lignin (Giri et al., 2013). Levoglucosan, a
7 combustion and pyrolysis product of cellulose, is the main biomarker used to track biomass
8 burning emissions (Schauer et al., 2001a). Levoglucosan was not detected in all collected
9 samples. The levoglucosan found in the samples indicates that biomass burning is impacting
10 the MMA to some extent (Table S1). The levoglucosan concentrations varied by sampling
11 dates, ranging from not detectable levels to 54 ng m⁻³ for spring. In contrast, levoglucosan
12 was detected in all fall samples, ranging from 0.14 to 28 ng m⁻³. The intermittent peaks of
13 levoglucosan concentrations during the springtime can be explained by the fact that
14 Northeastern Mexico's atmosphere is highly influenced by forest wildfires and prescribed
15 agricultural burnings during the spring (Mendoza et al., 2005); this is in line with the idea that
16 high OC/EC ratios obtained, in a parallel study, were influenced in part by regional transport
17 emissions (Mancilla et al., 2015). In the case of the fall seasons, the levoglucosan levels can
18 be associated with local biomass burning due to mild temperatures encountered during these
19 seasons; a local contribution can be associated with high OC/EC ratios and stagnation
20 conditions determined for this period (Mancilla et al., 2015). The high OC/EC ratios during
21 spring may have a contribution from primary sources with elevated OC/EC ratios. The low
22 and variable levoglucosan concentrations in this study indicate that wood/vegetation smoke
23 episodes were occasional at the urban site. Average levoglucosan concentrations of 112.9 ng
24 m⁻³ and 151.3 ng m⁻³ were reported at urban and peripheral sites for Mexico City,
25 respectively (Stone et al., 2008). Based on an average concentration of levoglucosan, Mexico
26 City exhibited from 5 to 7 times higher levels than the MMA. These results are consistent
27 with the concentrations of OC and EC obtained in Mexico City; the EC concentrations were
28 up to two times higher than those observed in the MMA, whereas the OC concentrations were
29 from 2 to 6 times higher. A study conducted in Houston, TX, during August-September
30 reported elevated concentrations of levoglucosan: up to 234 ng m⁻³ (Yue and Fraser, 2004).
31 Similarly, a study conducted for 14 cities in China during summer and winter, also reported
32 elevated levoglucosan concentrations of 259 ng m⁻³ (Wang et al., 2006). However, in those

1 studies the vegetation around the sampling sites included a vast number of parks and woody
2 shrubs, suggesting a major biomass burning contribution contrary to the MMA. Apart from
3 those studies, Zheng et al. (2002) reported elevated levoglucosan concentrations of 166–307
4 ng m^{-3} for urban areas of similar surroundings to the MMA. In this case, it is also possible
5 that the levoglucosan emissions reported come from industries that have implemented
6 biomass burning processes for energy generation. As can be seen from the previous
7 comparison, the contribution of biomass burning is minor for the MMA in comparison with
8 other urban locations. In addition, biomass burning contributions are inconsistent with those
9 reported in similar locations to the MMA.

10 The resin acids such as dehydroabietic acid, pimaric acid, and isopimaric acid (Table S1) are
11 secondary tracers from biomass burning (Schauer et al., 2001a). Dehydroabietic acid was the
12 most abundant resin acid, ranging from 1.94 to 4.39 ng m^{-3} and 1.95 to 3.69 ng m^{-3} for spring
13 and fall, respectively. Then, pimaric acid ranged from not detectable levels to 0.09 ng m^{-3} and
14 from 0.15 to 0.35 ng m^{-3} for spring and fall, respectively. Finally, isopimaric acid ranged
15 from not detectable levels to 0.03 ng m^{-3} and from 0.06 to 0.12 ng m^{-3} for spring and fall,
16 respectively. The results for resin acids are in line with those obtained for levoglucosan. These
17 results support the low impact from biomass burning emissions in the MMA, especially from
18 softwood burning (e.g., conifer wood) during the spring and fall campaigns. In addition, the
19 higher concentrations of resin acids in fall than in spring are associated with photochemical
20 activity due to stagnation events in fall.

21

22 **3.6 Source Apportionment**

23 CMB was applied using the quantification of individual organic compounds found in the
24 collected $\text{PM}_{2.5}$ samples. The relative contributions for gasoline-powered vehicles, diesel-
25 powered vehicles, natural gas combustion, fuel oil combustion, meat cooking operations,
26 vegetative detritus, and biomass burning were estimated. From the source categories selected,
27 the ones corresponding to natural gas and fuel oil combustion were not determined as
28 significant for some ambient samples. These two sources were determined to have
29 contributions that were not statistically different from zero or were slightly negative and thus
30 were excluded from the model. Model performance was determined by r^2 values ranging
31 between 0.58 and 0.85 and chi-squared (χ^2) values between 2.97 and 8.85. Similar values for

