

1 **RESPONSE TO EDITOR**

2  
3 **Ms. No.: acp-2015-282**

4 Title: Chemical characterization of fine organic aerosol for source apportionment at  
5 Monterrey, Mexico

6 Submitted to: *Atmospheric Chemistry and Physics*

7  
8 **Editor Decision: Reconsider after minor revisions (Editor review) (30 Dec 2015) by**  
9 **Willy Maenhaut**

10  
11 Comments to the Author:

12  
13 The authors have reasonably addressed the comments of the reviewers. However, many  
14 alterations and some clarifications are needed before the manuscript and its Supplement can  
15 be published in ACP.

16  
17 **C: we really appreciate all comments from the editor. We will attend every comment as**  
18 **the editor suggested. We thanked this opportunity for publishing our work.**

19  
20 For the main text:

21  
22 *1) Page 1, lines 1-3: There is too much "organic" in the title. I suggest replacing "organic*  
23 *aerosol" by "aerosol" in line 2.*

24  
25 **R: Done.**

26  
27 *2) Page 2, line 27: Replace "pyrolisis" by "pyrolysis".*

28  
29 **R: Done.**

30  
31 *3) Page 3, line 9: Replace "homologs" by "homologues".*

32  
33 **R: Done.**

1 4) Page 4, line 1: Replace "Anthony Chen" by "Chen".

2

3 **R:** Done.

4

5 5) Page 4, lines 3-4: "Viana et al., 2008" should be added as a reference here. The full  
6 reference is given below (see note for Page 32).

7

8 **R:** We agree with the editor. The reference was added.

9

10 6) Page 5, line 2: Replace "In addition, the" by "The".

11

12 **R:** Done.

13

14 7) Page 5, line 30: Replace "collected in" by "collected on".

15

16 **R:** Done.

17

18 8) Page 6, line 8: Replace "were carry" by "were carried".

19

20 **R:** Done.

21

22 9) Page 6, line 30: Replace "then they were subjected to ultrasonic agitation for 20 min" by  
23 "then ultrasonic agitation was applied for 20 min".

24

25 **R:** Done.

26

27 10) Page 7, line 1: Replace "flow ultra-high" by "flow of ultra-high".

28

29 **R:** Done.

30

31 11) Page 7, line 6: Replace "The another fraction" by "Another fraction".

32

33 **R:** Done.

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33

12) Page 7, line 9: Replace "Diazomethane (CH<sub>2</sub>N<sub>2</sub>) solution" by "CH<sub>2</sub>N<sub>2</sub> solution".

**R:** Done.

13) Page 7, line 15: Replace "Brown et al., 2002" by "Brown et al. (2002)".

**R:** Done.

14) Page 8, line 23: Replace "over determined" by "overdetermined".

**R:** Done.

15) Page 9, line 6: Replace "2015)." by "2015) and was also used in the current study.".

**R:** Done.

16) Page 9, line 14: Replace "based on" by "based their CMB on".

**R:** Here, it is important to clarify that Martínez et al. (2012) applied factor analysis instead of CMB to identified primary emission sources. Therefore, we consider to replace “based on” by “based their factor analysis on”.

17) Page 9, line 17: Replace "source profile" by "source profiles".

**R:** Done.

18) Page 9, line 19: Replace "while diesel" by "while the diesel".

**R:** Done.

19) Page 9, line 20: Replace "by heavy" by "of heavy".

1 **R:** Done.

2

3 20) Page 9, line 23: Replace "*a source profile*" by "*source profiles*".

4

5 **R:** Done.

6

7 21) Page 10, line 11: Replace "*of source profiles*" by "*of the source profiles*".

8

9 **R:** Done.

10

11 22) Page 10, line 29: Replace "*A detailed*" by "*Detailed*".

12

13 **R:** Done.

14

15 23) Page 11, line 1: Replace "*All the samples*" by "*All samples*".

16

17 **R:** Done.

18

19 24) Page 11, line 2: Replace "*of 2011*" by "*of the 2011*".

20

21 **R:** Done.

22

23 25) Page 11, line 5: Replace "*to the last*" by "*to that of the last*".

24

25 **R:** Done.

26

27 26) Page 11, lines 5-6: It say here "*eight*", but Fig. 2 contains only data for seven compound  
28 *classes*.

29

30 **R:** We agree with the reviewer, it should be seven resolved compound classes instead of eight.  
31 We replaced on page 11, line 1 and line 5 “eight organic compound” by “seven organic  
32 compound”.

33

1 27) Page 11, line 13: Replace "to some compounds" by "to the fact that some compounds".

2

3 **R:** Done.

4

5 28) Page 11, lines 19-20: Replace "sections will be analyzed the organic composition of the  
6 fine organic aerosols using" by "sections the organic composition of the fine organic aerosols  
7 will be analyzed using".

8

9 **R:** Done.

10

11 29) Page 12, line 5: Insert a space before "The average".

12

13 **R:** Done.

14

15 30) Page 12, line 9: Replace "emissions sources" by " emission sources".

16

17 **R:** Done.

18

19 31) Page 12, lines 18 and 20: Replace "of the 2011" by "of 2011".

20

21 **R:** Done.

22

23 32) Page 13, line 9: Replace "Benzo(a)pyrene + Benzo(e)pyrene" by "benzo(a)pyrene +  
24 benzo(e)pyrene".

25

26 **R:** Done.

27

28 33) Page 13, line 11: Replace "fine OC samples" by "fine samples".

29

30 **R:** Done.

31

32 34) Page 13, line 18: Replace "illustrated by" by "illustrated in".

33

1 **R:** Done.

2

3 35) Page 13, line 24: Replace "*due to PAHs*" by "*because PAHs*".

4

5 **R:** Done.

6

7 36) Page 13, line 26: Replace "*it would be determined the source origin (e.g.*" by "*the source*  
8 *could be determined (e.g.,*".

9

10 **R:** Done.

11

12 37) Page 14, line 2: Replace "*source for*" by "*sources for*".

13

14 **R:** Done.

15

16 38) Page 14, line 3: Replace "*Presence of*" by "*The presence of*".

17

18 **R:** Done.

19

20 39) Page 16, line 1: Replace "*included the cis-9-Octadecenoic acid*" by "*included cis-9-*  
21 *octadecenoic acid*".

22

23 **R:** Done.

24

25 40) Page 16, lines 2, 4, 10, 11, and 18: Replace "*cis-9-Octadecenoic acid*" by "*cis-9-*  
26 *octadecenoic acid*".

27

28 **R:** Done.

29

30 41) Page 16, line 6: Replace "*oxidation from gaseous precursors*" by "*oxidation*".

31

32 **R:** Done.

33

1 42) Page 16, line 8: Replace "while" by "versus".

2

3 **R:** Done.

4

5 43) Page 16, lines 11-13: I cannot follow the reasoning here. I would expect that high oxidant  
6 concentrations would lead to high ratios instead of to low ratios.

7

8 **R:** The editor is correct. We revised our notes and the references cited in this part. Therefore,  
9 we replaced on page 16, line 13 "low ratios" by "high ratios". In addition, we replaced on  
10 page 16, line 11, "By contrast" by "Similarly".

11

12 44) Page 16, line 25: Replace "product of" by "products of".

13

14 **R:** Done.

15

16 45) Page 16, line 26: Replace "The pinonic" by "Both pinonic".

17

18 **R:** Done.

19

20 46) Page 17, line 12: Replace "are the tracers" by "are tracers".

21

22 **R:** Done.

23

24 47) Page 17, line 13: Replace "the tracer" by "are a tracer".

25

26 **R:** Done.

27

28 48) Page 17, line 16: Replace "the OC samples" by "the samples".

29

30 **R:** Done.

31

32 49) Page 17, line 24: Replace "of fall" by "of the fall".

33

1 **R:** Done.

2

3 50) Page 17, line 26: Replace "*exhibited*" by "*encountered*".

4

5 **R:** Done.

6

7 51) Page 18, line 2: Replace "*in the Mexico*" by "*in Mexico*".

8

9 **R:** Done.

10

11 52) Page 18, line 3: Replace "*calculated in*" by "*observed in*".

12

13 **R:** Done.

14

15 53) Page 18, line 23: Replace "*for the levoglucosan*" by "*for levoglucosan*".

16

17 **R:** Done.

18

19 54) Page 19, line 17: Replace "*whilst 14*" by "*whereas 14*".

20

21 **R:** Done.

22

23 55) Page 19, lines 18-19: Replace "*Mancilla et al. (2015)*" by "*(Mancilla et al., 2015)*".

24

25 **R:** Done.

26

27 56) Page 19, line 24: Replace "*operations emissions for all monitoring campaigns were the*  
28 *highest. In analysis*" by "*operation emissions were the highest for all monitoring campaigns.*  
29 *When examining*".

30

31 **R:** Done.

32



1 57) Page 19, line 30: Replace *"In analysis of the"* by *"With regard to the"*.

2

3 **R:** Done.

4

5 58) Page 19, line 32: Replace *"some higher"* by *"somewhat higher"*.

6

7 **R:** Done.

8

9 59) Page 20, line 1: Replace *"There are not similar"* by *"There were no similar"*.

10

11 **R:** Done.

12

13 60) Page 20, line 3: Replace *"results were similar"* by *"results are similar"*.

14

15 **R:** Done.

16

17 61) Page 20, line 4: Replace *"for the Mexico"* by *"for Mexico"*.

18

19 **R:** Done.

20

21 62) Page 20, line 17: Replace *"to the secondary"* by *"to secondary"*.

22

23 **R:** Done.

24

25 63) Page 20, line 20: Replace *"The vegetative detritus"* by *"Vegetative detritus"*.

26

27 **R:** Done.

28

29 64) Page 20, line 21: Replace *"the less emitted"* by *"the least emitted"*.

30

31 **R:** Done.

32

1 65) Page 20, line 23: Replace "which contribute with" by " which contributes with".

2

3 **R:** Done.

4

5 66) Page 20, line 24: It is unclear what is meant by "types of biomass". Which types?  
6 Furthermore, I cannot follow the reasoning in lines 24-31. Clarification and rephrasing are  
7 needed.

8

9 **R:** We agree with the editor, the reasoning in lines 24-31 is confused. We clarified and  
10 rephrased this reasoning.

11

12 On page 20, lines 24-31, we replaced “The MMA as well as other urban areas can be affected  
13 by types of biomass burning, especially, when they are not surrounded by forests. For  
14 examples, several studies have demonstrated that Mexico City has a large contribution from  
15 biomass burning (Moffet et al., 2008; Stone et al., 2008; Yokelson et al., 2007) because it is  
16 affected by forests fires (Yokelson et al., 2007). Conversely, the MMA has no forests around,  
17 therefore, the contribution from biomass burning in the MMA might be higher because the  
18 source profile used for the CMB was only for wood combustion instead of using a source  
19 profile for garbage, industrial, and urban residues open fires (Simoneit et al., 2005).” by “With  
20 regard to biomass burning, several studies have demonstrated that Mexico City has a large  
21 contribution of biomass burning emissions due to forests fires (Moffet et al., 2008; Stone et  
22 al., 2008; Yokelson et al., 2007). However, the MMA can be affected by other types of  
23 biomass burning (e.g., shrub and grassland fires, agricultural waste and garbage burning, etc.)  
24 that may be ignored. Therefore, the contribution of biomass burning in the MMA might be  
25 higher because the source profile used for the CMB was only for wood combustion instead of  
26 using a source profile for other types of biomass burning (Simoneit et al., 2005).”

27

28 67) Page 20, line 26: Replace "has large" by "has a large".

29

30 **R:** Done.

31

32 68) Page 20, line 28: Replace "has not forests" by "has no forests".

33

1 **R:** Done.

2

3 69) Page 20, line 31: Replace "*here is*" by "*it is*".

4

5 **R:** Done.

6

7 70) Page 20, line 32: Replace "*due to prior*" by "*as appeared from previous*".

8

9 **R:** Done.

10

11 71) Page 21, line 4: Replace "*emits low*" by "*emits a low*".

12

13 **R:** Done.

14

15 72) Page 21, line 13: Replace "*e.g. plant*" by "*e.g., plant*".

16

17 **R:** Done.

18

19 73) Page 21, line 14: Replace "*some times*" by "*sometimes*".

20

21 **R:** Done.

22

23 74) Page 21, lines 24-25 and 26: Replace "*cis-9-Octadecenoic acid*" by "*cis-9-octadecenoic*  
24 *acid*".

25

26 **R:** Done.

27

28 75) Page 22, line 1: Replace "*for the 64%*" by "*for 64%*".

29

30 **R:** Done.

31

32 76) Page 22, line 2: Replace "*the vegetative detritus*" by "*vegetative detritus*".

33

1 **R:** Done.

2

3 77) Page 22, line 3: Replace "*less contributors*" by "*lowest contributors*".

4

5 **R:** Done.

6

7 78) Page 22, line 4: Replace "*the outcomes of a comparison with other studies were that*" by  
8 "*a comparison with other studies indicates that*".

9

10 **R:** Done.

11

12 79) Pages 22-33, Reference list:

13 *The initials for the authors are not always in the proper format; the first initial should be*  
14 *preceded by a comma, there should be period after each initial and there should be a space*  
15 *between subsequent initials.*

16 *Furthermore, titles of journal articles should be in lower case instead of in Title Case (e.g.,*  
17 *for Simoneit, 1985 and Simoneit, 1986).*

18

19 **R:** We appreciate the observation of the editor. All references were revised and now they  
20 have the proper format.

21

22 80) Page 23, line 6: Replace "*Antony Chen, L.-W.*" by "*Chen, L.-W. A.*".

23

24 **R:** Done.

25

26 81) Page 23, line 17: Replace "*Chen, W. A.*" by "*Chen, L. W. A.*".

27

28 **R:** Done.

29

30 82) Page 24, line 18: Replace "*A. (Eds):*" by "*A.:*".

31

32 **R:** Done.

33

1 83) Page 25, line 19: Replace "INEGI," by "INEGI:".

2

3 **R:** Done.

4

5 84) Page 25, lines 20 and 23: Replace "INEGI.. by "INEGI:".

6

7 **R:** Done.

8

9 85) Page 26, line 6: Replace "aerosols, .Environ." by "aerosols, Environ.".

10

11 **R:** Done.

12

13 86) Page 28, lines 9-10: "Paatero, 1997" should come on page 27 before "Park et al., 2006".

14

15 **R:** The reference was moved.

16

17 87) Page 29, lines 25-28: These two references should be moved down; they should come on  
18 page 31 after "Spurny, 2000".

19

20 **R:** The references were moved down.

21

22 88) Page 31, lines 28-30: "Stone et al., 2008" should come on page 32 after "Standley et al.,  
23 1987".

24

25 **R:** The reference was moved.

26

27 89) Page 32, between lines 13 and 14: The following reference should be added here:

28 Viana, M., Kuhlbusch, T. A. J., Querol, X., Alastuey, A., Harrison, R. M., Hopke, P. K.,  
29 Winiwarter, W., Vallius, M., Szidat, S., Prévôt, A. S. H., Hueglin, C., Bloemen, H., Wählin, P.,  
30 Vecchi, R., Miranda, A. I., Kasper-Giebl, A., Maenhaut, W., and Hitzenberger, R.: Source  
31 apportionment of particulate matter in Europe: A review of methods and results, *J. Aerosol*  
32 *Sci.* 39, 827-849, 2008.

