1 Organic composition and source apportionment of fine

2 organic aerosol at Monterrey, Mexico, based on organic

3 markers

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Abstract

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

- elemental carbon were correlated ($r^2 = 0.39-0.70$) across the monitoring periods, reinforcing
- 2 that motor vehicles are the major contributors of PAH. Cholesterol levels remained constant
- 3 during the spring and fall, showing evidence of the contribution of meat cooking operations,
- 4 while the isolated concentrations of levoglucosan suggested occasional biomass burning
- 5 events. Finally, source attribution results obtained using the CMB model indicate that
- 6 emissions from motor vehicle exhausts are the most important, accounting for the 64% of the
- 7 PM_{2.5}, followed by meat cooking operations with 31% The vegetative detritus and biomass
- 8 burning had the smallest contribution (2.2% of the PM_{2.5}). To our knowledge, this is the
- 9 second study to explore the organic composition and source apportionment of fine organic
- aerosol based on molecular markers in Mexico and the first for the MMA. Particularly
- molecular marker were quantified by solvent extraction with dichloromethane, derivatization,
- and gas chromatography with mass spectrometry (GC/MS). .

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1 Introduction

- 15 Fine organic aerosol (OA) has a major role in environmental and human health impacts (Peng
- et al., 2009). Some researchers have recently estimated that fine OA constitutes 23–38% of
- the PM_{2.5} mass in urban areas (Qin et al., 2006; Viana et al., 2006; Duan et al., 2007;
- Upadhyay et al., 2011). In addition, OA along with elemental carbon (EC) can account for up
- to 31-57% of the PM_{2.5} mass (Duan et al., 2007; Upadhyay et al., 2011; Martínez et al.,
- 20 2012).
- 21 Atmospheric fine OA is a complex mixture of hundreds of organic compounds that are
- 22 directly emitted or are generated by atmospheric chemical processes. Many of these organic
- compounds are toxic or carcinogenic (Spurny, 2000; Pope et al., 2002), but can be useful as
- 24 markers to identify the source of the aerosols being measured at a specific site. Organic
- 25 markers that have been used in the past include levoglucosan, cholesterol, nicotine, *n*-alkanes,
- 26 hopanes (pentacyclic triterpanes), and polycyclic aromatic hydrocarbons (PAHs).
- 27 Levoglucosan is a pyrolisis decomposition and combustion product of cellulose; therefore, it
- can be used as a tracer for biomass burning sources (Fraser et al., 2000; Robinson et al.,
- 29 2006a; Alves et al., 2011; Gonçalves et al., 2011). Cholesterol and nicotine are good markers
- for meat cooking operations (Rogge et al., 1991; Schauer et al., 2001b; Robinson et al.,
- 2006b) and cigarette smoke (Eatough et al., 1989; Hildemann et al., 1991; Rogge et al., 1994;
- 32 Kavouras et al., 1998), respectively. Hopanes are biomarkers of fuel oil combustion, coal

- 1 combustion and lubricants, and are useful to identify engine emissions (Rogge et al., 1993a;
- 2 Oros and Simoneit, 2000; Simoneit et al., 2004; Schnelle-Kreis et al., 2005). PAHs are semi-
- 3 volatile compounds formed from fossil fuel incomplete combustion processes (Rogge et al.,
- 4 1993a; Marr et al., 2004; Sklorz et al., 2007). Finally, *n*-alkanes are indicators of fossil fuel
- 5 utilization and biogenic emissions (Simoneit et al., 2004; Young and Wang, 2002). Additional
- 6 details about specific organic markers and their emission sources can be found elsewhere
- 7 (Simoneit et al., 1991; Simoneit, 1999; Lin et al., 2010; Blanchard et al., 2014).
- 8 Another feature used to identify the origin of fine OA are the diagnostic ratios between
- 9 homologs in series of biomolecules. For n-alkanes and alkanoic acids, the odd- and even-
- carbon preferences are indicators of biogenic sources (Tsapakis et al., 2002). A lack of carbon
- preference is indicative of fossil sources. For the case of PAHs, some ratios can be used to
- identify emissions from fossil fuel combustion (Zhang et al., 2005).
- Source apportionment studies based on organic molecular markers have accomplished a better
- understanding of the emission sources in urban areas. This approach considers two main
- principles: (1) that organic molecular markers are present in relatively high concentrations in
- emissions from a specific source and in lower concentrations in the remaining sources, and (2)
- that they react slowly enough in the atmosphere to be conserved during transport from the
- source to the observation/receptor site (Schauer et al., 1996; Lin et al., 2010). The use of
- organic molecular markers in the last decade has proven to be a powerful method to identify
- and attribute emission sources in urban areas (Alves et al., 2001; Fraser et al., 2003; Abas et
- 21 al., 2004; Kalaitzoglou et al., 2004; Zheng et al., 2005; Feng et al., 2006; Huang et al., 2006;
- 22 Li et al., 2006; Park et al., 2006; Alves et al., 2007; Chow et al., 2007; Ke et al., 2007; Stone
- 23 et al., 2008; Amador-Muñoz et al., 2010; Yin et al., 2010; Pietrogrande et al., 2011; Perrone et
- 24 al., 2012; Giri et al., 2013; Villalobos et al., 2015; Watson et al., 2015; Zheng et al., 2015).
- In spite of recent research interest on organic molecular markers for source apportionment, the
- application of this approach started in the 80s (Simoneit, 1985; Simoneit, 1986; Eatough et al.,
- 27 1989; Simoneit and Mazurek, 1989) and continued in the 90s (Simoneit et al., 1990; Simoneit
- 28 et al., 1991; Schauer et al., 1996; Simoneit, 1999; Schauer and Cass, 2000), especially, with
- 29 the development of organic source profiles for primary emission sources (Rogge et al., 1991;
- 30 Rogge et al., 1993a; Rogge et al., 1993b; Rogge et al., 1993c; Rogge et al., 1994; Rogge et al.,
- 31 1997; Fraser et al., 1999; Schauer et al., 1999) and alternative receptor models (Paatero 1997;
- Wold et al., 2001). Furthermore, improved source apportionment methods have been

developed (Antony Chen et al., 2011; Kelly et al., 2013; Watson et al., 2015) while other

2 methods have been suggested to be dropped as a receptor model (Hopke 2015). More detailed

3 information about source apportionment methods can be found elsewhere (Reff et al., 2007;

4 Lin et al., 2010; Nozière et al., 2015).

For the Monterrey Metropolitan Area (MMA), the third largest urban center of Mexico, there 5 is a growing concern to determine the emission sources of fine OA. It was recently 6 determined that fine OA accounts for 36-71% of PM_{2.5} mass in this urban center (Mancilla et 7 al., 2015). Previously, Martínez et al. (2012) estimated an OA fraction of ~40% of the PM_{2.5} 8 9 for the MMA. According to a recent tunnel study, PM2.5 emissions from gasoline-powered vehicles (one of the major emission sources in the MMA) contain as much as 55% of 10 carbonaceous material (Mancilla and Mendoza, 2012). To date, only one study has addressed 11 the chemical characterization of fine OA in the MMA, but it focused exclusively on the levels 12

of PAHs (González-Santiago, 2009). More importantly, the present study would be the second

of this kind in Mexico and the first one for the MMA; previously, Stone et al. (2008) reported

an evaluation of molecular organic markers for source apportionment at the Mexico City. This

city has a temperate and wet climate while the MMA has a dry and extreme climate with

scarce rains. It is well-known that climate conditions can affect the air quality in urban areas.

Extreme climates, including high temperatures, could increase the concentrations of air

pollutants. For example, warm and dry climates promote photochemical reactions in the

atmosphere producing secondary OA. The unique geography and the changeable climate as

well as its typical industries of the region make of the MMA unique and different from other

22 Mexican cities.

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2 Methodology

2.1 Sampling site

The MMA has a population of 4.2 million inhabitants (INEGI, 2011) and it is considered the

27 largest urban area in Northeastern Mexico and the third-largest urban center in the country.

