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New insights from seasonal and weekly evolutions of aerosol absorption properties and their association with PM2.5 and NO_2 concentrations at a central Mediterranean site

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A R T I C L E I N F O

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A B S T R A C T

Aerosol absorption parameters were investigated in this study using the measurements performed by an aethalometer during a monitoring campaign from December 2021 to July 2022 in a suburban area in south-eastern Italy. The aerosol absorption coefficient was compared to both PM2.5 and NO_2 concentrations from two nearby stations (a rural and an urban site). Different seasonal evolutions were identified for these extensive parameters, even if they also showed a common feature because all these parameters presented a higher variability in winter due to the highly variable meteorological conditions during that season. Intensive parameters like the aerosol absorption Ångström exponent and the PM2.5/PM10 ratio were also investigated showing the effects of wood burning from domestic heating and of vehicular traffic, especially both in the urban and in the suburban site. Then, the weekly evolution of both selected extensive and intensive parameters was also analyzed to identify potential impacts due to the weekly cycle of human activities. Most of the selected parameters presented a significant increase starting from Tuesday to Friday and then they generally decreased during the weekends due to the relevant reduction of the human activities. The selection of different types of monitoring sites (urban, suburban, and rural) and temporal scales (seasonal and weekly) has been proved for a proper characterization of the aerosol absorption properties at the monitored area due to its geographical location at the center of the Mediterranean area.

1. Introduction

One of the main atmospheric components among aerosol particles with light-absorbing properties is generally represented by elemental carbon (EC), also known as black carbon (BC). It has a significant effect on Earth's climate due to its contribution to atmospheric warming, which is in turn associated with glacier melting and perturbations in atmospheric circulation (e.g., Lüthi et al., 2015; Wang et al., 2020; Kaskaoutis et al., 2021). Open biomass burning (40%), diesel emissions (27%), and domestic solid-fuel combustion (25%) largely represent the most common sources of BC particles, according to Bond et al. (2013). Both BC and the other component of carbonaceous aerosols, referred to as organic carbon (OC), are generally identified within the aerosol fine mode (e.g., Wu et al., 2018; Kompalli et al., 2020). Their main sources are associated with various anthropogenic activities such as road traffic, industrial emissions, biomass burning, and some secondary processes in the atmosphere (Yan et al., 2018; Conte et al., 2020). Contrary to what is generally found for BC, OC is instead mainly characterized by light scattering properties, although it may also present absorption properties at UV wavelengths (e.g., Kaskaoutis et al., 2021). In fact, in this way it is defined the so-called brown carbon (BrC), which represents the light-absorbing component of OC (e.g., Laskin et al., 2015; Tang et al., 2016; Costabile et al., 2017; Pandey et al., 2020), with potential significant contributions also to radiative forcing as proved by some recent

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studies (e.g., Saleh et al., 2015; Zhang et al., 2017). Among the aerosol extensive parameters (defined as the parameters directly related to aerosol amount, e.g., Rajesh and Ramachandran, 2020), the aerosol absorption coefficient (σ_{abs}) is commonly used to quantify the light absorption by particulate matter. In more detail, the aethalometer represents the most used instrumentation for σ_{abs} determination at different wavelengths by using an optical methodology. Among the numerous intensive aerosol parameters (defined as the parameters not directly dependent on aerosol amount, but on other aerosol characteristics like size, type, and/or shape, e.g., Rajesh and Ramachandran, 2020) associated with absorption properties, Ångström absorption exponent (AAE) presents a particular importance since it is mainly associated with aerosol emission sources, combustion efficiency, and atmospheric aging (e.g., Pokhrel et al., 2016; Stockwell et al., 2016). About the carbonaceous aerosols with light absorption properties, several previous works were devoted to the BC source apportionment (Sciare et al., 2011; Healy et al., 2017; Liakakou et al., 2020a; Rajesh et al., 2021) and the BrC characterization (Massabo et al., 2015; Liakakou et al., 2020b; Pani et al., 2021), mostly associated with fossil fuel and biomass burning sources, respectively. Regarding the Mediterranean area, several recent studies have evaluated the main aerosol absorption parameters. For instance, Katsanos et al. (2019) and Liakakou et al. (2020b) reported significantly higher aerosol absorption levels in Athens (Greece) compared to other Southern European cities (e.g., Costabile et al., 2017; Titos et al., 2017; Romano et al., 2019). Milinković et al. (2021) investigated the temporal variation of aerosol optical properties and evaluated the main emission sources of BC, considering different seasons in a typical Mediterranean coastal environment. Their field campaign conducted in Sibenik (Croatia) during February–July 2019 provided valuable insights. In contrast, López-Caravaca et al. (2022) focused on characterizing the seasonal evolution of PM1 concentration, aerosol absorption coefficient, and AAE at the Aitana mountain site in Spain during 2018. They found that AAE exhibited opposite seasonality compared to the aerosol absorption coefficient, showing maximum values in winter, while PM1 concentrations and aerosol absorption coefficients were highest during some Saharan dust outbreaks. Several other studies have also examined the intensive aerosol absorption properties by determining the AAE values for various sites in Northern Italy. For example, Massabo et al., 2015 conducted research in Genoa, Bernardoni et al. (2017) in Milan, and Costabile et al. (2017) in Bologna. Another significant effect associated with anthropogenic sources of atmospheric aerosols is the relationship between their absorption properties and their weekly cycle, which mainly follows human activities with a significant reduction during weekends. For instance, Mbengue et al. (2020) analyzed the weekly variations of aerosol absorption properties during a 5-year monitoring campaign in the Czech Republic, while Popovicheva et al. (2022) conducted similar research in an urban site in Moscow (Russia), experiencing significant variations between weekday and weekend periods. The association of aerosol absorption properties with other gaseous pollutants like NO_2 has been widely investigated at different types of monitoring sites, as reported in several previous studies (e.g., Vestreng et al., 2009; McDuffie et al., 2020).