1 r^2 and χ^2 have been obtained in Fraser et al. (2003) and Schneidmesser et al. (2009). The
2 latter study used composites to perform the CMB. Another performance metric calculated by
3 EPA-CMB8.2 is the percent mass explained. Theoretically, values ranging from 80% to 120%
4 are acceptable. This ideally can occur when ambient data is not impacted heavily by SOA
5 because CMB is only able to account accurately for primary sources. In spite of this
6 limitation, CMB results with low percent mass explained values have been reported by some
7 studies. In these cases, the high levels of unexplained mass have been associated with
8 secondary production (Fraser et al., 2003; Zheng et al., 2005). For the 43 ambient samples fed
9 to CMB in this study, 18 samples exhibited low percent mass explained values (ranging from
10 20% to 77%), whereas samples had values around 100%. These results are in line with the
11 relative high and low OC/EC ratios obtained for spring and fall, respectively (Mancilla et al.,
12 2015). Finally, 11 samples were discarded due to poor performance parameters calculated.
13 These samples were not exclusively from a particular monitoring campaign; there were
14 samples from both springs and falls. A detailed description of the CMB performance and
15 relative contributions for each sample can be found in Table S2.

16 The average contributions of primary sources are shown in Table 5. The vehicle exhaust and
17 meat-cooking operation emissions were the highest for all monitoring campaigns. When
18 examining of the seasonal variation, the gasoline- and diesel-powered vehicles in falls were
19 up to five times higher than in springs, when cold weather increases the demand of petroleum
20 products due to low temperatures. The opposite occurred for meat-cooking operations, their
21 spring emissions were three times higher than in fall seasons. The natural gas combustion,
22 vegetative detritus and biomass burning emissions were very low and more constant
23 throughout the springs and falls. With regard to the daytime and nighttime variations, the
24 vehicle exhaust were much higher during daytime when traffic is heavier. For the meat-
25 cooking operations, the emissions were somewhat higher in nighttime during spring and more
26 constant between daytime and nighttime during fall. For the rest of the sources, the daytime
27 and nighttime emissions were relatively constant. There were no similar studies conducted in
28 the MMA, this is the first source apportionment study based on molecular organic markers for
29 this region. However, these results are similar to those obtained for the MMA using a factor
30 analysis based on trace elements (Martinez et al., 2012) and those for Mexico City based on
31 molecular organic markers (Stone et al., 2008).

1 The average contribution of each emission category to the identified PM_{2.5} mass is shown in
2 Fig. 6. The unidentified mass was on average 35±24% of the measured PM_{2.5} concentrations.
3 This value is 1.5 times greater than the ~23% of secondary organic aerosol contribution to the
4 total PM_{2.5} mass concentration (SOC/PM_{2.5}) estimated in Mancilla et al. (2015) for the MMA.
5 The average secondary contribution used for this comparison was based on the minimum
6 OC/EC ratios observed and reported in Mancilla et al. (2015). These ratios may take into
7 account primary sources with elevated values of OC/EC ratios such as biomass burning and
8 kitchen operations as well as fossil fuel combustion sources. The unidentified mass by CMB
9 may include secondary organic and inorganic aerosol and trace elements. Thus, the levels of
10 unidentified mass resolved by CMB are reasonable given that the secondary aerosol estimated
11 in Mancilla et al. (2015) was in fact only SOA. Therefore, the 12% of difference between 35%
12 and 23% might be attributed to secondary inorganic aerosol and other chemical species. As
13 indicated in Fig. 6, the emissions from motor vehicle exhausts (gasoline and diesel) are the
14 most important, accounting for the 64% of the identified PM_{2.5} emissions, followed by meat-
15 cooking operations (31%) and industries (2.8%). Vegetative detritus and biomass burning
16 were the least emitted with only 2.2% of the identified PM_{2.5} emissions. The relative high
17 contribution of the meat-cooking operations was expected given the high traditional restaurant
18 activity in the MMA which contributes with the 16% of the local growth domestic product.
19 With regard to biomass burning, several studies have demonstrated that Mexico City has a
20 large contribution of biomass burning emissions due to forests fires (Moffet et al., 2008; Stone
21 et al., 2008; Yokelson et al., 2007). However, the MMA can be affected by other types of
22 biomass burning (e.g., shrub and grassland fires, agricultural waste and garbage burning, etc.)
23 that may be ignored. Therefore, the contribution of biomass burning in the MMA might be
24 higher because the source profile used for the CMB was only for wood combustion instead of
25 using a source profile for other types of biomass burning (Simoneit et al., 2005). In addition,
26 it is important to point out the potential of industrial sources as appeared from previous
27 studies conducted in the MMA and the rest of the country. The MMA is the third largest
28 urban center of the country with approximately 9,700 industries (INEGI, 2005). In the MMA
29 the main emissions from industrial sources come from the combustion of natural gas; low
30 emissions come from the use of fuel oil. In this study the natural gas profile did not fit well
31 and it was discarded from the CMB, but the fuel oil did it. The combustion of natural gas
32 emits a low amount of particles, therefore, its contribution to the airborne particles is not
33 significant.

1

2 **4 Conclusions**

3 Spring and fall sampling campaigns were performed in 2011 and 2012 at one representative
4 site to conduct a chemical characterization of the fine OC in PM_{2.5} in the MMA. The
5 identified organic compound classes represented a low fraction of the ambient OC: 0.5% for
6 spring 2011 and 2.6 to 11% for the last three campaigns. The average CPI values derived from
7 the *n*-alkanes (0.9–1.7) and *n*-alkanoic acids (2.9–6.8) demonstrated that anthropogenic (e.g.,
8 fossil fuel combustion) were dominant while biogenic (e.g., plant waxes, microbial origin)
9 emission sources contribute at least sometimes to the fine OA in the MMA.

