High levels of black carbon from in-situ and column measurements in Barcelona

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Abstract: The highest values of black carbon (BC) concentration in Barcelona detected between 2019 and 2021 have been analyzed. BC concentrations overtook 8 $\mu g/m^3$ during the study period due to the development of the World Mobile Congress, higher than the maximum values of a period without additional urban sources, which usually graze 3 $\mu g/m^3$. Moreover, the influence of BC on aerosol optical properties such as the single scattering albedo (SSA) has been analyzed. Since BC particles absorb solar radiation, its presence decreases SSA values and its spectral variation. Finally, within the development of this study, it has been observed that, under certain circumstances, in-situ and column data can exhibit different results.

I. INTRODUCTION

Atmospheric aerosols play an important role in our environment, affecting air quality and health, and contributing to global climate. Aerosols impact on climate by modifying the Earth's radiative balance, directly through absorption and scattering of shortwave and longwave radiation, and indirectly by acting as a cloud condensation nuclei. Most particles scatter the sunlight, causing a net cooling at the top of the atmosphere (TOA), whereas certain atmospheric aerosols absorb solar radiation thus causing a net warming at the TOA. Aerosol light absorption is dominated by black carbon (BC), a carbonaceous light-absorbing aerosol produced as a result of the incomplete combustion of natural and anthropogenic substances, including the burning of fossil fuels, biofuels and biomass. Moreover, BC is the second most important warming agent after carbon dioxide.

Measurements of aerosol optical properties such as scattering, backscattering, absorption and extinction are important for aerosol characterization and model validation and, therefore, for yield further insight into the role of aerosols in the Earth-atmosphere system [1].

Due to the aforementioned reasons, the main aim of this project is to study an episode of high levels of BC in Barcelona and its influence on aerosol optical properties.

II. METHODOLOGY AND DATA

In this study, different aerosol parameters measured simultaneously using different instruments have been presented. In-situ measurements are carried out using two Aethalometers (AE33 model; Magee Scientific), and column integrated measurements performed by a sun photometer (CIMEL Electronique 318A) from Aerosol Robotic Network (AERONET). Moreover, planetary boundary layer (PBL) height data is retrieved from a ceilometer (Vaisala CL31) in order to further support the analysis of the results.

A. Instrumentation and Measuring sites

The Aethalometer is a filter-based instrument that continuously collects aerosol particles on a filter tape. The sampled air containing the aerosol particles passes through the filter tape where the particles impinge, creating a spot of increasing density, referred to as filter loading effect (k). The AE33 model used in this study has two filter spots with different sample flows, and one unloaded spot acting as a reference area, which allows for online correction of k. The attenuation of the projected light beam through the filter spots is measured at seven different wavelengths, ranging from 370 nm to 950 nm. From this attenuation measurement, the BC mass concentration is calculated taking into account the filter loading effect and the enhancement of optical absorption of aerosols due to the multiple scattering of light within the filter [2].

The data from both Aethalometers used in this study is from particles smaller than 1 μm (PM1), as it is conventionally assumed that BC is the only light-absorbing component of sub-micron aerosols [3]. At 880 nm, as other aerosol-absorbing particles (carbonaceous or mineral) absorb noticeably less at this wavelength, the BC can be considered the only particle that influences on the absorption [4].

The measurement stations are located in two different representative sites with different backgrounds: urban and regional. The urban background site, which is the reference station in this study, is located in the Institute of Environmental Assessment and Water Research (IDAEA-CSIC), in the metropolitan area of Barcelona (BCN; 41°23'15.15" N, 02°06'53.22" E, 80 m a.s.l.), 6 km far from the Mediterranean coast, 5 km west of the city center and 200 m distance from one of the most concurred avenues of the city: Diagonal Avenue. The data collected from this station goes from 13/02/2019 until 11/05/2021. In order to analyze a specific period of study, it has been decided to select the days with the highest values of BC. The regional background site is located in the Montseny Natural Park (MSY; 41°46'45.63" N, 02°21'28.92" E, 720 m a.s.l.), 50 km to the NNE of BCN and 25 km from the

Mediterranean coast. The data collected from this station span from 15/02/2019 until 01/06/2020.