The results reported in this study are based on the daily mean values of both aerosol absorption coefficient and absorption Ångström exponent from an 8-month monitoring campaign performed in a Central Mediterranean site, in south-eastern Italy, characterized by a mixed aerosol type, as discussed in Romano et al. (2019). The characterization of the aerosol absorption properties at the selected site was performed in relation to extensive parameters like PM2.5 and NO_2 concentrations and the intensive parameter denoted as PM2.5/PM10 ratio retrieved from two nearby monitoring stations. In more detail, both extensive and intensive parameters were analyzed considering their seasonal and weekly evolution to investigate the effects associated with meteorological and anthropic factors, respectively.

2. Material and methods

2.1. Site description

The monitoring area of this study is located in Lecce, a small-sized city (≈95,000 inhabitants), in a narrow and flat peninsula of south-eastern Italy, about 40 and 70 km away from large industrial areas of the Apulia region in Brindisi and Taranto, respectively, less than 100 km away from the Balkan and Greek coasts, and about 700 km away from the North African coast (Fig. S1). The monitoring campaign was carried out in an 8-month period from December 2021 to July 2022, to investigate the seasonal evolution of the analyzed parameters by dividing the dataset in winter (from December 2021 to February 2022), spring (from March to May 2022), and summer (June–July 2022). The measurements of aerosol absorption properties were performed by a 7-wavelength aethalometer at the monitoring station of the Mathematics and Physics Department of the University of Salento (40.33 °N, 18.11 °E), in an area of the university campus mainly affected by the vehicular traffic as local source of particulate matter and classified as suburban site. PM2.5, PM10, and NO_2 concentrations were instead monitored at the stations denoted as Lecce-Cerrate (40.46 °N, 18.12 °E, a rural background site only about 4 km from the Adriatic coast) and Lecce-Libertini (40.35 °N, 18.18 °E, an urban site frequently affected by an intense vehicular traffic) belonging to the ARPA (Agenzia Regionale per la Prevenzione e la Protezione dell'Ambiente) Puglia monitoring network (https://www.arpa.puglia.it/). The importance of the study area for the characterization of aerosol properties is due to its large variety of aerosol types, in turn due to its geographic location at the center of the Mediterranean basin, as clearly shown in Fig. S1. In more detail, the study area is generally affected by polluted particles from urban and industrial areas of Northern and Eastern Europe, sea salt and spray from the Mediterranean Sea or the Atlantic Ocean, mineral dust from the Sahara Desert and/or the surrounding arid regions, and biomass burning particles produced mostly in summer by forest fires, in addition to some local sources like vehicular traffic and domestic heating (e.g., Romano et al., 2019). Further details about the characterization of mean aerosol optical and physical properties and meteorological conditions at the study area were provided in previous works (e.g., Perrone et al., 2014, 2015).

2.2. Aethalometer measurements

An aethalometer model AE33 (Magee Scientific, Aerosol d. o.o., Drinovec et al., 2015) equipped with a PM2.5 sampling head was used to determine the aerosol absorption coefficient (σ_{abs}) at seven different wavelengths (370, 470, 520, 590, 660, 880, and 950 nm) with a temporal resolution of 1 min during an 8-month monitoring campaign from December 2021 to July 2022 at the monitoring station of the Mathematics and Physics Department of the University of Salento in Lecce (Italy). The used aethalometer continuously collects external airborne particles with a constant flowrate ($2\,l\,min^{-1}$) using a spot on a filter tape. The aerosol absorption can be estimated using the light transmission through both one section of the sample filter tape and an unloaded section of the filter tape considered as a reference spot. Consequently, the aethalometer can determine the instantaneous concentration of optically-absorbing aerosols using the rate of variation of the attenuation of light transmitted through the particle-laden filter tape. In more detail, the used aethalometer model performs two different measurements that are obtained at the same time from two sample spots with different rates of accumulation of the sample. Due to the particle deposition on the filter, the related radiation beam is attenuated for each of the seven used wavelengths. In more detail, the aerosol absorption coefficient σ_{abs} is determined using the optical attenuation ATN and the attenuation coefficient σ_{ATN} as follows:

$$ATN = -100 \cdot \ln (I/I_0) \quad [1]$$

$$\sigma_{ATN} = (S \cdot \Delta ATN/100) / (F_{in} \cdot \Delta t) \quad [2]$$

$$\sigma_{abs} = \sigma_{ATN} / C \quad [3]$$

where I and I_0 represent the spot and the reference signal, respectively, S is the spot area, F_{in} is the flow of the device, Δt is the selected interval time, while C is the multiple scattering parameter (Weingartner et al., 2003). The attenuation coefficient σ_{ATN} can be directly estimated from aethalometer measurements, as reported in some studies (e.g., Weingartner et al., 2003; Arnott et al., 2005; Schmid et al., 2006). However, this parameter does not correspond to the aerosol absorption coefficient σ_{abs} mainly because of some measurement artifacts defined by the C parameter, as described in Collaud-Coen et al. (2010). In more detail, the primary artifact arises from the loading effect induced by the accumulation of aerosol particles in the filter matrix (e.g., Virkkula et al., 2007). Following the deposition of particles, the detection of alterations in attenuation diminishes and eventually saturates, resulting in an underestimation of black carbon absorption and, consequently, reduced estimated elemental carbon concentrations (e.g., Drinovec et al., 2017). Therefore, it is important to highlight that the aethalometer AE33 incorporates an automated correction mechanism for the loading effect, alongside real-time computation of correction parameters across all seven wavelengths. This instrument operates by concurrently measuring attenuation through two sample spots, each with distinct rates of particulate accumulation, both sourced from the identical input air stream (Drinovec et al., 2015).

