耶鲁大学-南京信息工程大学大气环境中心

Yale-NUIST Center on Atmospheric Environment

Atmos. Chem. Phys., 16, 953–970, 2016
www.atmos-chem-phys.net/16/953/2016/
doi:10.5194/acp-16-953-2016

Atmospheric Chemistry and Physics
Open Access
EGU

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

Authors: Y. Mancilla, A. Mendoza, M. P. Fraser, and P. Herckes

Reporter: Wu Xia

2017.9.29

Outline

- 1 Background
- 2 Methodology
- 3 Results and discussion
- 4 Concluions

1 Background

- Primary emissions from anthropogenic and biogenic sources as well as secondary formation are responsible for the pollution levels of ambient air in major urban areas.These sources release fine particles into the air that negatively impact human health and the environment.

- Organic molecular markers, which are compounds that are unique to specific PM 2.5 sources, can be utilized to identify the major emission sources in urban areas.

- Fine organic aerosol (OA) has a major role in environmental and human health impacts.For the MMA, there is a growing concern to determine the emission sources of fine OA.

2 Methodology

2.1 Sampling site

Location: at only one site placed in the facilities of the downtown monitoring station of the SIMA network (25 °40’32 ”N, 100°20 ’18”W), 556m.a.s.l.(meters above sea level).

Period： during the spring and fall of 2011 and 2012

Samplers： 43 representative PM 2.5 samples, for both daytime and nighttime periods