AERONET is a global network of different ground-based sun photometers that perform column integrated measurements in order to provide information about optical and physical aerosol properties [5]. The instrument used is designed to perform spectral measurements at different wavelengths from 300 nm to 1020 nm of the sun and sky radiances at different angles. Finally, AERONET continuously provides different cloud-screened aerosol properties that represent an average of the total aerosol column within the atmosphere.

The AERONET station is located at the roof of the Universitat Politècnica de Catalunya (41°23'20.4" N, 02°06'43.2" E, 125 m a.s.l.), in Barcelona, at a distance of around 267 m from the Aethalometer station.

The Ceilometer allows to determine cloud base and PBL height from the analysis of the vertical profile of backscattering. Data is automatically calculated by the Vaisala BL-View software.

B. Aerosol optical properties

Different column integrated aerosol optical properties from AERONET are handled within this study.

The extinction of direct solar radiation throughout the atmosphere is determined by the photometer according to the Beer law:

$$V(\lambda) = V_0(\lambda)e^{-\tau_\lambda m}, \tag{1}$$

where $V(\lambda)$ and $V_0(\lambda)$ are the in-situ measured potential and the constant initial value of the potential on the TOA for a certain wavelength, τ_λ is the optical depth and $m = 1/\cos\theta$, where θ is the solar zenith angle in a particular moment. The optical depth under clear conditions is the sum of multiple contributions: aerosol particles, air molecules (Rayleigh) and other gases ($\tau_\lambda = \tau_{aer,\lambda} + \tau_{R,\lambda} + \tau_{gases,\lambda}$).

As an increase of BC particles involves an increase of the extinction of radiation that travels through the atmosphere, the $V(\lambda)$ term becomes smaller because less amount of radiation reaches the surface. Therefore, according to Eq. (1), if $V(\lambda)$ becomes smaller, the optical depth should increase. Assuming that the contributions of air and gases remained constant, this increase can be attributed to an increase of aerosol particle concentration. Therefore, as previously reported [6], a high optical thickness implies a higher concentration of aerosols.

The spectral variation of $\tau_{aer,\lambda}$ can provide insight into the aerosol particle size distribution. This spectral variation is given by the Ångström power law:

$$\tau_{aer,\lambda} = \beta\lambda^{-\alpha}, \tag{2}$$

where β is the turbidity parameter that shows the aerosol content of the atmosphere in a vertical column and α is the Ångström exponent.

In particular, α is an indicator of the aerosol particle size distribution: a distribution dominated by fine mode aerosols (radius ≤ 1 μm) is indicated by $\alpha > 1$ and is typically associated with urban pollution and biomass burning. In contrast, a size distribution dominated by coarse mode particles (radius ≥ 1 μm) is characterized by $\alpha < 1$ and is usually associated with dust and sea salt particles.

The single scattering albedo (SSA) is a spectral parameter that represents the ratio between the scattering efficiency and the total extinction (scattering and absorption) efficiency, and it is given by:

$$\text{SSA} = \frac{\sigma_{sp}}{\sigma_{sp} + \sigma_{ap}}, \tag{3}$$

where σ_{sp} is the particles scattering coefficient and σ_{ap} is the particles absorption coefficient.

The SSA indicates the potential of aerosols for warming or cooling the atmosphere: a SSA = 1 means that the aerosol cools the atmosphere and is related to non-absorbing particles, whereas the lower SSA values become, the more absorbing particles in the atmosphere coexist. The value for pure BC particles is about 0.2 (warming). Furthermore, its spectral dependence is used to deduce aerosol composition and particle size distribution. Since particles' absorption usually decreases with wavelength, the spectral variation of SSA for coarser aerosol particles presents an increase as the scattering increases with the wavelength. On the other hand, the scatte-ring coefficient of finer aerosol particles tends to decrease at a faster rate than its corresponding absorption coefficient. In particular, BC particles, which are usually very fine aerosols (radius < 1 μm), are equally efficient at absorbing at every wavelength, thus an aerosol mixture dominated by BC presents a decreasing SSA spectrum.