33

1 R: The reference was added.

2

3 90) Page 33, lines 13-16: *"Yunker et al." should start on a new line; the publication year of*  
4 *the reference is missing and "Geochemistry 33," should be replaced by " Geochemistry, 33,".*

5

6 R: The reference was moved and the corresponding year were also added.

7

8 91) Page 36, line 2: *There is something wrong with the explanation given here; also "curly*  
9 *brackets" should be replaced by "parentheses".*

10

11 **R:** We agree with the editor. This explanation was for a column that was deleted given some  
12 comments from other reviewers. Therefore, on page 36, the line 2 was deleted.

13

14 92) Page 36, line 5: Replace "that dates" by "that the dates".

15

16 R: Done.

17

18 93) Page 37, line 4: *"Akyüz and Cabuk, 2010" is missing in the Reference list.*

19

20 **R:** The editor is correct, the reference is missing. Therefore, the reference was added in the  
21 reference list.

22

23 95) Page 37, line 6: Replace "BaP" by "BeP".

24

25 **R:** Done.

26

27 96) Page 41, line 4: Replace *"line is the daytime concentrations while the dot line is the"* by  
28 *"line represents the daytime concentrations while the dotted line represents the".*

29

30 **R:** Done.

31

32 For the Supplement:

33

1 *1) Pages 1-4, Table S1: Consistency is needed here. Therefore, all names of the organic*  
2 *compounds should start with a lower case letter instead of with a capital.*

3

4 **R:** Done.

5

# 1 Organic composition and source apportionment of fine 2 ~~organic aerosol~~aerosol at Monterrey, Mexico, based on 3 organic markers

4  
5 Y. Mancilla<sup>1</sup>, A. Mendoza<sup>1</sup>, M. P. Fraser<sup>2</sup> and P. Herckes<sup>3</sup>

6 [1]{School of Engineering and Sciences, Tecnológico de Monterrey, Monterrey, Mexico}

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

9 [3]{Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona}

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

## 11 12 **Abstract**

13 Primary emissions from anthropogenic and biogenic sources as well as secondary formation  
14 are responsible for the pollution levels of ambient air in major urban areas. These sources  
15 release fine particles into the air that negatively impact human health and the environment.  
16 Organic molecular markers, which are compounds that are unique to specific PM<sub>2.5</sub> sources,  
17 can be utilized to identify the major emission sources in urban areas. In this study, 43  
18 representative PM<sub>2.5</sub> samples, for both daytime and nighttime periods, were built from  
19 individual samples collected in an urban site of the Monterrey Metropolitan Area (MMA)  
20 during the spring and fall of 2011 and 2012. The samples were analyzed for organic carbon,  
21 elemental carbon, and organic molecular markers. Several diagnostic tools were employed for  
22 the preliminary identification of emission sources. Organic compounds for eight compound  
23 classes were quantified. The *n*-alkanoic acids were the most abundant, followed by *n*-alkanes,  
24 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  
28 engines. In addition, the contribution of gasoline and diesel vehicle exhaust was confirmed  
29 and identified by the PAH concentrations in PM<sub>2.5</sub>. Diagnostic ratios of PAH showed  
30 emissions from burning coal, wood, biomass, and other fossil fuels. The total PAH and



1 elemental carbon were correlated ( $r^2 = 0.39\text{--}0.70$ ) 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  $\text{PM}_{2.5}$ , followed by meat cooking operations with 31%. The vegetative detritus and biomass  
8 burning had the smallest contribution (2.2% of the  $\text{PM}_{2.5}$ ). To our knowledge, this is the  
9 second study to explore the organic composition and source apportionment of fine organic  
10 aerosol based on molecular markers in Mexico and the first for the MMA. Particularly  
11 molecular marker were quantified by solvent extraction with dichloromethane, derivatization,  
12 and gas chromatography with mass spectrometry (GC/MS).

13

## 14 **1 Introduction**

15 Fine organic aerosol (OA) has a major role in environmental and human health impacts (Peng  
16 et al., 2009). Some researchers have recently estimated that fine OA constitutes 23–38% of  
17 the  $\text{PM}_{2.5}$  mass in urban areas (Qin et al., 2006; Viana et al., 2006; Duan et al., 2007;  
18 Upadhyay et al., 2011). In addition, OA along with elemental carbon (EC) can account for up  
19 to 31–57% of the  $\text{PM}_{2.5}$  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  
23 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 ~~pyrolysis~~-pyrolysis decomposition and combustion product of cellulose;  
28 therefore, it can be used as a tracer for biomass burning sources (Fraser et al., 2000; Robinson  
29 et al., 2006a; Alves et al., 2011; Gonçalves et al., 2011). Cholesterol and nicotine are good  
30 markers for meat cooking operations (Rogge et al., 1991; Schauer et al., 2001b; Robinson et  
31 al., 2006b) and cigarette smoke (Eatough et al., 1989; Hildemann et al., 1991; Rogge et al.,  
32 1994; Kavouras et al., 1998), respectively. Hopanes are biomarkers of fuel oil combustion,

1 coal combustion and lubricants, and are useful to identify engine emissions (Rogge et al.,  
2 1993a; Oros and Simoneit, 2000; Simoneit et al., 2004; Schnelle-Kreis et al., 2005). PAHs are  
3 semi-volatile compounds formed from fossil fuel incomplete combustion processes (Rogge et  
4 al., 1993a; Marr et al., 2004; Sklorz et al., 2007). Finally, *n*-alkanes are indicators of fossil  
5 fuel utilization and biogenic emissions (Simoneit et al., 2004; Young and Wang, 2002).  
6 Additional details about specific organic markers and their emission sources can be found  
7 elsewhere (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~~ homologues in series of biomolecules. For *n*-alkanes and alkanolic acids, the odd-  
10 and even- carbon preferences are indicators of biogenic sources (Tsapakis et al., 2002). A lack  
11 of carbon preference is indicative of fossil sources. For the case of PAHs, some ratios can be  
12 used to identify emissions from fossil fuel combustion (Zhang et al., 2005).

13 Source apportionment studies based on organic molecular markers have accomplished a better  
14 understanding of the emission sources in urban areas. This approach considers two main  
15 principles: (1) that organic molecular markers are present in relatively high concentrations in  
16 emissions from a specific source and in lower concentrations in the remaining sources, and (2)  
17 that they react slowly enough in the atmosphere to be conserved during transport from the  
18 source to the observation/receptor site (Schauer et al., 1996; Lin et al., 2010). The use of  
19 organic molecular markers in the last decade has proven to be a powerful method to identify  
20 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).  
25 In spite of recent research interest on organic molecular markers for source apportionment, the  
26 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;  
32 Wold et al., 2001). Furthermore, improved source apportionment methods have been

1 developed ([Antony-ChenChen](#) 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 [Viana et al., 2008](#); Lin et al., 2010; Nozière et al., 2015).

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

## 24 **2 Methodology**

### 25 **2.1 Sampling site**

26 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 km<sup>2</sup>  
29 (SEDESOL et al., 2007), as shown in Fig. 1. The MMA has a vehicular fleet of 1.7 million  
30 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

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

## 13 **2.2 Sampling periods and instruments**

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

22 Carbonaceous aerosol samples were collected using high-volume filter-based instruments with  
23 PM<sub>2.5</sub> inlet (TE-6001-2.5, Tisch Environmental Inc), operating at a flow of 1.13 m<sup>3</sup>/min. The  
24 flow rates for the high-volume samplers were calibrated at the start and end of each  
25 monitoring campaign. For each high-volume sampler, the calibration was carried out using a  
26 calibration orifice (NIST Traceable Calibration Certificate). The samplers were mounted on  
27 the rooftop of the monitoring station three meters above the ground. One high-volume  
28 sampler was used for each campaign, except for the campaign of fall 2012, in which two high-  
29 volume samplers were deployed and operated simultaneously to collect pairs of samples for  
30 each diurnal and nighttime sampling period. Fine particles were ~~collected~~incollected on  
31 8"×10" quartz microfibre filters (Whatman QMA). Filters were previously pre-fired for 8 hrs

1 at 600°C in a furnace to remove residual carbon and stored in baked aluminum foil within  
2 sealed plastic bags (Ziploc®) until they were used. After sampling, loaded 8”×10” filters were  
3 stored in tall 8 oz. glass jars (VWR, IR221-0250). Loaded filters were placed in a cooler with  
4 blue ice for immediate transport from the sampling site to the laboratory. All loaded filters  
5 were stored in a freezer at –20°C to prevent the evaporation of volatile compounds until they  
6 were analyzed. A total of 111 samples and 10 field blanks were collected throughout the  
7 study.

### 8 **2.3 Ambient measurements**

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

23 Solvent-extractable molecular markers were quantified using gas chromatography mass  
24 spectrometry (GC/MS) using dichloromethane (DCM), and methanol (MeOH) (high purity  
25 99.9%, Fisher Scientific). Filters were spiked with 50 µL of the following deuterated internal  
26 standards (Sigma Aldrich): *n*-hexadecane-d34, *n*-hexatriacontane-d74, *n*-eicosane-d42, *n*-  
27 triacontane-d62, vanillin-d3, benzophenone-d5, chrysene-d12, dibenz(a,h)anthracene-d14,  
28 naphthalene-d8, pyrene-d10, benzo(e)pyrene-d12, coronene-d12, decanoic acid-d19, palmitic  
29 acid-d31, stearic acid-d35, levoglucosan-13c6, and cholesterol-d6. Each individual filter or  
30 sample composite was extracted three times with DCM. During each extraction, enough DCM  
31 was added and ~~then they were subjected to ultrasonic agitation for 20 min~~then ultrasonic

1 agitation was applied for 20 min using a sonicator (Bransonic®, model 5510R-DTH). The  
2 extracts were combined and then concentrated by evaporation under a gentle ~~flow ultra-~~  
3 highflow of ultra-high purity nitrogen until the extract reached a volume of ~5 mL. The  
4 extracts were filtered through a pre-fired quartz filter, subsequently reduced in volume to 250  
5 µL, and then separated into three fractions. One fraction was a direct portion of the 250 µL  
6 extract for direct analysis by GC/MS, and the other two fractions were used for chemical  
7 derivatizations. One fraction was methylated using diazomethane (CH<sub>2</sub>N<sub>2</sub>) to convert  
8 carboxylic acids to their respective methyl esters. ~~The another fraction~~Another fraction was  
9 silylated using a combination of BSTFA (N, O-bis(trimethylsilyl)trifluoroacetamide) and  
10 TMCS (trimethylchlorosilane) to convert sterols and sugars to their respective trimethylsilyl  
11 esters. For methylation, 50 µL of a ~~Diazomethane (CH<sub>2</sub>N<sub>2</sub>) solution~~CH<sub>2</sub>N<sub>2</sub> solution was  
12 combined in a vial with 50 µL of extract. For the silylation, 50 µL of BSTFA+TMCS (molar  
13 ratio 99:1) was combined with 50 µL sample extract. Then, the mixture was allowed to react  
14 for 3 h at 65°C. The quantification and identification of organic compounds was based on  
15 comparisons with authentic standards, retention times, literature mass spectra, and  
16 fragmentation patterns using HP chemstation. A detailed description of the extraction and  
17 analysis procedures as well as the chromatograph and column used can be found in ~~Brown et~~  
18 al., 2002; Brown et al. (2002).

## 19 **2.4 Molecular diagnostic ratios**

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

### 21 **2.4.1 Carbon Preference Index (CPI)**

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

$$26 \text{ CPI} = \frac{\sum(\text{C}_{17} \text{ to } \text{C}_{33})}{\sum(\text{C}_{16} \text{ to } \text{C}_{32})} \quad (1)$$

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

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

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  $\text{CPI} > 1$  indicate that hydrocarbons and carboxylic acids are emitted from natural sources. In contrast, values of  $\text{CPI} \leq 1$  (or close to one) indicate that they are emitted from anthropogenic sources (Gogou et al., 1996; Alves et al., 2001; Gelencsér, 2004).

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

#### 2.4.2 Diagnostic ratios of PAHs

Other indicators that have been used as markers of different source emissions of OA are the 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).

### 2.5 Chemical Mass Balance model

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

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

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 the model error. This model considers a prior knowledge of the source profiles and that the 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 the ~~over-determined~~ overdetermined set of mass balance equations (Eq. 1). CMB takes into



1 account the known uncertainties in the ambient measurements and the source emission data to  
2 minimize the chi-square ( $\chi^2$ ) goodness-of-fit parameter for each sample  $i$ :

$$3 \quad \chi^2 = \sum_{j=1}^m \left[ \frac{x_j - \sum_{k=1}^p g_{jk} f_k}{\sigma_{x_j}^2 + \sum_{k=1}^p \sigma_{g_{jk}}^2 f_k} \right] \quad (2)$$

4 where  $\sigma_{x_j}$  is the standard deviation of the concentration of species  $j$ ,  $\sigma_{g_{jk}}$  is the standard  
5 deviation of the  $g_{jk}$ , and  $m$  the total number of species. The U.S. EPA-CMB8.2 software has  
6 been successfully used to apportion source contributions to ambient PM<sub>2.5</sub> (Ke et al., 2007;  
7 Stone et al., 2008; Watson et al., 2008; Kleeman et al., 2009; Schneidmesser et al., 2009; Yin  
8 et al., 2010; Perrone et al., 2012; Villalobos et al., ~~2015~~, 2015) and was also used in the  
9 current study. More details about CMB can be found elsewhere (e.g., Henry et al., 1984;  
10 Watson et al., 2008).

## 11 **2.6 Source profiles**

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

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

26 From evidence of industrial sources in Mexican urban atmospheres, ~~a source profiles~~ source  
27 profiles for natural gas combustion and fuel oil combustion were taken from Rogge et al.  
28 (1993c) and Rogge et al. (1997), respectively.



1 Finally, source profiles for meat cooking operations, vegetative detritus, and biomass burning  
2 were taken from Schauer et al. (1999), Rogge et al. (1993b) and Schauer et al. (2001a),  
3 respectively. Most traditional restaurants activities of the region of study include meat  
4 charbroiling operations. For biomass burning, given the existence of softwood and hardwood  
5 sources in the region (Zurita, 2009), the softwood pine and hardwood oak profiles were used  
6 in this study. These last profiles were used separately because they are highly collinear.  
7 Regarding vegetative detritus, a source profile was included based on the contributions  
8 determined by Stone et al. (2008) in Mexico City along with the fact that the MMA is  
9 surrounded by rural areas with vast green covers. Therefore, it is possible to have an impact  
10 from transport of biogenic emissions.