28 The MMA is composed of 12 municipalities that overall cover an area of 6,680 km²

(SEDESOL et al., 2007), as shown in Fig. 1. The MMA has a vehicular fleet of 1.7 million

vehicles (INEGI, 2010) with a composition of approximately 73% gasoline-powered vehicles

31 (car passengers), 25% diesel-powered vehicles (buses and trucks) and 3% motorcycles. In

addition, the MMA has an industrial activity dominated by manufacturing industries, 1 construction and electricity, transport, restaurants and other local services. In addition, the 2 MMA has a network of air quality monitoring stations (Sistema Integral de Monitoreo 3 Ambiental, SIMA). For this study, PM_{2.5} samples were collected at only one site placed in the 4 5 facilities of the downtown monitoring station of the SIMA network (25° 40' 32" N, 100° 20' 18" W), 556 meters above sea level. The sampling site is affected mainly by traffic and 6 emissions from a wide range of industrial activities (e.g., steel and cement production). The 7 vegetation around the sampling site includes dispersed and scarce grass, shrubs, and street tree 8 systems in the immediate vicinity as well as in the periphery. The sampling site selection was 9 based on coefficients of divergence (COD) analysis using the 24-hour average PM_{2.5} 10 concentrations recorded in 2009 by the SIMA network. Details about this analysis can be 11 found elsewhere (Mancilla et al., 2015). 12

2.2 Sampling periods and instruments

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The samples were collected during the spring and fall of 2011 and 2012 (Table 1). For every 14 sampling day two consecutive twelve-hour samples were taken to obtain information for 15 daytime and nighttime periods. The daytime sampling was performed from 06:00 a.m. to 16 06:00 p.m. (local time), while nighttime samples were collected from 06:00 p.m. to 06:00 a.m. 17 the next day. For the spring and fall 2011 campaigns, sampling periods were performed on 18 alternate days. For example, for the spring of 2011, the first sampling day was on May 28, the 19 second on May 30, and so on. For the campaigns of 2012, both were conducted for 14 20 consecutive sampling days. 21 22 Carbonaceous aerosol samples were collected using high-volume filter-based instruments with PM_{2.5} inlet (TE-6001-2.5, Tisch Environmental Inc), operating at a flow of 1.13 m³/min. The 23 24 flow rates for the high-volume samplers were calibrated at the start and end of each monitoring campaign. For each high-volume sampler, the calibration was carried out using a 25 26 calibration orifice (NIST Traceable Calibration Certificate). The samplers were mounted on the rooftop of the monitoring station three meters above the ground. One high-volume 27 sampler was used for each campaign, except for the campaign of fall 2012, in which two high-28 volume samplers were deployed and operated simultaneously to collect pairs of samples for 29 each diurnal and nighttime sampling period. Fine particles were collected in 8"×10" quartz 30 microfiber filters (Whatman QMA). Filters were previously pre-fired for 8 hrs at 600°C in a 31

- 1 furnace to remove residual carbon and stored in baked aluminum foil within sealed plastic
- 2 bags (Ziploc®) until they were used. After sampling, loaded 8"×10" filters were stored in tall
- 8 oz. glass jars (VWR, IR221-0250). Loaded filters were placed in a cooler with blue ice for
- 4 immediate transport from the sampling site to the laboratory. All loaded filters were stored in
- 5 a freezer at -20° C to prevent the evaporation of volatile compounds until they were analyzed.
- 6 A total of 111 samples and 10 field blanks were collected throughout the study.

2.3 Ambient measurements

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

- 22 Solvent-extractable molecular markers were quantified using gas chromatography mass
- spectrometry (GC/MS) using dichloromethane (DCM), and methanol (MeOH) (high purity
- 99.9%, Fisher Scientific). Filters were spiked with 50 μL of the following deuterated internal
- standards (Sigma Aldrich): n-hexadecane-d34, n-hexatriacontane-d74, n-eicosane-d42, n-
- triacontane-d62, vanillin-d3, benzophenone-d5, chrysene-d12, dibenz(a,h)anthracene-d14,
- 27 naphthalene-d8, pyrene-d10, benzo(e)pyrene-d12, coronene-d12, decanoic acid-d19, palmitic
- acid-d31, stearic acid-d35, levoglucosan-13c6, and cholesterol-d6. Each individual filter or
- sample composite was extracted three times with DCM. During each extraction, enough DCM
- was added and then they were subjected to ultrasonic agitation for 20 min using a sonicator
- 31 (Bransonic®, model 5510R-DTH). The extracts were combined and then concentrated by

evaporation under a gentle flow ultra-high purity nitrogen until the extract reached a volume 1 of ~5 mL. The extracts were filtered through a pre-fired quartz filter, subsequently reduced in 2 volume to 250 µL, and then separated into three fractions. One fraction was a direct portion of 3 the 250 µL extract for direct analysis by GC/MS, and the other two fractions were used for 4 chemical derivatizations. One fraction was methylated using diazomethane (CH₂N₂) to 5 6 convert carboxylic acids to their respective methyl esters. The another fraction was silylated using a combination of BSTFA (N, O-bis(trimethylsilyl)trifluoroacetamide) and TMCS 7 (trimethylchlorosilane) to convert sterols and sugars to their respective trimethylsilyl esters. 8 For methylation, 50 µL of a Diazomethane (CH₂N₂) solution was combined in a vial with 50 9 μL of extract. For the silvlation, 50 μL of BSTFA+TMCS (molar ratio 99:1) was combined 10 with 50 µL sample extract. Then, the mixture was allowed to react for 3 h at 65°C. The 11 quantification and identification of organic compounds was based on comparisons with 12 authentic standards, retention times, literature mass spectra, and fragmentation patterns using 13 14 HP chemstation. A detailed description of the extraction and analysis procedures as well as the chromatograph and column used can be found in Brown et al., 2002. 15

2.4 Molecular diagnostic ratios

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

2.4.1 Carbon Preference Index (CPI)

The CPI is an indicator of the measure of odd or even carbon homologues series of organic compounds within a sample. Based on several studies (Abas and Simoneit, 1996; Tsapakis et

al., 2002; Harrad et al., 2003), the CPI for n-alkanes (odd to even ratio) was calculated as

22 follows:

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

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

$$\mathbf{CPI} = \frac{\sum (C_{10} \text{ to } C_{32})}{\sum (C_{11} \text{ to } C_{31})}$$
(2)

The CPI is an important indicator that is used to determine whether emissions come from natural or anthropogenic sources. For both n-alkanes and n-alkanoic acids, values of CPI > 1

- 1 indicate that hydrocarbons and carboxylic acids are emitted from natural sources. In contrast,
- values of $CPI \le 1$ (or close to one) indicate that they are emitted from anthropogenic sources
- 3 (Gogou et al., 1996; Alves et al., 2001; Gelencsér, 2004).
- 4 Another useful indicator that is used to specify the origin of the emissions is the carbon
- 5 number with maximum concentration (C_{max}). Hydrocarbons and carboxylic acids of high
- 6 molecular weight (> C₂₅) are emitted from biogenic sources, while those with lower molecular
- 7 weight ($\leq C_{25}$) are mainly emitted from fossil fuel combustion processes (Alves et al., 2001;
- 8 Young and Wang, 2002; Gelencsér, 2004).