The light attenuation at the 880 nm channel is generally considered standard for BC concentration calculations because other aerosol species do not exhibit absorption properties at this wavelength (Hansen et al., 1984). The aerosol absorption coefficients estimated by the aethalometer at different wavelengths (λ_1 and λ_2) can be used to calculate an aerosol optical intensive parameter like the aerosol absorption Ångström exponent AAE using the following formula:

$$AAE\ (\lambda_1, \lambda_2) = -\ln\,[\sigma_{abs}(\lambda_1)/\sigma_{abs}(\lambda_2)]\ /\ \ln\,(\lambda_1/\lambda_2) \quad [4]$$

More specifically, note that in this study the AAE estimated at the 470–660 nm wavelength pair was analyzed because it takes into account the closest wavelengths of the used aethalometer to those used in some previous reference studies (e.g., Bahadur et al., 2012; Cazorla et al., 2013; Costabile et al., 2013; Lee et al., 2012). The AAE values are generally investigated in a specific site because they can be related to the chemical composition of particulate matter (Ealo et al., 2016; Schmeisser et al., 2017) and can be used to determine the major absorbing type in a mixture of different aerosols (Cazorla et al., 2013). An AAE of ~1 is generally associated with pure black carbon since the absorption by these particles usually follows a λ^{-1} spectral dependence (Bergstrom et al., 2002). On the contrary, AAE values larger than 1 are generally typical of OC as BrC (e.g., Cappa et al., 2016; Costabile et al., 2017) and mineral dust because these last types of aerosol particles contribute to light absorption mainly in both ultraviolet and blue spectral regions (Kirchstetter et al., 2004; Kim et al., 2012). Note also that mineral dust typically presents AAE values in the 1.5–6.5 range, as proved by Collaud Coen et al. (2004), Petzold et al. (2009), and Yang et al. (2009). Therefore, the urban pollution particles can be associated with AAE values close to 1, while biomass smoke particles like those from wood burning in cities are instead associated with AAE values close to 2 (Bergstrom et al., 2007; Russell et al., 2010; Clarke et al., 2007; Martinsson et al., 2017). It is also worth observing that each AAE value is strictly dependent on the selected wavelength pair (Cazorla et al., 2013).

3. Main results and discussion on the aerosol absorption properties

3.1. Seasonal evolution and correlation analysis for aerosol extensive parameters

The temporal evolution of the three aerosol extensive parameters analyzed in this study (aerosol absorption coefficient σ_{abs} at 470 nm from the monitoring station of the University of Salento and PM2.5 concentrations from Lecce-Cerrate and -Libertini stations) is reported in Fig. 1a using different colors. The analyzed period was divided in three seasons (December 2021 and January–February 2022 for winter, March-April-May 2022 for spring, and June–July 2022 for summer) according to the grouping adopted in previous works at the same study site (Romano et al., 2019, 2020). Note from the evolution based on the daily mean values from December 2021 to July 2022 (Fig. 1a) that the aerosol absorption coefficient presented a significant decrease from winter to spring-summer. In more detail, the winter mean value of σ_{abs} at 470 nm was 37.5 ± 3.3 Mm^{-1} that drastically decreased up to 19.2 ± 3.3 Mm^{-1} in summer. This marked decrease could be explained considering the main sources of PM that generally are associated with an increase of the aerosol absorption properties. In fact, at the study area the domestic heating is a relevant PM source during the winter period and typically represents the key factor for the larger values of σ_{abs} at 470 nm in winter with respect to their values in summer (Romano et al., 2019). On the contrary, both PM2.5 concentrations from the rural (Lecce-Cerrate) and the urban site (Lecce-Libertini) showed a less marked difference in their mean values between winter and summer. More specifically, a slightly larger mean value in summer (11.6 ± 0.5 μg/m^3) than in winter (9.1 ± 0.5 μg/m^3) was observed for the rural site probably due to the larger effect of forest fires in the warm period, while a similar value of 13.7 ± 0.7 μg/m^3 was detected in winter and 14.2 ± 0.5 μg/m^3 in summer for the urban site, which is strictly affected by the vehicular traffic for all the year. About these last observed differences, we are aware that the aerosol absorption and the PM2.5-NO_2 measurements were performed in different sites, however their distance is very limited (a few kilometers) and, therefore, we believe that this aspect cannot represent a factor significantly affecting the results reported in this study. Indeed, they

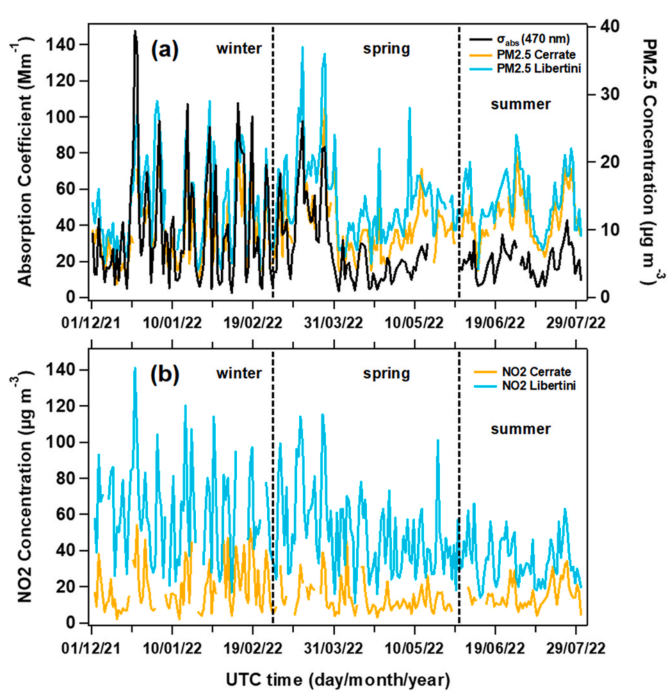

Fig. 1. Temporal evolution of the daily mean values of (a) aerosol absorption coefficient σ_{abs} at 470 nm (black line) at the monitoring station of the Mathematics and Physics Department of the University of Salento in Lecce and PM2.5 concentration from the Lecce-Cerrate (background site, orange line) and the Lecce-Libertini (urban site, light blue line) stations belonging to the ARPA Puglia monitoring network in the period from December 2021 to July 2022. The corresponding time evolution of the daily mean values of NO_2 concentration at the same ARPA Puglia stations was reported in (b). The vertical black and dashed lines separate the different seasons of the monitoring campaign.