III. RESULTS AND DISCUSSION

A. Diurnal variation of mass BC

The average BC concentration at BCN exhibits two well-marked peaks throughout its diurnal evolution (Fig. 1, 2a whole period). The first peak, which also presents the maximum value of the time series, coincides with the rush hour tra-ffic between 5 and 10 UTC, when the highest number of vehicles are being driven by people who have to commute. Similarly, the second peak also concurs with the second peak traffic time of the day, emphasizing the relevance of BC emission due to the incomplete combustion of diesel engines. However, the fact that a minimum is shown during the central hours of the day is closely related to both fewer traffic and the daily variations of the PBL. At noon, the increased solar heating warms the air cells close to the surface, which increases the air molecules near the surface kinetic energy, thus favoring vertical movements of these air parcels. Taking into consideration that the Aethalometer used to measure

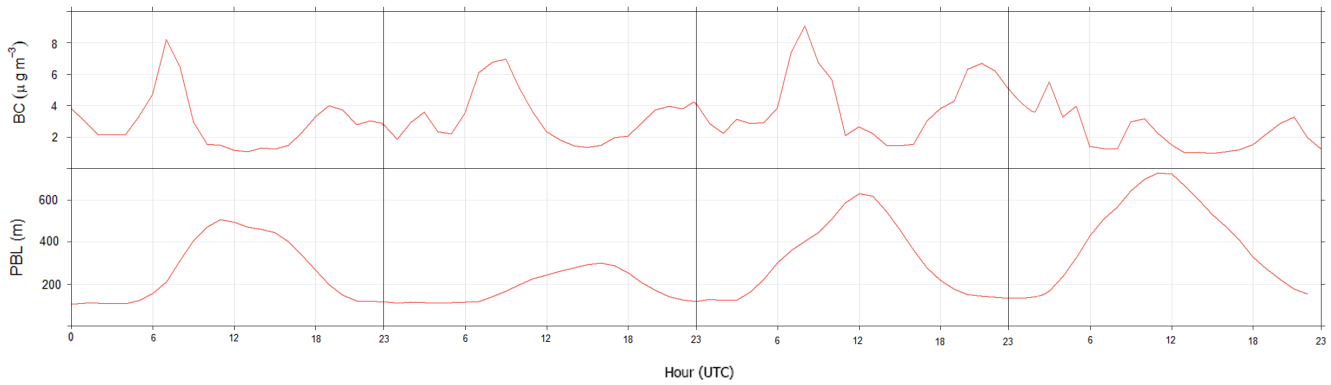

FIG. 1: Daily cycle of BC concentration and PBL height within each day of the study period at BCN. In the x axis, the hours from 26/02/2019 to 01/03/2019 are represented.

BC concentration is located near the surface, it captures higher concentration within the first and last hours of the day, when the particles are diluted in a shallower PBL.