10 The PAH diagnostic ratios indicate that gasoline- and diesel-powered vehicles are the main
11 emission sources of this class of organic compounds in PM_{2.5}. However, other pyrogenic
12 sources such as coal, grass, and wood combustion were also identified as contributors to the
13 fine OA. The quantified levels of cholesterol and levoglucosan confirm the high and low
14 contribution of cooking operations and biomass burning, respectively. Low levoglucosan
15 concentrations suggest low episodic or transport effects of emissions of biomass burning on
16 PM_{2.5} in the MMA.

17 In a parallel study, significant SOA formation was found in the MMA. The chemical
18 speciation of the OC confirmed the aging of primary emissions and the SOA from biogenic
19 volatile organic compounds. On one hand, the identified octadecanoic acid and *cis*-9-
20 octadecenoic acid along with other secondary organic markers point out the SOA formation in
21 the MMA atmosphere. The average ratios of octadecanoic acid to *cis*-9-octadecenoic acid
22 (3.8–21) indicate aging of the fine OA due to photochemical activity and transport. On the
23 other hand, the presence of the *cis*-pinonic and pinic acids confirmed the SOA derived from
24 biogenic sources. This is in line with the transport and stagnation events that predominated
25 during spring and fall, respectively.

26 The emissions from vehicle exhausts are the most important, accounting for 64% of the
27 identified PM_{2.5} emissions. By contrast, vegetative detritus and biomass burning were the
28 lowest contributors with barely 2.2% of the identified PM_{2.5} emissions.

29 Finally, a comparison with other studies indicates that the MMA exhibits similar
30 concentrations patterns of the organic molecular markers identified in this study.

31

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7

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1 Table 1. Monitoring experiments conducted for this study.

Campaign	Period	Sampling Days	Samples	Field blanks
Spring 2011	May 28 to June 11	7 ^a	14	2
Fall 2011	October 22 to November 3	7 ^a	14	2
Spring 2012	June 6 to June 19	14	27	2
Fall 2012	October 13 to October 26	14	56	4

2 ^a Non-consecutive days.

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1 Table 2. Characteristics of individual and composite samples for each monitoring campaign.

Campaign	Description	Dates included	PM _{2.5}		OC	
			($\mu\text{g m}^{-3}$)	SD	($\mu\text{g m}^{-3}$)	SD
Spring 2011	ID1	May 30, Jun 01, Jun 09, Jun 11	20.3	8.7	8.2	2.7
	ID2	May 28, Jun 03, Jun 05	22.5	15.1	10.7	5.7
	IN1	May 30, Jun 01, Jun 09, Jun 11	25.1	10.2	6.3	1.5
	IN2	May 28, Jun 03, Jun 05	31.7	22.6	8.5	4.3
Fall 2011	CD1	Oct 24, Nov 01	18.5	3.2	8.7	1.6
	CD1	Oct 26, Nov 03	18.1	12.4	8.2	5.4
	CN1	Oct 24, Nov 01	13.5	1.6	4.7	0.3
	CN1	Oct 26, Nov 03	12.9	9.4	5.5	2.5
	CD2	Oct 22, Oct 28, Oct 30	20.8	11.6	9.3	3.3
	CN2	Oct 22, Oct 28, Oct 30	15.1	6.1	6.7	2.1
Spring 2012	CD1	Jun 11, Jun 12	17.1	3.7	7.6	2.5
	CD1	Jun 13, Jun 14	19.3	1.7	6.2	0.6
	CD1	Jun 18, Jun 19	12.6	0.7	5.1	0.9
	CD1	Jun 06, Jun 07	18.3	2.0	8.8	1.0
	CN1	Jun 11, Jun 12	20.3	0.5	4.3	0.8
	CN1	Jun 13, Jun 14	15.2	0.1	3.3	0.1
	CN1	Jun 18, Jun 06, Jun 07	9.3	1.5	4.0	0.8
	CD2	Jun 08, Jun 09, Jun 10	18.4	3.7	8.3	0.7
	CD2	Jun 15, Jun 16, Jun 17	10.7	2.2	4.6	0.6
	CN2	Jun 08, Jun 09, Jun 10	18.8	6.6	5.3	1.0
	CN2	Jun 15, Jun 16, Jun 17	9.3	3.1	2.8	0.6
	Fall 2012	CD2	Oct 13, Oct 14, Oct 27	15.8	2.9	9.3
CN2		Oct 13, Oct 14, Oct 28	8.9	2.7	6.8	1.1
CD1		Oct 15, Oct 16	17.6	4.1	10.1	3.1
CN1		Oct 15, Oct 16	23.4	11.4	11.4	3.9
CD1		Oct 17, Oct 18	17.6	11.9	13.7	6.2
CN1		Oct 17, Oct 18	13.4	2.4	8.7	1.9
CD2		Oct 19, Oct 20, Oct 21	29.7	5.5	10.9	2.1
CN2		Oct 19, Oct 20, Oct 21	23.1	1.1	6.6	2.1
CD1		Oct 22, Oct 23	23.6	3.9	8.1	0.2
CN1		Oct 22, Oct 23	13.7	2.2	4.5	0.3
CD1		Oct 24, Oct 25	13.9	1.6	9.3	3.9
CN1		Oct 24, Oct 25	10.8	1.0	5.3	0.6

