Source Apportionment and Diurnal Variability of Autumn-Time Black Carbon in a Coastal City of Salé, Morocco †

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Abstract: This research aims to understand the temporal variation of concentrations of equivalent black carbon (eBC) and to calculate the fossil fuel (BCff) and biomass combustion (BCwb) contribution to eBC during the 2020 autumn season. In-situ measurements of eBC and NO\textsubscript{2} were performed for this aim in Sale, Morocco. The contribution of BCff and BCwb was assigned based on the spectrum dependence of BC absorption. The average eBC concentration was 1.9 ± 2.2 µg/m\textsuperscript{3} with a contribution of 13% for BCwb. The eBC was strongly correlated with NO\textsubscript{2} (R\textsuperscript{2} = 0.63). Fossil fuel combustion is the most significant contributor to eBC and NO\textsubscript{2} concentrations.

Keywords: black carbon; source apportionment; Morocco

1. Introduction

Air pollution, mainly from traffic combustion processes, is a serious environmental problem in Salé, the second densest city in Morocco (8163 hab/km\textsuperscript{2}), as in other major urban areas worldwide. Air pollution in cities leads to increased atmospheric concentrations of combustion products such as nitrogen dioxide (NO\textsubscript{2}) and particulate matter (PM). The latter includes primary particles generated by combustion, secondary particles, and mineral dust particles. Black carbon (BC) is identified as a large amount of carbonaceous aerosols, and consequently, the fine PM2.5 [1] comes mainly from the combustion of fossil fuels and biomass [2].

Studies [3,4] stated that BC concentrations are proportional to traffic emissions, which allows inferring BC levels from traffic. However, the contribution of biomass-burning activities may affect both the daily cycles of BC and the BC/NO\textsubscript{2} ratios.

Among the methods of apportionment techniques based on observation, the aethalometer model has been adopted in different studies [5,6] to assess the contributions of fossil fuel and biomass combustion to equivalent black carbon (eBC) by analyzing light absorption at multiple wavelengths.

In this context, the goal of this research is to look at the influence of biomass burning vs. fossil fuel consumption on the Salé air pollution during the 2020 autumn season.
2. Materials and Methods

2.1. Sampling Site

The Médersa of Mérinides (34°02'23.4" N 6°49'38.5" W) was built in 1341 JC/733 h by the mérinide sultan Abou'l Hassan, and it represents the architectural masterpiece of the medina of Salé. It offers a unique decoration including Andalusian excellence in architecture and spatial organization as shown in Figure 1. A preliminary census campaign outlined two types of anthropogenic sources of pollution that may be identified during the measurement: (1) Fixed sources implemented inside the Medina, including traditional hammams (Moroccan public bathhouses) and ovens (use of combustion wood); and (2) Mobile sources (cars, trucks, buses, motorcycles, etc.) circulating inside the city and in the surrounding area parallel to the historical wall of the medina.

![Figure 1. Location map of the measurement site at The Médersa of Mérinides in Salé.](image)

2.2. Data Collection

The field campaign in Salé was performed from 14 October to 27 November 2020. Black carbon continuous measurements were carried out using a multiple spectrum carbon analyzer (The BC1054 by Met One Instruments, USA) on the terraced roof of Mderssa at the height of around 12 m-agl. The BC1054 analyzer automatically measures optical transmission at ten wavelengths ranging from 370 nm to 950 nm through a filter on which particles have been deposited. The absorption at 880 nm in the near-infrared computes the equivalent black carbon (eBC) content.

ENVEA Cairpol’s low-cost electrochemical sensors were employed for continuous and high-resolution temporal NO$_2$ monitoring. For each gas measurement, the uncertainty was on the order of $+/-25$ to $30\%$.

Meteorological data, such as temperatures, wind speed, and direction, were collected from the International Meteorology website (http://www.wunderground.com (accessed on 7 March 2022) and from (NOAA Air Resources Laboratory) with processing by R software [7]. Wind rose and hourly change in temperature and humidity in October and November 2020 are illustrated in Figures 2 and 3, respectively.
3. Results and Discussion

3.1. Characteristics of eBC and NO\textsubscript{2} Concentrations and Sources

Numerous studies have shown that BC concentration is related to the site type (urban, suburban, rural, downtown) \cite{8,9} and prevailing weather conditions \cite{6,8}. The first method used in this study to apportion the sources of eBC is based on the correlations between eBC and traffic combustion tracer NO\textsubscript{2}. Figure 4 shows the hourly variation of BC and NO\textsubscript{2}, and Figure 5 shows their linear regression. A strong relationship between eBC and NO\textsubscript{2} was observed during this study ($R^2 \approx 0.63$), close to the values reported in Malaysian ($R^2 = 0.71$) \cite{10} and English ($R^2 = 0.88$) \cite{1} suburban areas, as shown in Table 1. The ratio between eBC and NO\textsubscript{2} is 0.17, equivalent to a value of 0.14 according to the results obtained in Doha, Qatar \cite{2}, characterizing diesel fuel. The average eBC values recorded during this study were $1.9 \pm 2.2 \mu g/m^3$, which are comparable to the values recorded at an urban site in Milan, Italy ($1.92 \pm 0.88 \mu g/m^3$) \cite{11} and during periods of winter biomass burning ($1.89 \pm 0.5 \mu g/m^3$) at residential urban areas in Kwadela, South Africa \cite{12}.
Table 1. Comparison of eBC values measured in Salé and worldwide cities. The table covers the type of sites, study period, measurement techniques, and the eBC concentrations. The table is ordered according to eBC mass concentration.