11 For individual organic compound quantification, an uncertainty of  $\pm 20\%$  of the measured  
12 concentration was used for all ambient samples and source profiles (Schauer et al., 2000;  
13 SRM 1649a, 2007; SRM 1649b, 2009; Fraser et al., 2003; Schantz et al., 2005). A detailed  
14 description ~~of source profiles~~ of the source profiles and settings used to perform the CMB in  
15 this study can be found in Fraser et al. (2003). For the current application, the fitting species  
16 for CMB included 20 organic compounds along with EC and overall OC. The molecular  
17 markers included seven *n*-alkanes (C27-C33), four petroleum biomarkers (17a(H),21b(H)-29-  
18 norhopane, 17a(H),21b(H)-hopane, 22R+S 17a(H),21b(H)-30-homohopane, and 22R+S  
19 17a(H),21b(H)-30-bishomohopane), five polycyclic aromatic hydrocarbons  
20 (benzo[a]anthracene, benzofluoranthenes, benzo[a]pyrene, indeno[123-cd]pyrene and  
21 benzo[ghi]perylene), two saturated fatty acids (C16:0 and C18:0), cholesterol and  
22 levoglucosan.

### 23 **3 Results and discussion**

#### 24 **3.1 Resolved organic aerosols**

25 The results for the chemical characterization of the fine organic aerosol for the MMA are  
26 summarized in Table S1. In this and other sections, averaged values for concentrations and  
27 other parameters are given  $\pm$  one standard deviation. Most of the PM<sub>2.5</sub> daytime  
28 concentrations were 20% higher than nighttime concentrations. The concentrations of OC and  
29 EC were on average 32% higher during the daytime than the nighttime. In addition, the OC  
30 and EC accounted together for 28–49% and 46–55% of the PM<sub>2.5</sub> for spring and fall,  
31 respectively. In the spring, the daytime carbonaceous fraction was 1.6–1.8 times higher than

1 the corresponding nighttime fraction, whereas during the fall, it was 1.1–1.2 times higher. The  
2 average OC/EC ratios ranged from 7.4 to 12.6 during this study. ~~A detailed~~Detailed  
3 information and analysis of the carbonaceous aerosol for this study can be found in Mancilla  
4 et al. (2015).

5 ~~All the samples~~All samples collected during this study were analyzed for ~~eight-seven~~ organic  
6 compound classes except those samples collected in the spring ~~of 2011~~of the 2011 campaign,  
7 for which carboxylic acids, wood smoke markers, and nitro-PAH compounds were not  
8 included for the chemical analysis. Therefore, the overall contribution of the resolved organic  
9 compounds to OC in the spring of 2011 is not directly comparable ~~to the last~~to that of the last  
10 three campaigns. For the ~~eight-seven~~ resolved compound classes in the last three campaigns  
11 (Fig. 2), the *n*-alkanoic acids were the most abundant, followed by *n*-alkanes, wood smoke  
12 markers, and levoglucosan/alkenoic acids. The PAHs and triterpanes hydrocarbons were less  
13 abundant. The same tendency was observed in the spring of 2011, except that the *n*-alkanes  
14 were the most abundant. The concentrations of nitro-PAH were neglected because their levels  
15 were below the detection limit of the method.

16 The daytime and nighttime concentrations of the resolved organics for the spring 2011  
17 accounted for  $0.49\pm 0.52\%$  and  $0.46\pm 0.41\%$  of the ambient OC, respectively. These  
18 contributions were much lower than the following three campaigns due ~~to some compounds~~to  
19 the fact that some compounds classes were not included. For spring 2012 and all fall  
20 campaigns, the total daytime concentrations of the resolved organics accounted for  
21  $7.58\pm 4.89\%$  and  $2.64\pm 1.82\%$  to  $4.67\pm 1.76\%$ , respectively, while the total nighttime  
22 concentrations accounted for  $11.0\pm 6.3\%$  and  $3.2\pm 2.4\%$  to  $8.0\pm 4.0\%$ , respectively. These  
23 observations are consistent with the findings that typically, around 84% of the fine OC is  
24 either non-extractable or will not elute from the GC column (Schauer and Cass, 2000). In the  
25 following ~~sections will be analyzed the organic composition of the fine organic aerosols~~  
26 using sections the organic composition of the fine organic aerosols will be analyzed using  
27 several diagnostic ratios to identify the primary emission sources. Then the relative  
28 contribution of each primary source to the PM<sub>2.5</sub> will be calculated by using the CMB receptor  
29 model.

### 1 3.2 *n*-Alkanes and Hopanes

2 The *n*-alkanes have two main sources: petroleum product utilization and natural vegetation  
3 waxes. The latter source consists of the longer chain plant lipids ( $>C_{20}$ ) as *n*-alkanes (Simoneit  
4 and Mazurek, 1982). In this study, the *n*-alkanes in the range of  $C_{17}$ – $C_{33}$  were detected. For  
5 the samples collected for spring 2011 and fall 2011, the average daytime and nighttime  
6 concentrations of *n*-alkanes were 1.6 and 2.3 times higher for the fall than the spring,  
7 respectively. This is consistent with the high contribution of the OC to  $PM_{2.5}$  and the lowest  
8 OC/EC ratios exhibited during the fall (Mancilla et al., 2015). In addition, the average  
9 temperature in the fall was 18.7–22.1°C versus 27.8–29.4°C in the spring. Low temperatures  
10 typically promote the utilization of petroleum products. In Mexico, the government sets the  
11 tariff-rates for the electric energy consumption with regard to the temperature; during the cold  
12 seasons the government removes the subsidy to the domestic electric energy due to the  
13 demand on fossil fuels in those seasons, and the sampling years of this study were not the  
14 exception (SENER, 2013). The average CPI values of *n*-alkanes in the spring were  $1.5 \pm 0.3$   
15 (range: 1.1–1.9) in the daytime and  $1.7 \pm 0.5$  (range: 1.1–2.6) in the nighttime, while the CPI  
16 values in the fall were  $1.0 \pm 0.3$  (range: 0.7–1.2) in the daytime and  $0.9 \pm 0.1$  (range: 0.7–1.0) in  
17 the nighttime. The CPI values in the spring suggest the mixed contribution of anthropogenic  
18 and biogenic ~~emissions sources~~ emission sources, whereas those values in the fall indicated a  
19 dominance of anthropogenic emissions. In addition, the contribution of anthropogenic  
20 emission sources is confirmed by the presence of petroleum biomarkers (hopanes: range of  
21 0.06 to 2.36  $ng\ m^{-3}$ ) and *n*-alkanes  $\leq C_{25}$  (Fig. 3). For the fall, the average daytime and  
22 nighttime concentrations of hopanes were 2.3 and 4.2 times higher than in the spring,  
23 respectively. Similarly, the presence of biogenic emissions due to  $C_{max}$  was found at  $C_{27}$ ,  $C_{29}$ ,  
24 or  $C_{31}$  (Fig. 3). These carbons' number dominance and trace levels of hopanes are  
25 characteristics of plant wax emissions and urban traffic emissions, respectively (Standley and  
26 Simoneit, 1987; Cass, 1998; Simoneit et al., 2004).

27 For the spring 2012 and fall 2012, the behavior of *n*-alkanes was the opposite ~~of the 2011 of~~  
28 2011. The average daytime and nighttime concentrations of *n*-alkanes were 1.5 and 2.0 times  
29 higher in the spring than in the fall, respectively. The EC levels remained similar to those ~~of~~  
30 the 2011 of 2011, but the OC levels were higher during the fall 2012 increasing the OC/EC  
31 ratios. Some of these ratios exhibited high peaks suggesting a contribution from primary  
32 emission sources with elevated OC/EC ratios like biomass burning (Mancilla et al., 2015).

1 The average temperature in the fall was 23.5–26.4°C versus 28.0–30.7°C in the spring. The  
2 average fall temperatures were not consistent with the average of 2011. In the fall of 2012, the  
3 warmer temperatures might have promoted less utilization of some fuels compared to the  
4 2011 in which lower temperatures could have promoted their utilization, increasing the *n*-  
5 alkanes' concentrations in fall 2011. The average CPI values of *n*-alkanes in the spring 2012  
6 were 0.9±0.1 (range: 0.8–1.1) in the daytime and 1.2±0.1 (range: 1.2–1.3) in the nighttime,  
7 while the CPI values in the fall 2012 were 1.3±0.1 (range: 1.0–1.4) in the daytime and 1.5±0.2  
8 (range: 1.3–1.6) in the nighttime. From these CPI values, it appears that biogenic emissions  
9 are relevant in all sampling periods. For spring 2012 daytime, the emissions appear to be  
10 heavily dominated by anthropogenic emissions due to the low CPI value exhibited. The  
11 presence of petroleum biomarkers supports the relative contribution of anthropogenic  
12 emissions. However, in 2012 the hopanes levels were ~35% lower at daytime and ~43%  
13 lower at nighttime than those in the previous year. The low hopane levels (range of 0.10 to  
14 1.49 ng m<sup>-3</sup>) highlight the possible presence of biogenic emissions (Fig. 2).

### 15 **3.3 PAHs**

16 Twelve PAH compounds, fluoranthene (FLT), acephenanthrylene (ACE), pyrene (PYR),  
17 benzo(a)anthracene (BAA), chrysene (CRY), benzo(k)fluoranthene + benzo(b)fluoranthene  
18 (BFA), **b**Benzo(a)pyrene + **b**Benzo(e)pyrene (BaP+BeP), perylene (PER),  
19 indeno(123cd)pyrene (IP), benzo(ghi)perylene (BgP), dibenz(ah)anthracene (DaA), and  
20 coronene (Cor), were identified in the MMA ~~fine OC samples~~fine samples. For both sampling  
21 years, the average daytime and nighttime concentrations of PAHs were 1.4–5.9 and 1.4–2.4  
22 times higher in the fall than in the spring, respectively. This is consistent with the high  
23 contribution of the OC to the PM<sub>2.5</sub> during the falls. Independently of the season, the daytime  
24 concentrations were 1.3–1.6 times higher than nighttime concentrations. These seasonal  
25 differences are consistent with the results of Guo et al. (2003) and Li et al. (2006), where PAH  
26 levels were 2–4 and 14.4 times higher in the cold seasons than in the warm seasons,  
27 respectively.

28 As ~~illustrated by~~illustrated in Fig. 4, the high molecular weight (HMW) PAHs were the most  
29 abundant for the MMA. The presence of HMW PAHs such as BaP+BeP, IP, and BgP is an  
30 indication of gasoline-powered vehicle emissions (Katsoyiannis et al, 2011; Tobiszewski and  
31 Namieśnik, 2012). In addition, a possible contribution of diesel-powered vehicles is indicated

1 by the low concentrations of the low molecular weight (LMW) PAHs such as FLT, PYR, and  
2 CRY. To identify the emission sources of PAH, diagnostic ratios were calculated (Table 4).  
3 These ratios should be used with caution ~~due to PAHs~~because PAHs are emitted from a  
4 variety of emission sources, particularly combustion sources, and their profiles can be  
5 modified due to their reactivity (Tsapakis et al., 2002). From these ratios, ~~it would be~~  
6 ~~determined the source origin (e.g. the source could be determined (e.g.,~~ pyrogenic and  
7 petrogenic sources). Then, these qualitative conclusions will be considered for the source  
8 apportionment to estimate the relative contribution of primary emission sources. The average  
9 ratios of IP/(IP+BgP) indicate that ambient PAHs in the MMA originated from gasoline and  
10 diesel combustion, whereas the ratios of BAA/(BAA+CRY) show the presence of petrogenic  
11 sources as well as vehicle emissions. To complement these results, the ratios of  
12 (BaP+BeP)/BgP identified a marked contribution of non-traffic sources for the spring of 2011,  
13 traffic ~~source for~~sources for the fall 2011 and the spring 2012, and mixed-sources for the fall  
14 2012. ~~Presence of~~the presence of gas-phase PAHs was not evaluated and thus no  
15 information on gas/particle partitioning of these semivolatile species is available. Thus, only  
16 diagnostic ratios for HMW PAHs were calculated for this study because those PAHs exhibit  
17 low volatility (Kavouras et al, 1999).

18 In this study, the average total concentrations of the quantified PAHs (TPAHs) were  
19  $2.42 \pm 2.45 \text{ ng m}^{-3}$  (range: 0.65–8.31  $\text{ng m}^{-3}$ ) and  $4.11 \pm 2.62 \text{ ng m}^{-3}$  (range: 1.42–11.97  $\text{ng m}^{-3}$ )  
20 during 2011 and 2012, respectively, whilst those quantified by González-Santiago (2009) at  
21 two different sites in the MMA were  $1.30 \pm 1.64 \text{ ng m}^{-3}$  (range: 0.05–6.93  $\text{ng m}^{-3}$ ) and  
22  $1.70 \pm 1.88 \text{ ng m}^{-3}$  (range: 0.07–9.14  $\text{ng m}^{-3}$ ). The lowest concentrations were obtained during  
23 the spring because its average temperature was statistically higher than during the fall seasons  
24 ( $p < 0.05$ ). The volatility of PAH increases with temperature; as a result low concentrations are  
25 obtained in comparison with fall and winter seasons. For this study the concentrations of PAH  
26 were lower during the spring than concentrations during fall; this pattern was exhibited during  
27 the two sampling years. González-Santiago (2009) identified only six PAHs, while in this  
28 study were identified twelve. In the current study, the total concentrations calculated for the  
29 six common PAHs were from 3 to 8 times higher than those estimated by González-Santiago  
30 (2009). Similar concentrations (between  $0.04 \text{ ng/m}^3$  and  $1.78 \text{ ng/m}^3$ ) were also reported for  
31 six individual PAHs in urban samples collected in Mexico City (Stone et al., 2008). Of the  
32 same PAHs identified among these studies, their levels were in the same concentration range.

1 However, the TPAH levels in the MMA compared to those calculated by Marr et al. (2006)  
2 (20–100 ng m<sup>-3</sup>) in Mexico City were found at appreciably lower concentrations. In addition,  
3 Marr et al. (2006) suggest that vehicles are the major source of PAHs. They demonstrated that  
4 PAHs and carbon monoxide (CO) concentrations are well correlated in Mexico City and,  
5 given that 99% of CO emissions are emitted by motor vehicles, this source is a major  
6 contribution of PAH emissions. For the current study, daytime correlations ( $r$ ) of +0.76 ( $p >$   
7 0.05) were found between TPAH and CO, reinforcing the conclusion that motor vehicles are  
8 one major source of PAH emissions for the MMA. The concentrations of CO during this  
9 study were obtained from the SIMA network.

10 The total PAH (TPAH) concentrations were compared with the EC and OC levels. TPAH  
11 concentrations measured in the MMA exhibited fair daytime correlations with EC ( $r=+0.79$ ;  
12  $p>0.05$ ), but low correlations with OC ( $r=+0.57$ ;  $p>0.05$ ). According to Marr et al. (2004), the  
13 strong correlation between TPAH and EC indicated the relative contribution of diesel-  
14 powered vehicle exhaust, while weak correlations may be due to the low concentrations of EC  
15 determined during this study (Mancilla et al., 2015). Furthermore, the weak correlation  
16 between TPAH and EC suggests the presence of emission sources with an elevated OC/EC.