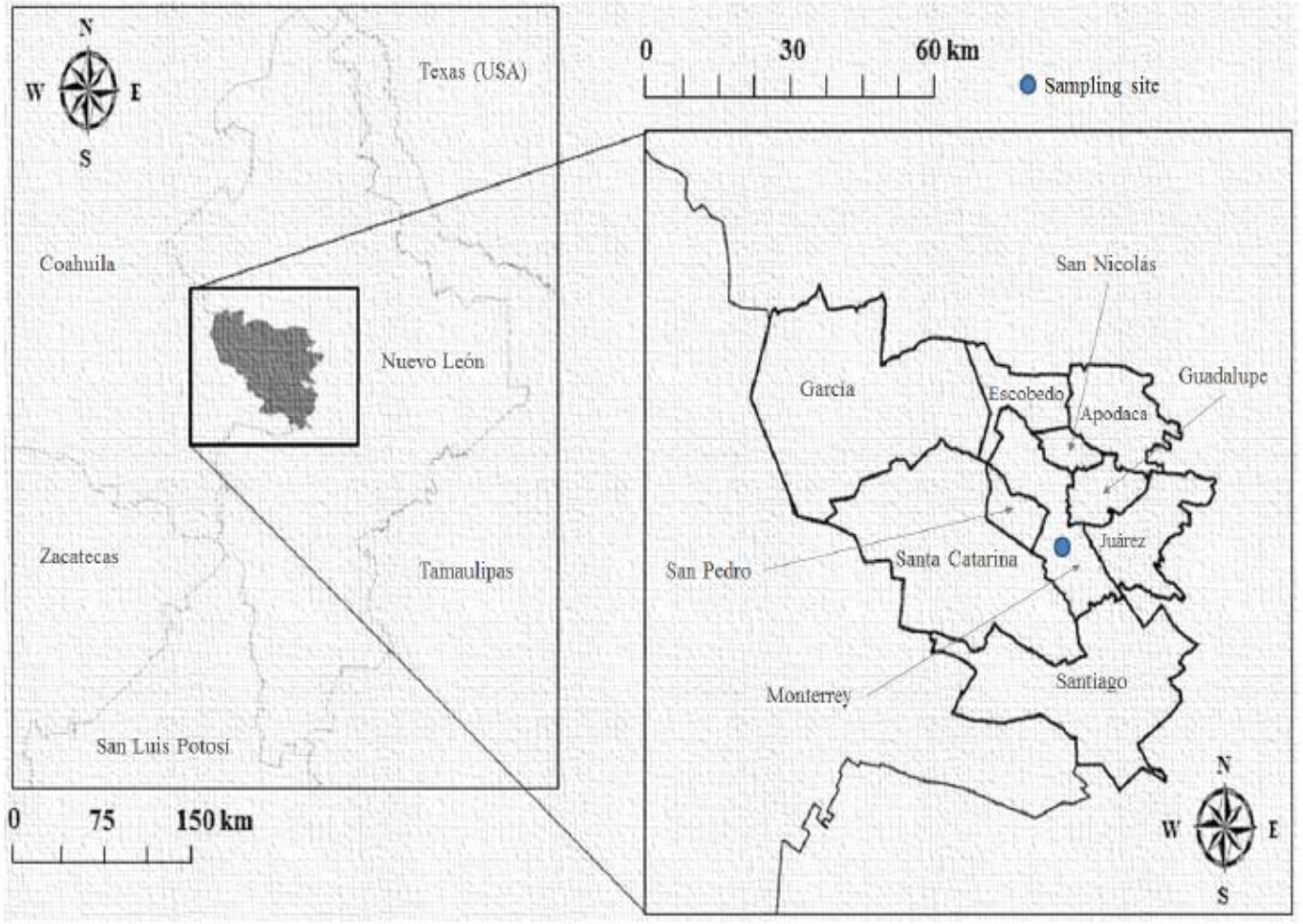


Fig.1 Location and municipalities of the MMA; the sampling site was set up in the downtown.

2.2 Molecular diagnostic ratios

2.2.1 Carbon preference index （CPI）

The CPI for n-alkanes (odd to even ratio) : $$\mathrm{CPI} = \frac{\sum(C_{17} \text{ to } C_{33})}{\sum}(C_{16} \text{ to } C_{32})$$

The CPI for n-alkanoic acids (even to odd ratio) : $$\mathrm{CPI} = \frac{\sum (C_{10} \text{ to } C_{32})}{(C_{11} \text{ to } C_{31})}$$

values of CPI>1: hydrocarbons and carboxylic acids are emitted from natural sources;

values of CPI≤1(or close to 1): they are emitted from anthropogenic sources .

Another useful indicator 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.

2.2.2 Diagnostic ratios of PAHs

The diagnostic ratios(DRs) calculated in this study are shown in Table 1 (Ravindra et al., 2008; Tobiszewski and Namie´ snik, 2012).

Table 1 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? .50	Petroleum combustion	Yunker et al. (2002)
	> 0.50	Coal, grass, and wood combustion	Yunker et al. (2002)
BAA / (BAA + CRY)	< 0.20	Petrogenic	Katsoyiannis et al. (2011)
	0.20? .35	Coal combustion	Aky 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? .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)

2.3 Chemical mass balance model

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

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
e_{ij} is the model error.

CMB takes into account the known uncertainties in the ambient measurements and the source emission data to minimize the chisquare (χ^2) goodness-of-fit parameter for each sample i:

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

σ_{xj} is the standard deviation of the concentration of species j
σ_{gjk} is the standard deviation of the g_{jk}
m is the total number of species.

3 Results and discussion

3.1 Resolved organic aerosols

	Spring 2011				Fall 2011				Spring 2012				Fall 2012			
	Daytime		Nighttime		Daytime		Nighttime		Daytime		Nighttime		Daytime		Nighttime	
	Avg	SD	Avg	SD	Avg	SD	Avg	SD	Avg	SD	Avg	SD	Avg	SD	Avg	SD
Identified OC	45.27	27.98	31.83	22.83	408	127	447	152	512	200	436	142	270	135	232	94.42
OC	9200	800	7300	700	8800	500	5800	300	6700	400	4000	300	10200	600	7100	400
EC	1300	400	600	300	900	100	700	100	500	100	10	100	900	100	700	100
$PM_{2.5}$	21300	3400	27900	3300	19400	2800	14000	1400	15800	2200	13700	1800	20100	3000	16000	1800

- Most of the PM 2.5 daytime concentrations were 20% higher than nighttime concentrations.
- The concentrations of OC and EC were on average 32% higher during the daytime than the nighttime.
- The OC and EC accounted together for 28–49 and 46–55% of the PM 2.5 for spring and fall,respectively.