2.4.2 Diagnostic ratios of PAHs

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

14 2.5 Chemical Mass Balance model

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

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

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

$$\chi^{2} = \sum_{j=1}^{m} \left| \frac{x_{j} - \sum_{k=1}^{p} g_{jk} f_{k}}{\sigma_{x_{j}}^{2} + \sum_{k=1}^{p} \sigma_{g_{jk}} f_{k}} \right|$$
(2)

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

2.6 Source profiles

- 9 The source profiles used in this work were taken from the most comprehensive studies
- available. The selection of the source profiles was based on previous source apportionment
- 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,
- Martinez et al. (2012) based on trace elements identified primary sources such as industrial
- sources, motor vehicle exhaust and biomass burning in the MMA. Finally, from these studies,
- seven primary source profiles were selected.
- 17 The source profile 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
- be rather well maintained and of a recent model year, while diesel vehicle fleet is composed
- 20 by heavy duty vehicle trucks and buses. Therefore, the profiles reported for catalyst-equipped
- 21 gasoline-powered motor vehicles emissions and heavy duty trucks from dynamometer tests
- were used.
- 23 From evidence of industrial sources in Mexican urban atmospheres, a source profile for
- 24 natural gas combustion and fuel oil combustion were taken from Rogge et al. (1993c) and
- 25 Rogge et al. (1997), respectively.
- 26 Finally, source profiles for meat cooking operations, vegetative detritus, and biomass burning
- 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

- 1 charbroiling operations. For biomass burning, given the existence of softwood and hardwood
- 2 sources in the region (Zurita, 2009), the softwood pine and hardwood oak profiles were used
- 3 in this study. These last profiles were used separately because they are highly collinear.
- 4 Regarding vegetative detritus, a source profile was included based on the contributions
- 5 determined by Stone et al. (2008) in Mexico City along with the fact that the MMA is
- 6 surrounded by rural areas with vast green covers. Therefore, it is possible to have an impact
- 7 from transport of biogenic emissions.
- 8 For individual organic compound quantification, an uncertainty of $\pm 20\%$ of the measured
- 9 concentration was used for all ambient samples and source profiles (Schauer et al., 2000;
- 10 SRM 1649a, 2007; SRM 1649b, 2009; Fraser et al., 2003; Schantz et al., 2005). A detailed
- description of source profiles and settings used to perform the CMB in this study can be found
- in Fraser et al. (2003). For the current application, the fitting species for CMB included 20
- organic compounds along with EC and overall OC. The molecular markers included seven n-
- 14 alkanes (C27-C33), four petroleum biomarkers (17a(H),21b(H)-29-norhopane,
- 15 17a(H),21b(H)-hopane, 22R+S 17a(H),21b(H)-30-homohopane, and 22R+S 17a(H),21b(H)-
- 16 30-bishomohopane), five polycyclic aromatic hydrocarbons (benzo[a]anthracene,
- benzofluoranthenes, benzo[a]pyrene, indeno[123-cd]pyrene and benzo[ghi]perylene), two
- saturated fatty acids (C16:0 and C18:0), cholesterol and levoglucosan.

19 3 Results and discussion

20 3.1 Resolved organic aerosols

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

- 1 All the samples collected during this study were analyzed for eight organic compound classes
- 2 except those samples collected in the spring of 2011 campaign, for which carboxylic acids,
- 3 wood smoke markers, and nitro-PAH compounds were not included for the chemical analysis.
- 4 Therefore, the overall contribution of the resolved organic compounds to OC in the spring of
- 5 2011 is not directly comparable to the last three campaigns. For the eight resolved compound
- 6 classes in the last three campaigns (Fig. 2), the *n*-alkanoic acids were the most abundant,
- 7 followed by *n*-alkanes, wood smoke markers, and levoglucosan/alkenoic acids. The PAHs and
- 8 triterpanes hydrocarbons were less abundant. The same tendency was observed in the spring
- 9 of 2011, except that the *n*-alkanes were the most abundant. The concentrations of nitro-PAH
- were neglected because their levels were below the detection limit of the method.
- 11 The daytime and nighttime concentrations of the resolved organics for the spring 2011
- accounted for 0.49±0.52% and 0.46±0.41% of the ambient OC, respectively. These
- contributions were much lower than the following three campaigns due to some compounds
- 14 classes were not included. For spring 2012 and all fall campaigns, the total daytime
- 15 concentrations of the resolved organics accounted for 7.58±4.89% and 2.64±1.82% to
- 4.67 \pm 1.76%, respectively, while the total nighttime concentrations accounted for 11.0 \pm 6.3%
- and 3.2±2.4% to 8.0±4.0%, respectively. These observations are consistent with the findings
- that typically, around 84% of the fine OC is either non-extractable or will not elute from the
- 19 GC column (Schauer and Cass, 2000). In the following sections will be analyzed the organic
- 20 composition of the fine organic aerosols using several diagnostic ratios to identify the primary
- emission sources. Then the relative contribution of each primary source to the $PM_{2.5}$ will be
- calculated by using the CMB receptor model.

3.2 *n*-Alkanes and Hopanes

- 24 The *n*-alkanes have two main sources: petroleum product utilization and natural vegetation
- waxes. The latter source consists of the longer chain plant lipids (>C₂₀) as n-alkanes (Simoneit
- and Mazurek, 1982). In this study, the n-alkanes in the range of C_{17} – C_{33} were detected. For
- the samples collected for spring 2011 and fall 2011, the average daytime and nighttime
- 28 concentrations of n-alkanes were 1.6 and 2.3 times higher for the fall than the spring,
- respectively. This is consistent with the high contribution of the OC to PM_{2.5} and the lowest
- 30 OC/EC ratios exhibited during the fall (Mancilla et al., 2015). In addition, the average
- 31 temperature in the fall was 18.7–22.1°C versus 27.8–29.4°C in the spring. Low temperatures

typically promote the utilization of petroleum products. In Mexico, the government sets the 1 tariff-rates for the electric energy consumption with regard to the temperature; during the cold 2 seasons the government removes the subsidy to the domestic electric energy due to the 3 demand on fossil fuels in those seasons, and the sampling years of this study were not the 4 5 exception (SENER, 2013). The average CPI values of *n*-alkanes in the spring were 1.5±0.3 (range: 1.1–1.9) in the daytime and 1.7±0.5 (range: 1.1–2.6) in the nighttime, while the CPI 6 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 7 the nighttime. The CPI values in the spring suggest the mixed contribution of anthropogenic 8 and biogenic emissions sources, whereas those values in the fall indicated a dominance of 9 anthropogenic emissions. In addition, the contribution of anthropogenic emission sources is 10 confirmed by the presence of petroleum biomarkers (hopanes: range of 0.06 to 2.36 ng m⁻³) 11 and n-alkanes $\leq C_{25}$ (Fig. 3). For the fall, the average daytime and nighttime concentrations of 12 hopanes were 2.3 and 4.2 times higher than in the spring, respectively. Similarly, the presence 13 of biogenic emissions due to C_{max} was found at C_{27} , C_{29} , or C_{31} (Fig. 3). These carbons' 14 number dominance and trace levels of hopanes are characteristics of plant wax emissions and 15 urban traffic emissions, respectively (Standley and Simoneit, 1987; Cass, 1998; Simoneit et 16 al., 2004). 17 For the spring 2012 and fall 2012, the behavior of *n*-alkanes was the opposite of the 2011. The 18 average daytime and nighttime concentrations of *n*-alkanes were 1.5 and 2.0 times higher in 19 the spring than in the fall, respectively. The EC levels remained similar to those of the 2011, 20 but the OC levels were higher during the fall 2012 increasing the OC/EC ratios. Some of these 21 22 ratios exhibited high peaks suggesting a contribution from primary emission sources with elevated OC/EC ratios like biomass burning (Mancilla et al., 2015). The average temperature 23 in the fall was 23.5–26.4°C versus 28.0–30.7°C in the spring. The average fall temperatures 24 were not consistent with the average of 2011. In the fall of 2012, the warmer temperatures 25 might have promoted less utilization of some fuels compared to the 2011 in which lower 26 temperatures could have promoted their utilization, increasing the *n*-alkanes' concentrations in 27 fall 2011. The average CPI values of *n*-alkanes in the spring 2012 were 0.9 ± 0.1 (range: 0.8-28 1.1) in the daytime and 1.2±0.1 (range: 1.2–1.3) in the nighttime, while the CPI values in the 29 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 30 nighttime. From these CPI values, it appears that biogenic emissions are relevant in all 31 sampling periods. For spring 2012 daytime, the emissions appear to be heavily dominated by 32

- anthropogenic emissions due to the low CPI value exhibited. The presence of petroleum
- biomarkers supports the relative contribution of anthropogenic emissions. However, in 2012
- 3 the hopanes levels were ~35% lower at daytime and ~43% lower at nighttime than those in
- 4 the previous year. The low hopane levels (range of 0.10 to 1.49 ng m⁻³) highlight the possible
- 5 presence of biogenic emissions (Fig. 2).