exhibited analogous characteristics, as discernible in Fig. 1a, wherein a notably pronounced decrease in all analyzed parameters was observed starting from April. Taking into account that the vehicular traffic is a PM source during all the year at the study sites investigated in this work, the marked difference between March and April 2022 for the analyzed parameters could be due to the significant decrease in the domestic heating starting from April due to a significant increase of the mean temperatures at the study area. Another common feature between the aerosol absorption coefficient and the PM2.5 concentrations is represented by the higher variability experienced in winter than that observed in summer. In fact, the larger winter variability is generally associated with variable meteorological conditions at the study area during the “cold” period, while a larger atmospheric stability with stagnant conditions and low variability is typically observed in the “warm” period (Romano et al., 2019). A similar evolution of PM2.5 concentration and the proportional aerosol scattering coefficient retrieved by an integrating nephelometer at the study area was also found and described in previous studies (e.g., Perrone et al., 2014, 2015; Romano et al., 2019). A significant decrease of the NO_2 concentration at the study sites from the “cold” to the “warm” seasons can be also observed from Fig. 1b. In fact, the NO_2 concentration decreased from 19 ± 1 μg/m^3 in winter to 15 ± 1 μg/m^3 in summer for the rural site of Lecce-Cerrate and from 61 ± 3 μg/m^3 in winter to 35 ± 2 μg/m^3 in summer for the urban site of Lecce-Libertini. In detail, note that this decrease was more marked for the urban site considering that the domestic heating generally associated with an increase of the NO_2 concentration could present a lower effect in a rural area (e.g., Vestreng et al., 2009; Ruberti and Romano, 2020; Ravina et al., 2022). Therefore, σ_{abs} at 470 nm from the university suburban site and NO_2 concentrations from Lecce-Cerrate rural site and Lecce-Libertini urban site presented a similar season evolution, probably due to their common sources like vehicular traffic and domestic heating (e.g., McDuffie et al., 2020; Bertazza et al., 2023; Morillas et al., 2024). In addition, the main differences in meteorological effects between winter and spring-summer could also represent a significant factor in determining the seasonal differences between the investigated parameters. When comparing the trends shown in Fig. 1a and b, it is evident that the concentrations of PM2.5 and NO_2 are notably higher in Lecce-Libertini, an urban site, compared to Lecce-Cerrate, a rural site. This difference can be attributed to the typical sources and environmental conditions associated with urban areas. In fact, the larger effects of vehicular traffic and domestic heating in the urban site are only partially offset by the larger effects of forest fires in the rural site in summer. Note also from Fig. 1 that all the spring and summer values in the plots presented similar values and evolutions considering that in the investigated area these two seasons generally present similar features. The only relevant difference in this aspect is represented by the NO_2 concentration in the selected urban site (light blue line in Fig. 1b) with larger values in spring than in summer, as also reported by Kalabokas et al. (2023) in another Mediterranean site.

The correlation analyses reported in Fig. 2 allowed us to better understand the relationships between σ_{abs} at 470 nm and PM2.5 and NO_2 concentrations at the selected study area. Pairwise comparisons by the Mann-Whitney test (e.g., Cheung and Klotz, 1997) indicated that all the analyzed parameters were not significantly different at a *p*-level <0.05. As one can observe from Fig. 2a and c, a higher correlation between σ_{abs} at 470 nm and PM2.5 concentration was found in winter than in spring and in summer both in the rural (Lecce-Cerrate) and in the urban site (Lecce-Libertini). This result could be associated with the similar winter sources of both optical and physical aerosol parameter examined in this section such as vehicular traffic and domestic heating. By comparing Fig. 2a and c, observe also that the correlation coefficients between σ_{abs} at 470 nm and PM2.5 concentration were similar in Lecce-Cerrate and in Lecce-Libertini, except for spring because probably this season is generally characterized by a marked variability in the aerosol sources. In addition, both in the analyzed rural and urban site, we experienced lower correlation coefficients for the relationships between σ_{abs} at 470 nm and NO_2 concentration (Fig. 2b–d) than those between σ_{abs} at 470 nm and PM2.5 concentration (Fig. 2a–c). In any case, note by the comparison of Fig. 2b and d that the correlation coefficients between σ_{abs} at 470 nm and NO_2 concentration were higher in Lecce-Libertini than in Lecce-Cerrate since the aerosol absorption properties and NO_2 concentrations generally present similar sources in an urban site (mainly the vehicular traffic). In addition, observe also from Fig. 2b and d that the correlation coefficients between σ_{abs} and NO_2 concentration did not show any seasonal dependence because these coefficients presented similar values among the studied seasons.

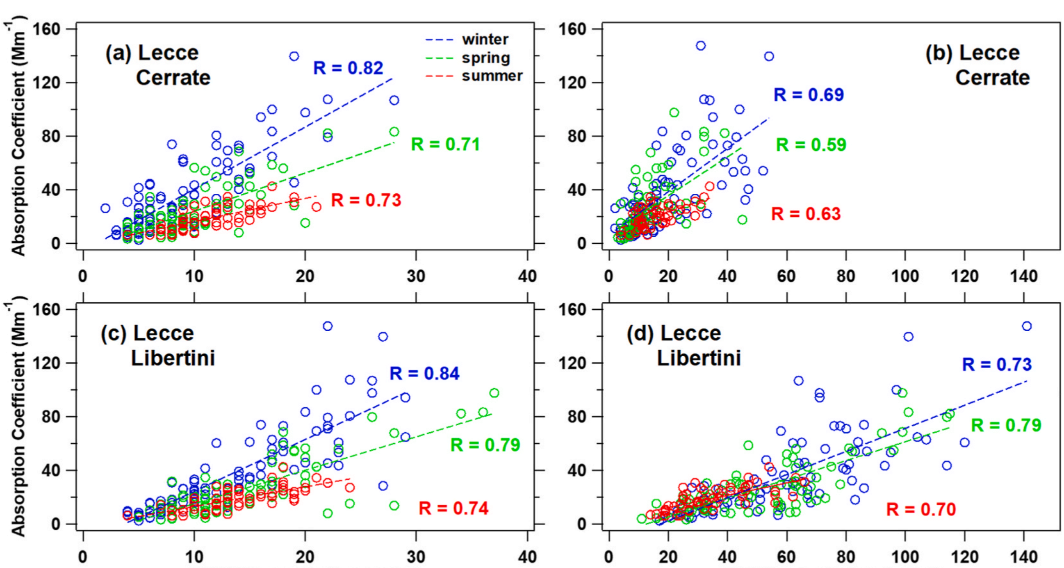

Fig. 2. Scatterplot of the daily mean values of aerosol absorption coefficient σ_{abs} at 470 nm at the monitoring station of the Mathematics and Physics Department of the University of Salento in Lecce as a function of the corresponding daily means of (a) PM2.5 and (b) NO_2 concentration from Lecce-Cerrate (background site) and of (c) PM2.5 and (d) NO_2 concentration from Lecce-Libertini (urban site) for winter (December 2021–February 2022, blue circles), spring (March–May 2022, green circles), and summer (June–July 2022, red circles). The corresponding linear correlation coefficients R have been provided for each season.