### 17 **3.4 *n*-Alkanoic acids**

18 The carboxylic acids or *n*-alkanoic acids are mainly derived from biogenic emissions (Rogge  
19 et al., 1993b). However, these acids have also been identified in several primary sources such  
20 as cooking operations (Rogge et al., 1991; Schauer et al., 2001b) and fossil fuel combustion  
21 (Schauer et al., 2002). The *n*-alkanoic acids from C<sub>10</sub> to C<sub>32</sub> were quantified only for the three  
22 last monitoring campaigns. The *n*-alkanoic acids were the most abundant, accounting for  
23 69±16% at daytime and 78±11% of the total resolved organics at nighttime for both spring  
24 and fall. The daytime and nighttime concentration levels were two times higher in the spring  
25 than in the fall. As can be seen in Fig. 5, the *n*-alkanoic acids measured in the MMA were  
26 dominated by hexadecanoic acid (palmitic acid) and octadecanoic acid (stearic acid). This  
27 dominance is consistent with measurements in other locations (Fraser et al., 2002; Simoneit  
28 2004; Li et al., 2006).

29 The average CPI values of *n*-alkanoic acids in the fall of 2011 were 4.3±1.0 (range: 3.3–5.3)  
30 during the day and 5.0±0.4 (range: 4.6–5.4) at night. For the 2012 year the CPI values in the  
31 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,

1 while the CPI values in the fall were  $4.7 \pm 0.3$  (range: 4.3–5.1) during the day and  $5.3 \pm 1.1$   
2 (range: 4.0–6.8) at night. These elevated CPI values indicated the significant influence of  
3 biogenic sources such as microbial and plant wax sources. The *n*-alkanoic acids  $<C_{20}$  are  
4 derived in part from microbial sources while those  $>C_{20}$  are from vascular plant waxes (Guo  
5 et al., 2003; Yue and Fraser, 2004; Simoneit et al., 2004). Fig. 5 clearly shows influence of  
6 long chain ( $>C_{20}$ ) plant wax particles for the MMA. The CPI values in this study were  
7 consistent with those obtained by Wang and Kawamura (2005) (CPI: 5.3–10) and Yue and  
8 Fraser (2004) (CPI: 3.2–11.2). Regardless of the elevated CPI values obtained for the MMA,  
9 the values were not as high as those reported by the other mentioned studies due to a scarcity  
10 of green vegetation covers in the MMA.

11 The *n*-alkenoic acids only ~~included the cis-9-Octadecenoic acid~~included cis-9-octadecenoic  
12 acid (oleic acid) and trans-9-octadecenoic acid (elaidic acid). The concentrations of cis-9-  
13 octadecenoic acid~~is-9-Octadecenoic acid~~ ranged from  $0.96 \text{ ng m}^{-3}$  to  $15.38 \text{ ng m}^{-3}$ , while  
14 the concentrations of trans-9-octadecenoic acid ranged from  $2.11 \text{ ng m}^{-3}$  to  $13.35 \text{ ng m}^{-3}$ . The  
15 ratio of octadecanoic acid to cis-9-octadecenoic acid~~is-9-Octadecenoic acid~~ has been used as  
16 an indicator of the atmospheric chemical processing (aging) of aerosols, since the unsaturated  
17 acids are susceptible to atmospheric ~~oxidation from gaseous precursors~~oxidation (Brown et  
18 al., 2002; Yue and Fraser, 2004). In this study, the average ratios were 5.0 (range: 1.5–9.4)  
19 during the day and 3.8 (range: 2.5–4.9) at night for the spring, ~~while versus~~ 20.3 (range: 4.7–  
20 38.6) during the day and 21.0 (range: 10.5–29.1) at night for the fall. The transport of aerosols  
21 from local and rural sources can lead to the loss of cis-9-octadecenoic acid~~is-9-Octadecenoic~~  
22 ~~acid~~ producing high octadecanoic acid to cis-9-octadecenoic acid~~is-9-Octadecenoic acid~~  
23 ratios. ~~By contrast~~Similarly, the stagnation of aerosols may reflect the impact of high oxidant  
24 concentrations in an urban atmosphere producing ~~low ratios~~high ratios (Brown et al., 2002;  
25 Yue and Fraser, 2004). Therefore, these ratios suggest that the ambient organic aerosols for  
26 the MMA were aged and might be produced from transport and atmospheric oxidation. Air  
27 circulation patterns (Hysplit backward trajectories) during these monitoring campaigns  
28 suggested a long-range transport from the northeast and southeast (Mancilla et al., 2015). As  
29 expected, the lowest and highest octadecanoic acid to cis-9-octadecenoic acid~~is-9-~~  
30 ~~Octadecenoic acid~~ ratios obtained for the MMA were consistent with the highest OC/EC  
31 ratios estimated for the MMA for the same campaign; high OC/EC ratios identified transport  
32 and stagnation scenarios for the spring and fall, respectively (Mancilla et al., 2015). In



1 addition, these results are in line with those reported by Brown et al. (2002) and Yue and  
2 Fraser (2004), who obtained ratios of 5-11 and 1.0–21.5, respectively.

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

9

### 10 **3.5 Meat cooking and biomass burning tracers**

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

14 There was not a clear trend between spring and fall samples during the two sampling years for  
15 steroids (Table S1). However, the evidence of cooking operations' impact on the MMA was  
16 confirmed by the presence of cholesterol and stigmasterol along with hexadecanoic acid,  
17 octadecanoic acid, and oleic acid. Although cholesterol is considered a good marker for meat  
18 cooking, studies have reported unexpectedly high levels of cholesterol from non-cooking  
19 related sources such as soil and prescribed burns (Sheesley et al., 2004; Lee et al., 2005;  
20 Robinson et al., 2006a).

21 Anhydrosaccharides are the tracers from burning cellulose and hemicelluloses, whereas the  
22 methoxyphenols the tracer from burning of lignin (Giri et al., 2013). Levoglucosan, a  
23 combustion and pyrolysis product of cellulose, is the main biomarker used to track biomass  
24 burning emissions (Schauer et al., 2001a). Levoglucosan was not detected in all collected  
25 samples. The levoglucosan found in ~~the OC sample~~the samples indicates that biomass  
26 burning is impacting the MMA to some extent (Table S1). The levoglucosan concentrations  
27 varied by sampling dates, ranging from not detectable levels to 54 ng m<sup>-3</sup> for spring. In  
28 contrast, levoglucosan was detected in all fall samples, ranging from 0.14 to 28 ng m<sup>-3</sup>. The  
29 intermittent peaks of levoglucosan concentrations during the springtime can be explained by  
30 the fact that Northeastern Mexico's atmosphere is highly influenced by forest wildfires and  
31 prescribed agricultural burnings during the spring (Mendoza et al., 2005); this is in line with



1 the idea that high OC/EC ratios obtained, in a parallel study, were influenced in part by  
2 regional transport emissions (Mancilla et al., 2015). In the case ~~of fall~~of the fall seasons, the  
3 levoglucosan levels can be associated with local biomass burning due to mild temperatures  
4 ~~exhibited~~encountered during these seasons; a local contribution can be associated with high  
5 OC/EC ratios and stagnation conditions determined for this period (Mancilla et al., 2015). The  
6 high OC/EC ratios during spring may have a contribution from primary sources with  
7 elevated OC/EC ratios. The low and variable levoglucosan concentrations in this study  
8 indicate that wood/vegetation smoke episodes were occasional at the urban site. Average  
9 levoglucosan concentrations of 112.9 ng m<sup>-3</sup> and 151.3 ng m<sup>-3</sup> were reported at urban and  
10 peripheral sites for Mexico City, respectively (Stone et al., 2008). Based on an average  
11 concentration of levoglucosan, Mexico City exhibited from 5 to 7 times higher levels than the  
12 MMA. These results are consistent with the concentrations of OC and EC obtained ~~in the~~  
13 ~~Mexico~~in Mexico City; the EC concentrations were up to two times higher than those  
14 ~~calculated~~inobserved in the MMA, whereas the OC concentrations were from 2 to 6 times  
15 higher. A study conducted in Houston, TX, during August-September reported elevated  
16 concentrations of levoglucosan: up to 234 ng m<sup>-3</sup> (Yue and Fraser, 2004). Similarly, a study  
17 conducted for 14 cities in China during summer and winter, also reported elevated  
18 levoglucosan concentrations of 259 ng m<sup>-3</sup> (Wang et al., 2006). However, in those studies the  
19 vegetation around the sampling sites included a vast number of parks and woody shrubs,  
20 suggesting a major biomass burning contribution contrary to the MMA. Apart from those  
21 studies, Zheng et al. (2002) reported elevated levoglucosan concentrations of 166–307 ng m<sup>-3</sup>  
22 for urban areas of similar surroundings to the MMA. In this case, it is also possible that the  
23 levoglucosan emissions reported come from industries that have implemented biomass  
24 burning processes for energy generation. As can be seen from the previous comparison, the  
25 contribution of biomass burning is minor for the MMA in comparison with other urban  
26 locations. In addition, biomass burning contributions are inconsistent with those reported in  
27 similar locations to the MMA.

28 The resin acids such as dehydroabietic acid, pimaric acid, and isopimaric acid (Table S1) are  
29 secondary tracers from biomass burning (Schauer et al., 2001a). Dehydroabietic acid was the  
30 most abundant resin acid, ranging from 1.94 to 4.39 ng m<sup>-3</sup> and 1.95 to 3.69 ng m<sup>-3</sup> for spring  
31 and fall, respectively. Then, pimaric acid ranged from not detectable levels to 0.09 ng m<sup>-3</sup> and  
32 from 0.15 to 0.35 ng m<sup>-3</sup> for spring and fall, respectively. Finally, isopimaric acid ranged

1 from not detectable levels to 0.03 ng m<sup>-3</sup> and from 0.06 to 0.12 ng m<sup>-3</sup> for spring and fall,  
2 respectively. The results for resin acids are in line with those obtained ~~for the levoglucosan for~~  
3 ~~levoglucosan~~. These results support the low impact from biomass burning emissions in the  
4 MMA, especially from softwood burning (e.g., conifer wood) during the spring and fall  
5 campaigns. In addition, the higher concentrations of resin acids in fall than in spring are  
6 associated with photochemical activity due to stagnation events in fall.

7

### 8 **3.6 Source Apportionment**

9 CMB was applied using the quantification of individual organic compounds found in the  
10 collected PM<sub>2.5</sub> samples. The relative contributions for gasoline-powered vehicles, diesel-  
11 powered vehicles, natural gas combustion, fuel oil combustion, meat cooking operations,  
12 vegetative detritus, and biomass burning were estimated. From the source categories selected,  
13 the ones corresponding to natural gas and fuel oil combustion were not determined as  
14 significant for some ambient samples. These two sources were determined to have  
15 contributions that were not statistically different from zero or were slightly negative and thus  
16 were excluded from the model. Model performance was determined by  $r^2$  values ranging  
17 between 0.58 and 0.85 and chi-squared ( $\chi^2$ ) values between 2.97 and 8.85. Similar values for  
18  $r^2$  and  $\chi^2$  have been obtained in Fraser et al. (2003) and Schneidmesser et al. (2009). The  
19 latter study used composites to perform the CMB. Another performance metric calculated by  
20 EPA-CMB8.2 is the percent mass explained. Theoretically, values ranging from 80% to 120%  
21 are acceptable. This ideally can occur when ambient data is not impacted heavily by SOA  
22 because CMB is only able to account accurately for primary sources. In spite of this  
23 limitation, CMB results with low percent mass explained values have been reported by some  
24 studies. In these cases, the high levels of unexplained mass have been associated with  
25 secondary production (Fraser et al., 2003; Zheng et al., 2005). For the 43 ambient samples fed  
26 to CMB in this study, 18 samples exhibited low percent mass explained values (ranging from  
27 20% to 77%), ~~whilst 14~~ ~~whereas~~ samples had values around 100%. These results are in line  
28 with the relative high and low OC/EC ratios obtained for spring and fall, respectively  
29 ~~Mancilla et al. (2015)~~ ~~(Mancilla et al., 2015)~~. Finally, 11 samples were discarded due to poor  
30 performance parameters calculated. These samples were not exclusively from a particular

1 monitoring campaign; there were samples from both springs and falls. A detailed description  
2 of the CMB performance and relative contributions for each sample can be found in Table S2.  
3 The average contributions of primary sources are shown in Table 5. The vehicle exhaust and  
4 meat-cooking ~~operations emissions for all monitoring campaigns were the highest. In~~  
5 ~~analysis~~operation emissions were the highest for all monitoring campaigns. When examining  
6 of the seasonal variation, the gasoline- and diesel-powered vehicles in falls were up to five  
7 times higher than in springs, when cold weather increases the demand of petroleum products  
8 due to low temperatures. The opposite occurred for meat-cooking operations, their spring  
9 emissions were three times higher than in fall seasons. The natural gas combustion, vegetative  
10 detritus and biomass burning emissions were very low and more constant throughout the  
11 springs and falls. ~~In analysis of the~~With regard to the daytime and nighttime variations, the  
12 vehicle exhaust were much higher during daytime when traffic is heavier. For the meat-  
13 cooking operations, the emissions were ~~some higher~~some what higher in nighttime during  
14 spring and more constant between daytime and nighttime during fall. For the rest of the  
15 sources, the daytime and nighttime emissions were relatively constant. ~~There are not~~  
16 ~~similar~~There were no similar studies conducted in the MMA, this is the first source  
17 apportionment study based on molecular organic markers for this region. However, these  
18 ~~results were similar~~results are similar to those obtained for the MMA using a factor analysis  
19 based on trace elements (Martinez et al., 2012) and those ~~for the Mexico~~for Mexico City  
20 based on molecular organic markers (Stone et al., 2008).