3.3 PAHs

- 7 Twelve PAH compounds, fluoranthene (FLT), acephenanthrylene (ACE), pyrene (PYR),
- 8 benzo(a)anthracene (BAA), chrysene (CRY), benzo(k)fluoranthene + benzo(b)fluoranthene
- 9 (BFA), Benzo(a)pyrene + Benzo(e)pyrene (BaP+BeP), perylene (PER), indeno(123cd)pyrene
- 10 (IP), benzo(ghi)perylene (BgP), dibenz(ah)anthracene (DaA), and coronene (Cor), were
- identified in the MMA fine OC samples. For both sampling years, the average daytime and
- nighttime concentrations of PAHs were 1.4–5.9 and 1.4–2.4 times higher in the fall than in the
- spring, respectively. This is consistent with the high contribution of the OC to the PM_{2.5}
- during the falls. Independently of the season, the daytime concentrations were 1.3–1.6 times
- 15 higher than nighttime concentrations. These seasonal differences are consistent with the
- results of Guo et al. (2003) and Li et al. (2006), where PAH levels were 2-4 and 14.4 times
- 17 higher in the cold seasons than in the warm seasons, respectively.
- As illustrated by Fig. 4, the high molecular weight (HMW) PAHs were the most abundant for
- the MMA. The presence of HMW PAHs such as BaP+BeP, IP, and BgP is an indication of
- 20 gasoline-powered vehicle emissions (Katsoyiannis et al, 2011; Tobiszewski and Namieśnik,
- 21 2012). In addition, a possible contribution of diesel-powered vehicles is indicated by the low
- concentrations of the low molecular weight (LMW) PAHs such as FLT, PYR, and CRY. To
- 23 identify the emission sources of PAH, diagnostic ratios were calculated (Table 4). These ratios
- should be used with caution due to PAHs are emitted from a variety of emission sources,
- 25 particularly combustion sources, and their profiles can be modified due to their reactivity
- 26 (Tsapakis et al., 2002). From these ratios, it would be determined the source origin (e.g.
- 27 pyrogenic and petrogenic sources). Then, these qualitative conclusions will be considered for
- 28 the source apportionment to estimate the relative contribution of primary emission sources.
- 29 The average ratios of IP/(IP+BgP) indicate that ambient PAHs in the MMA originated from
- 30 gasoline and diesel combustion, whereas the ratios of BAA/(BAA+CRY) show the presence
- of petrogenic sources as well as vehicle emissions. To complement these results, the ratios of

- 1 (BaP+BeP)/BgP identified a marked contribution of non-traffic sources for the spring of 2011,
- traffic source for the fall 2011 and the spring 2012, and mixed-sources for the fall 2012.
- 3 Presence of gas-phase PAHs was not evaluated and thus no information on gas/particle
- 4 partitioning of these semivolatile species is available. Thus, only diagnostic ratios for HMW
- 5 PAHs were calculated for this study because those PAHs exhibit low volatility (Kavouras et
- 6 al, 1999).
- 7 In this study, the average total concentrations of the quantified PAHs (TPAHs) were
- 8 $2.42\pm2.45 \text{ ng m}^{-3}$ (range: $0.65-8.31 \text{ ng m}^{-3}$) and $4.11\pm2.62 \text{ ng m}^{-3}$ (range: $1.42-11.97 \text{ ng m}^{-3}$)
- 9 during 2011 and 2012, respectively, whilst those quantified by González-Santiago (2009) at
- 10 two different sites in the MMA were 1.30±1.64 ng m⁻³ (range: 0.05-6.93 ng m⁻³) and
- 1.70 \pm 1.88 ng m⁻³ (range: 0.07–9.14 ng m⁻³). The lowest concentrations were obtained during
- the spring because its average temperature was statistically higher than during the fall seasons
- 13 (p<0.05). The volatility of PAH increases with temperature; as a result low concentrations are
- obtained in comparison with fall and winter seasons. For this study the concentrations of PAH
- were lower during the spring than concentrations during fall; this pattern was exhibited during
- the two sampling years. González-Santiago (2009) identified only six PAHs, while in this
- study were identified twelve. In the current study, the total concentrations calculated for the
- six common PAHs were from 3 to 8 times higher than those estimated by González-Santiago
- 19 (2009). Similar concentrations (between 0.04 ng/m³ and 1.78 ng/m³) were also reported for
- six individual PAHs in urban samples collected in Mexico City (Stone et al., 2008). Of the
- same PAHs identified among these studies, their levels were in the same concentration range.
- However, the TPAH levels in the MMA compared to those calculated by Marr et al. (2006)
- 23 (20–100 ng m⁻³) in Mexico City were found at appreciably lower concentrations. In addition,
- Marr et al. (2006) suggest that vehicles are the major source of PAHs. They demonstrated that
- 25 PAHs and carbon monoxide (CO) concentrations are well correlated in Mexico City and,
- 26 given that 99% of CO emissions are emitted by motor vehicles, this source is a major
- 27 contribution of PAH emissions. For the current study, daytime correlations (r) of +0.76 (p >
- 28 0.05) were found between TPAH and CO, reinforcing the conclusion that motor vehicles are
- one major source of PAH emissions for the MMA. The concentrations of CO during this
- 30 study were obtained from the SIMA network.
- 31 The total PAH (TPAH) concentrations were compared with the EC and OC levels. TPAH
- 32 concentrations measured in the MMA exhibited fair daytime correlations with EC (r=+0.79;

- 1 p>0.05), but low correlations with OC (r=+0.57; p>0.05). According to Marr et al. (2004), the
- 2 strong correlation between TPAH and EC indicated the relative contribution of diesel-
- 3 powered vehicle exhaust, while weak correlations may be due to the low concentrations of EC
- 4 determined during this study (Mancilla et al., 2015). Furthermore, the weak correlation
- 5 between TPAH and EC suggests the presence of emission sources with an elevated OC/EC.

3.4 *n*-Alkanoic acids

- 7 The carboxylic acids or *n*-alkanoic acids are mainly derived from biogenic emissions (Rogge
- 8 et al., 1993b). However, these acids have also been identified in several primary sources such
- 9 as cooking operations (Rogge et al., 1991; Schauer et al., 2001b) and fossil fuel combustion
- 10 (Schauer et al., 2002). The n-alkanoic acids from C_{10} to C_{32} were quantified only for the three
- last monitoring campaigns. The *n*-alkanoic acids were the most abundant, accounting for
- 12 69±16% at daytime and 78±11% of the total resolved organics at nighttime for both spring
- and fall. The daytime and nighttime concentration levels were two times higher in the spring
- than in the fall. As can be seen in Fig. 5, the *n*-alkanoic acids measured in the MMA were
- dominated by hexadecanoic acid (palmitic acid) and octadecanoic acid (stearic acid). This
- dominance is consistent with measurements in other locations (Fraser et al., 2002; Simoneit
- 17 2004; Li et al., 2006).
- The average CPI values of *n*-alkanoic acids in the fall of 2011 were 4.3 ± 1.0 (range: 3.3-5.3)
- during the day and 5.0±0.4 (range: 4.6–5.4) at night. For the 2012 year the CPI values in the
- 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,
- 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
- 22 (range: 4.0–6.8) at night. These elevated CPI values indicated the significant influence of
- biogenic sources such as microbial and plant wax sources. The n-alkanoic acids <C₂₀ are
- 24 derived in part from microbial sources while those >C₂₀ are from vascular plant waxes (Guo
- et al., 2003; Yue and Fraser, 2004; Simoneit et al., 2004). Fig. 5 clearly shows influence of
- long chain (>C₂₀) plant wax particles for the MMA. The CPI values in this study were
- 27 consistent with those obtained by Wang and Kawamura (2005) (CPI: 5.3-10) and Yue and
- Fraser (2004) (CPI: 3.2–11.2). Regardless of the elevated CPI values obtained for the MMA,
- 29 the values were not as high as those reported by the other mentioned studies due to a scarcity
- of green vegetation covers in the MMA.