3.2. Seasonal evolution and correlation analysis for aerosol intensive parameters

Fig. 3a shows the temporal evolution of the daily mean values of the two aerosol intensive parameters, i.e. aerosol absorption Ångström exponent AAE estimated at the 470–660 nm wavelength pair for the suburban monitoring station of the University of Salento and the PM2.5/PM10 ratio for the urban site of Lecce-Libertini and the rural site of Lecce-Cerrate, analyzed in this study for the period December 2021–July 2022. Observe from the AAE temporal evolution in Fig. 3a that this intensive aerosol parameter presented a clear seasonal variation with larger values in the "coldest" months (from December to March), a rapid decrease in April and, then, lower values in the "warmest" months (from May to June). In more detail, the AAE mean seasonal value significantly decreased from 1.71 ± 0.01 in winter to 1.43 ± 0.01 in summer, which corresponds to a decrease of about 16%. The main aerosol sources at the selected site can explain this seasonal behavior since the winter months are largely affected by the domestic heating with wood burning effects that highly increase the AAE values (brown carbon usually presents AAE values larger than 1.5), while the summer months can present larger AAE value only if some forest fire events occur. The summer AAE mean values are typically in the range of urban/suburban sites largely affected by the vehicular traffic since the AAE value for black carbon particles and other fossil fuel related aerosol particles are generally very close to 1. Observe from Fig. 3a that this AAE reduction from winter to summer was also associated with a corresponding reduction of PM2.5/PM10 ratios. In fact, in both the urban site of Lecce-Libertini and the rural-background site of Lecce-Cerrate a PM2.5/PM10 ratio average decrease of about 10% from winter to summer was observed. Therefore, the average size of the collected aerosol particles was lower in winter due to a larger concentration of fine-mode particles associated with the wood burning related to the domestic heating effects, in addition to a significant effect of desert dust particles in summer that generally contribute to an increase of the mean aerosol size and, therefore, a decrease of the PM2.5/PM10 ratio. On the contrary, the effects of the vehicular traffic cannot be considered in the explanation of these seasonal variations because it is a common effect in all the year. The vehicular traffic is instead determinant in the explanation of the higher PM2.5/PM10 ratios in the urban site than in the rural site since it generally produces fine-mode particles mostly in an urban area. Observing Fig. 3a note that both AAE and PM2.5/PM10 values presented a larger variability in winter than in summer months considering the related higher variability of the meteorological conditions in winter at the monitoring sites, as also reported in the previous section. Considering the marked seasonality of the selected parameters, we decided to perform the respective correlation analyses dividing the data per season. Analogously to what was found for the extensive parameters (Section 3.1), pairwise comparisons by the Mann-Whitney test indicated