21 The average contribution of each emission category to the identified PM<sub>2.5</sub> mass is shown in  
22 Fig. 6. The unidentified mass was on average 35±24% of the measured PM<sub>2.5</sub> concentrations.  
23 This value is 1.5 times greater than the ~23% of secondary organic aerosol contribution to the  
24 total PM<sub>2.5</sub> mass concentration (SOC/PM<sub>2.5</sub>) estimated in Mancilla et al. (2015) for the MMA.  
25 The average secondary contribution used for this comparison was based on the minimum  
26 OC/EC ratios observed and reported in Mancilla et al. (2015). These ratios may take into  
27 account primary sources with elevated values of OC/EC ratios such as biomass burning and  
28 kitchen operations as well as fossil fuel combustion sources. The unidentified mass by CMB  
29 may include secondary organic and inorganic aerosol and trace elements. Thus, the levels of  
30 unidentified mass resolved by CMB are reasonable given that the secondary aerosol estimated  
31 in Mancilla et al. (2015) was in fact only SOA. Therefore, the 12% of difference between 35%  
32 and 23% might be attributed ~~to the secondary~~to secondary inorganic aerosol and other

1 chemical species. As indicated in Fig. 6, the emissions from motor vehicle exhausts (gasoline  
2 and diesel) are the most important, accounting for the 64% of the identified PM<sub>2.5</sub> emissions,  
3 followed by meat-cooking operations (31%) and industries (2.8%). ~~The vegetative~~  
4 ~~detritus~~ Vegetative detritus and biomass burning were ~~the less emitted~~ the least emitted with  
5 only 2.2% of the identified PM<sub>2.5</sub> emissions. The relative high contribution of the meat-  
6 cooking operations was expected given the high traditional restaurant activity in the MMA  
7 ~~which contribute with~~ which contributes with the 16% of the local growth domestic product.  
8 With regard to biomass burning, several studies have demonstrated that Mexico City has a  
9 large contribution of biomass burning emissions due to forests fires (Moffet et al., 2008; Stone  
10 et al., 2008; Yokelson et al., 2007). However, the MMA can be affected by other types of  
11 biomass burning (e.g., shrub and grassland fires, agricultural waste and garbage burning, etc.)  
12 that may be ignored. Therefore, the contribution of biomass burning in the MMA might be  
13 higher because the source profile used for the CMB was only for wood combustion instead of  
14 using a source profile for other types of biomass burning (Simoneit et al., 2005). ~~The MMA as~~  
15 ~~well as other urban areas can be affected by types of biomass burning, especially, when they~~  
16 ~~are not surrounded by forests. For examples, several studies have demonstrated that Mexico~~  
17 ~~City has large contribution from biomass burning (Moffet et al., 2008; Stone et al., 2008;~~  
18 ~~Yokelson et al., 2007) because it is affected by forests fires (Yokelson et al., 2007).~~  
19 ~~Conversely, the MMA has not forests around, therefore, the contribution from biomass~~  
20 ~~burning in the MMA might be higher because the source profile used for the CMB was only~~  
21 ~~for wood combustion instead of using a source profile for garbage, industrial, and urban~~  
22 ~~residues open fires (Simoneit et al., 2005).~~ In addition, ~~here is~~ it is important to point out the  
23 potential of industrial sources ~~due to prior~~ as appeared from previous studies conducted in the  
24 MMA and the rest of the country. The MMA is the third largest urban center of the country  
25 with approximately 9,700 industries (INEGI, 2005). In the MMA the main emissions from  
26 industrial sources come from the combustion of natural gas; low emissions come from the use  
27 of fuel oil. In this study the natural gas profile did not fit well and it was discarded from the  
28 CMB, but the fuel oil did it. The combustion of natural gas ~~emits low~~ emits a low amount of  
29 particles, therefore, its contribution to the airborne particles is not significant.

30

#### 31 **4 Conclusions**

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

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

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

24 The emissions from vehicle exhausts are the most important, accounting ~~for the~~for 64% of the  
25 identified PM<sub>2.5</sub> emissions. By contrast, ~~the vegetative detritus~~vegetative detritus and biomass  
26 burning were the ~~less contributors~~lowest contributors with barely 2.2% of the identified PM<sub>2.5</sub>  
27 emissions.

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

31

## 1 **Acknowledgements**

2 This work was supported by the Mexican National Council for Science and Technology  
3 (CONACYT) through grant number CB-2010-154122 and Tecnológico de Monterrey through  
4 grant number 0020CAT186. Yasmany Mancilla received additional support (a scholarship)  
5 through CONACYT. We appreciate the Integral System of Environmental Monitoring's  
6 support of the MMA during the field campaigns conducted in this study.

7

## 8 **References**

9 Abas, M. R. B., and Simoneit, B.: Composition of extractable organic matter of air particles  
10 from Malaysia: initial study, *Atmos. Environ.*, 30, 2779-2793, 1996.

11 Abas, M. R. B., Rahman, N. A., Omar, N. Y. M. J., Maah, M. J., Samah, A. A., Oros, D. R.,  
12 Otto, A., and Simoneit, B. R. T.: Organic composition of aerosol particulate matter during a  
13 haze episode in Kuala Lumpur, Malaysia-, *Atmos. Environ.*, 38, 4223-4241, doi:  
14 10.1016/j.atmosenv.2004.01.048, 2004.

15 [Akyüz, M., and Çabuk, H.: Gas-particle partitioning and seasonal variation of polycyclic](#)  
16 [aromatic hydrocarbons in the atmosphere of Zonguldak, Turkey., \*Sci. Total Environ.\* 408,](#)  
17 [5550-5558, 2010.](#)

18 Alves, C., Pio, C., and Duarte, A.: Composition of extractable organic matter of air particles  
19 from rural and urban pPortuguese areas, *Atmos. Environ.*, 35, 5485-5496, 2001.

20 Alves C., Oliveira, T., Pio, C., Silvestre, A. J. D., Fialho, P., Barata, F., and Legrand, M.:  
21 Characterisation of carbonaceous aerosols from the Azorean Island of Terceira, *Atmos.*  
22 *Environ.*, 41, 1359-1373, 2007.

23 Alves, C. A., Vicente, A., Monteiro, C., Gonçalves, C., Evtyugina, M., and Pio, C.: Emission  
24 of trace gases and organic components in smoke particles from wildfire in a mixed-evergreen  
25 forest in Portugal, *Sci. Total Environ.*, 409, 1466-1475, 2011.

26 Amador-Muñoz, O., Villalobos-Pietrini, R., Agapito-Nadales, M. C., Munive-Colín, Z.,  
27 Hernández-Mena, L., Sánchez-Sandoval, M., Gómez-Arroyo, S., Bravo-Cabrera, J. L., and  
28 Guzmán-Rincón, J.: Solvent extracted organic matter and polycyclic aromatic hydrocarbons  
29 distributed in size-segregated airborne particles in a zone of México City: sSeasonal behavior  
30 and human exposure, *Atmos. Environ.*, 44, 122-130, 2010.

1 ~~Antony Chen, L. W., Watson, J. G., Chow, J. C., DuBois, D. W., and Herschberger, L.:~~  
2 ~~PM2.5 source apportionment: reconciling receptor models for U. S. nonurban and urban long-~~  
3 ~~term networks, J. Air Waste Manage. Assoc. 61, 1204-1217, 2011.~~

4 Blanchard, C. L., Chow, J. C., Edgerton, E. S., Watson, J. G., Hidy, G. M., and Shaw, S.:  
5 Organic aerosols in the southeastern United States: sSpeciated particulate carbon  
6 measurements from the SEARCH network 2006-2010, Atmos. Environ., 95, 327-333, 2014.

7 Brown, S. G., Herckes, P., Ashbaugh, L., Hannigan, M. P., Kreidenweis, S. M., and Collett Jr,  
8 J. L.: Characterization of organic aerosol in Big Bend National Park, Texas, Atmos. Environ.,  
9 36, 5807-5818, doi: 10.1016/s1352-2310(02)00578-2, 2002.

10 Cass, G. R.: Organic molecular tracers for particulate air pollution sources, Trend. Anal.  
11 Chem., 17, 356-366, 1998.

12 Chen, L.-W. A., Watson, J. G., Chow, J. C., DuBois, D. W., and Herschberger, L.: PM2.5  
13 source apportionment: reconciling receptor models for U. S. nonurban and urban long-term  
14 networks, J. Air Waste Manage. Assoc. 61, 1204-1217, 2011.

15 Chow, J. C., Watson, J. G., Lowenthal, D. H., ~~Chen, W. A.~~ Chen, L. W. A., Zielinska, D.,  
16 Mazzoleni, L. R., Magliano, K. L.: Evaluation of organic markers for chemical mass balance  
17 source apportionment at the Fresno Supersite, Atmos. Chem. Phys., 7, 1741-1754, 2007.

18 Dvorská, A., Lammel, G., and Klánová, J.: Use of diagnostic ratios for studying source  
19 apportionment and reactivity of ambient polycyclic aromatic hydrocarbons over cCentral  
20 Europe, Atmos. Environ., 45, 420-427, doi: 10.1016/j.atmosenv.2010.09.063, 2011.

21 Duan, J., Tan, J., Cheng, D., Bi, X., Deng, W., Sheng, G., Fu, J., and Wong, M. H.: Sources  
22 and characteristics of carbonaceous aerosol in two largest cities in Pearl River Delta Region,  
23 China, Atmos. Environ., 41, 2895-2903. doi: 10.1016/j.atmosenv.2006.12.017, 2007.

24 Eatough, D. J., Benner, C. L., Tang, H., Landon, V., Richards, G., Caka, F. M., Crawford, J.,  
25 Lewis, E. A., Hansen, L. D., and Eatough, N. L.: The chemical composition of environmental  
26 tobacco smoke III. Identification of conservative tracers of environmental tobacco smoke,  
27 Environ. Int., 15, 19-28, 1989.

28 Feng, J., Hu, M., Chan, C. K., Lau, P. S., Fang, M., He, L., and Tang, X.: A comparative  
29 study of the organic matter in PM2.5 from three cChinese megacities in three different  
30 climatic zones, Atmos. Environ., 40, 3983-3994, doi: 10.1016/j.atmosenv.2006.02.017, 2006.



1 Fraser, M. P., Cass, G. R., and Simoneit, B. R. T.: Particulate organic compounds emitted  
2 from motor vehicle exhaust and in the urban atmosphere, *Atmos. Environ.*, 33, 2715-2724,  
3 1999.

4 Fraser, M. P. and Lakshmanan, K.: Using levoglucosan as a molecular marker for the long-  
5 range transport of biomass combustion aerosols, *Environ. Sci. Technol.*, 34, 4560-4564, 2000.

6 Fraser, M. P., Yue, Z. W., Tropp, R. J., Kohl, S. D., and Chow, J. C.: Molecular composition  
7 of organic fine particulate matter in Houston, TX, *Atmos. Environ.*, 36, 5751-5758, doi:  
8 10.1016/S1352-2310(02)00725-2, 2002.

9 Fraser, M. P., Yue, Z. W., and Buzcu, B.: Source apportionment of fine particulate matter in  
10 Houston, TX, using organic molecular markers, *Atmos. Environ.*, 37, 2117-2123, doi:  
11 10.1016/S1352-2310(03)00075-X, 2003.

12 García, C. D., Engling, G., Herckes, P., Collett, J. L., and Henry, C. S.: ~~Henry~~, Determination  
13 of ~~I~~levoglucosan from ~~s~~Smoke ~~s~~Samples ~~u~~Using ~~m~~Microchip ~~c~~Capillary ~~e~~Electrophoresis  
14 with ~~p~~Pulsed ~~a~~Amperometric ~~d~~Detection, *Environ. Sci. Technol.*, 39, 618-623, 2005.

15 Gelencsér, A. (Eds) A.: Carbonaceous aerosol: ~~a~~Atmospheric and ~~o~~Oceanographic ~~s~~Sciences  
16 ~~L~~ibrary, Springer Publications, Dordrecht, The Netherlands, 2004.

17 Giri, B., Patel, K. S., Jaiswal, N. K., Sharma, S., Ambade, B., Wang, W., Simonich, S. L. M.,  
18 Simoneit, B. R. T.: Composition and sources of organic tracers in aerosol particles of  
19 industrial central India, *Atmos. Res.*, 120-121, 312-324, 2013.

20 Gogou, A., Stratigakis, N., Kanakidou, M., and Stephanou, E. G.: Organic aerosols in  
21 ~~e~~Eastern Mediterranean: components source reconciliation by using molecular markers and  
22 atmospheric back trajectories, *Org. Geochem.*, 25, 79-96, doi:  
23 [http://dx.doi.org/10.1016/S0146-6380\(96\)00105-2](http://dx.doi.org/10.1016/S0146-6380(96)00105-2), 1996.

24 Gonçalves, C., Alves, C., Fernandes, A. P., Monteiro, C., Tarelho, L., Evtugina, M., and Pio,  
25 C.: Organic compounds in PM<sub>2.5</sub> emitted from fireplace and woodstove combustion of  
26 typical ~~p~~Portuguese ~~w~~Wood species, *Atmos. Environ.*, 45, 4533-4545, 2011.

27 González-Santiago, O.: Determinación del contenido de PAH's en partículas PM<sub>2.5</sub> en una  
28 zona de alto tráfico vehicular y otra con potencial exposición industrial del Área  
29 Metropolitana de Monterrey, Ph.D. thesis, Facultad de Ciencias Químicas, Universidad  
30 Autónoma de Nuevo León (UANL), Mexico, 104 pp., 2009.



1 Guo, Z. G., Sheng, L. F., Feng, J. L., and Fang, M.: Seasonal variation of solvent extractable  
2 organic compounds in the aerosols in Qingdao, China, *Atmos. Environ.*, 37, 1825-1834, 2003.

3 Harrad, S., Hassoun, S., Callén Romero, M. S., and Harrison, R. M.: Characterisation and  
4 source attribution of the semi-volatile organic content of atmospheric particles and associated  
5 vapour phase in Birmingham, UK, *Atmos. Environ.*, 37, 4985-4991, 2003.

6 Henry, R. C., Lewis, C. W., Hopke, P. K., and Williamson, H. J.: Review of receptor model  
7 fundamentals, *Atmos. Environ.*, 18, 1507-1515, 1984.

8 Hildemann, L. M., Markowski, G. R., and Cass, G. R.: Chemical composition of emissions  
9 from urban sources of fine organic aerosol, *Environ. Sci. Technol.*, 25, 744-759, 1991.

10 Hopke, P. K.: It is time to drop principal components analysis as a “receptor model”, *J.*  
11 *Atmos. Chem.*, 72, 127-128, 2015.

12 Huang, X.-F., He, L.-Y., Hu, M., and Zhang, Y.-H.: Annual variation of particulate organic  
13 compounds in PM<sub>2.5</sub> in the urban atmosphere of Beijing, *Atmos. Environ.*, 40, 2449-2458.  
14 doi: 10.1016/j.atmosenv.2005.12.039, 2006.

15 ~~INEGI~~, INEGI: Annual statistics of Nuevo Leon, Monterrey, Nuevo León, Mexico, 2005.

16 ~~INEGI~~, INEGI: Estadísticas de vehículos de motor registrados en circulación. Available in:  
17 [http://www.inegi.org.mx/est/contenidos/espanol/proyectos/continuas/economicas/bd/transporte/  
18 Vehiculos.asp?s=est&c=13158](http://www.inegi.org.mx/est/contenidos/espanol/proyectos/continuas/economicas/bd/transporte/Vehiculos.asp?s=est&c=13158), 2010.

19 ~~INEGI~~, INEGI: Censo de población y vivienda 2010. Available in:  
20 [www.inegi.org.mx/sistemas/consulta\\_resultados/iter2010.aspx?c=27329&s=est](http://www.inegi.org.mx/sistemas/consulta_resultados/iter2010.aspx?c=27329&s=est), 2011.

21 Kalaitzoglou, M., Terzi, E., and Samara, C.: Patterns and sources of particle-phase aliphatic  
22 and polycyclic aromatic hydrocarbons in urban and rural sites of western Greece, *Atmos.*  
23 *Environ.*, 38, 2545-2560, 2004.

24 Katsoyiannis, A., Sweetman, A. J., and Jones, K. C.: PAH molecular diagnostic ratios applied  
25 to atmospheric sources: a critical evaluation using two decades of source inventory and air  
26 concentration data from UK, *Environ. Sci. Technol.*, 45, 8897-8906, 2011.