The *n*-alkenoic acids only included the cis-9-Octadecenoic acid (oleic acid) and trans-9octadecenoic acid (elaidic acid). The concentrations of cis-9-Octadecenoic acid ranged from 0.96 ng m⁻³ to 15.38 ng m⁻³, while the concentrations of trans-9-octadecenoic acid ranged from 2.11 ng m⁻³ to 13.35 ng m⁻³. The ratio of octadecanoic acid to cis-9-Octadecenoic acid has been used as an indicator of the atmospheric chemical processing (aging) of aerosols, since the unsaturated acids are susceptible to atmospheric oxidation from gaseous precursors (Brown et al., 2002; Yue and Fraser, 2004). In this study, the average ratios were 5.0 (range: 1.5–9.4) during the day and 3.8 (range: 2.5–4.9) at night for the spring, while 20.3 (range: 4.7–38.6) during the day and 21.0 (range: 10.5–29.1) at night for the fall. The transport of aerosols from local and rural sources can lead to the loss of cis-9-Octadecenoic acid producing high octadecanoic acid to cis-9-Octadecenoic acid ratios. By contrast, the stagnation of aerosols may reflect the impact of high oxidant concentrations in an urban atmosphere producing low ratios (Brown et al., 2002; Yue and Fraser, 2004). Therefore, these ratios suggest that the ambient organic aerosols for the MMA were aged and might be produced from transport and atmospheric oxidation. Air circulation patterns (Hysplit backward trajectories) during these monitoring campaigns suggested a long-range transport from the northeast and southeast (Mancilla et al., 2015). As expected, the lowest and highest octadecanoic acid to cis-9-Octadecenoic acid ratios obtained for the MMA were consistent with the highest OC/EC ratios estimated for the MMA for the same campaign; high OC/EC ratios identified transport and stagnation scenarios for the spring and fall, respectively (Mancilla et al., 2015). In addition, these results are in line with those reported by Brown et al. (2002) and Yue and Fraser (2004), who obtained ratios of 5-11 and 1.0–21.5, respectively. In addition, a minor biogenic contribution can be identified by the presence of terpenoic acids such as cis-pinonic acid and pinic acid. These acids are known to be a secondary, particlephase product of pinene, which is emitted from plants, particularly conifers (Plewka et al., 2006; Sheesley et al., 2004). The pinonic acid and pinic acid exhibited higher concentrations in the spring than in the fall (Table S1), indicating biogenic emissions from softwood sources.

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1 3.5 Meat cooking and biomass burning tracers

- 2 The major tracers for meat cooking particles are the steroids, while for biomass burning are
- 3 the anhydrosaccharides and methoxyphenols. All of these organic tracers were intermittent in
- 4 only 80% of the total OA samples/composites collected during this study.
- 5 There was not a clear trend between spring and fall samples during the two sampling years for
- 6 steroids (Table S1). However, the evidence of cooking operations' impact on the MMA was
- 7 confirmed by the presence of cholesterol and stigmasterol along with hexadecanoic acid,
- 8 octadecanoic acid, and oleic acid. Although cholesterol is considered a good marker for meat
- 9 cooking, studies have reported unexpectedly high levels of cholesterol from non-cooking
- related sources such as soil and prescribed burns (Sheesley et al., 2004; Lee et al., 2005;
- 11 Robinson et al., 2006a).
- Anhydrosaccharides are the tracers from burning cellulose and hemicelluloses, whereas the 12 methoxyphenols the tracer from burning of lignin (Giri et al., 2013). Levoglucosan, a 13 combustion and pyrolysis product of cellulose, is the main biomarker used to track biomass 14 burning emissions (Schauer et al., 2001a). Levoglucosan was not detected in all collected 15 samples. The levoglucosan found in the OC samples indicates that biomass burning is 16 impacting the MMA to some extent (Table S1). The levoglucosan concentrations varied by 17 sampling dates, ranging from not detectable levels to 54 ng m⁻³ for spring. In contrast, 18 levoglucosan was detected in all fall samples, ranging from 0.14 to 28 ng m⁻³. The 19 intermittent peaks of levoglucosan concentrations during the springtime can be explained by 20 the fact that Northeastern Mexico's atmosphere is highly influenced by forest wildfires and 21 prescribed agricultural burnings during the spring (Mendoza et al., 2005); this is in line with 22 23 the idea that high OC/EC ratios obtained, in a parallel study, were influenced in part by regional transport emissions (Mancilla et al., 2015). In the case of fall seasons, the 24 25 levoglucosan levels can be associated with local biomass burning due to mild temperatures exhibited during these seasons; a local contribution can be associated with high OC/EC ratios 26 27 and stagnation conditions determined for this period (Mancilla et al., 2015). The high OC/EC rations during spring may have a contribution from primary sources with elevated OC/EC 28 29 ratios. The low and variable levoglucosan concentrations in this study indicate that wood/vegetation smoke episodes were occasional at the urban site. Average levoglucosan 30 concentrations of 112.9 ng m⁻³ and 151.3 ng m⁻³ were reported at urban and peripheral sites 31 32 for Mexico City, respectively (Stone et al., 2008). Based on an average concentration of

levoglucosan, Mexico City exhibited from 5 to 7 times higher levels than the MMA. These 1 results are consistent with the concentrations of OC and EC obtained in the Mexico City; the 2 EC concentrations were up to two times higher than those calculated in the MMA, whereas 3 the OC concentrations were from 2 to 6 times higher. A study conducted in Houston, TX, 4 during August-September reported elevated concentrations of levoglucosan: up to 234 ng m⁻³ 5 6 (Yue and Fraser, 2004). Similarly, a study conducted for 14 cities in China during summer and winter, also reported elevated levoglucosan concentrations of 259 ng m⁻³ (Wang et al., 7 2006). However, in those studies the vegetation around the sampling sites included a vast 8 9 number of parks and woody shrubs, suggesting a major biomass burning contribution contrary to the MMA. Apart from those studies, Zheng et al. (2002) reported elevated levoglucosan 10 concentrations of 166–307 ng m⁻³ for urban areas of similar surroundings to the MMA. In this 11 case, it is also possible that the levoglucosan emissions reported come from industries that 12 have implemented biomass burning processes for energy generation. As can be seen from the 13 previous comparison, the contribution of biomass burning is minor for the MMA in 14 comparison with other urban locations. In addition, biomass burning contributions are 15 inconsistent with those reported in similar locations to the MMA. 16 17 The resin acids such as dehydroabietic acid, pimaric acid, and isopimaric acid (Table S1) are secondary tracers from biomass burning (Schauer et al., 2001a). Dehydroabietic acid was the 18 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 19 and fall, respectively. Then, pimaric acid ranged from not detectable levels to 0.09 ng m⁻³ and 20 from 0.15 to 0.35 ng m⁻³ for spring and fall, respectively. Finally, isopimaric acid ranged 21 from not detectable levels to 0.03 ng m⁻³ and from 0.06 to 0.12 ng m⁻³ for spring and fall. 22 respectively. The results for resin acids are in line with those obtained for the levoglucosan. 23 24 These results support the low impact from biomass burning emissions in the MMA, especially from softwood burning (e.g., conifer wood) during the spring and fall campaigns. In addition, 25 the higher concentrations of resin acids in fall than in spring are associated with 26 photochemical activity due to stagnation events in fall. 27