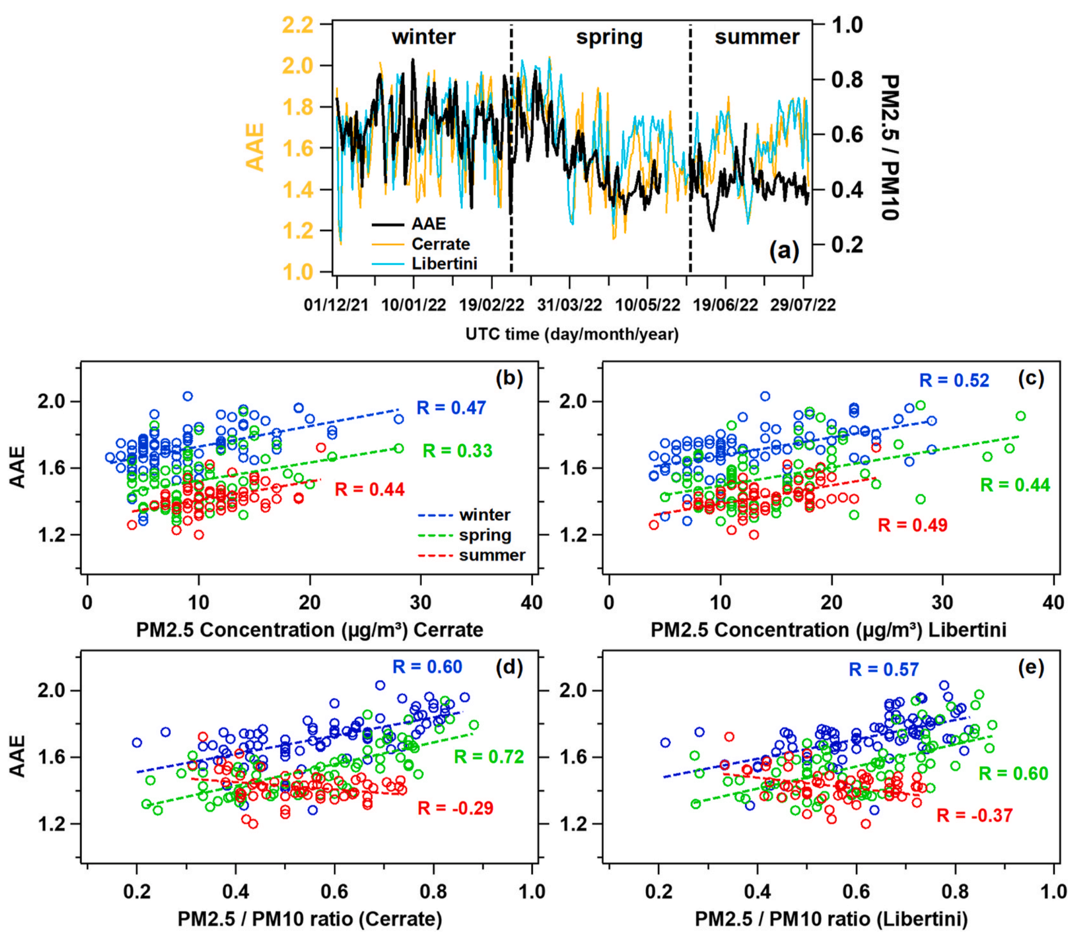

Fig. 3. (a) Temporal evolution of the daily mean values of absorption Ångstrom exponent AAE estimated at the 470–660 nm wavelength pair (black line) at the monitoring station of the Mathematics and Physics Department of the University of Salento in Lecce and PM2.5/PM10 ratio from the Lecce-Cerrate (background site, orange line) and the Lecce-Libertini (urban site, light blue line) stations belonging to the ARPA Puglia monitoring network in the period from December 2021 to July 2022. The vertical black and dashed lines in (a) separate the different seasons of the monitoring campaign. The scatterplot of AAE daily mean values has been reported as a function of the corresponding daily means of PM2.5 concentration from (b) Lecce-Cerrate and (c) Lecce-Libertini, and PM2.5/PM10 ratio from (d) Lecce-Cerrate and (e) Lecce-Libertini for winter (December 2021–February 2022, blue circles), spring (March–May 2022, green circles), and summer (June–July 2022, red circles). The corresponding linear correlation coefficients R have been provided for each season.

that all the parameters reported in Fig. 3 were not significantly different at a *p*-level <0.05. Firstly, we compared the AAE daily means with the corresponding values of PM2.5 concentration in the selected rural site (Fig. 3b) and urban site (Fig. 3c). Note from Fig. 3b and c that in both the selected sites a discrete correlation between AAE values and PM2.5 concentrations was observed because larger AAE values (larger OC contribution) are generally associated to an increase of PM2.5 concentrations (possible effect of the increase in domestic heating with wood burning). On the contrary, lower AAE values (typical of fossil fuel combustion) appeared associated with lower values of PM2.5 concentrations in the selected sites. By comparing Fig. 3b and c, it is also worth observing that the correlation AAE vs PM2.5 concentration was not largely affected by some seasonal variations and that the selection of a rural or urban site did not present a marked effect in this correlation. Then, by comparing Fig. 3d and e, note that we found similar correlations between AAE daily means and corresponding PM2.5/PM10 daily means if we compare the selected rural site of Cerrate and the urban one of Libertini. Therefore, this last result highlights that the monitoring site location is not a significant factor in the correlation between the AAE and the PM2.5/PM10 values. In addition, observe both from Fig. 3d and from Fig. 3e that the positive correlation between the optical parameter AAE and the physical parameter PM2.5/PM10 was found only in winter and in spring, while on the contrary a negative correlation between these two parameters was detected in summer, probably because of the forest fires that generally occur during the “warm” seasons.

Fig. S2 in the supplementary material provides a scatterplot illustrating the relationship between the daily mean values of aerosol absorption coefficient σ_{abs} at 470 nm and the corresponding daily means of absorption Ångström exponent AAE estimated at the 470–660 nm wavelength pair at the university station in Lecce. The plot also incorporates the NO_2 concentrations from both the rural site (Lecce-Cerrate) and the urban site (Lecce-Libertini) using a color scale. By visually representing the correlation between aerosol absorption properties and NO_2 concentrations, Fig. S2 offers valuable insights into the atmospheric composition and pollutant levels at the monitoring site. Observe that larger AAE values are associated with larger σ_{abs} values indicating that atmospheric particles from domestic heating in winter and forest fires in spring/summer (i.e., brown carbon, generally with AAE values larger than 1.5) present larger absorption properties at the study site. Fig. S2 also shows that the increase of AAE and σ_{abs} values was also associated with larger NO_2 values. As reported in the previous section, this last result could be due to their common sources like domestic heating (e.g., McDuffie et al., 2020). Therefore, Fig. S2 serves as a useful visualization tool to understand the connections between aerosol properties and pollutant concentrations, contributing to a better comprehension of the air quality dynamics at the studied Central Mediterranean site.

3.3. Weekly evolution for aerosol extensive parameters

The weekly evolution of the extensive aerosol parameters analyzed in this study was reported in Fig. 4 to verify if they were significantly affected the corresponding weekly cycle of the human activities. By comparing Fig. 4a–c, observe that the weekly cycle of the σ_{abs} at 470 nm detected in the suburban university site was similar to that of the PM2.5 concentration detected both in the rural and in the urban site investigated in this study. Note also that the weekly evolution presented similar values in the 3 selected sites even if we consider separately each season. In more detail, in winter and in spring all the 3 selected sites presented