2 Values for PM_{2.5} are the averages obtained from the SIMA network. OC concentration values
3 are the average values reported by Mancilla et al. (2015). SD represents standard deviation, I
4 indicates that the dates included were analyzed individually, C indicates that dates included
5 were pooled to form a composite, D represents daytime sampling, N represents nighttime
6 sampling, 1 refers to weekday sampling, 2 refers to weekend sampling.

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2 Table 3. PAH diagnostic ratios for different source categories.

Diagnostic Ratio	Value	Source	Reference
IP/(IP+BgP)	< 0.20	Petrogenic	Katsoyiannis et al., 2011
	> 0.20	Pyrogenic	Katsoyiannis et al., 2011
	0.20–0.50	Petroleum combustion	Yunker et al., 2002
	> 0.50	Coal, grass, and wood combustion	Yunker et al., 2002
BAA/(BAA+CRY)	< 0.20	Petrogenic	Katsoyiannis et al., 2011
	0.20–0.35	Coal combustion	Akyüz and Cabuk, 2010
	> 0.35	Pyrogenic, vehicle emissions	Katsoyiannis et al., 2011
FLT/(FLT+PYR)	< 0.40	Petrogenic	Katsoyiannis et al., 2011
	> 0.40	Pyrogenic	Katsoyiannis et al., 2011
	0.40–0.50	Fuel combustion	Katsoyiannis et al., 2011
	> 0.50	Diesel emissions	Ravindra et al., 2008
(BaP+BeP)/BgP	> 0.60	Traffic	Katsoyiannis et al., 2011
	< 0.60	Non-traffic	Katsoyiannis et al., 2011

3 The PAH abbreviations are IP: Indeno(123cd)pyrene, BgP: Benzo(ghi)perylene, BAA:
4 Benz(a)anthracene, CRY: Chrysene, FLT: Fluranthene, PYR: Pyrene, BeP: Benzo(e)pyrene,
5 BaP: Benzo(a)pyrene.

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1 Table 4. Average diagnostic ratios of PAHs in MMA

Season	Period	IP/(IP+BgP)	BAA/(BAA+CRY)	FLT/(FLT+PYR)	(BaP+BeP)/BgP
Spring 2011	D	0.41±0.05	0.34±0.28	0.50±0.03	0.19±0.24
	N	0.46±0.02	0.62±0.30	0.49±0.10	0.07±0.06
Fall 2011	D	0.35±0.10	0.50±0.03	0.55±0.12	2.67±0.75
	N	0.51±0.26	0.17±0.29	0.66±0.25	4.63±4.49
Spring 2012	D	0.33±0.13	0.01±0.003	0.72±0.20	4.48±2.19
	N	0.47±0.34	0.06±0.12	0.89±0.02	10.40±2.45
Fall 2012	D	0.34±0.04	0.35±0.07	0.60±0.06	0.55±0.08
	N	0.36±0.02	0.40±0.09	0.68±0.05	0.52±0.13

2 D represents daytime, N represents nighttime

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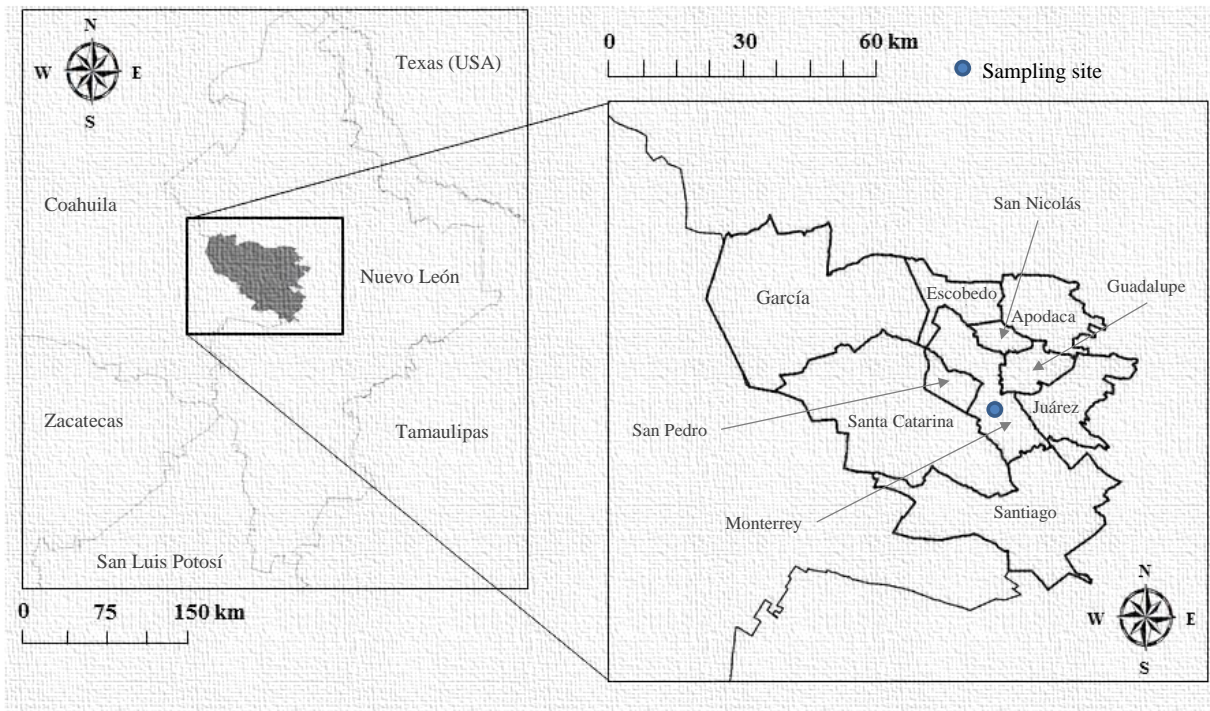
4 Table 5. Contributions and uncertainty of primary sources to seasonal average ambient PM_{2.5}