3.2 n-Alkanes and hopanes

Seasons \ CPI	Daytime	Nighttime
Spring	1.5±0.3 (range:1.1-1.9)	1.7±0.5 (range:1.1-2.6)
Fall	1.0±0.3 (range:0.7-1.2)	0.9±0.1 (range:0.7-1.0)

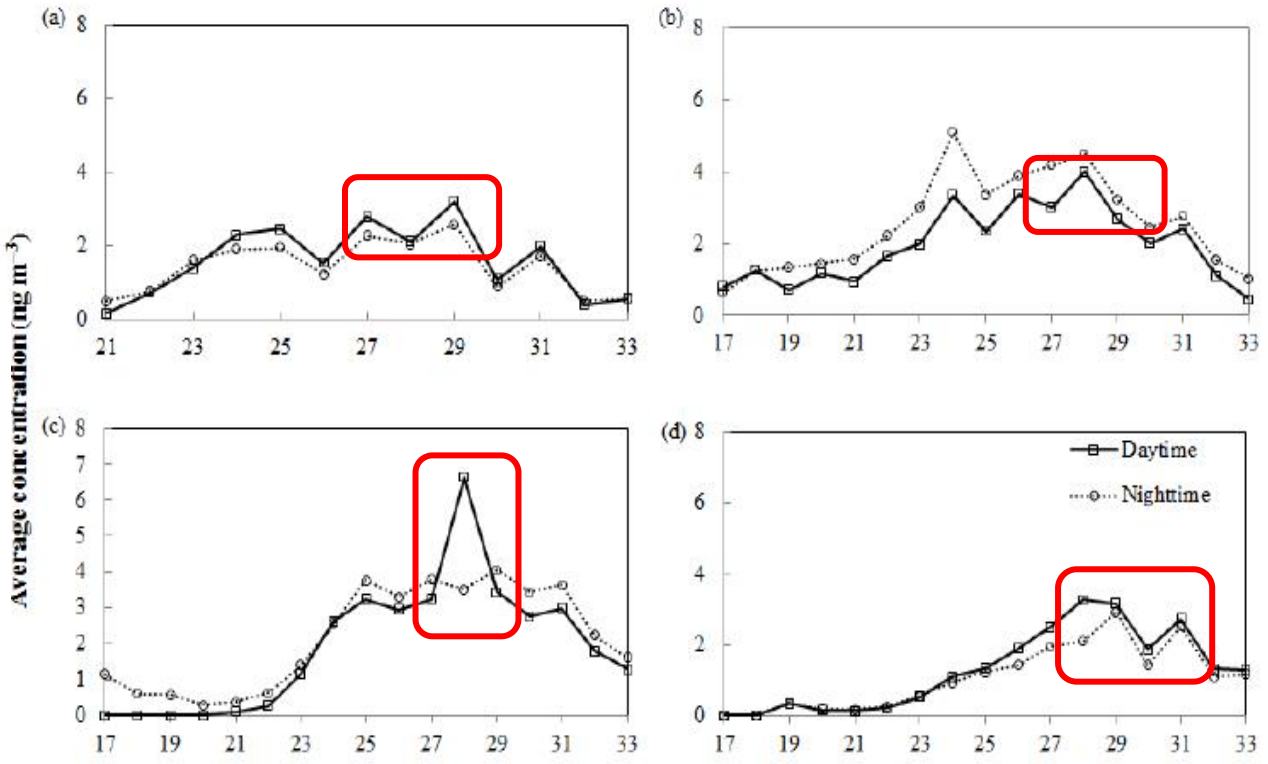


Fig.2 Carbon number distribution of n-alkanes in the MMA, for (a) spring 2011, (b) fall 2011, (c) spring 2012, and (d) fall 2012.

- spring----the mixed contribution of anthropogenic and biogenic emission sources
- fall ---- a dominance of anthropogenic emissions.
- the presence of biogenic emissions due to C_{max} was found at C_{27} , C_{29} , or C_{31}