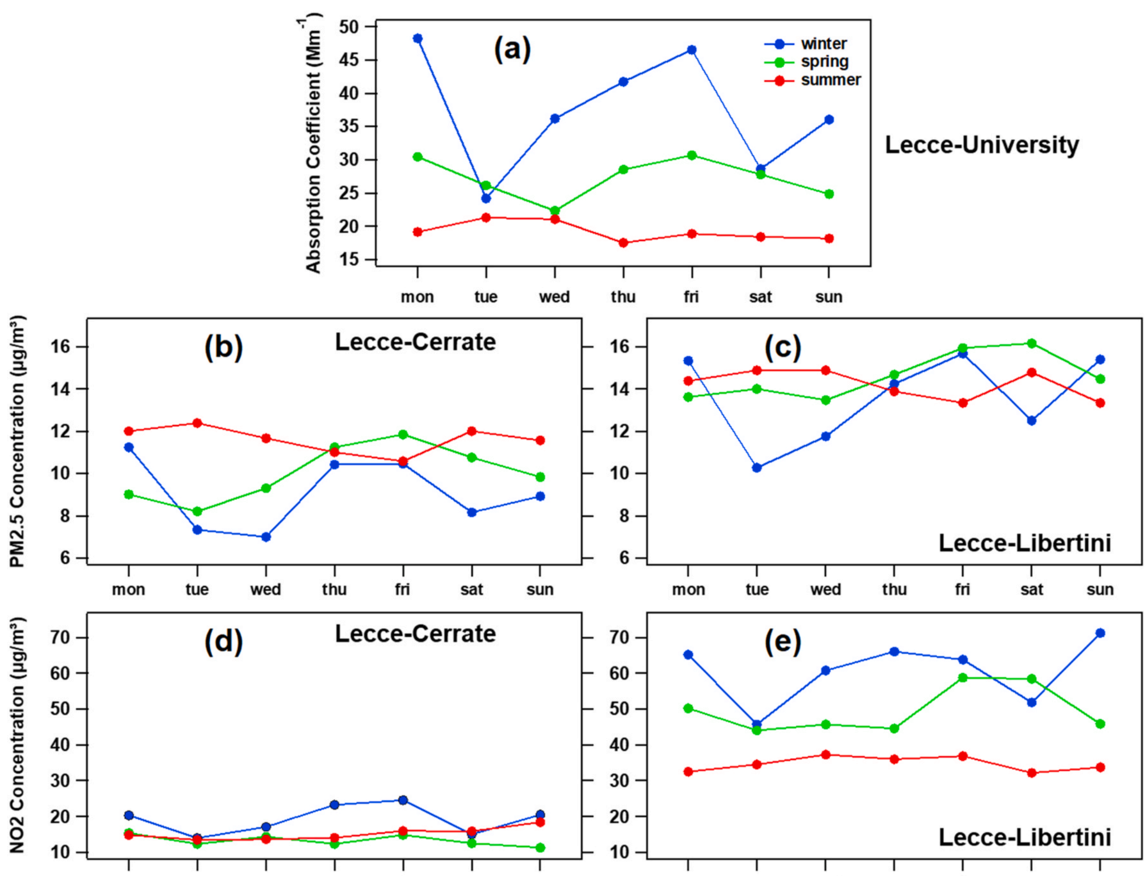

Fig. 4. Weekly mean evolution of (a) aerosol absorption coefficient σ_{abs} at 470 nm at the monitoring station of the Mathematics and Physics Department of the University of Salento in Lecce, PM2.5 concentration in (b) Lecce-Cerrate and (c) Lecce-Libertini, and NO_2 concentration in (d) Lecce-Cerrate and (e) Lecce-Libertini for winter (December 2021–February 2022, blue), spring (March–May 2022, green), and summer (June–July 2022, red).

larger values on Friday, while all the investigated parameters generally decrease during the weekends due to the relevant reduction of the human activities. In winter and in spring, this last anthropic effect was also proved by the significant increase of the studied parameters from Tuesday to Friday. On the contrary, from Fig. 4a–c a different mean weekly evolution was detected in summer, characterized by both a reduced variability and a significant decrease from the first days of the week up to Friday. In addition, the significant reduction on Friday was then followed by a slight increase of σ_{abs} at 470 nm and PM2.5 concentration during the weekends, probably due to the increase of the vehicular traffic in the summer weekends in the monitoring area for touristic reasons. The weekly mean evolution of NO_2 concentration was also analyzed in Fig. 4d and e for the rural site of Lecce-Cerrate and the urban one of Lecce-Libertini, respectively. This parameter showed a larger weekly variability only in winter, since it is also strictly related to the weekly cycle of the human activities. In fact, NO_2 concentration presented a significant increase from Tuesday to Friday only in winter, as also reported in previous studies (e.g., Stavrakou et al., 2020; Wang et al., 2022; Di Bernardino et al., 2023) with the exception of spring for the urban site of Libertini that also presented higher values on Saturday. The remaining weekly evolutions of NO_2 were instead characterized by a lower variability, especially in summer. In conclusion, by comparing the weekly cycles of aerosol extensive parameters like aerosol absorption coefficient and PM2.5 concentration, in addition to NO_2 concentration, we proved that all the investigated parameters presented a reduced weekly variability in summer, while the urban/suburban sites generally were associated with a more marked variability than the corresponding rural site in winter and in spring.

3.4. Weekly evolution for aerosol intensive parameters

Finally, the weekly mean evolution of the investigated aerosol intensive parameters (AAE at the wavelength pair 470–660 nm and the PM2.5/PM10 ratio at the urban site of Lecce-Libertini and the rural one of Lecce-Cerrate) was also analyzed to study their potential relationships with the corresponding weekly cycle of the human activities. Note by comparing Fig. 5a with Fig. 5b and c that the weekly evolution of AAE was significantly less marked with respect to those of the PM2.5/PM10 ratio for all the 3 investigated seasons. In more detail, as one can observe from Fig. 5a, AAE showed a larger variability only in winter, with a significant increase from Tuesday to Friday. This last result proved an increase of the OC concentration during the weekdays, probably associated with the increase of human activities from Monday-Tuesday to Friday, followed by their significant reduction during the weekends. On the contrary, AAE did not show a significant variation in spring and in summer during the week. Regarding the PM2.5/PM10 ratio, different trends in its weekly evolution were observed for the 3 different selected seasons. In winter, a significant increase from Tuesday to Friday was observed both in the rural and in the urban site, while the PM2.5/PM10 presented higher values in the weekends only in the urban site that is affected by a larger vehicular traffic also in the weekend days. In spring, both the rural and the urban investigated sites presented higher values of PM2.5/PM10 at the beginning of the week, then a significant reduction followed by a new increase was observed in the weekend days. Conversely, in summer lower values of PM2.5/PM10 ratio were detected during the central days of the week (Wednesday and Thursday) probably related to an increase of the road dust that generally increases the aerosol mean size.

4. Conclusion

In this study, we investigated both aerosol absorption coefficient and absorption Ångström exponent during a monitoring campaign from December 2021 to July 2022 performed in a university campus at the center of the Mediterranean area in Lecce (in south-eastern Italy). The results obtained by analyzing the evolutions of the selected absorption properties monitored at the university site were compared to both PM2.5 and NO_2 mass concentrations and the PM2.5/PM10 ratio at two nearby stations belonged to the ARPA Puglia monitoring network. In more detail, both seasonal and weekly evolutions of the selected parameters were analyzed to investigate their potential impacts associated with meteorological and anthropic factors, respectively.