5 for daytime and nighttime in the MMA (in $\mu\text{g m}^{-3}$)

Source category	Spring 2011		Fall 2011		Spring 2012		Fall 2012	
	Daytime	Nighttime	Daytime	Nighttime	Daytime	Nighttime	Daytime	Nighttime
Gasoline-powered vehicles	2.37 ± 0.56	2.46 ± 0.46	3.70 ± 0.78	2.24 ± 0.51	1.43 ± 0.41	*	7.51 ± 1.27	3.19 ± 0.51
Diesel-powered vehicles	7.34 ± 0.86	3.81 ± 0.53	13.67 ± 1.59	13.10 ± 1.55	2.93 ± 0.41	*	13.85 ± 1.58	5.15 ± 0.51
Vegetative detritus	0.22 ± 0.04	0.22 ± 0.04	0.13 ± 0.03	0.27 ± 0.05	0.40 ± 0.06	*	0.42 ± 0.07	0.31 ± 0.03
Meat-cooking operations	8.24 ± 1.54	11.13 ± 1.85	3.26 ± 0.71	3.86 ± 0.71	9.74 ± 1.20	*	3.22 ± 0.53	3.37 ± 0.51
Natural gas combustion	0.01 ± 0.01	N.I.	0.05 ± 0.03	0.03 ± 0.01	0.01 ± 0.01	*	0.10 ± 0.02	0.04 ± 0.01
Biomass burning	0.20 ± 0.05	0.17 ± 0.05	0.17 ± 0.05	0.07 ± 0.02	0.16 ± 0.04	*	0.01 ± 0.01	0.01 ± 0.01
Fuel oil combustion	N.I.	N.I.	4.18 ± 3.55	3.60 ± 1.20	N.I.	*	N.I.	0.22 ± 0.03

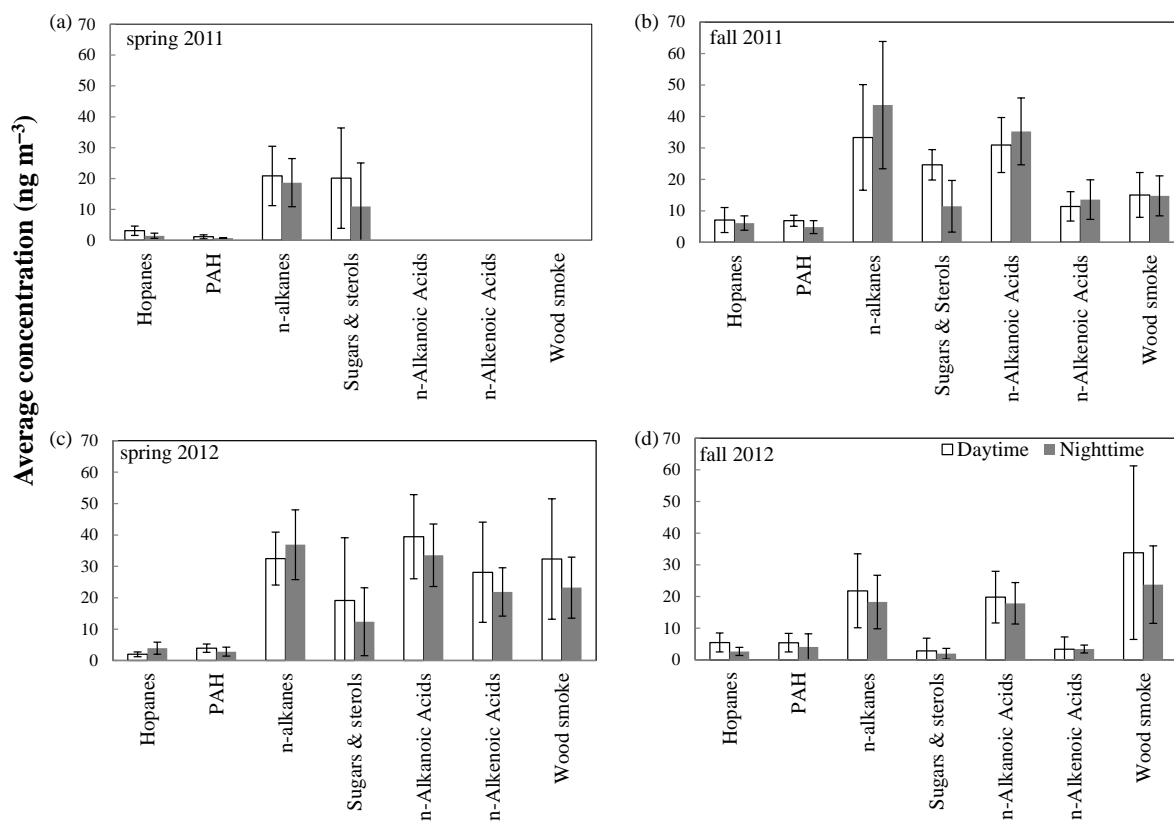
6 N. I. means Not Important. * samples were discarded due to poor CMB performance.