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3.6 Source Apportionment

CMB was applied using the quantification of individual organic compounds found in the collected $PM_{2.5}$ samples. The relative contributions for gasoline-powered vehicles, diesel-

powered vehicles, natural gas combustion, fuel oil combustion, meat cooking operations, 1 vegetative detritus, and biomass burning were estimated. From the source categories selected, 2 the ones corresponding to natural gas and fuel oil combustion were not determined as 3 significant for some ambient samples. These two sources were determined to have 4 contributions that were not statistically different from zero or were slightly negative and thus 5 were excluded from the model. Model performance was determined by r^2 values ranging 6 between 0.58 and 0.85 and chi-squared (χ^2) values between 2.97 and 8.85. Similar values for 7 r^2 and χ^2 have been obtained in Fraser et al. (2003) and Schneidemesser et al. (2009). The 8 latter study used composites to perform the CMB. Another performance metric calculated by 9 EPA-CMB8.2 is the percent mass explained. Theoretically, values ranging from 80% to 120% 10 are acceptable. This ideally can occur when ambient data is not impacted heavily by SOA 11 because CMB is only able to account accurately for primary sources. In spite of this 12 limitation, CMB results with low percent mass explained values have been reported by some 13 studies. In these cases, the high levels of unexplained mass have been associated with 14 secondary production (Fraser et al., 2003; Zheng et al., 2005). For the 43 ambient samples fed 15 to CMB in this study, 18 samples exhibited low percent mass explained values (ranging from 16 20% to 77%), whilst 14 samples had values around 100%. These results are in line with the 17 relative high and low OC/EC ratios obtained for spring and fall, respectively Mancilla et al. 18 19 (2015). Finally, 11 samples were discarded due to poor performance parameters calculated. These samples were not exclusively from a particular monitoring campaign; there were 20 21 samples from both springs and falls. A detailed description of the CMB performance and relative contributions for each sample can be found in Table S2. 22 The average contributions of primary sources are shown in Table 5. The vehicle exhaust and 23 meat-cooking operations emissions for all monitoring campaigns were the highest. In analysis 24 of the seasonal variation, the gasoline- and diesel-powered vehicles in falls were up to five 25 times higher than in springs, when cold weather increases the demand of petroleum products 26 due to low temperatures. The opposite occurred for meat-cooking operations, their spring 27 emissions were three times higher than in fall seasons. The natural gas combustion, vegetative 28 detritus and biomass burning emissions were very low and more constant throughout the 29 springs and falls. In analysis of the daytime and nighttime variations, the vehicle exhaust were 30 31 much higher during daytime when traffic is heavier. For the meat-cooking operations, the emissions were some higher in nighttime during spring and more constant between daytime 32 and nighttime during fall. For the rest of the sources, the daytime and nighttime emissions 33

were relatively constant. There are not similar studies conducted in the MMA, this is the first 1 source apportionment study based on molecular organic markers for this region. However, 2 these results were similar to those obtained for the MMA using a factor analysis based on 3 trace elements (Martinez et al., 2012) and those for the Mexico City based on molecular 4 organic markers (Stone et al., 2008). 5 The average contribution of each emission category to the identified PM_{2.5} mass is shown in 6 Fig. 6. The unidentified mass was on average 35±24% of the measured PM_{2.5} concentrations. 7 This value is 1.5 times greater than the ~23% of secondary organic aerosol contribution to the 8 9 total PM_{2.5} mass concentration (SOC/PM_{2.5}) estimated in Mancilla et al. (2015) for the MMA. The average secondary contribution used for this comparison was based on the minimum 10 OC/EC ratios observed and reported in Mancilla et al. (2015). These ratios may take into 11 account primary sources with elevated values of OC/EC ratios such as biomass burning and 12 kitchen operations as well as fossil fuel combustion sources. The unidentified mass by CMB 13 may include secondary organic and inorganic aerosol and trace elements. Thus, the levels of 14 unidentified mass resolved by CMB are reasonable given that the secondary aerosol estimated 15 in Mancilla et al. (2015) was in fact only SOA. Therefore, the 12% of difference between 35% 16 and 23% might be attributed to the secondary inorganic aerosol and other chemical species. 17 As indicated in Fig. 6, the emissions from motor vehicle exhausts (gasoline and diesel) are the 18 most important, accounting for the 64% of the identified PM_{2.5} emissions, followed by meat-19 cooking operations (31%) and industries (2.8%). The vegetative detritus and biomass burning 20 were the less emitted with only 2.2% of the identified PM_{2.5} emissions. The relative high 21 22 contribution of the meat-cooking operations was expected given the high traditional restaurant activity in the MMA which contribute with the 16% of the local growth domestic product. 23 24 The MMA as well as other urban areas can be affected by types of biomass burning, especially, when they are not surrounded by forests. For examples, several studies have 25 26 demonstrated that Mexico City has large contribution from biomass burning (Moffet et al., 2008; Stone et al., 2008; Yokelson et al., 2007) because it is affected by forests fires 27 (Yokelson et al., 2007). Conversely, the MMA has not forests around, therefore, the 28 contribution from biomass burning in the MMA might be higher because the source profile 29 30 used for the CMB was only for wood combustion instead of using a source profile for garbage, industrial, and urban residues open fires (Simoneit et al., 2005). In addition, here is 31 important to point out the potential of industrial sources due to prior studies conducted in the 32

MMA and the rest of the country. The MMA is the third largest urban center of the country

- with approximately 9,700 industries (INEGI, 2005). In the MMA the main emissions from
- 2 industrial sources come from the combustion of natural gas; low emissions come from the use
- 3 of fuel oil. In this study the natural gas profile did not fit well and it was discarded from the
- 4 CMB, but the fuel oil did it. The combustion of natural gas emits low amount of particles,
- 5 therefore, its contribution to the airborne particles is not significant.

7

4 Conclusions

- 8 Spring and fall sampling campaigns were performed in 2011 and 2012 at one representative
- 9 site to conduct a chemical characterization of the fine OC in PM_{2.5} in the MMA. The
- identified organic compound classes represented a low fraction of the ambient OC: 0.5% for
- spring 2011 and 2.6 to 11% for the last three campaigns. The average CPI values derived from
- the *n*-alkanes (0.9–1.7) and *n*-alkanoic acids (2.9–6.8) demonstrated that anthropogenic (e.g.,
- 13 fossil fuel combustion) were dominant while biogenic (e.g. plant waxes, microbial origin)
- emission sources contribute at least some times to the fine OA in the MMA.
- 15 The PAH diagnostic ratios indicate that gasoline- and diesel-powered vehicles are the main
- emission sources of this class of organic compounds in PM_{2.5}. However, other pyrogenic
- sources such as coal, grass, and wood combustion were also identified as contributors to the
- 18 fine OA. The quantified levels of cholesterol and levoglucosan confirm the high and low
- 19 contribution of cooking operations and biomass burning, respectively. Low levoglucosan
- 20 concentrations suggest low episodic or transport effects of emissions of biomass burning on
- 21 $PM_{2.5}$ in the MMA.
- 22 In a parallel study, significant SOA formation was found in the MMA. The chemical
- speciation of the OC confirmed the aging of primary emissions and the SOA from biogenic
- volatile organic compounds. On one hand, the identified octadecanoic acid and cis-9-
- Octadecenoic acid along with other secondary organic markers point out the SOA formation
- in the MMA atmosphere. The average ratios of octadecanoic acid to cis-9-Octadecenoic acid
- 27 (3.8–21) indicate aging of the fine OA due to photochemical activity and transport. On the
- other hand, the presence of the cis-pinonic and pinic acids confirmed the SOA derived from
- 29 biogenic sources. This is in line with the transport and stagnation events that predominated
- 30 during spring and fall, respectively.