Considering the main results obtained about the aerosol extensive parameters investigated in this work, the aerosol absorption coefficient from the university suburban site presented a significant decrease from winter to spring-summer that was mainly associated with the decrease of the domestic heating effect. On the contrary, both PM2.5 concentrations from the rural (Lecce-Cerrate) and the urban site (Lecce-Libertini) showed a less marked difference in their mean values between winter and summer due to the effects of forest fires in summer for the rural site

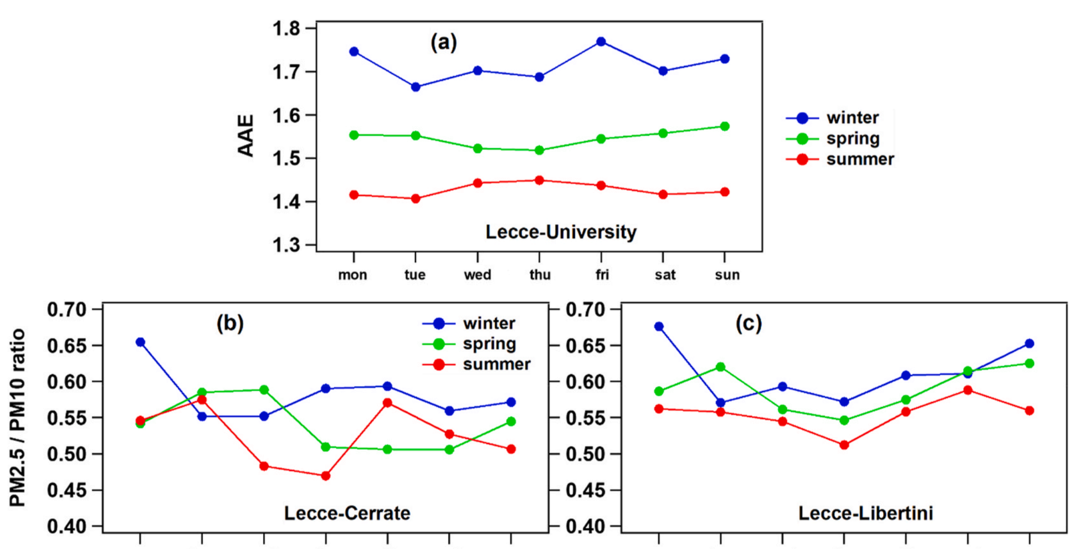

Fig. 5. Weekly mean evolution of (a) absorption Ångstrom exponent AAE estimated at the 470–660 nm wavelength pair at the monitoring station of the Mathematics and Physics Department of the University of Salento in Lecce and PM2.5/PM10 ratio from the (b) Lecce-Cerrate (background site) and (c) Lecce-Libertini (urban site) stations belonging to the ARPA Puglia monitoring network for winter (December 2021–February 2022, blue), spring (March–May 2022, green), and summer (June–July 2022, red).

and the effects of vehicular traffic for all the studied period in the case of the urban site. A common feature between the aerosol absorption coefficient and the PM2.5-NO_2 concentrations was also observed in relation to the higher variability in winter than that observed in summer. This last result could be explained considering the highly variable meteorological conditions at the study area during the "cold" period, while a larger atmospheric stability with stagnant conditions and low variability is typically observed in the "warm" period. Another interesting result was that the σ_{abs} at 470 nm from the university suburban site and the NO_2 concentrations from both Lecce-Cerrate (rural site) and Lecce-Libertini (urban site) presented a similar seasonal evolution, probably due to their common sources like vehicular traffic and domestic heating.

Then, considering the main results obtained about the aerosol intensive parameters investigated in this work, the AAE parameter presented a clear seasonal variation with larger values in the "coldest" months, a rapid decrease in April and, then, lower values in the "warmest" months. In fact, the winter months are largely affected by the domestic heating with wood burning effects that highly increase the AAE values, while the summer AAE mean values are typically in the range of urban/suburban sites largely affected by the vehicular traffic, generally very close to 1. Both AAE and PM2.5/PM10 values presented a larger variability in winter than in summer that could be associated with the higher variability of the meteorological conditions in winter at the study sites. Similar correlations between AAE daily means from the university suburban site and corresponding PM2.5/PM10 daily means were observed if we compare the selected rural site of Lecce-Cerrate and the urban one of Lecce-Libertini.

Finally, the weekly evolution of both aerosol extensive and intensive parameters analyzed in this work was investigated to detect possible effects associated with the weekly cycle of human activities. About the studied extensive parameters, we proved that they presented a reduced weekly variability in summer, while the urban/suburban sites generally were associated with a more marked variability than the corresponding rural site in winter and in spring. In more detail, both in winter and in spring all the parameters in the 3 selected sites increase from Tuesday up to Friday showing the largest weekly values on Friday and, then, they generally decrease during the weekends due to the relevant reduction of the human activities. About the studied intensive parameters, AAE showed a larger variability in its weekly evolution only in winter, with a significant increase from Tuesday to Friday. This last result proved an increase of the OC concentration during the weekday, probably associated with the increase of human activities from Monday-Tuesday to Friday, followed by their significant reduction during the weekends. On the contrary, AAE did not show a significant variation in spring and in summer during the week.

In conclusion, this study has highlighted the main features of both extensive and intensive parameters associated with aerosol absorption properties at some south-eastern Italy monitoring sites that can be considered as representative of the Central Mediterranean coastal areas. The reported results have suggested the importance of considering different types of monitoring sites (urban, suburban, and rural) for a proper characterization of the aerosol absorption properties at the selected area. In addition, the results of this study have also revealed the need for including aerosol intensive properties to obtain a proper aerosol typing and for including aerosol weekly evolution to properly define the impact of the weekly cycle of human activities on the main air quality parameters.

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CRediT authorship contribution statement

Dalila Peccarrisi: Data curation, Formal analysis, Investigation, Methodology, Software, Validation, Visualization. **Salvatore Romano:** Conceptualization, Formal analysis, Funding acquisition, Methodology, Resources, Software, Validation, Writing – original draft. **Mattia Fragola:** Data curation, Formal analysis, Investigation, Methodology, Visualization. **Alessandro Buccolieri:** Data curation, Investigation, Methodology, Validation. **Gianluca Quarta:** Conceptualization, Funding acquisition, Project administration, Supervision. **Lucio Calcagnile:** Conceptualization, Funding acquisition, Investigation, Project administration, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apr.2024.102131.

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