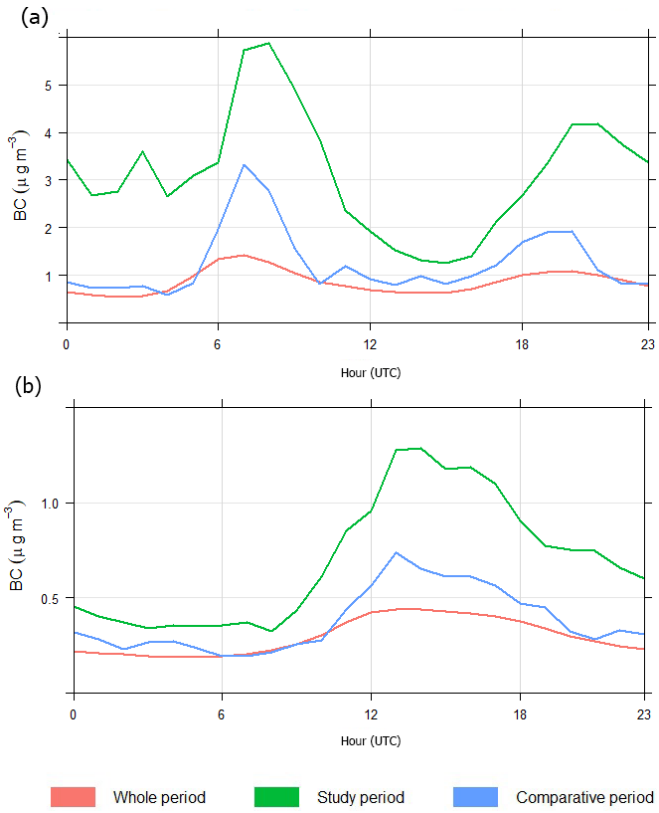

FIG. 2: Daily cycle of BC average mass concentration from 13/02/2019 to 27/05/2021 (whole period), 26/02/2019 to 01/03/2019 (study period) and 18/02/2020 to 21/02/2020 (comparative period) at BCN (a) and MSY (b), where the y axis is adjusted for an optimal presentation of the daily variations.

Otherwise, the daily cycle of mean BC concentration from the study period, with values that almost reach 6 μg/m^3 (Fig. 2a), brings into prominence the remarkable difference between the BC concentrations within both time series. This contrast arises from the fact that the period herein selected includes the last 3 days in which the World Mobile Congress (WMC) took place. The number of attendees that went to this influential event in 2019 got to 109.000 [7], thus causing a meaningful increase of traffic on both characteristic rush hours of weekdays. Furthermore, the fact that the average values of the whole period are determined including the COVID-19 lockdown, when the main source of BC in an urban city such as BCN (the fossil fuels incomplete combustion) was almost drastically reduced [8], also contributes to this difference between the peaks of both series. Hence, it has also been aimed to yield insight into the everyday life daily cycle within weekdays at BCN, when the aerosols concentrations are not hugely influenced by any external event. To this aim, an equivalent period to the study one displaced a year (comparative period) has been represented in Fig. 2. The diurnal variation of BC presents the same cycle that has been previously discussed and highlights the e-ffect that a large event such as the WMC can have on the increase of BC within the traffic rush hours.

In order to further understand the influence of the PBL on aerosol dilution and, therefore, on BC capture, its diurnal variation within the study period is presented in Fig. 1. Since the BC concentration measured by the Aethalometer is represented simultaneously, it can be seen that the maximum values of the PBL height coincide with the minimum BC concentrations. In addition, this representation clearly shows the difference between the BC concentration within the days when the WMC was being carried out (26-28/02) and the day it ended (01/03), since the peak values are halved.

Finally, we can see the appearance of a new peak in the study period located in the dawn hours (not observed in the whole period average), related with the night events that took place during the WMC (Fig. 2) and caused a boom of incomplete combustion of diesel engines in an unusual time of the day. However, this peak is not as remarkable as the other two.

On the other hand, this pattern exhibited in the daily

cycle at BCN is only characteristic of urban sites and can not be seen in other sites such as MSY regional site (Fig. 2b). The average BC concentration at MSY presents lower values at night and higher values in the afternoon throughout its diurnal evolution. This is caused by the thermally driven upslope winds that promote the transport of anthropogenic pollutants from the industrialized coastline and valleys to inland areas during the warmest hours of the day. Other factors that make this possible are the proximity of the MSY station to BCN and other principal urbanized sites and its altitude, which is not high enough to avoid that the height of the polluted PBL reaches it [1].