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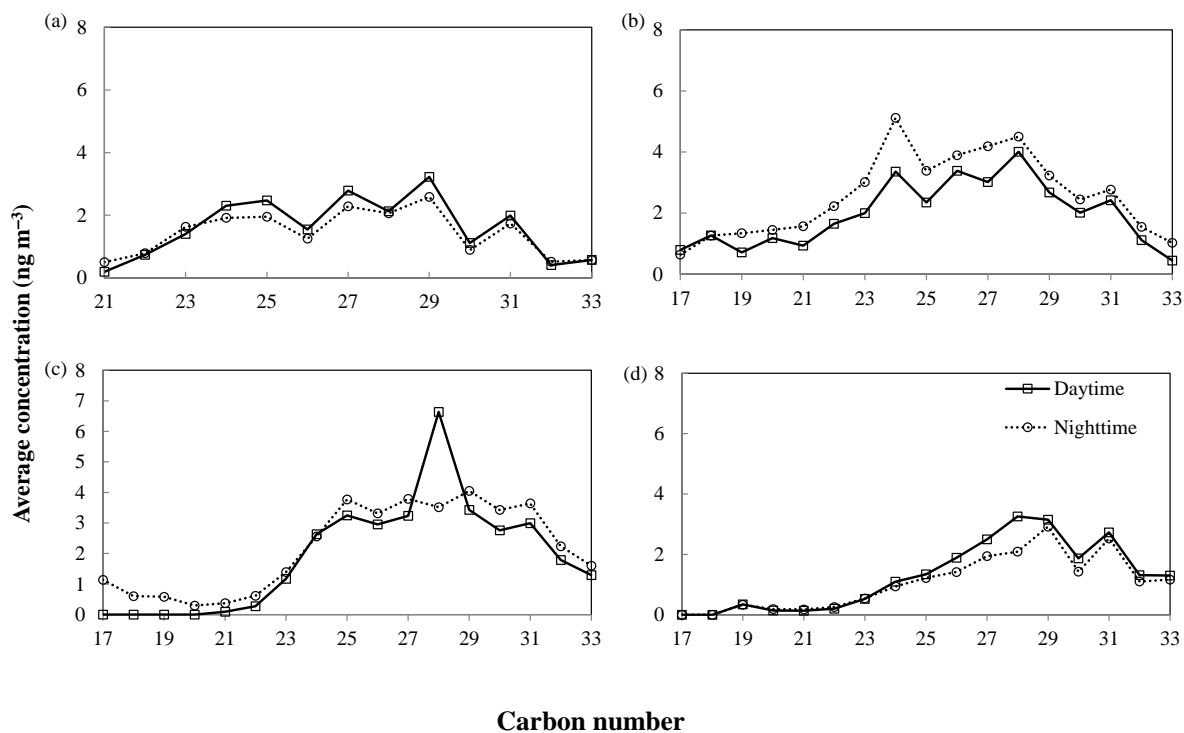


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Figure 1. Location and municipalities of the Monterrey Metropolitan Area (MMA); the sampling site was set up in the downtown.