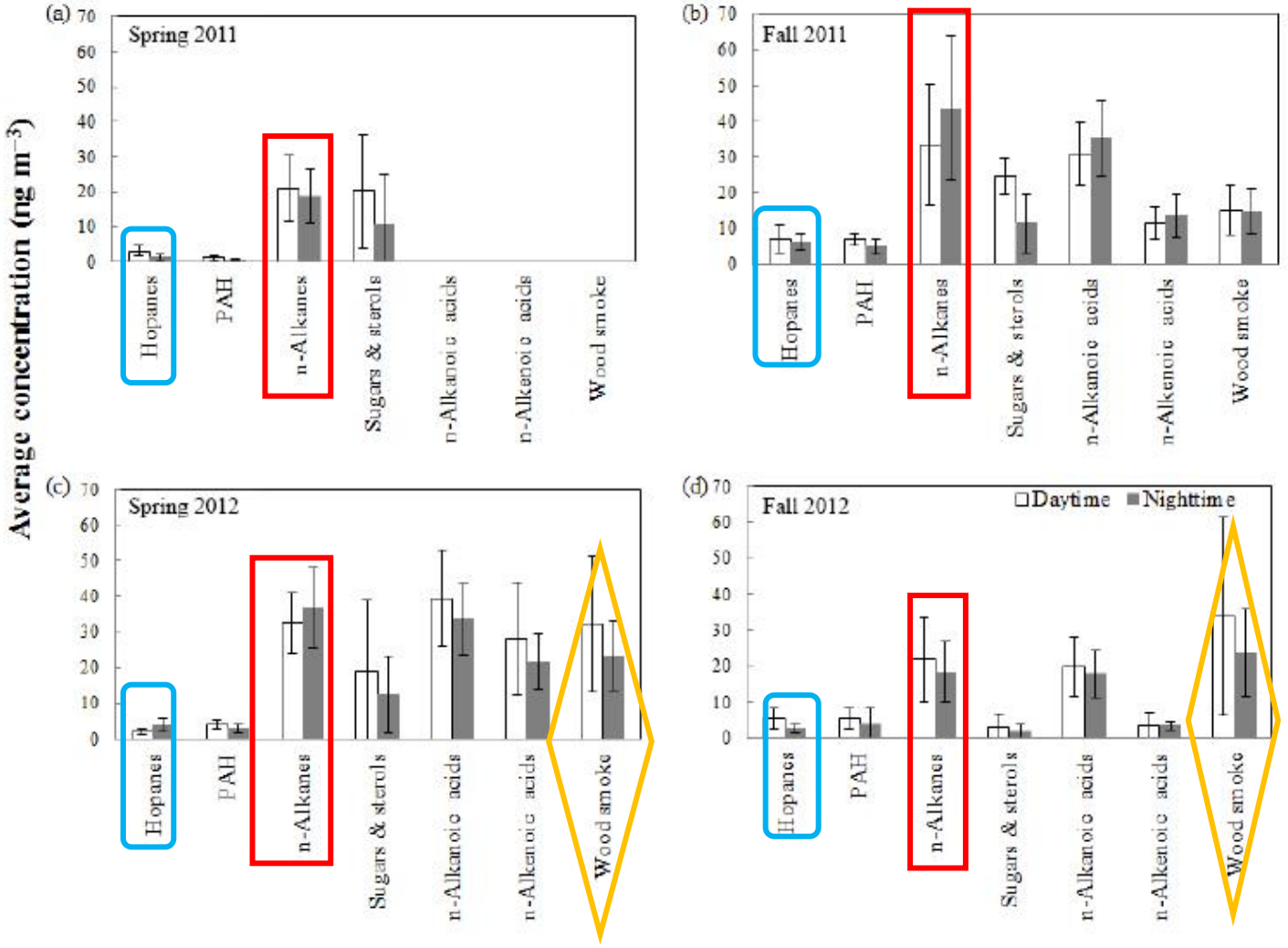


Fig.3 Concentrations of the resolved organic compound classes in the MMA. For (a) the n-alkanoic and alkenoic acids and wood smoke tracer were not included in the chemical analysis. For (b), (c) and (d) the n-alkanoic acids are divided by a factor of 10.

- For spring and fall 2012, the behavior of n-alkanes was the opposite of 2011.
- The EC levels remained similar to those of 2011, but the OC levels were higher during fall 2012.
- Some of these ratios exhibited high peaks suggesting a contribution from primary emission sources with elevated OC/EC ratios like biomass burning (Mancilla et al., 2015).
- In 2012 the hopane levels were lower than in 2011. The low hopane levels highlight the possible presence of biogenic emissions.

3.3 PAHs

- The high-molecular-weight(HMW) PAHs were the most abundant. The presence of HMW PAHs such as BaP+BeP, IP, and BgP is an indication of gasoline-powered vehicle emissions (Katsoyiannis et al.,2011).

- A possible contribution of diesel-powered vehicles is indicated by the low concentrations of the low-molecular-weight (LMW)PAHs such as FLT, PYR, and CRY.

