Black carbon in PM$_{2.5}$, data from two urban sites in Guadalajara, Mexico during 2008

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ABSTRACT

The BC and PM$_{2.5}$ concentrations in Guadalajara, Mexico were measured in 2008 using a two–wavelength Aethalometer and a Partisol sampler, respectively. The aerosols were collected within two sites of the local Network Monitoring Stations, Centro in downtown and Miravalle in the south. BC was measured from January to December and PM$_{2.5}$ from January to August. The 24–h PM$_{2.5}$ mean concentrations were 73 and 90 $\mu$g m$^{-3}$ at Centro and Miravalle, respectively. Mexican air quality 24–h standard (65 $\mu$g m$^{-3}$) was exceeded by 79% of the PM$_{1.0}$ samples. The BC study period was divided into three seasons: two dry seasons (DS1 and DS2) and one rainy season (RS). The hourly BC median concentrations at Centro and Miravalle were 1.3–8.7 and 1.5–13.8 $\mu$g m$^{-3}$ in DS1 while 1.4–3.3 and 1.9–6.4 $\mu$g m$^{-3}$ in RS, and 1.4–7.0 $\mu$g m$^{-3}$ in DS2. When the 24–h mean BC concentration is compared to the mass concentration of PM$_{2.5}$, it shows that BC comprises less than 10% of the fine particles measured at the same period. Considering the meteorological parameters wind speed and wind direction, data analysis indicates that the BC concentration is mainly influenced by local sources at Centro, but by regional and/or long–range transport and local sources at Miravalle site. The strong correlation between BC and carbon monoxide concentrations confirmed that these two species at the two sites have common sources.

Keywords: Black carbon aerosol, PM$_{2.5}$ Aethalometer, Urban atmosphere Guadalajara air pollution

Article History:
Received: 14 June 2010
Revised: 22 August 2010
Accepted: 25 August 2010

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1. Introduction

Black carbon aerosol, hereafter referred to as BC, is a term used to describe the refractory carbonaceous residues resulting from incomplete combustion of biomass and fossil fuels (Cooke et al., 1999; Chang et al., 2008). Since BC is relatively resistant to degradation, it can be used as a tracer for the burning of biomass, and processes of human pollution in natural environments including the atmosphere, soils, sediments, ice and seawater (Schmidt and Noach, 2000).

Aerosol particles are important for climate because of their ability to both scatter and absorb solar radiation, effects that may extend over regional to global scales (Cao et al., 2006). While some aerosol (e.g., sulfate) scattering is primarily dependent on particle size, aerosol absorption is largely dependent upon chemical composition. Those aerosols that have no significant absorption in the near–UV/Visible spectral region act to scatter solar radiation, reducing the amount of sunlight reaching the Earth’s surface and resulting in an overall cooling effect. Other aerosols, such as BC, can both scatter and absorb solar radiation, resulting in a cooling of the surface while simultaneously warming the atmosphere. BC aerosols, produced from incomplete combustion, can reduce the amount of sunlight reaching the Earth’s surface by as much as 10% (Bergstrom et al., 2007; Marley et al., 2009b). In addition, it can affect cloud albedo by changing the hygroscopicity of cloud condensation nuclei (Lioussse et al., 1996; Bergstrom et al., 2002). The BC can reduce crop yields (Chameides et al., 1999) and contaminate building materials (Ghedini et al., 2000).

BC– and organic carbon–containing aerosols often comprise a major fraction of atmospheric particulate matter, especially in polluted regions such as Mexico City (70%) (Marley et al., 2009b), Los Angeles (44%) (Larson et al., 1989), Shanghai (41.4%) (Ye et al., 2003), Beijing (35%) (He et al., 2001) and Southwestern Pennsylvania (22.9%) (Allen et al., 1999). They can reduce atmospheric visibility (Reddy and Venkataraman, 2000) and indicate the presence of combustion particles (Chow et al., 2006).

Small carbonaceous aerosols (less than 1 $\mu$m in aerodynamic diameter) can penetrate deep into the lungs; hence, their potential adverse health effect can be much greater than that of larger particles (Pope III and Dockery, 2006).