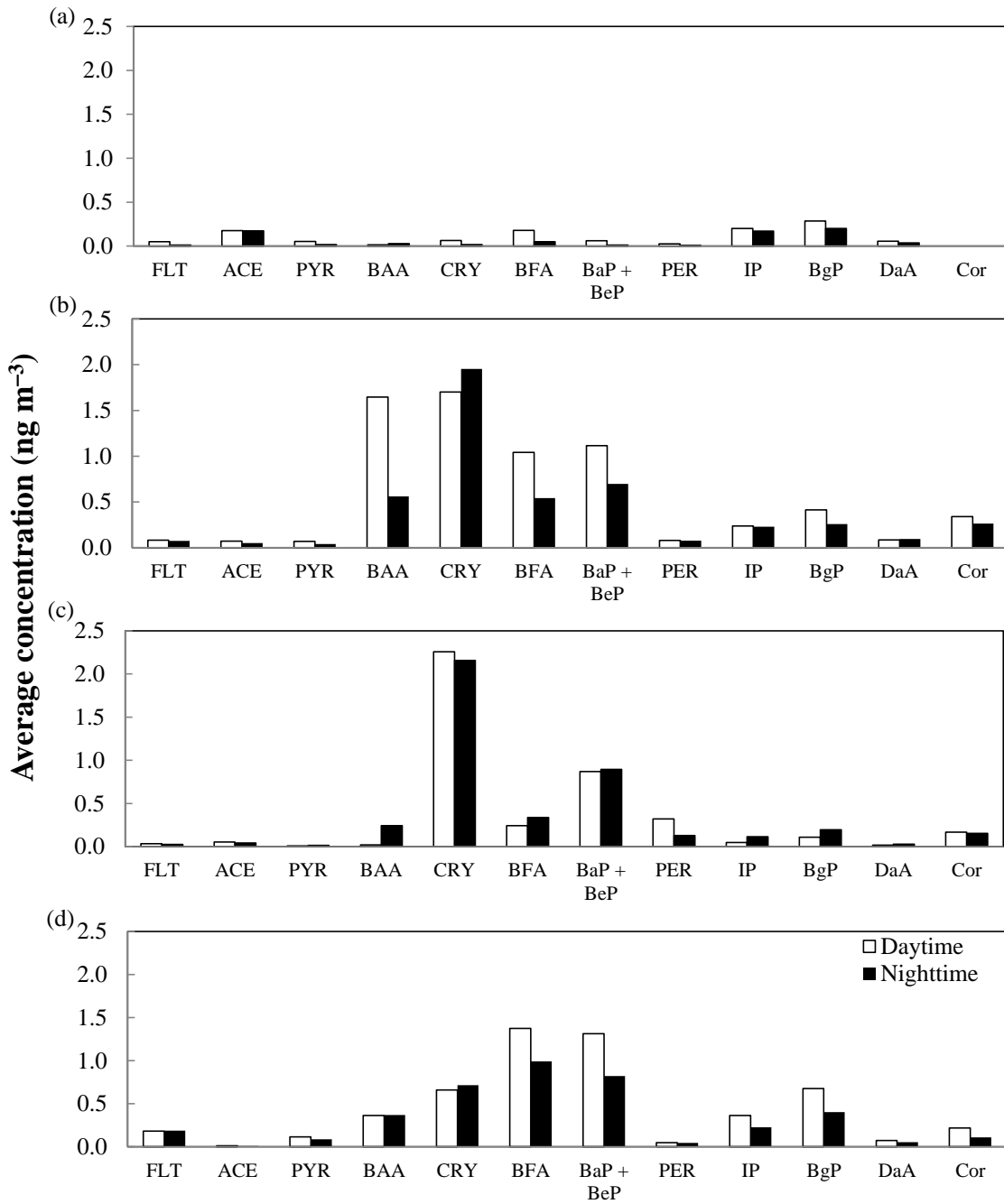


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 2 Figure 2. Concentrations of the resolved organic compound classes in the MMA. For (a) the
 3 n-Alkanoic and Alkenoic acids and wood smoke tracer were not included in the chemical
 4 analysis. For (b), (c) and (d) the *n*-alkanoic acids are divided by a factor of 10.
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Figure 3. Carbon number distribution of *n*-alkanes in the Monterrey Metropolitan Area (MMA) for (a) spring 2011, (b) fall 2011, (c) spring 2012 and (d) fall 2012. The black line represents the daytime concentrations while the dotted line represents the nighttime concentrations.



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Figure 4. Mass concentration distribution of PAHs in the Monterrey Metropolitan Area