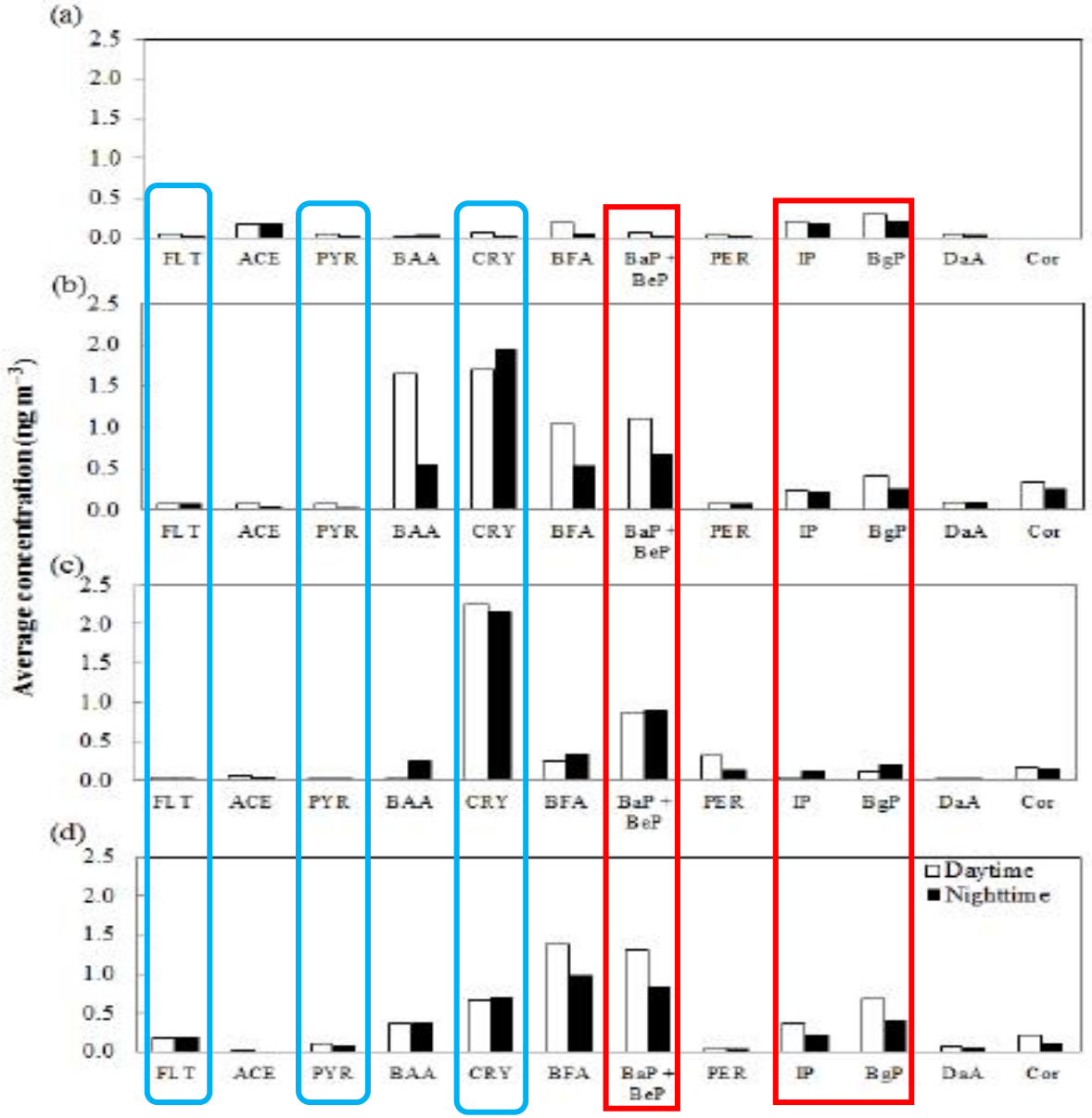


Fig.4 Mass concentration distribution of PAHs in the MMA, for (a) spring 2011, (b) fall 2011,(c) spring 2012, and (d) fall 2012. Coronene was included in all monitoring campaigns except in spring 2011.

Table 4 Average diagnostic ratios of PAHs in MMA. D represents daytime and N represents nighttime.

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

- The average ratios of IP/(IP+BgP) indicate that ambient PAHs in the MMA originated from gasoline and diesel combustion.

- The ratios of BAA/(BAA+CRY) show the presence of petrogenic sources as well as vehicle emissions.

- The ratios of (BaP+BeP)/BgP identified a marked contribution of non-traffic sources for the spring of 2011, traffic sources for fall 2011 and spring 2012, and mixed sources for fall 2012.

3.4 n-Alkanoic acids

- The n-alkanoic acids measured in the MMA were dominated by hexadecanoic acid (palmitic acid) and octadecanoic acid (stearic acid).