Incomplete combustion of carbonaceous fuels such as fossil fuels and biomass releases anthropogenic BC aerosols. Submicron carbonaceous particles have an atmospheric residence time of 6–10 days (Cooke et al., 2002) and therefore may be transported over distances of hundreds to thousands of kilometers.
In this work, the BC and PM$_{2.5}$ concentrations were determined by using the absorption of fine aerosols measurements in the field with a 2–wavelength Aethalometer and a Partisol sampler, respectively. The aerosols were collected within two sites of the local Network Monitoring Stations, Centro in downtown and Miravalle in the south. BC was measured from January to December and PM$_{2.5}$ from January to August, both in 2008. This study presents the time series of hourly BC concentration, and its correlations with meteorological parameters, wind speed and wind direction, and carbon monoxide (CO).

The objectives of this study are: (1) to provide quantitative information about the major contributor to light absorption in the visible region; and (2) to find the fraction of BC in the fine particles in sites mainly affected by vehicular traffic and industrial sources, in Guadalajara.

2. Experimental

2.1. Sites description

Guadalajara is considered the second largest city in Mexico, with 1,600,894 inhabitants; it occupies 187.91 km$^2$ and the 2005 inventory reported 712,886 gasoline and diesel vehicles (INEGI, 2005), where continuous periods of unhealthy air quality levels have been registered by the local air pollution control agency (Mendoza and García, 2009).

The sampling sites are part of the Guadalajara air quality–monitoring network. The Centro site is located downtown (20°40′20,5200″N 103°20′09,18″W at 1,582 m above mean sea level). This area is characterized by high commercial activity and both heavy and light gasoline and diesel vehicular traffic, it is surrounded by large avenues. The second site is Miravalle (20°36′47,1740″N 103°20′39″W at 1,622 m above mean sea level) located in the Southern part of the city, with large industrial and vehicular activity as well as exposure to re–suspension of dust from the ground. Figure 1 shows the Guadalajara map, both sampling sites Centro and Miravalle are highlighted by black rectangles.

2.2. Sample collection

PM$_{2.5}$ sampling. The PM$_{2.5}$ sample collection was performed simultaneously at Centro (8 m above ground level) and Miravalle (10 m above ground level) sites, by means of a Partisol 2300 model (Rupprecht and Patashnick Co.) sampler, for 24 h (00:00 to 24:00 h) at a rate of 16.7 L min$^{-1}$ every six days between January and August 2008. The Teflon filters 47 mm in diameter with a pore size of 2 μm (Whatman) used, were allowed to stabilize for 24 h. Gravimetric analysis was carried out with a Sartorius microbalance (model SE2F), under controlled room temperature (295.15 ± 3 K) and humidity (40±5%). Twenty percent of the total filters were used as laboratory and field blanks to correct the mass of the exposed filters for matter introduced during handling. The detection limit, calculated as 3xSD of the mass change in the blank filters divided by the volume of 24–h sampling, was 0.92 μg m$^{-3}$. All concentrations reported in this paper were adjusted to standard temperature (298.15 K) and pressure (101.325 Pa).

BC monitoring. The BC concentration was determined by using the absorption of fine aerosols measurements in the field with a 2–wavelength Aethalometer (Model AE–21, Magee Scientific, Berkeley, CA). Air sample flows through a cyclone, installed at the inlet port, to remove particles higher than 2.5 μm in aerodynamic diameter. A flow rate of 2.4 L min$^{-1}$ produced by a small internal pump was monitored by an internal mass flow meter. The instrument collects the sample on a quartz–fiber filter tape, and performs a continuous optical analysis at 370 and 880 nm. The analysis gives a new reading every 5 minutes.

At constant air stream velocity, the attenuation is linearly proportional to the mass of BC. The technique assumes that the multiple–scattering characteristics of the fibrous filter material are not influenced by non–absorbing particles. Rosen et al. (1978) found that the removal of a non–absorbing aerosol, like ammonium bisulfate, from a filter did not appreciably affect the attenuation.