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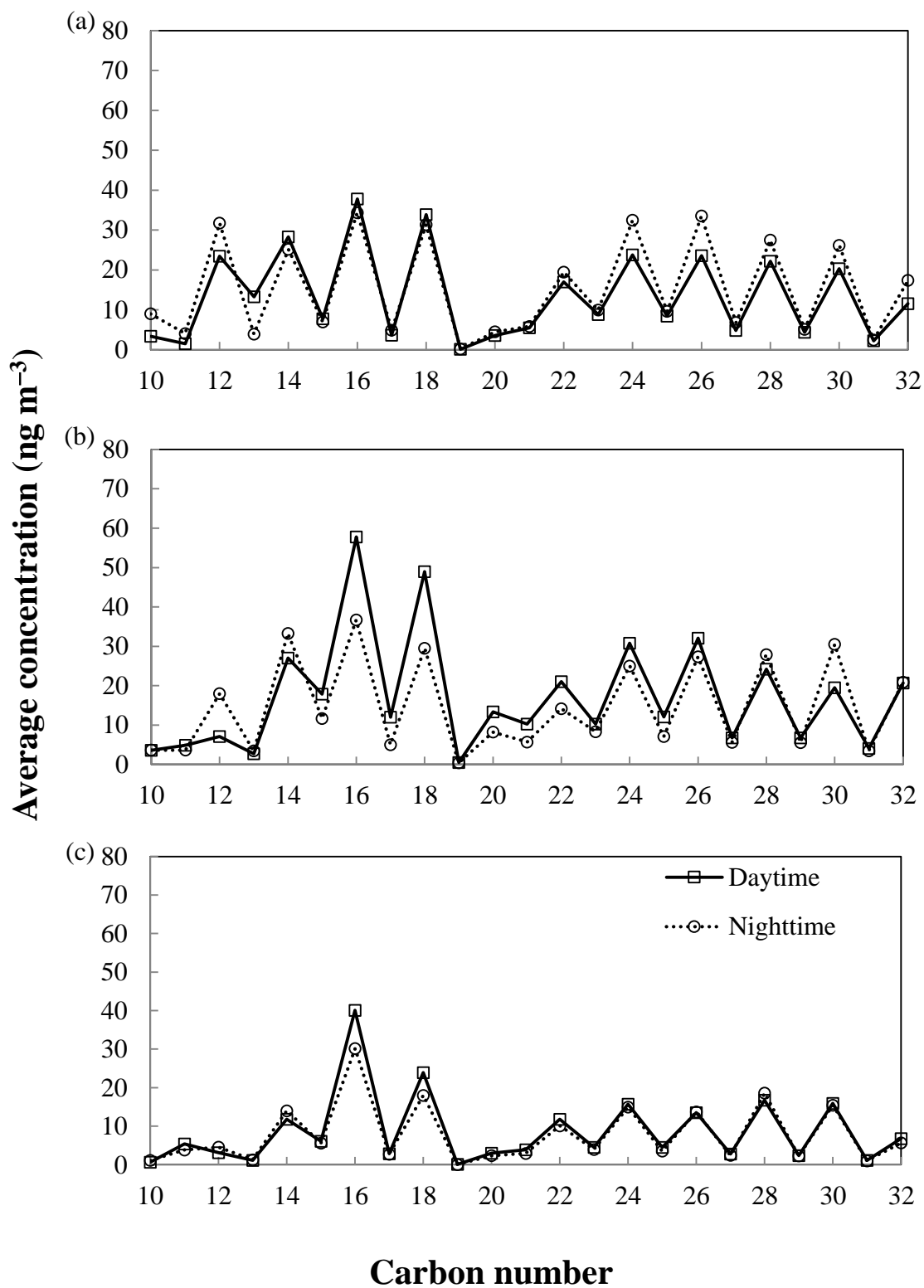
(MMA) for (a) spring 2011, (b) fall 2011, (c) spring 2012 and (d) fall 2012. Coronene was

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included in all monitoring campaigns, except in the spring 2011.

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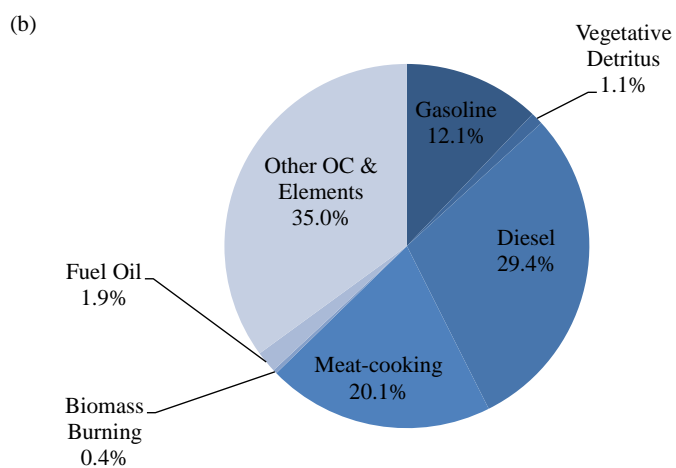
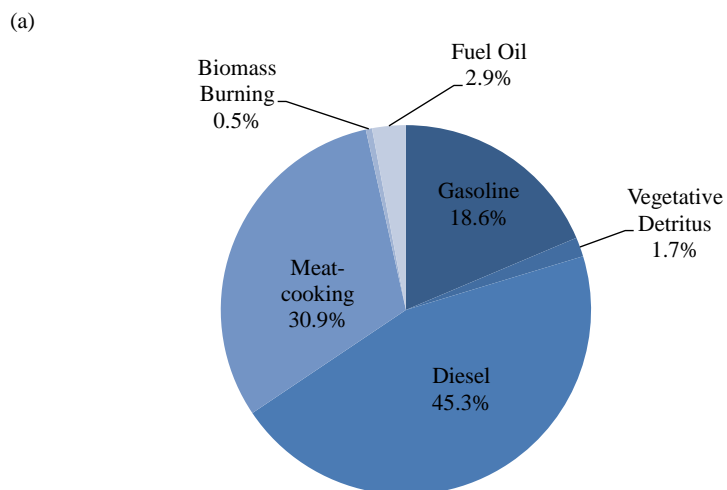


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2 Figure 5. Carbon number distribution of *n*-alkanoic acids in the Monterrey Metropolitan Area

3 (MMA) for (a) fall 2001, (b) spring 2012 and (c) fall 2012. The black line represents the

4 daytime concentrations while the dot line represents the nighttime concentrations.



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 2 Figure 6. CMB contributions to the (a) average identified ambient $PM_{2.5}$ in the MMA and to
 3 the (b) overall $PM_{2.5}$ including the unidentified mass of the measured $PM_{2.5}$ concentrations.

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