27 Kavouras, I. G., Lawrence, J., Koutrakis, P., Stephanou, E. G., Oyola, P.: Measurements of  
28 particulate aliphatic and polynuclear aromatic hydrocarbons in Santiago de Chile: source  
29 reconciliation and evaluation of sampling artifacts, *Atmos. Environ.*, 33, 4977-4986, 1999.

1 Kavouras, I. G., Stratigakis, N., and Stephanou, E. G.: Iso and anteiso-Alkanes: specific  
2 tracers of environmental tobacco smoke in indoor and outdoor particle-size distributed urban  
3 aerosols, *Environ. Sci. Technol.*, 32, 1369-1377, 1998.

4 Ke, L., Ding, X., Tanner, R. L., Schauer, J. J., and Zheng, M.: Source contributions to  
5 carbonaceous aerosols in the Tennessee Valley Region, *Atmos. Environ.*, 41, 8898-8923,  
6 2007.

7 Kelly, K. E., Kotchenruther, R., Kuprov, R., and Silcox, G. D.: Receptor model source  
8 attributions for Utah's Salt Lake City airshed and the impacts of wintertime secondary  
9 ammonium nitrate and ammonium chloride aerosol, *J. Air Waste Manage. Assoc.*, 63, 575-  
10 590, 2015.

11 Kleeman, M. J., Riddle, S. G., Robert, M. A., Jakober, C. A., Fine, P. M., Hays, M. D.,  
12 Schauer, J. J., Hannigan, M. P.: Source apportionment of fine (PM<sub>1.8</sub>) and ultrafine (PM<sub>0.1</sub>)  
13 airborne particulate matter during a severe winter pollution episode, *Environ. Sci. Technol.*,  
14 43, 272-279, 2009.

15 Lee, S., Baumann, K., Schauer, J. J., Sheesley, R. J., Naeher, L. P., Meinardi, S., Blake, D. R.,  
16 Edgerton, E. S., Russell, A. G., Clements, M.: Gaseous and particulate emissions from  
17 prescribed burning in Georgia, *Environ. Sci. Technol.*, 39, 9049-9056, 2005.

18 Li, M., McDow, S. R., Tollerud, D. J., and Mazurek, M. A.: Seasonal abundance of organic  
19 molecular markers in urban particulate matter from Philadelphia, PA, *Atmos. Environ.*, 40,  
20 2260-2273, doi: 10.1016/j.atmosenv.2005.10.025, 2006.

21 Lin, L., Lee, M. L., and Eatough, D. J.: Review of recent advances in detection of organic  
22 markers in fine particulate matter and their use for source apportionment, *J. Air Waste  
23 Manage. Assoc.*, 60, 3-25, 2010.

24 Mancilla, Y., and Mendoza, D.: A tunnel study to characterize PM<sub>2.5</sub> emissions from gasoline-  
25 powered vehicles in Monterrey, Mexico, *Atmos. Environ.*, 59, 449-460, 2012.

26 Mancilla, Y., Herckes, P., Fraser, M. P., and Mendoza, A.: Secondary organic aerosol  
27 contributions to PM<sub>2.5</sub> in Monterrey, Mexico: Temporal and seasonal variation, *Atmos. Res.*,  
28 153, 348-359, 2015.

29 Marr, L. C., Grogan, L. A., Wöhrnschimmel, H., Molina, L. T., Molina, M. J., Smith, T. J.,  
30 and Garshick, E.: Vehicle Traffic as a Source of Particulate Polycyclic Aromatic

1 [hHydrocarbon eExposure in the Mexico City mMetropolitan aArea](#), Environ. Sci. Technol.,  
2 38, 2584-2592, doi: 10.1021/es034962s, 2004.

3 Marr, L. C., Dzepina, K., Himenez, J. L., Reisen, F., Bethel, H. L., Arey, J., Gaffney, J. S.,  
4 Marley, N. A., Molina, L. T., and Molina, M. J.: Sources and transformations of particle-  
5 bound polycyclic aromatic hydrocarbons in Mexico City, Atmos. Chem. Phys., 6, 1733-1745,  
6 2006.

7 Martinez, M. A., Caballero, P., Carrillo, O., Mendoza, A., and Mejía, M. [G.](#): Chemical  
8 characterization and factor analysis of PM<sub>2.5</sub> in two sites of Monterrey, Mexico, J. Air Waste  
9 Manage. Assoc., 62, 817-827, 2012.

10 Mendoza, A., García, M. R., Vela, P., Lozano, D. F., and Allen, D.: Trace gases and  
11 particulate matter emissions from wildfires and agricultural burning in northeastern Mexico  
12 during the 2000 fire season, J. Air Waste Manage. Assoc., 55, 1797-1808, 2005.

13 Moffet, R. C., de Foy, B., Molina, L. T., Molina, M. J., and Prather, K. A.: Measurement of  
14 ambient aerosols in northern Mexico City by single particle mass spectrometry, Atmos. Chem.  
15 Phys., [8](#), 4499-4516, 2008.

16 Noziere, B., Kalberer, M., Claeys, M., Allan, J., D'Anna, B., Decesari, S., Finessi, E., Glasius,  
17 M., Grgic, I., Hamilton, J. F., Hoffmann, T., Linuma, Y., Jaoui, M., Kahnt, A., Kampf, C. J.,  
18 Kourtchev, I., Maenhaut, W., Marsden, N., Saarikoski, S., Schnelle-Kreis, J., Surratt, J. D.,  
19 Szidat, Sönke, Szmigielski, R., and Wisthalder, A.: The molecular identification of organic  
20 compounds in the atmosphere: state of the art and challenges, Chemical Reviews, 115, 3919-  
21 3983, 2015.

22 Oros, D. R., and Simoneit, B. R. T.: Identification and emission rates of molecular tracers in  
23 coal smoke particulate matter, Fuel, 79, 515-536, 2000.

24 [Paatero, P.: Least squares formulation of robust non-negative factor analysis. Chemometr.](#)  
25 [Intell. Lab., 37, 23-35, 1997.](#)

26 Park, S. S., Bae, M.-S., Schauer, J. J., Kim, Y. J., Yong Cho, S. and Jai Kim, S.: Molecular  
27 composition of PM<sub>2.5</sub> organic aerosol measured at an urban site of Korea during the ACE-  
28 Asia campaign, Atmos. Environ., 40, 4182-4198, doi: 10.1016/j.atmosenv.2006.02.012, 2006.

29 Peng, R. D., Bell, M. L., Geyh, A. S., McDermott, A., Zeger, S. L., Samet, J. M. and  
30 Dominici, F.: Emergency admissions for cardiovascular and respiratory diseases and the

1 chemical composition of fine particle air pollution, *Environ. Health Persp.*, 117, 957-963,  
2 2009.

3 Perrone, M. G., Larsen, B. R., Ferrero, L., Sangiorgi, G., De Gennaro, G., Udisti, R.,  
4 Zangrano, R., Gambaro, A., Bolzacchini, E.: Source of high PM<sub>2.5</sub> concentrations in Milan,  
5 ~~n~~Northern Italy: Molecular marker data and CMB modelling, *Sci. Total Environ.*, 414, 343-  
6 355, 2012.

7 ~~Paatero, P.: Least squares formulation of robust non-negative factor analysis. *Chemometr.*  
8 *Intell. Lab.*, 37, 23-35, 1997.~~

9 Pietrogrande, M. C., Abbaszade, G., Schnelle-Kreis, J., Bacco, D., Mercuriali, M., and  
10 Zimmermann, R.: Seasonal variation and source estimation of organic compounds in urban  
11 aerosol of Augsburg, Germany. *Environ. Pollut.*, 159, 1861-1868, 2011.

12 Plewka, A., Gnauk, T., Brüggemann, E., and Herrmann, H.: Biogenic contributions to the  
13 chemical composition of airborne particles in a coniferous forest in Germany, *Atmos.*  
14 *Environ.*, 40, 103-115. doi: <http://dx.doi.org/10.1016/j.atmosenv.2005.09.090>, 2006.

15 Pope, C. A. III, Burnett, R. T., Thun, M. J., Calle, E. E., Krewski, D., Ito, K., and Thurston,  
16 G. D.: Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air  
17 pollution, *J. Amer. Med. Assoc.*, 287, 1132-1141, 2002.

18 Qin, Y., Kim, E., and Hopke, P. K.: The concentrations and sources of PM<sub>2.5</sub> in metropolitan  
19 New York City, *Atmos. Environ.*, 40, S312-S332, 2006.

20 Ravindra, K., Sokhi, R., and Van Grieken, R.: Atmospheric polycyclic aromatic  
21 hydrocarbons: ~~s~~Source attribution, emission factors and regulation, *Atmos. Environ.*, 42,  
22 2895-2921. doi: [10.1016/j.atmosenv.2007.12.010](https://doi.org/10.1016/j.atmosenv.2007.12.010), 2008.

23 Reff, A., Eberly, S. I., and Bhave, P. V.: Receptor modeling of ambient particulate matter data  
24 using positive matrix factorization: review of existing methods, *J. Air Waste Manage. Assoc.*,  
25 57, 146-154, 2007.

26 Robinson, A. L., Subramanian, R., Donahue, N. M., Bernardo-Bricker, A., and Rogge, W. F.:  
27 Source ~~a~~Apportionment of ~~m~~Molecular ~~m~~Markers and ~~o~~Organic ~~a~~Aerosol. 2. Biomass  
28 ~~s~~Smoke, *Environ. Sci. Technol.*, 40, 7811-7819. doi: [10.1021/es060782h](https://doi.org/10.1021/es060782h), 2006a.

1 Robinson, A. L., Subramanian, R., Donahue, N. M., Bernardo-Bricker, A. and Rogge, W. F.:  
2 Source aApportionment of mMolecular mMarkers and oOrganic aAerosol. 3. Food cCooking  
3 eEmissions, Environ. Sci. Technol., 40, 7820-7827. doi: 10.1021/es060781p, 2006b.

4 Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simoneit, B. R. T.:  
5 Sources of fine organic aerosol. 1. Charbroilers and meat cooking operations, Environ. Sci.  
6 Technol., 25, 1112-1125, doi: 10.1021/es00018a015, 1991.

7 Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simoneit, B. R. T.:  
8 Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and Heavy-  
9 duty diesel trucks, Environ. Sci. Technol., 27, 636-651, 1993a.

10 Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simoneit, B. R. T.:  
11 Sources of fine organic aerosol. 4. Particulate abrasion products from leaf surfaces of urban  
12 plants, Environ. Sci. Technol., 27, 2700-2711, doi: 10.1021/es00049a008, 1993b.

13 Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simoneit, B. R. T.:  
14 Sources of fine organic aerosol. 5. Natural gas home appliances, Environ. Sci. Technol., 27,  
15 2736-2744, 1993c.

16 Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R. and Simoneit, B. R. T.:  
17 Sources of fine organic aerosol. 6. Cigarette smoke in the urban atmosphere, Environ. Sci.  
18 Technol., 28, 1375-1388, 1994.

19 Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simoneit, B. R. T.:  
20 Sources of fine organic aerosol. 8. Boilers burning No. 2 distillate fuel oil, Environ. Sci.  
21 Technol., 31, 2731-2737, 1997.

22 Schantz, M., Poster, D., Kucklick, J., Wise, S., McDow, S., Lewtas, J.: NISTIR 7303,  
23 Intercomparison program for organic speciation in PM<sub>2.5</sub> air particulate matter: description  
24 and results for trial III. NIST, 2005.

25 ~~SRM 1649a; Urban Dust/Organics; National Institute of Standards and Technology; U.S.~~  
26 ~~Department of Commerce; Gaithersburg, MD (06 December 2007)~~

27 ~~SRM 1649b; Urban Dust/Organics; National Institute of Standards and Technology; U.S.~~  
28 ~~Department of Commerce; Gaithersburg, MD (23 February 2009)~~

29 Schauer, J. J. and Cass, G. R.: Source apportionment and particle-phase air pollutants using  
30 organic compounds as tracers, Environ. Sci. Technol., 34, 1821-1832, 2000.

1 Schauer, J. J., Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simoneit,  
2 B. R. T.: Source apportionment of airborne particulate matter using organic compounds as  
3 tracers, *Atmos. Environ.*, 30, 3837-3855, 1996.

4 Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of Emissions  
5 from Air Pollution Sources. 1. C1 through C29 organic compounds from meat charbroiling,  
6 *Environ. Sci. Technol.*, 33, 1566-1577, 1999.

7 Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of Emissions  
8 from Air Pollution Sources. 3. C1–C29 Organic Compounds from Fireplace Combustion of  
9 Wood, *Environ. Sci. Technol.*, 35, 1716-1728. doi: 10.1021/es001331e, 2001a.

10 Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of Emissions  
11 from Air Pollution Sources. 4. C1–C27 Organic Compounds from Cooking with Seed Oils,  
12 *Environ. Sci. Technol.*, 36, 567-575, doi: 10.1021/es002053m, 2001b.

13 Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of Emissions  
14 from Air Pollution Sources. 5. C1–C32 Organic Compounds from Gasoline-Powered Motor  
15 Vehicles, *Environ. Sci. Technol.*, 36, 1169-1180, doi: 10.1021/es0108077, 2002.

16 Schneidmesser, E. von., Schauer, J. J., Hagler, G. S. W., and Bergin, M.: Concentrations and  
17 sources of carbonaceous aerosol in the atmosphere of Summit, Greenland, *Atmos. Environ.*,  
18 43, 4155-4162, 2009.

19 Schnelle-Kreis, J., Sklorz, M., Peters, A., Cyrys, J., and Zimmermann, R.: Analysis of  
20 particle-associated semi-volatile aromatic and aliphatic hydrocarbons in urban particulate  
21 matter on a daily basis, *Atmos. Environ.*, 39, 7702-7714, 2005.

22 SEDESOL, INEGI & CONAPO.: Delimitación de las zonas metropolitanas en México 2005.  
23 México. 38 pp., 2007.

24 SENER. Prospectiva del sector eléctrico 2013-2027. Available in:  
25 [http://www.sener.gob.mx/res/pe\\_y\\_dt/pub/2013/prospectiva\\_del\\_sector\\_electrico\\_2013-](http://www.sener.gob.mx/res/pe_y_dt/pub/2013/prospectiva_del_sector_electrico_2013-2027.pdf)  
26 [2027.pdf](http://www.sener.gob.mx/res/pe_y_dt/pub/2013/prospectiva_del_sector_electrico_2013-2027.pdf), 2013.

27 Sheesley, R. J., Schauer, J. J., Bean, E., and Kenski, D.: Trends in secondary organic aerosol  
28 at a remote site in Michigan's Upper Peninsula, *Environ. Sci. Technol.*, 38, 6941-6500,  
29 2004.