-

Time \ CPI	Daytime	Nighttime
Fall,2011	4.3 ±1.0 (range:3.3-5.3)	5.0 ±0.4 (range:4.6-5.4)
Spring,2012	3.6 ±0.6 (range:2.9-4.5)	4.7 ±0.8 (range:3.9-5.8)
Fall,2012	4.7 ±0.3 (range:4.3-5.1)	5.3 ±1.1 (range:4.0-6.8)

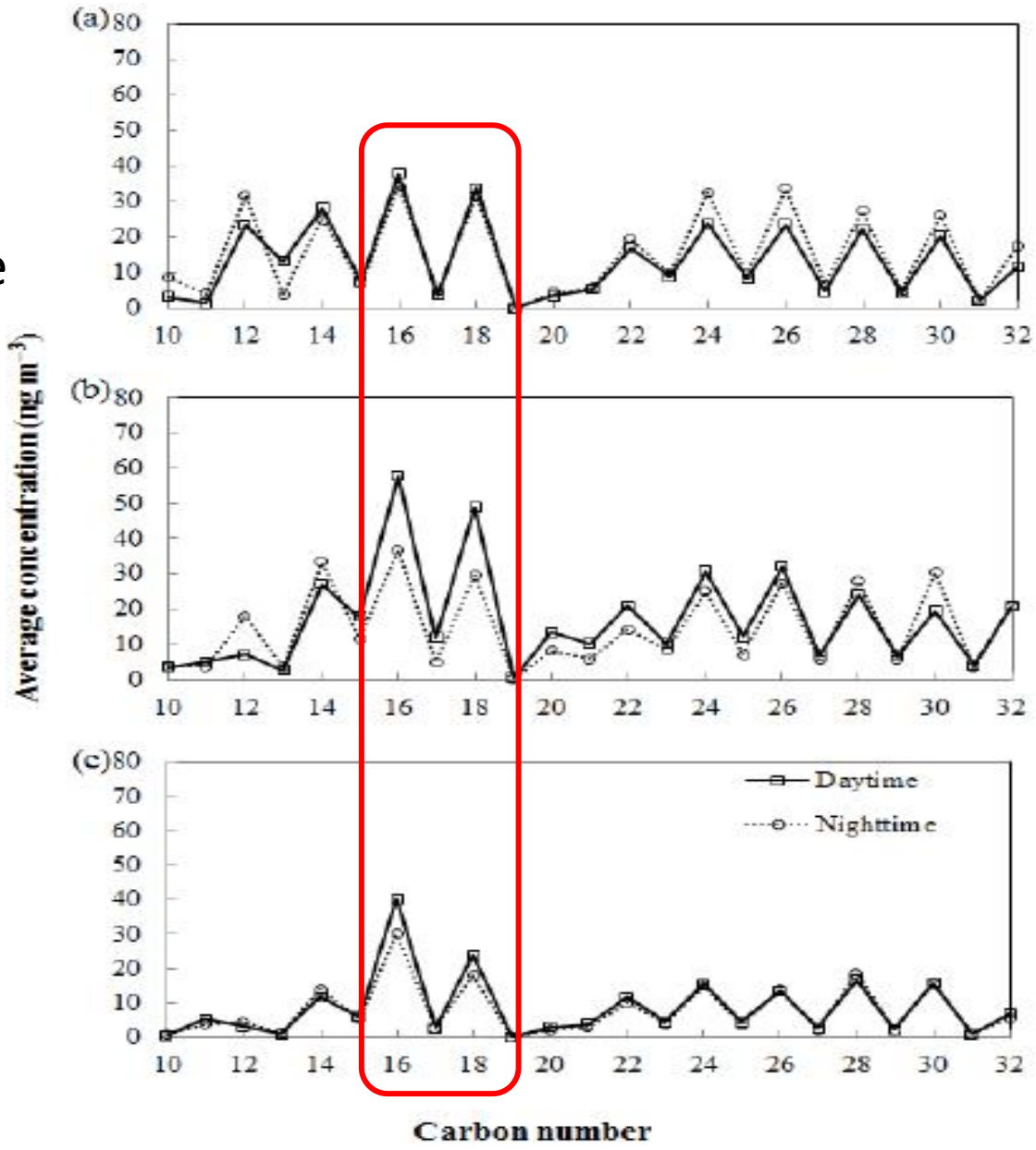


Fig.5 Carbon number distribution of n-alkanoic acids in the MMA, for (a) fall 2001,(b) spring 2012, and (c) fall 2012

- These elevated CPI values indicated the significant influence of biogenic sources such as microbial and plant wax sources. The n-alkanoic acids <C_{20} are derived in part from microbial sources, while those >C_{20} are from vascular plant waxes.