Nevertheless, as being located within a Natural Park, not close to large emission sources, the BC concentration is much lower than in BCN, where its minimum value within the whole time series is higher than the maximum value in MSY. However, there is an increase of BC concentration within the time periods presented in Fig. 2b, where the peak in the selected period of study almost overtakes for 1 μg/m^3 the peak in the whole time series.

B. BC influence on aerosol optical properties

As BC absorbs solar radiation, it causes the variation of different aerosol optical properties such as the AOD, AE or SSA, whose values determine the magnitude of the influence of aerosols on radiative forcing.

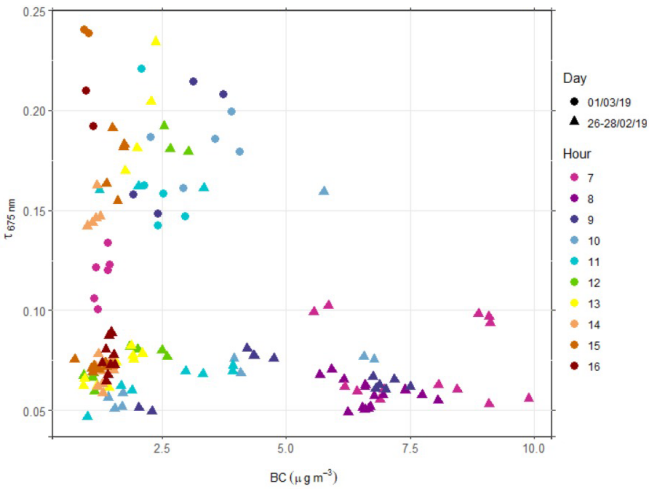

FIG. 3: Scatter diagram of AOD at 675 nm versus BC mass concentration distinguished by hours and days.

An increase in BC concentration should imply higher values of AOD, thus a positive correlation between both variables is expected [6]. However, Fig. 3 shows two different behaviors within the days of the study period. On one hand, there is a null relation between the variables during the first hours (from 7 to 10 UTC) of the 26-28 of February. On the other hand, the remaining hours of 26-28 of February and all the hours collected from 01 of March exhibit, as expected, a positive correlation between AOD and BC concentrations.

As it has been previously seen, the main source of BC particles measured in BCN comes from traffic, which occurs near the surface. Nevertheless, since the AERONET photometer is located at a certain height above the surface, it can not detect the variation in the atmospheric composition until enough vertical development of the PBL is produced. Moreover, it must be taken into account that the AOD is a variable that provides information about the whole atmosphere column, whereas the BC concentration is limited to surface measurements. Thus, if the fact that BC particles are not the only aerosols that influence on the AOD, it is clear that significant differences can be displayed.

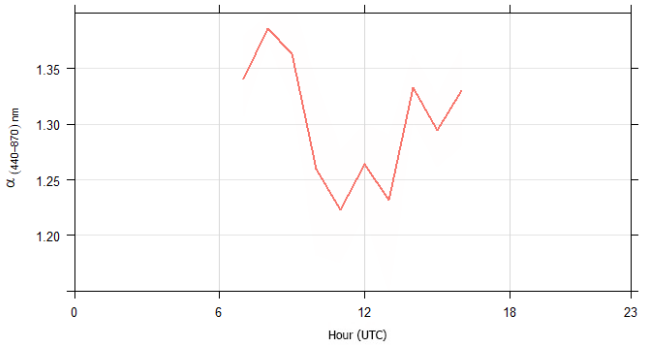

FIG. 4: Mean Ångström exponent (440-870 nm) daily cycle within the study period (26/02/2019 to 01/03/2019).