- 1 Simoneit, B. R. T.: Application of mMolecular Marker aAnalysis to vehicular eExhaust  
2 for sSource rReconciliations, *Int. J. Environ. An. Ch.*, 22: 203-233, 1985.
- 3 Simoneit, B. R. T.: Characterization of oOrganic-cConstituents in aAerosols in rRelation to  
4 their oOrigin and transport - a rReview, *Int. J. Environ. An. Ch.*, 23: 207-237, 1986.
- 5 Simoneit, B. R. T.: A review of biomarker compounds as source indicators and tracers for air  
6 pollution, *Environ. Sci. Pollut. R.*, 6: 159-169, 1999.
- 7 Simoneit, B. R. T., and Mazurek, M. A.: Organic matter of the troposphere-II. Natural  
8 background of biogenic lipid matter in aerosols over the rural western United States, *Atmos.*  
9 *Environ.*, 16, 2139-2159, 1982.
- 10 Simoneit, B. R. T., and Mazurek, M. A.: Organic tracers in ambient aerosols and rain,  
11 *Aerosol Sci. Tech.*, 10, 267-291, 1989.
- 12 Simoneit, B. R. T., Cardoso, J. N., and Robinson, N.: An assessment of the origin and  
13 composition of higher molecular weight organic matter in aerosols over Amazonia,  
14 *Chemosphere*, 21, 1285-1301, 1990.
- 15 Simoneit, B. R. T., Sheng G. Y., Chen, X. J., Fu, J. M., Zhang, J., Xu, Y. P.: Molecular  
16 mMarker study of eExtractable oOrganic-mMatter in aAerosols from uUrban areas of  
17 China. *Atmospheric Environment Part a- General Topics*, 25: 2111-2129, 1991.
- 18 Simoneit, B. R. T., Kobayashi, M., Mochida, M., Kawamura, K., Lee, M., Lim, H.-J., Turpin,  
19 B., and Komazaki, Y.: Composition and major sources of organic compounds of aerosol  
20 particulate matter sampled during the ACE-Asia campaign, *J. Geophys. Res-Atmos.*, 109, 1-  
21 22, doi: 10.1029/2004JD004598, 2004.
- 22 Simoneit, B. R. T., Medeiros, O. M., and Didyk, B., M.: Combustion products of plastics as  
23 indicators for refuse burning in the atmosphere, *Environ. Sci. Technol.* 39, 6961-6970, 2005.
- 24 Sklorz, M., Schnelle-Kreis, J., Liu, Y., Orasche, J., and Zimmermann, R.: Daytime resolved  
25 analysis of polycyclic aromatic hydrocarbons in urban aerosol samples — Impact of sources  
26 and meteorological conditions, *Chemosphere*, 67, 934-943, 2007.
- 27 Spurny, K. R.: Aerosol chemistry and its environmental effects. In Spurny, K. R. (Ed).  
28 *Aerosol Chemical Processes in the Environment* (3-21). Florida: Lewis, 2000.
- 29 [SRM 1649a; Urban Dust/Organics; National Institute of Standards and Technology; U.S.](#)  
30 [Department of Commerce: Gaithersburg, MD \(06 December 2007\)](#)



1 [SRM 1649b; Urban Dust/Organics; National Institute of Standards and Technology; U.S.](#)  
2 [Department of Commerce: Gaithersburg, MD \(23 February 2009\)](#)

3 ~~[Stone, E. A., Snyder, D. C., Sheesley, R. J., Sullivan, A. P., Weber, R. J. and Schauer, J. J.:](#)~~  
4 ~~[Source apportionment of fine aerosol in Mexico City during the MILAGRO experiment 2006,](#)~~  
5 ~~[Atmos. Chem. Phys., 8, 1249-1259, 2008.](#)~~

6 Standley, L. J., and Simoneit, B. R. T.: Characterization of extractable plant wax, resin, and  
7 thermally matured components in smoke particles from prescribed burns, Environ. Sci.  
8 Technol., 21, 163-169, 1987.

9 ~~[Stone, E. A., Snyder, D. C., Sheesley, R. J., Sullivan, A. P., Weber, R. J., and Schauer, J. J.:](#)~~  
10 ~~[Source apportionment of fine aerosol in Mexico City during the MILAGRO experiment 2006,](#)~~  
11 ~~[Atmos. Chem. Phys., 8, 1249-1259, 2008.](#)~~

12 Tobiszewski, M., and Namieśnik, J.: PAH diagnostic ratios for the identification of pollution  
13 emission sources, Environ. Pollut., 162, 110-119. doi: 10.1016/j.envpol.2011.10.025, 2012.

14 Tsapakis, M., Lagoudaki, E., Stephanou, E. G., Kavouras, I. G., Koutrakis, P., Oyola, P., and  
15 von Baer, D.: The composition and sources of PM<sub>2.5</sub> organic aerosol in two urban areas of  
16 Chile, Atmos. Environ., 36, 3851-3863, doi: Doi: 10.1016/s1352-2310(02)00269-8, 2002.

17 Upadhyay, N., Clements, A., Fraser, M., and Herckes, P.: Chemical speciation of PM<sub>2.5</sub> and  
18 PM<sub>10</sub> in south Phoenix, AZ, J. Air Waste Manage. Assoc., 61, 302-310, 2011.

19 Viana, M., Chi, X., Maenhaut, W., Querol, X., Alastuey, A., Mikuška, P., and Večeřa, Z.:  
20 Organic and elemental carbon concentrations in carbonaceous aerosols during summer and  
21 winter sampling campaigns in Barcelona, Spain, Atmos. Environ., 40, 2180-2193, 2006.

22 ~~[Viana, M., Kuhlbusch, T. A. J., Querol, X., Alastuey, A., Harrison, R. M., Hopke, P. K.,](#)~~  
23 ~~[Winiwarter, W., Vallius, M., Szidat, S., Prévôt, A. S. H., Hueglin, C., Bloemen, H., Wählin,](#)~~  
24 ~~[P., Vecchi, R., Miranda, A. I., Kasper-Giebl, A., Maenhaut, W., and Hittenberger, R.: Source](#)~~  
25 ~~[apportionment of particulate matter in Europe: A review of methods and results, J. Aerosol](#)~~  
26 ~~[Sci. 39, 827-849, 2008.](#)~~

27 Villalobos, A. M., Amonov, M. O., Shafer, M. M., Devi, J. J., Gupta, T., Tripathi, S. N.,  
28 Rana, K. S., McKenzie, M., Bergin, M. H., Schauer, J. J.: Source apportionment of  
29 carbonaceous fine particulate matter (PM<sub>2.5</sub>) in two contrasting cities across the Indo-  
30 Gangetic Plain, Atmos. Pollut. Res., 6, ~~398-405~~~~xx-xx~~, 2015.



1 Wang, G., and Kawamura, K.: Molecular characteristics of urban organic aerosols from  
2 Nanjing: a case study of a mega-city in China, *Environ. Sci. Technol.*, 39, 7430-7438, 2005.

3 Wang, G., Kawamura, K., Lee, S., Ho, K. and Cao, J.: Molecular, seasonal, and spatial  
4 distributions of organic aerosols from fourteen Chinese cities, *Environ. Sci. Technol.*, 40,  
5 4619-4625, 2006.

6 Watson, J. G., Chen, L.-W. A., Chow, J. C., Doraiswamy, P., and Lowenthal, D. H.: Source  
7 apportionment: Findings from the U. S. supersites program, *J. Air Waste Manage. Assoc.*, 58,  
8 265-288, 2008.

9 Watson, J. G, Chow, J. C., Lowenthal, D. H., Antony Chen, L.-W., Shaw, S., Edgerton, E. S.,  
10 and Blanchard, C. L.: PM<sub>2.5</sub> source apportionment with organic markers in the southeastern  
11 aerosol research and characterization (SEARCH) study, *J. Air Waste Manage. Assoc.*, 65,  
12 1104-1118, 2015.

13 Wold, S., Sjöström, M., and Eriksson, L., ~~2001~~: PLS-regression: a basic tool of  
14 chemometrics, *Chemometr. Intell. Lab.* 58, 109-130, ~~2001~~.

15 Yin, J., Harrison, R. M., Chen, Q., Rutter, A., and Schauer, J. J.: Source apportionment of fine  
16 particles at urban background and rural sites in the UK atmosphere, *Atmos. Environ.*, 44, 841-  
17 851, 2010.

18 Yokelson, R. J., Urbanski, S. P., Atlas, E. L., Toohey, D. W., Alvarado, E. C., Crouse, J. D.,  
19 Wennberg, P. O., Fisher, M. E., Wold, C. E., Campos, T. L., Adachi, K., Buseck, P. R., and  
20 Hao, W. M.: Emissions from forest fires near Mexico City, *Atmos. Chem. Phys.*, 7, 5569-  
21 5584, 2007.

22 Young, L.-H., and Wang, C.-S.: Characterization of n-alkanes in PM<sub>2.5</sub> of the Taipei aerosol,  
23 *Atmos. Environ.*, 36, 477-482, doi: Doi: 10.1016/s1352-2310(01)00298-9, 2002.

24 Yue, Z., and Fraser, M. P.: Polar organic compounds measured in fine particulate matter  
25 during TexAQS 2000, *Atmos. Environ.*, 38, 3253-3261, 2004.

26 Yunker, M. B., Macdonald, R. W., Vingarzan, R., Mitchell, R. H., Goyette, D., and Sylvestre,  
27 S.: PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH  
28 source and composition, *Organic Geochemistry*, 33, 489-515, ~~2002~~.

- 1 Zhang, X. L., Tao, S., Liu, W. X., Yang, Y., Zuo, Q., and Liu, Z.: Source diagnostic of  
2 polycyclic aromatic hydrocarbons based on species ratios: a multimedia approach, *Environ.*  
3 *Sci. Technol.*, 39, 9109-9114, 2005.
- 4 Zheng, M., Cass, G. R., Ke, L., Wang, F., Schauer, J. J., Edgerton, E. S., and Russell, A. G.:  
5 Source apportionment of daily fine particulate matter at Jefferson Street, Atlanta, GA, during  
6 summer and winter, *J. Air Waste Manage. Assoc.*, 57, 228-242, 2015.
- 7 Zheng, M., Cass, G. R., Schauer, J. J., and Edgerton, E. S.: Source apportionment of PM<sub>2.5</sub> in  
8 the southeastern United States using solvent-extractable organic compounds as tracers,  
9 *Environ. Sci. Technol.*, 36, 2361-2371, 2002.
- 10 Zheng, M., Salmon, L. G., Schauer, J. J., Zeng, L., Kiang, C. S., Zhang, Y., and Cass, G. R.  
11 Seasonal trends in PM<sub>2.5</sub> source contributions in Beijing, China, *Atmos. Environ.*, 39, 3967-  
12 3976, 2005.
- 13 Zurita, O.: Guía de árboles y otras plantas nativas en la zona metropolitana de Monterrey,  
14 Fondo Editorial de Nuevo León, ISBN 978-607-7577-15-7, pp. 82, 2009.
- 15  
16  
17

1 Table 1. Monitoring experiments conducted for this study.

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

2 <sup>a</sup> Non-consecutive days.

3

4

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

Campaign	Description	Dates included	PM <sub>2.5</sub>		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 in curly brackets are the mass ranges for the mass of OC collected per filter included.~~

3 Values for PM<sub>2.5</sub> 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~~that the dates included were analyzed individually, C indicates that dates

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

3

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., 2002 <del>5</del>
	> 0.50	Coal, grass, and wood combustion	Yunker et al., 2002 <del>5</del>
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

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

8

9

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

3

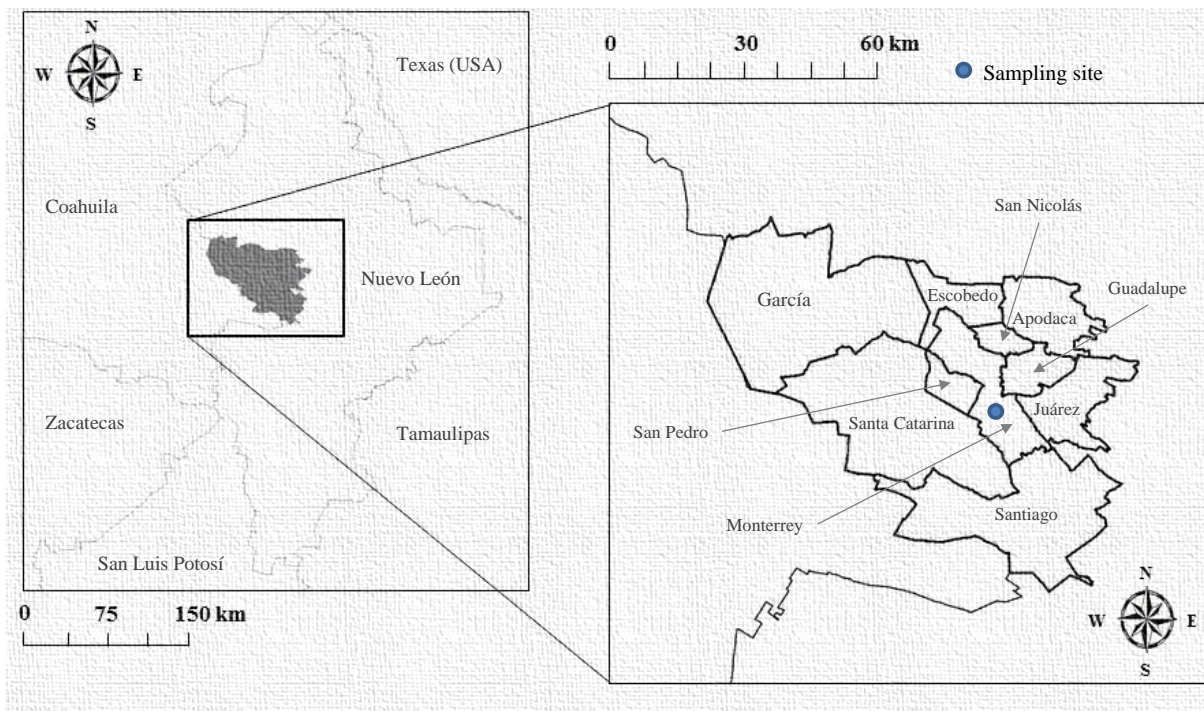
4 Table 5. Contributions and uncertainty of primary sources to seasonal average ambient PM<sub>2.5</sub>

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

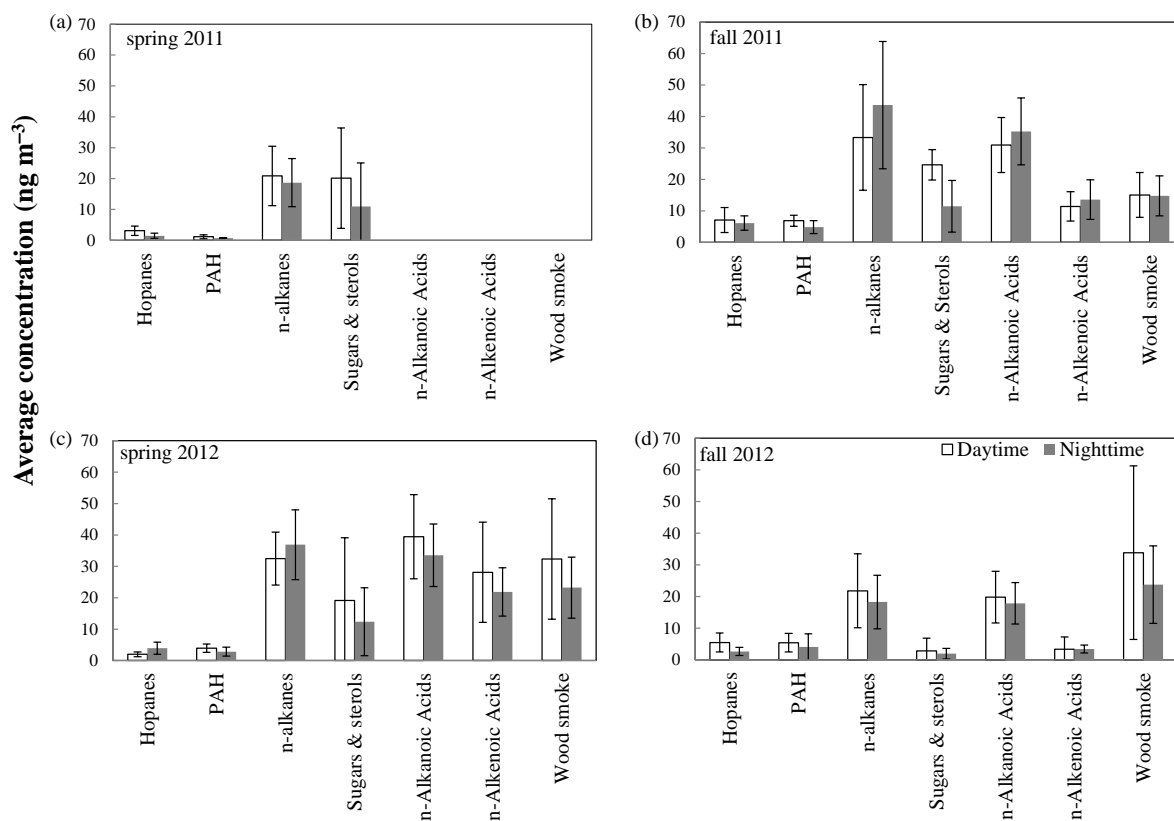
6 N. I. means Not Important. \* samples were discarded due to poor CMB performance.