	Spring 2011				Fall 2011				Spring 2012				Fall 2012			
	Daytime		Nighttime		Daytime		Nighttime		Daytime		Nighttime		Daytime		Nighttime	
	Avg	SD	Avg	SD	Avg	SD	Avg	SD	Avg	SD	Avg	SD	Avg	SD	Avg	SD
n-Alkenoic acids																
cis-9-octadecenoic acid	NA		NA		3.83	1.83	4.77	3.52	15.38	8.44	8.50	2.72	1.22	1.83	0.94	0.39
trans-9-octadecenoic acid	NA		NA		7.57	2.85	8.81	2.76	12.74	7.51	13.35	4.97	2.11	2.04	2.45	0.87
total					11.40	4.67	13.57	6.28	28.12	15.95	21.85	7.69	3.33	3.87	3.40	1.27
octadecanoic acid/cis-9-octadecenoic acid					10.6	5.9	8.2	3.6	5.0	3.4	3.8	1.3	20.3	17.1	21.0	6.7

- The ratio of octadecanoic acid to cis-9-octadecenoic acid has been used as an indicator of the atmospheric chemical processing (aging) of aerosols, since the unsaturated acids are susceptible to atmospheric oxidation (Brown et al., 2002; Yue and Fraser, 2004).

Ratio / Seasons	Daytime	Nighttime
Spring	5.0 (range:1.5-9.4)	3.8 (range:2.5-4.9)
Fall	20.3 (range:4.7-38.6)	21.0 (range:10.5-29.1)

- These ratios suggest that the ambient organic aerosols for the MMA were aged and might be produced from transport and atmospheric oxidation.

- The lowest and highest octadecanoic acid to cis-9-octadecenoic acid ratios were consistent with the highest OC/EC ratios for the same campaign; High OC/EC ratios identified transport and stagnation scenarios for the spring and fall, respectively (Mancilla et al., 2015).

3.5 Meat-cooking and biomass burning tracers

- It is possible that the levoglucosan emissions reported come from industries that have implemented biomass burning processes for energy generation.

- The results for resin acids are in line with those obtained for levoglucosan. These results support the low impact from biomass burning emissions in the MMA.

- The higher concentrations of resin acids in fall than in spring are associated with photochemical activity due to stagnation events in fall.

3.6 Source apportionment

- The vehicle exhaust and meat-cooking operation emissions were the highest.
- The gasoline- and diesel-powered vehicles in falls were higher than in springs.
- For meat-cooking operations, their spring emissions were higher than in falls.