![Figure 1. Guadalajara sampling sites: Centro and Miravalle.](Image 126x91 to 483x349)
The Aethalometer measures optical aerosol absorption by quantifying the attenuation of light transmitted through a filter tape on which aerosol particles are collected (Hansen, 2005). Once the spot monitored on the filter tape exceeds a certain optical density, the equipment automatically advances the tape to a new spot. In this manner, the Aethalometer can perform months of ambient monitoring without operator attention. The BC concentration, measured as optical attenuation, is the result of conversion with an empirically determined factor obtained by comparison with TOR–EC measurements. Hansen (2005) and Allen et al. (1999) suggest a filter loading correction to account for the multiple scattering effects of filter material in the Aethalometer. A 50% reduction occurs between when the filter is pristine and white after a filter change, and when it is dark right before a filter change. In this work, two calibration factors were used, δ = 39.5 m² g⁻¹ at 370 nm and 16.6 m² g⁻¹ at 880 nm, as given by the manufacturer. A similar procedure was previously used and reported by Marley et al. (2007; 2009b); Madhavi Latha et al. (2005); Eidels–Dubovoi (2002); Derwent et al. (2001) and Bhugwant and Bremaud (2001). The detection limit calculated according to Hansen (2005) was 0.06 µg m⁻³.

Carbon monoxide and meteorological parameters. The Secretary of the Environment for Sustainable Development for the State of Jalisco (SEMADES, by its Spanish acronym) reports levels of criteria pollutant concentrations and meteorological parameter measurements in Guadalajara (SINAT, 2008). The wind speed, wind direction and carbon monoxide concentrations were used to obtain Pearson correlations with BC. The temperature and pressure were necessary to reduce concentrations to standard conditions. Mixing heights and lapse rates for Guadalajara were obtained from outputs of the North American Mesoscale (NAM) Computer Weather Model, operated by the National Weather Service, NOAA, Camp Springs, Maryland, USA.

Statistical analysis. The BC seasonal, monthly, weekly and diurnal variations were compared using the Mann–Whitney and Kruskal–Wallis tests (Conover, 1980). The associations of BC concentration with wind speed and with CO concentration were evaluated by the Pearson correlation coefficient. All basic and non-parametric statistical tests were carried out using the software, INSTAT+, version 3.36.

3. Results and Discussion

Figure 2 presents a summary of the mean PM₁.₅ concentrations measured at the two sites in Guadalajara. Individual PM₁.₅ concentrations ranged from 35 to 179 µg m⁻³ at Centro (n=37) and from 22 to 214 µg m⁻³ at Miravalle (n=39). The PM₁.₅ concentration results indicate that 79% of the samples are above the Mexican air quality standard of 65 µg m⁻³ during 24-h, not to be exceeded by more than 2% of the measurements in a year (NOM–025–SSA1–1993).

Considering the annual rainfall Guadalajara report, prepared by the National Water Commission (CNA, by its Spanish acronym), the BC study period was divided in three seasons: two dry seasons, the first one from January to May (DS1) and the second one from November to December (DS2), while the period from June to October was considered the rainy season (RS).

The hourly BC basic statistics such as data number (n), mean, median and standard deviation, during the three seasons at Centro and Miravalle sites are shown in Table 1.

To better visualize the trends in the median hourly of the BC concentrations, measured for the period of 24–h, the complete data set is plotted for each site in Figure 3a (Centro) and in Figure 3b (Miravalle). During the 2–time periods 00:00–05:00 h and 14:00–18:00 h approximately, the median BC concentration exhibits lower levels and varies between 1.3–2.1 µg m⁻³ in DS1 and 1.4–1.9 µg m⁻³ in RS, at Centro (Figure 3a) while it varies between 1.5–3.6 µg m⁻³ in DS1 and 1.9–2.4 µg m⁻³ in RS, at Miravalle (Figure 3b). These results are a direct image of the city activities, mainly when the vehicular traffic flow shows a net decrease. Evidently, in the 14:00–18:00 h period there is no difference considering site or season.