7



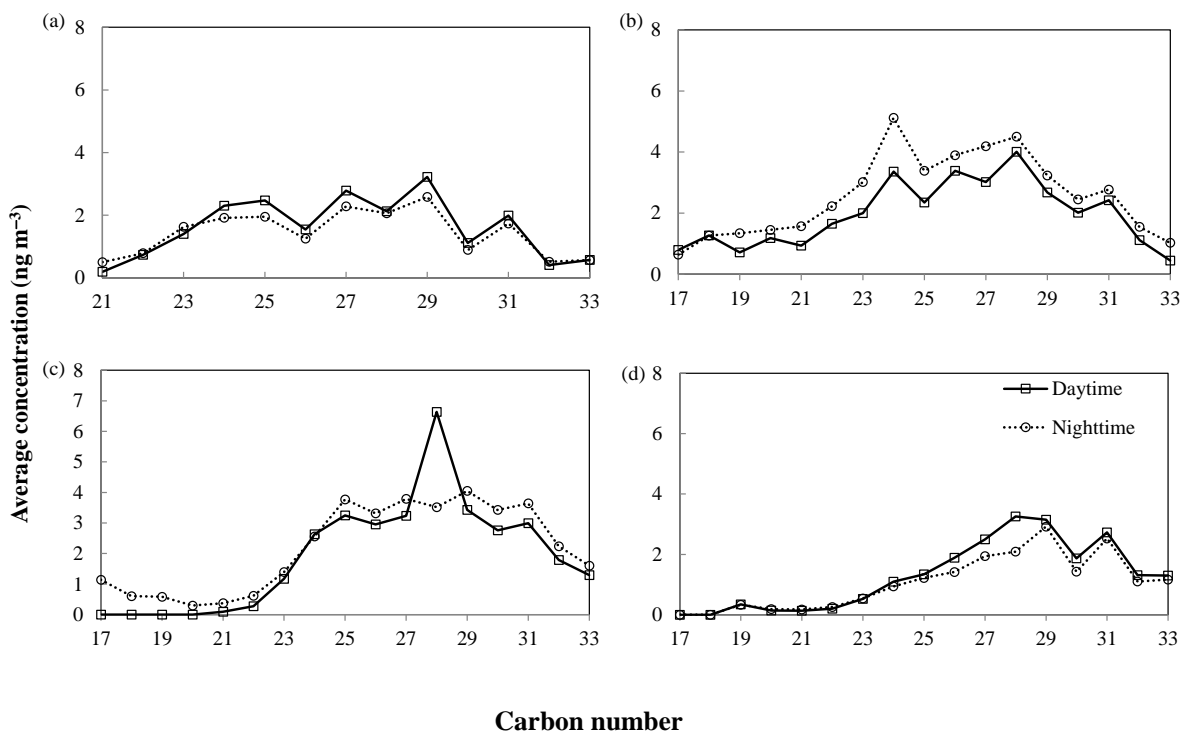
1  
2  
3  
4  
5  
6

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



1  
 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.  
 5





1

2

Figure 3. Carbon number distribution of *n*-alkanes in the Monterrey Metropolitan Area

3

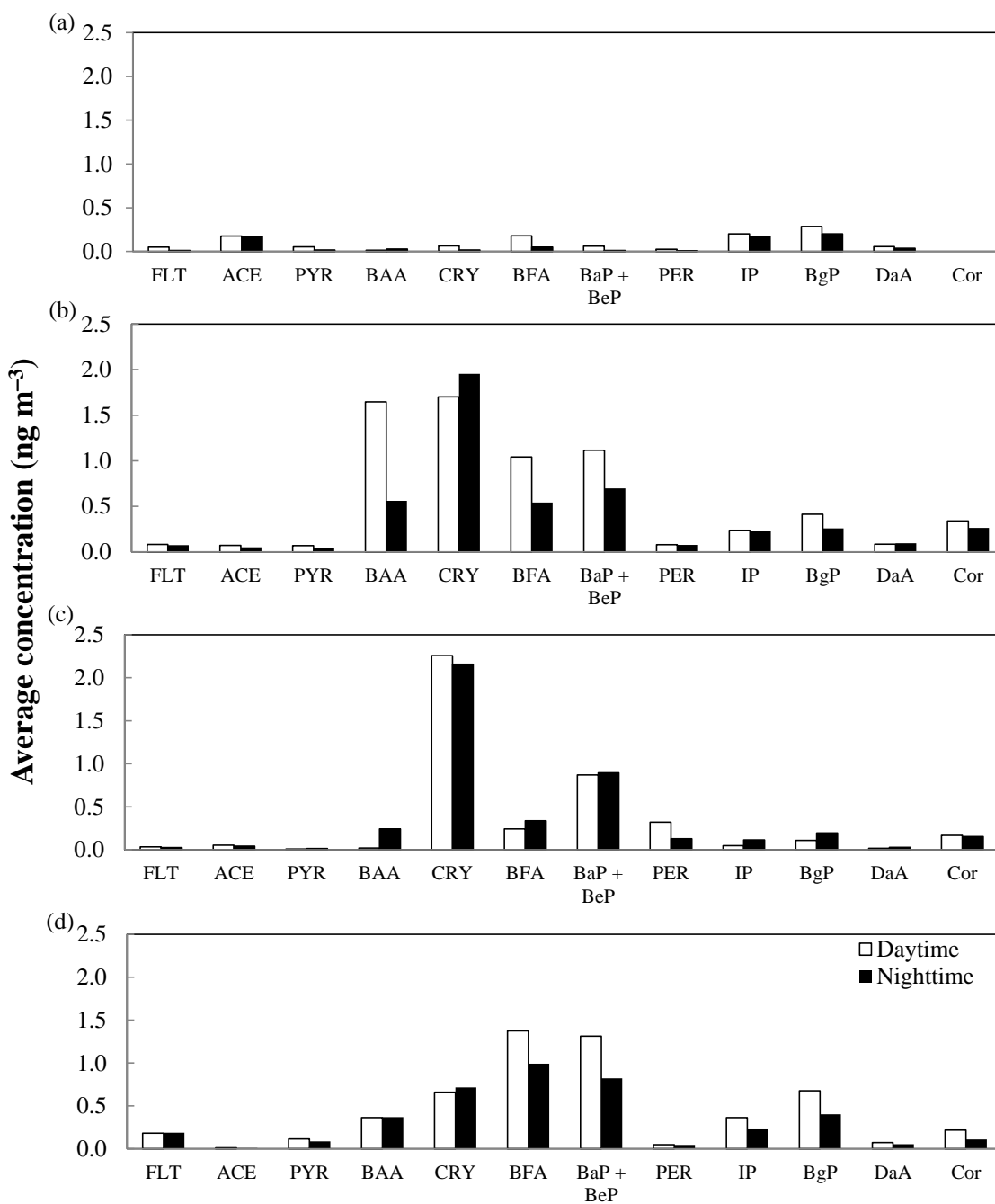
(MMA) for (a) spring 2011, (b) fall 2011, (c) spring 2012 and (d) fall 2012. The black

4

line is the daytime concentrations while the dot line is the

5

line represents the daytime concentrations while the dotted line represents the nighttime concentrations.



1

2

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

3

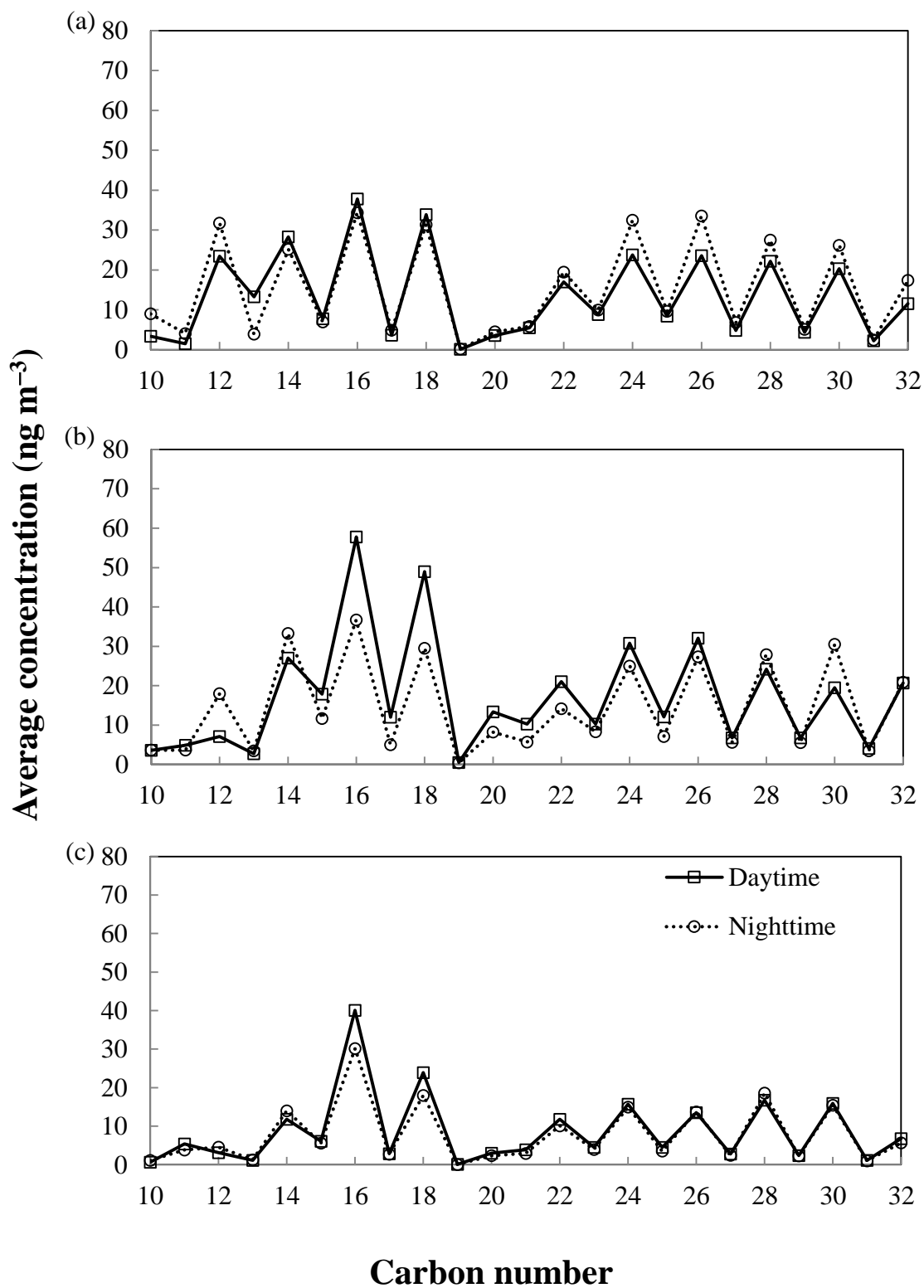
(MMA) for (a) spring 2011, (b) fall 2011, (c) spring 2012 and (d) fall 2012. Coronene was

4

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

5

6

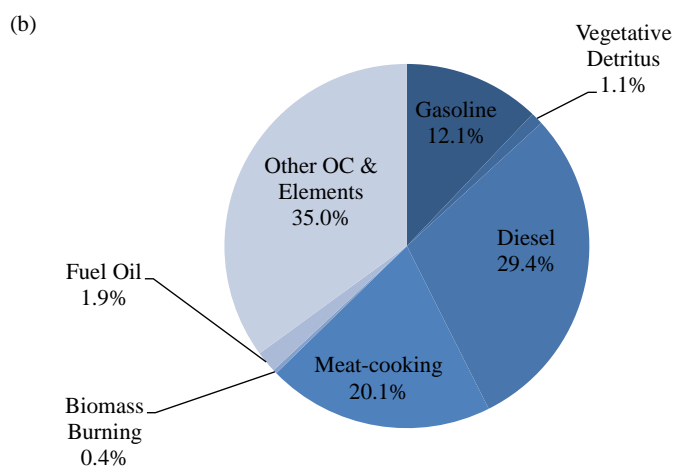
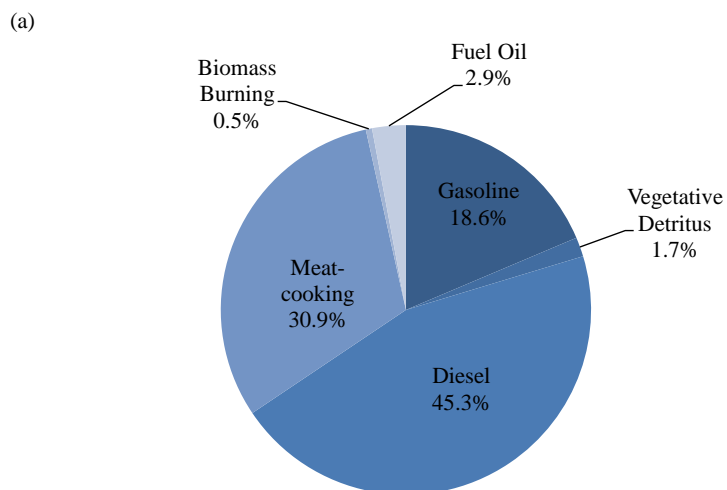


1

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.



1

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.

4