| Location                        | Type of Location                | Study Period                  | Measurement Techniques/Methods | Mass Concentration Range (µg/m³) of eBC, BCff, BCwb, and NO₂ | Reference |
|---------------------------------|---------------------------------|-------------------------------|--------------------------------|---------------------------------------------------------------|-----------|
| British Columbia, Canada        | Lower Fraser Valley             | September 2016 to August 2017 | Aethalometer AE22              | BC: 0.3–0.8, BCff: 70–84%                                      | [13]      |
| Dacheng Township, Taiwan        | Rural site                      | 1 January to 31 December 2019 | Aethalometer AE31              | BC: 0.793 ± 0.638, BCff: 0.709 ± 0.567 (89.4%), BCff: 0.084 ± 0.196 (10.6%) | [14]      |
| London, England                 | Suburban background             | 1 January 2013 to 1 April 2015| Magee Aethalometer AE22        | BC: 1.0–2.4, R² (BC and NO₂) = 0.88                           | [1]       |
| Helsinki, Finland               | Suburban                        | October 2015 to May 2017      | Aethalometer AE33              | BC: 1.04 ± 2.13, BCwb: 46 ± 15%                                | [15]      |
| Kwadela, South Africa           | Kwadela low-income settlement   | 18 February to 13 April 2015  | Aethalometer AE-22 (winter)    | BC: 1.89 ± 0.5                                                  | [12]      |
| Salé, Morocco                   | Urban                           | 14 October to 27 November 2020| BC1054                         | eBC: 1.9 ± 2.2, BCff: 1.6 ± 2.5, BCwb 0.25 ± 0.72, R² (BC and NO₂) ≈ 0.63 | This study|
| Milan, Italy                    | Main roads                      | July 2008                     | Aethalometer AE51             | 1.92 ± 0.88                                                    | [11]      |
| Klang Valley, Malaysia          | Suburban location               | 1 January to 31 May 2020      | Aethalometer AE33              | BC: 2.34, BCff = 79%, R² (BC and NO₂) = 0.71                   | [10]      |
| Nairobi, Kenya                  | Rural background                | July 2009                     | Teflon filters at LDEO         | BC: 3.2 ± 1.1                                                   | [16]      |

Figure 4. Hourly mean variation of eBC and NO₂.
The eBC pollutant rose shown in Figure 6 indicates that the highest levels of eBC concentrations are recorded when the wind speed is low (not exceeding 3 m/s) and comes from the southeast. Daily and hourly pollutant rose diagrams (not shown), show that eBC concentrations peaked at midnight (~23:00 h–00:00 h) when the winds were from the south and southeast.

Figure 6. Rose pollutant of eBC depicting the relationships between mean eBC concentrations (ng/m³), wind speed, and wind direction over the study period.

3.2. eBC Source Apportionment

Significant day-night variation in eBC levels was observed during the sampling period (mean night/day ratio = 1.4). This variability could be due to two processes: (a) the atmospheric boundary layer is shallower at night and retains pollutants in a smaller volume, and (b) the transport of emissions from fossil fuels produced at the local scale by the nighttime land breeze (Figure 6). A third option is the higher emissions from fossil fuels during the night (possibly due to transportation engines). To discuss these hypotheses involved in the observed eBC changes and to assess eBC source apportionment, the exponent of the absorption Ångström was used as a source-specific parameter to distinguish between wood combustion (BCwb) and fossil fuel (BCff) aerosols [17]. In this study, we used absorption Ångström exponents of 1.0 and 2.0 for pure traffic (BCff) and wood burning (BCwb), respectively.

We tracked the evolution of concentrations of the eBC, BCff, and BCwb by studying their hourly changes during the period October 14 to 27 November 2020. The diurnal variations of the mean values are presented in Figure 7. Significant diurnal cycles in eBC and BCwb and BCff concentration were recorded with two peaks, around 8 a.m. and 11 p.m.
For non-reactive pollutants like BC, the concentration increases at night when the boundary layer gets shallower than it is throughout the day [1]. Average eBC, BCff, and BCwb values range from $1.9 \pm 2.2$, $1.6 \pm 2.5$, and $0.25 \pm 0.72 \mu g/m^3$, respectively.

![Figure 7](image)

**Figure 7.** The diurnal distribution of BC, BCff, and BCwb. The horizontal lines represent the medians; the limits of the boxes are the 1st and 3rd quartiles. The whiskers extend to one and a half times the interquartile range. Hours are in local time, LT.

The primary contribution to BC concentrations in this study is fossil fuel use, with more than 86%, particularly in the morning and evening hours. Although our census campaign outlined 12 ovens and eight traditional hammams within a radius of 400 m of the sampling site, biomass burning makes a non-significant contribution of about 13% to autumn-time eBC.

### 4. Conclusion

This study demonstrated that the concentration of black carbon comes from a large percentage of vehicle fuel combustion. The contribution of biomass burning and hammams located around the Médersa site of Salé was evaluated by 13%. The average values of eBC, BCff, and BCwb ranged from $1.9 \pm 2.2$, $1.6 \pm 2.5$, and $0.25 \pm 0.72 \mu g/m^3$. It was also determined that the increase in the concentration of eBC remains local and not related to wind gusts. There is a significant correlation between eBC concentration and NO$_2$ with a value of 0.63 and an inverse asymmetric relationship with the atmospheric boundary layer.
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