In general, BC exhibits maximum values in two well defined time–periods. The first peak section starts increasing sharply from “background” level nearly at 05:00 h and reaches a maximum value (around 08:00–09:00 h) of 8.7 and 3.3 µg m⁻³ in DS1 and RS respectively, at Centro; and 13.8 and 6.4 µg m⁻³ in DS1 and RS, at Miravalle. Thereafter, the BC concentration decreased down to the “background” level at 14:00 h approximately. Second peak sections with lower intensity take place in the last period from 18:00 to 24:00 h, the BC concentration in DS1 and RS at Centro and Miravalle are in the range 1.6–7.0 µg m⁻³. The first peak section is a feature of the daily starting activities, coinciding with the morning rush hours at both sites investigated. On the other hand, the second peak section is a consequence of the return from work activities. Overall, the highest BC values observed are from Miravalle throughout DS1. The difference in BC concentration is a clear indication of the contrasting traffic density and the influence of the industrial activities. The lower BC concentrations detected in RS are ascribed to the wet deposition and the reduced biomass burning (i.e., grazing and agricultural burning, and forest fires in the metropolitan area) (Ballesteros, 2009).

Finally, the second dry season DS2 showed an atypical BC–time profile at Centro. The BC concentrations are almost twice higher than the values recorded in DS1, during the first period of the day (00:00–05:00 h). Then, a typical peak is formed as in DS1 and RS, between 05:00–14:00 h, with a maximum BC of 6.8 µg m⁻³. Surprisingly, from 14:00 to 18:00 h the BC tendency is similar to DS1 and RS. A second peak appear in the last time–period (18:00–24:00 h) which shows unusually high concentrations than those observed in DS1 and RS, the top values are in the range of 6.0–7.0 µg m⁻³. These highest concentrations can be attributed to the Mexican traditional use of fireworks and a higher recurrence of vehicles and people at downtown in December. Also, the lower wind speeds favor pollutant accumulation.

Comparison with Miravalle site was not possible due to technical problems, the values during DS2 at Miravalle are not statistically representative (n=4–7 per month), therefore November and December data are not plotted (see Table 1). In general, the daily diurnal pattern is a repetitive phenomenon that was also previously observed at different urban cities such as Mexico City (Eidels–Dubovoi, 2002), Fresno, CA (Chow et al., 2009) and Seoul and Kwangju, Korea (Park et al., 2002).
<table>
<thead>
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<th>MIRAVALLE</th>
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</tr>
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<tr>
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<td>2.5</td>
</tr>
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</table>

For Pollution Median 358 2 4 365
With respect to the BC fraction present in the fine particles, it was necessary to calculate the 24-h BC and the PM$_{2.5}$ mean concentrations, considering just those days when both BC and PM$_{2.5}$ data were available. The Figure 4 summarizes the BC in PM$_{2.5}$ ratios in a box and whisker plot, the medians are 3.5 and 4.9 µg m$^{-3}$ at Centro and Miravalle, respectively. Slightly higher values resulted at the second site. However, all ratios indicate that BC comprises less than 10% of the PM$_{2.5}$ mass concentration measured. Similar data has been reported for other urban areas with similar or higher population than Guadalajara, as Mexico City, Santiago, Beijing, Helsinki, Hong Kong, Los Angeles and Xi’an. Table 2 shows PM$_{2.5}$ and BC concentrations and their ratio measured in different urban cities.

The Mann–Whitney and Kruskal Wallis tests applied to seasonal, monthly and weekly variation show that there is not a significant statistical difference ($p > 0.05$) between the BC concentrations at Centro and Miravalle. The Table 3 contains the BC non-parametric statistics.