The maximum value of the AE, which almost reaches 1.4, is presented at 8 UTC (Fig. 4). Furthermore, the higher values are located from 7 to 9 UTC, which coincide with the highest peak of BC concentration within the study period (Fig. 2a). As expected, the AE values show that this is the period of time when fine mode aerosols are more dominant, which include BC particles. Straightaway, the AE sharply decreases thus exhibiting its lower values at the central hours of the day. As already mentioned, the increased solar heating within these hours leads to a faster dispersion of aerosols, causing a mixture and redistribution of them into higher heights. Therefore, due to this dilution of aerosols and the scarce sources of BC particles within the central hours, the AE values indicate that such hours present the least dominance of fine mode aerosols within the day. Finally, the second peak also concurs with the second peak of BC concentration within the study period, making evident that a period of time when an abundant incomplete combustion by diesel engines is produced implies a higher dominance of fine mode aerosols than the rest of the day.

It must be taken into consideration that, as the AE value does not drop below 1, it indicates that the study period is not dominated by coarse mode aerosols such as dust or sea salt, which could also influence on radiation absorption.

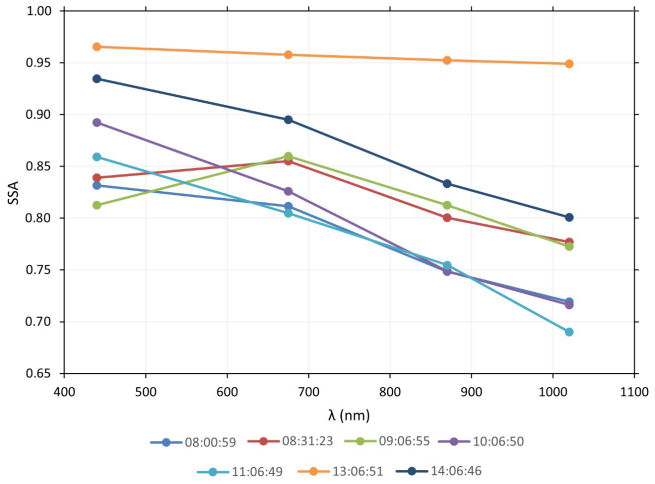

FIG. 5: SSA wavelength dependence (440, 675, 870, 1020 nm) within seven different hours of 26/02/2019. The legend indicates the observation hours in UTC.

Since most of the atmospheric aerosols have a scattering behavior and SSA is a column-integrated parameter, the first hours of the day, which have been previously discussed to present huge concentrations of BC, do not show SSA values close to 0.2, as it would be representative of a pure column of BC particles (Fig. 5). Nevertheless, the values below 0.9 exhibited within the five first hours in Fig. 5 indicate the relevant presence of absorbing aerosols as the scattering percentage has been noticeably reduced.

On the other hand, the high SSA values near 0.95 observed within 13 and 14 UTC at 440 nm reconfirm the fact that there is less concentration of BC within the central hours of the day. Moreover, the low spectral dependence shown at 13 UTC indicates an almost non-existence of absorbing particles within that hour. However, the rest of the hours show a decreasing spectral variation of SSA, in agreement with an aerosol mixture dominated by BC particles. It should be noticed that, although the expected spectral dependence is a monotonically increase or decrease, the SSA at 8:30 and 9 UTC increases for shorter wavelengths and then decreases. However, this behavior is reported [9] to be shown occasionally.

IV. CONCLUSIONS

This study has shown the following:

1. The BC daily cycle in an urban site is strongly conditioned by traffic and regulated by the diurnal evolution of the PBL.

2. Since BC particles present a high absorptive capacity, their presence in the atmosphere decreases the SSA but increases the AOD. Aforesaid absorptive capacity remains constant with wavelength variation, whereas the scattering reduces thus causing a decreasing SSA spectral dependence. Moreover, as BC particles usually are finer particles, their presence produces an increase of the AE.

3. The analysis of column-integrated data implies the study of an aerosol mixture in a vertical column where BC does not always have an essential role, whereas the analysis of in-situ data just collects aerosols near the surface. Therefore, in-situ and column-integrated measurements must be analyzed with carefulness since the results can lead to different conclusions. Moreover, if the instruments are located far from each other or at different heights, the chance of these differences within the results increases.

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