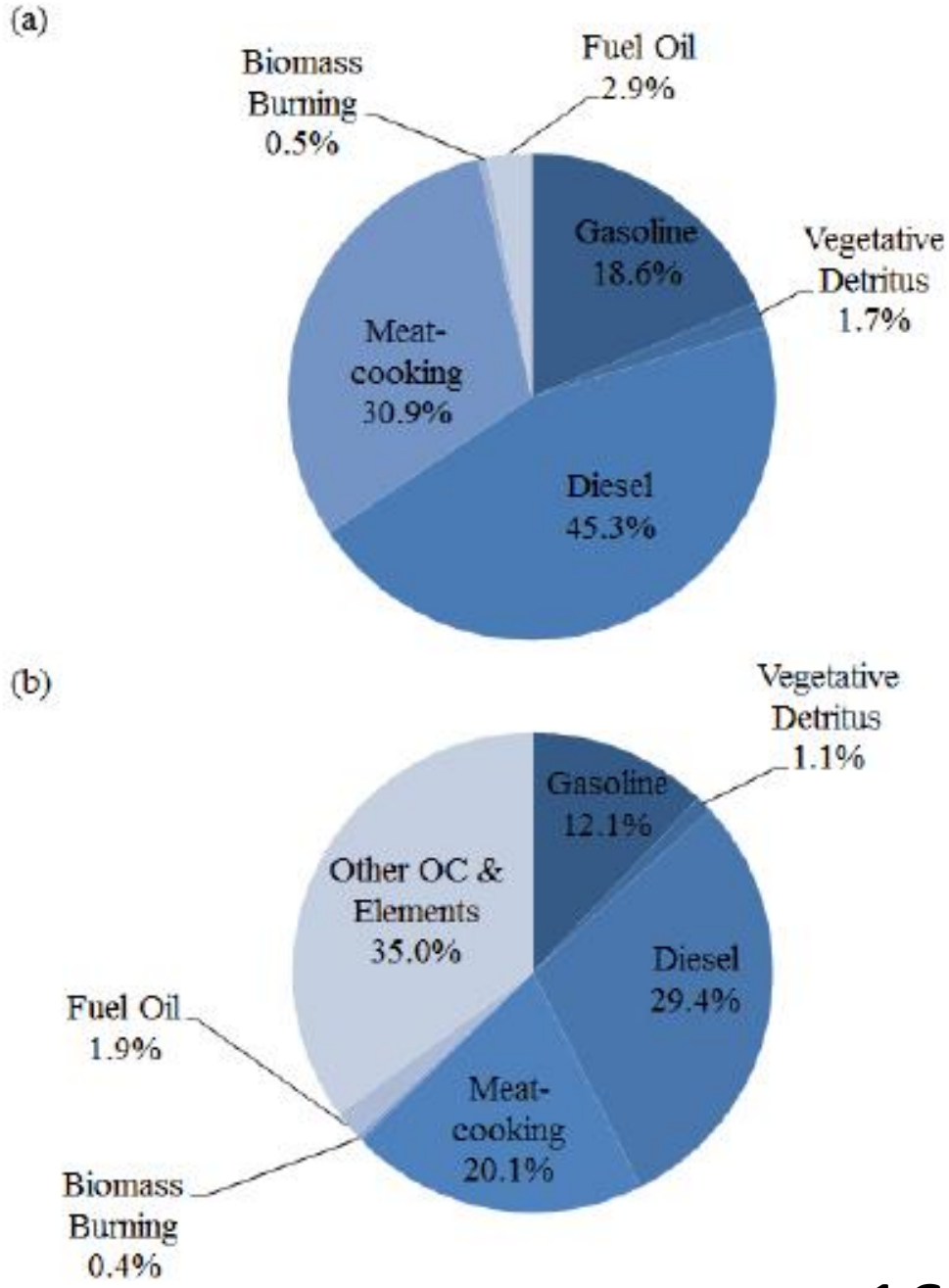
Table 5 Contributions and uncertainty of primary sources to seasonal average ambient PM 2.5 for daytime and nighttime in the MMA (in μgm $^{-3}$).

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 ± 0.54
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 ± 0.62
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 ± 0.05
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 ± 0.47
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 ± 0.48

N.I. means not important. * Samples were discarded due to poor CMB performance.

- The natural gas combustion, vegetative detritus, and biomass burning emissions were very low and constant.
- The vehicle exhaust were much higher during daytime when traffic is heavier.
- For the meat-cooking operations, the emissions were somewhat higher during nighttime during spring and more constant between daytime and nighttime during fall.
- For the rest of the sources, the daytime and nighttime emissions were relatively constant.

Fig. 6 CMB contributions to the (a) average identified ambient PM 2.5 in the MMA and to the (b) overall PM 2.5 including the unidentified mass of the measured PM 2.5 concentrations.



- The emissions from motor vehicle exhausts (gasoline and diesel) are the most important(64%), followed by meat-cooking operations (31%) and industries (2.8%). Vegetative detritus and biomass burning were the least emitted(2.2.%).

- The relatively high contribution of the meat-cooking operations was expected given the high traditional restaurant activity in the MMA.

4 Conclusions

- The average CPI values derived from the n-alkanes and n-alkanoic acids demonstrated that anthropogenic emission sources were dominant, while biogenic emission sources contribute at least sometimes to the fine OA in the MMA.

- The PAH diagnostic ratios indicate that gasoline- and diesel-powered vehicles are the main emission sources o f this class of organic compounds in PM 2.5 . Other pyrogenic sources were also identified as contributors to the fine OA.

- The average ratios of octadecanoic acid to cis-9-octadecenoic acid indicate aging of the fine OA due to photochemical activity and transport.

- The emissions from vehicle exhausts are the most important, vegetative detritus and biomass burning were the lowest contributors.

耶鲁大学-南京信息工程大学大气环境中心

Yale-NUIST Center on Atmospheric Environment

Thank you for listening!

Questions and suggestions are welcome.