BC is a tracer of primary anthropogenic emissions, and its variability reflects changes in source strengths, long-range transport, and atmospheric mixing characteristics (Viidanoja et al., 2002). Guadalajara’s diurnal meteorological factors have a strong effect on air quality. Inversions form at ground level during the nighttime and influence the morning increase in concentrations of pollutants. The sharp drop in these concentrations in the late mornings coincides with solar heating and the dissipation of these nighttime inversions. The mixing layer during the afternoon–evening rush hours is high, around 2–3 km, (NOAA NAM model) contributing to a decrease in the afternoon peak concentrations. Daily wind speeds are slow and variable in the early mornings (less than 1 m s$^{-1}$) and increase throughout the day, reaching 2–3 m s$^{-1}$ around 22:00 h, then the wind speed begins to decrease as the nighttime inversion forms (SIMAT, 2008). Higher wind speeds in the afternoon and evenings during DS1 as compared to DS2 can partially account for concentration differences during these periods at Centro. Weather patterns during the wet or rainy season are more variable as upper airflows shift to the East and Southeast, bringing in moist air from the Gulf of Mexico, replacing the dryer westerly airflow experienced during the dry seasons. Torrential rainstorms may accompany a much more turbulent boundary layer at any time throughout this period.
Table 3. BC non-parametric statistics

<table>
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</table>

When the median BC concentration is related to wind speed (24-h median wind speeds are rounded to the closest integer value), a good inverse correlation resulted ($r^2 = 0.675, p < 0.05$) between BC and wind speed at Centro (Figure 5a). This means that local emissions (traffic) are most likely dominant over all other sources and, external combustion sources did not have an important impact on BC concentrations. On the other hand, considering the whole Miravalle data, it shows a moderate $r^2 = 0.514$ and not significant $p > 0.05$ correlation. There is no clear dependency between BC and local/external sources (industrial and traffic), indicating that there are significant regional and/or long-range transport sources that influence concentrations at this site, as compared to local sources (industrial and traffic) (see Figure 5b).

![Figure 5. (a) Median BC concentration variation with wind speed at Centro site. (b) Median BC concentration variation with wind speed at Miravalle site.](image)

There is another industrial area called El Salto, located in the Southeast that contributes to Miravalle pollution. This is accentuated due to the effect of a hill, called Cerro del Cuatro (20°36’N 103°22’W at 1,870 m above mean sea level), situated close to the monitoring site and causes some turbulence and channeling of the winds near the study area.

Figure 6 shows the strong positive correlation found between BC and CO concentrations, $r^2 = 0.721$ at Centro and $r^2 = 0.670$ at Miravalle, also with significant $p$ values ($<0.05$) at both sites. This confirms common sources for the two species, both produced in the combustion of fossil fuels and biomass burning and both have a relatively long atmospheric lifetimes (BC = 6–10 days and CO = 1–3 months), that varies with season and location (Zhou et al., 2009; Edwards et al., 2004). Consequently, no significant chemical reactions and transformations are expected to change the BC and CO concentrations during their transport between the emission sources and sampling sites.

![Figure 6. (a) Median diurnal BC concentration vs. CO at Centro site. (b) Median diurnal BC concentration vs. CO at Miravalle site.](image)

4. Summary and Conclusions

This study has quantified the PM$_{10}$ and black carbon concentrations at a commercial and an industrial site during the dry and rainy seasons at Guadalajara, Mexico in 2008. The PM$_{10}$ mass concentration ranged from 22 to 214 µg m$^{-3}$ and BC concentration from 1.3 to 13.9 µg m$^{-3}$. BC has a similar diurnal and nocturnal trend during the dry and rainy seasons, although high concentrations are measured in dry season. The mean 24-h BC and PM$_{10}$ concentrations indicate that BC comprises less than 10% of the total fine particles. The meteorology analysis showed that the main BC source is due to local traffic emissions at Centro site. On the other hand, no clear BC dependency with local and external sources (industrial and traffic) was observed at Miravalle site. Finally, a strong correlation was found between BC and CO concentrations at Centro and Miravalle that confirms common sources for the two species, both produced during combustion of fossil fuels and biomass burning.
Acknowledgements

The authors would like to express their appreciation to the Secretaría de Medio Ambiente para el Desarrollo del Estado de Jalisco (SEMADES), for allowing the installation of the equipment in their locations and use of their data bases. Special thanks to CONACyT for the financial support of this project.

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