- 1 The emissions from vehicle exhausts are the most important, accounting for the 64% of the
- 2 identified PM_{2.5} emissions. By contrast, the vegetative detritus and biomass burning were the
- 3 less contributors with barely 2.2% of the identified PM_{2.5} emissions.
- 4 Finally, the outcomes of a comparison with other studies were that the MMA exhibits similar
- 5 concentrations patterns of the organic molecular markers identified in this study.

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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	7ª	14	2
Fall 2011	October 22 to November 3	7ª	14	2
Spring 2012	June 6 to June 19	14	27	2
Fall 2012	October 13 to October 26	14	56	4

^a Non-consecutive days.

3

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

Campaign	Description	Description Dates included		PM _{2.5}		OC	
Spring 2011	ID1	May 30, Jun 01, Jun 09, Jun 11	$(\mu g m^{-3})$ 20.3	SD 8.7	$(\mu g m^{-3})$ 8.2	SD 2.7	
	ID2 IN1	May 28, Jun 03, Jun 05 May 30, Jun 01, Jun 09, Jun 11	22.5 25.1	15.1 10.2	10.7 6.3	5.7 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	1.3	
	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 in curly brackets are the mass ranges for the mass of OC collected per filter included.
- 3 Values for PM_{2.5} are the averages obtained from the SIMA network. OC concentration values
- 4 are the average values reported by Mancilla et al. (2015). SD represents standard deviation, I
- 5 indicates that dates included were analyzed individually, C indicates that dates included were

- 1 pooled to form a composite, D represents daytime sampling, N represents nighttime sampling,
- 2 1 refers to weekday sampling, 2 refers to weekend sampling.

4 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., 2005
	> 0.50	Coal, grass, and wood	Yunker et al., 2005
		combustion	
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

The PAH abbreviations are IP: Indeno(123cd)pyrene, BgP: Benzo(ghi)perylene, BAA:

⁶ Benz(a)anthracene, CRY: Chrysene, FLT: Fluranthene, PYR: Pyrene, BaP: Benzo(e)pyrene,

⁷ BaP: Benzo(a)pyrene.

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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7

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

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

Comin								
Spring 2011		Fall	Fall 2011		Spring 2012		Fall 2012	
Daytime	Nighttime	Daytime	Nighttime	Daytime	Nighttime	Daytime	Nighttii	
		-				-		
							!	
2.37 ± 0.56	2.46 ± 0.46	3.70 ± 0.78	2.24 ± 0.51	1.43 ± 0.41	*	7.51 ± 1.27	$3.19 \pm 0.$	
							ļ	
7.34 ± 0.86	3.81 ± 0.53	13.67 ± 1.59	13.10 ± 1.55	2.93 ± 0.41	*	13.85 ± 1.58	$5.15 \pm 0.$	
0.22 ± 0.04	0.22 ± 0.04	0.13 ± 0.03	0.27 ± 0.05	0.40 ± 0.06	*	0.42 ± 0.07	$0.31 \pm 0.$	
8.24 ± 1.54	11.13 ± 1.85	3.26 ± 0.71	3.86 ± 0.71	9.74 ± 1.20	*	3.22 ± 0.53	$3.37 \pm 0.$	
0.01 ± 0.01	N.I.	0.05 ± 0.03	0.03 ± 0.01	0.01 ± 0.01	*	0.10 ± 0.02	$0.04 \pm 0.$	
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	
N.I.	N.I.	4.18 ± 3.55	3.60 ± 1.20	N.I.	*	N.I.	0.22 ± 0	
	Daytime 2.37 ± 0.56 7.34 ± 0.86 0.22 ± 0.04 8.24 ± 1.54 0.01 ± 0.01 0.20 ± 0.05	Daytime Nighttime 2.37 ± 0.56 2.46 ± 0.46 7.34 ± 0.86 3.81 ± 0.53 0.22 ± 0.04 0.22 ± 0.04 8.24 ± 1.54 11.13 ± 1.85 0.01 ± 0.01 N.I. 0.20 ± 0.05 0.17 ± 0.05 N.I. N.I.	Daytime Nighttime Daytime 2.37 ± 0.56 2.46 ± 0.46 3.70 ± 0.78 7.34 ± 0.86 3.81 ± 0.53 13.67 ± 1.59 0.22 ± 0.04 0.22 ± 0.04 0.13 ± 0.03 8.24 ± 1.54 11.13 ± 1.85 3.26 ± 0.71 0.01 ± 0.01 N.I. 0.05 ± 0.03 0.20 ± 0.05 0.17 ± 0.05 0.17 ± 0.05 N.I. N.I. 4.18 ± 3.55	Daytime Nighttime Daytime Nighttime 2.37 ± 0.56 2.46 ± 0.46 3.70 ± 0.78 2.24 ± 0.51 7.34 ± 0.86 3.81 ± 0.53 13.67 ± 1.59 13.10 ± 1.55 0.22 ± 0.04 0.22 ± 0.04 0.13 ± 0.03 0.27 ± 0.05 8.24 ± 1.54 11.13 ± 1.85 3.26 ± 0.71 3.86 ± 0.71 0.01 ± 0.01 N.I. 0.05 ± 0.03 0.03 ± 0.01 0.20 ± 0.05 0.17 ± 0.05 0.17 ± 0.05 0.07 ± 0.02 N.I. N.I. 4.18 ± 3.55 3.60 ± 1.20	Daytime Nighttime Daytime Nighttime Daytime 2.37 ± 0.56 2.46 ± 0.46 3.70 ± 0.78 2.24 ± 0.51 1.43 ± 0.41 7.34 ± 0.86 3.81 ± 0.53 13.67 ± 1.59 13.10 ± 1.55 2.93 ± 0.41 0.22 ± 0.04 0.22 ± 0.04 0.13 ± 0.03 0.27 ± 0.05 0.40 ± 0.06 8.24 ± 1.54 11.13 ± 1.85 3.26 ± 0.71 3.86 ± 0.71 9.74 ± 1.20 0.01 ± 0.01 N.I. 0.05 ± 0.03 0.03 ± 0.01 0.01 ± 0.01 0.20 ± 0.05 0.17 ± 0.05 0.17 ± 0.05 0.07 ± 0.02 0.16 ± 0.04 N.I. N.I. 4.18 ± 3.55 3.60 ± 1.20 N.I.	Daytime Nighttime Daytime Nighttime Daytime Nighttime 2.37 ± 0.56 2.46 ± 0.46 3.70 ± 0.78 2.24 ± 0.51 1.43 ± 0.41 * 7.34 ± 0.86 3.81 ± 0.53 13.67 ± 1.59 13.10 ± 1.55 2.93 ± 0.41 * 0.22 ± 0.04 0.22 ± 0.04 0.13 ± 0.03 0.27 ± 0.05 0.40 ± 0.06 * 8.24 ± 1.54 11.13 ± 1.85 3.26 ± 0.71 3.86 ± 0.71 9.74 ± 1.20 * 0.01 ± 0.01 N.I. 0.05 ± 0.03 0.03 ± 0.01 0.01 ± 0.01 * 0.20 ± 0.05 0.17 ± 0.05 0.17 ± 0.05 0.07 ± 0.02 0.16 ± 0.04 * N.I. N.I. 4.18 ± 3.55 3.60 ± 1.20 N.I. *	Daytime Nighttime Daytime Nighttime Daytime Nighttime Daytime Daytime	

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

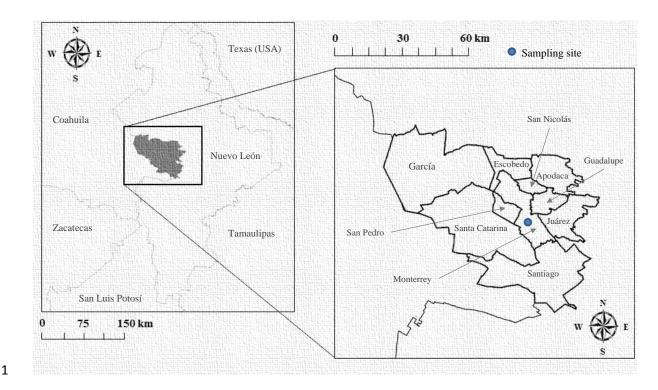


Figure 1. Location and municipalities of the Monterrey Metropolitan Area (MMA); the sampling site was set up in the downtown.

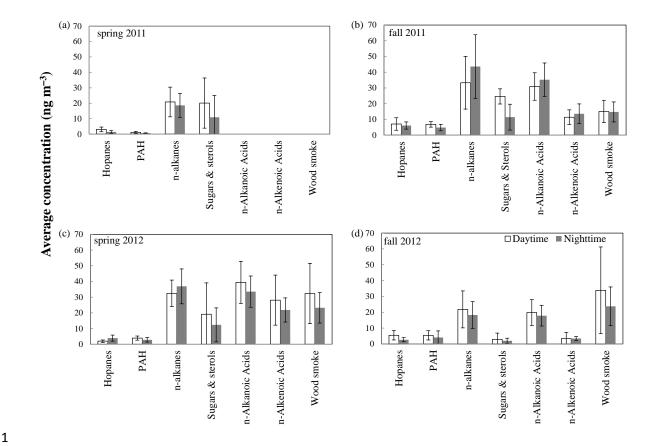


Figure 2. Concentrations of the resolved organic compound classes in the MMA. For (a) the n-Alkanoic and Alkenoic acids and wood smoke tracer were not included in the chemical analysis. For (b), (c) and (d) the *n*-alkanoic acids are divided by a factor of 10.

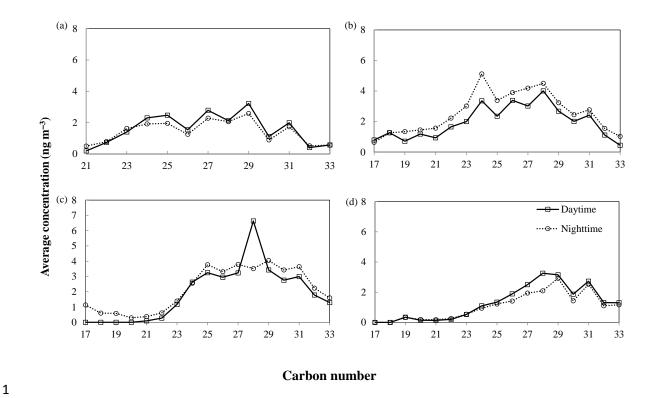


Figure 3. Carbon number distribution of *n*-alkanes in the Monterrey Metropolitan Area (MMA) for (a) spring 2011, (b) fall 2011, (c) spring 2012 and (d) fall 2012. The black line is the daytime concentrations while the dot line is the nighttime concentrations.

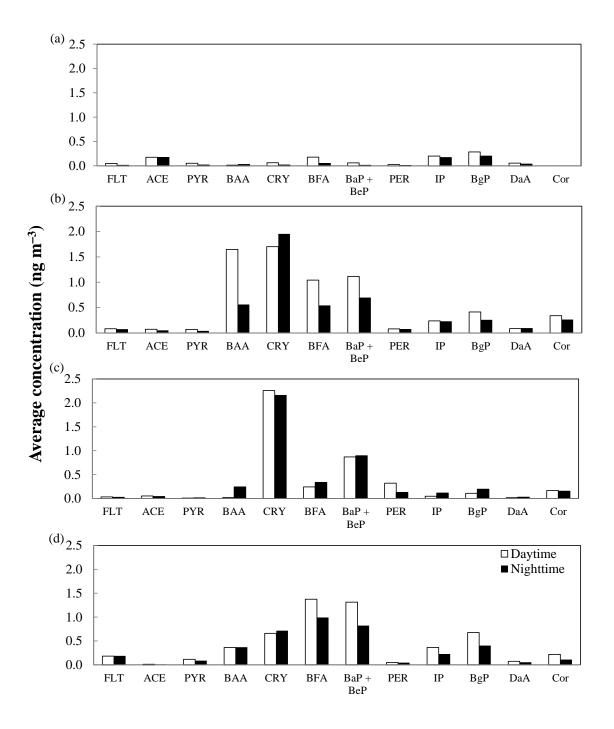


Figure 4. Mass concentration distribution of PAHs in the Monterrey Metropolitan Area (MMA) for (a) spring 2011, (b) fall 2011, (c) spring 2012 and (d) fall 2012. Coronene was included in all monitoring campaigns, except in the spring 2011.

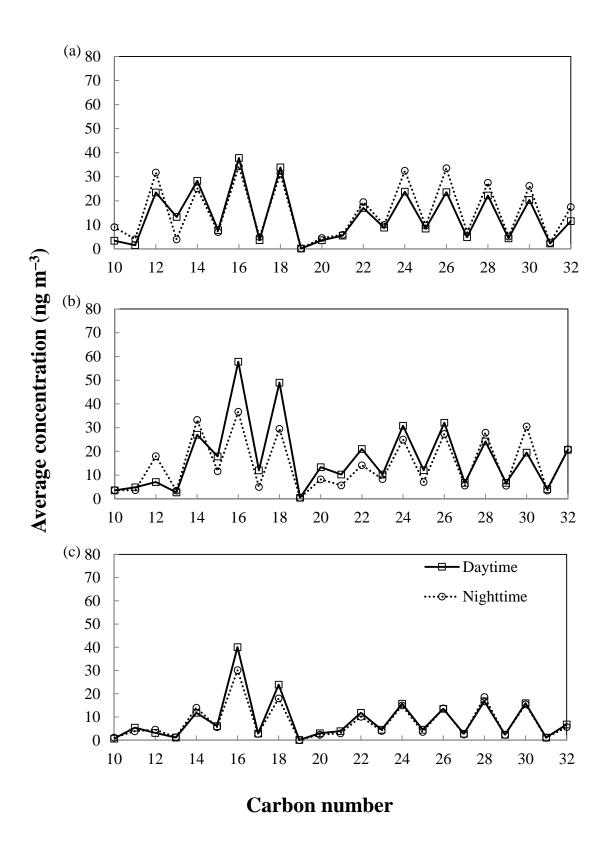
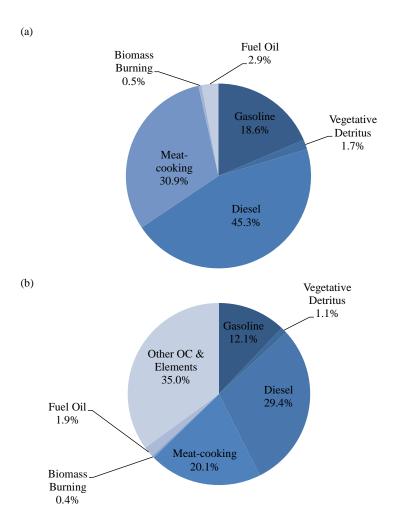


Figure 5. Carbon number distribution of *n*-alkanoic acids in the Monterrey Metropolitan Area (MMA) for (a) fall 2001, (b) spring 2012 and (c) fall 2012. The black line represents the daytime concentrations while the dot line represents the nighttime concentrations.



4

2 Figure 6. CMB contributions to the (a) average identified ambient PM_{2.5} in the MMA and to

3 the (b) overall PM2.5 including the unidentified mass of the measured $PM_{2.5}$ concentrations.