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Spatial Characteristics of PM_1 Aerosol Chemical Composition over the Greater Athens Area †

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Abstract: Airborne sub-micrometer particles (PM_1) have been documented to exert adverse impacts on human health, including respiratory and cardiovascular disease and premature mortality. The Greater Athens Area (GAA), characterized by topographic and meteorological conditions which frequently obstruct the effective dispersion of ambient pollutants, hosts approximately 40% of Greece's population. It can be considered an "ambient laboratory" for studying PM_1 pollution events, given the intensity and diversity of submicron aerosol sources and processing. Fine aerosol chemical composition is continuously monitored at the National Observatory of Athens Air Monitoring Station in Thissio, an urban background site in Central Athens. Furthermore, two intensive monthly campaigns were held at a central site in Piraeus, where Greece's busiest passenger port is located, during both winter (December 2018–January 2019) and summer (June–July 2019) periods. Organic aerosol (OA), sulfate, nitrate, ammonium, and chloride were measured using an aerosol chemical speciation monitor (ACSM), while black carbon (BC and source-specific components) was measured using a multi-wavelength aethalometer (AE-33). The variability of concentrations at different temporal scales was examined, revealing differences for primary aerosol components, depending on site type and location, and related to local sources and transport processes. Biomass burning for domestic heating was found to be a key factor during wintertime, leading to uniform OA and BC levels at both sites, while the local sources in Piraeus (traffic, port activity) lead to substantially increased levels during the summer. Secondary sources were found to affect both sites in a relatively homogeneous manner.

Keywords: ACSM; NR-PM1; organic aerosol; black carbon

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1. Introduction

Ambient fine particles are recognized to exert seriously adverse health effects, with results of epidemiological studies suggesting a causal link between human exposure and increased premature mortality [1]. The chemical composition and sources of aerosols to which humans are exposed at various time scales are considered to play an important role in the observed cardiorespiratory effects [2]. At the same time, the role of atmospheric aerosols in the atmospheric radiation budget has come under scrutiny [3].

The acknowledged human health effects, together with the wider impacts on the climate, have highlighted particulate matter as a high-priority pollutant at the European level and especially in Southern Europe [4]. To address these important effects, it is crucial to characterize the chemical composition of particles, which are closely related to the toxicity-inducing pathways and their optical properties. Moreover, it is necessary to identify

and assess the contribution of particle pollution sources so as to be able to design appropriate air quality managements strategies.

Regarding aerosol chemical composition, a large contribution of the organic fraction is recognized, with hundreds of compounds—of different atmospheric activity and toxicity characteristics—being classified in organic aerosol (OA). The fine particle mass is complemented by major ionic compounds and elemental carbon [5]. An important characteristic of organic and ionic aerosols is their atmospheric activity, since they participate in physicochemical processes, and therefore, being able to dynamically record their concentrations in high temporal resolution is highly important. Aerosol mass spectrometric techniques have provided a valuable solution toward this direction, with the aerosol chemical speciation monitor (ACSM), specifically, having the capability to track the temporal variability of major aerosol components, in near real-time and under continuous long-term operation [6].

Given the intensity of primary sources and its topographic and meteorological characteristics [7], the Athens basin is a particularly suitable field of study of dynamic atmospheric pollution phenomena at a large urban scale. The Greater Athens Area (GAA) is populated by 3.8 million inhabitants and has about 3 million vehicles registered [8]. Industrial activity within the basin, but also in the neighboring Thriassion Plain, was greatly reduced in previous decades. However, in recent years, the renewed development of the commercial port of Piraeus, which led to increased shipping and port terminal activity, has established this area as a pollution source, with an impact both locally and on the wider area [9].

The general characteristics of the air pollution issue in the GAA have been extensively researched in the past [9,10]. However, the available information regarding the short-term variability of aerosol chemical composition and related sources and processes is limited [11,12]. Moreover, a new challenge in the study of atmospheric aerosols in the GAA has emerged, due to the economic recession that prevailed for the larger part of the previous decade. Following large hikes in the excise duty on heating oil since 2011, there has been a major shift toward biomass burning for space heating, with the appearance of intense winter "smog" episodes [13], characterized by high concentrations of organic aerosols and black carbon (BC). At the same time, the restriction of road transport activity due to the recession, in combination with European legislation aimed at reducing vehicle emissions and improving fuel quality, has significantly altered the relative impact of primary sources and has decreased PM levels in the long-term. Road traffic has been recognized in the past as a controlling factor that was effective for PM levels all over the Athens basin [14]; however, it has to be reaffirmed whether this remains a valid assessment in the evolving air quality landscape.

It is therefore imperative to implement characterization methods for aerosol composition and sources with high temporal resolution, but also to expand the assessment on the spatial scale, a venture that, due to the cost of the advanced instrumentation required, is rather demanding. The spatial characterization should involve both primary pollutant hotspots and urban background locations, which are more relevant for the exposure of the general population. Only a few studies that used aerosol mass spectrometric techniques attempted till now to assess the spatial characteristics of aerosol composition and sources within larger geographical areas, but in most cases without conducting concurrent measurements at multiple locations [15,16].

In the present work, we report data on the chemical composition of fine aerosol at two representative locations in the Athens basin, in hourly temporal resolution, using online instrumentation (ACSM and multi-wavelength aethalometer for source-specific BC components). The first site, where long-term measurements have been performed since December 2015, is the urban background supersite of the National Observatory of Athens, in Central Athens (Thissio). The second is an urban traffic site located in Central Piraeus, close to the passenger port, where two intensive monthly measurement campaigns were performed in December 2018–January 2019 and June–July 2019. More emphasis is placed

on the analysis of the Piraeus dataset, since it is a new measurement location in the GAA, characterized for the first time, while the Thissio (a well-studied site) dataset is mainly used for inter-site comparisons. We explored the temporal variability of major aerosol components at the two sites and analyzed the inter-site differences, in order to highlight the relative impacts at two locations of different type within the same airshed.

2. Experiments

2.1. Study Sites

Two sites within the Athens basin (Figure 1) were examined in the present study, namely Thissio (THI) and Piraeus (PIR). THI is an urban background site, in the historic center of Athens. It is located in the premises of the National Observatory of Athens in Thissio. It is in a relatively large distance (>200m) from major roads and surrounded by pedestrian zones, in a moderately populated neighborhood [10,13]. The site has been found to be representative for urban background conditions in the central part of the Athens basin [17].

Measurements at PIR were carried out at the building (1st floor) of the terminal station of the Athens Metro in Piraeus. The site is characterized as urban traffic, being at a distance of approximately 50 m from the Piraeus coastal avenue, which is adjacent to the port zone where passenger ships are berthing. The site, due to its central placement in a transportation hub, is also characterized by intense human and commercial activity. Moreover, Piraeus is the second most-densely populated municipality in the GAA, with the greater area of Piraeus having almost 450,000 residents. Therefore, an important input from residential emissions during the heating season should be also expected.

Measurements in Piraeus were conducted during two season-specific monthly periods of the year: winter (12 December 2018–15 January 2019) and summer (12 June 2019–8 July 2019). To perform a comparative analysis and assess the general spatial characteristics of the pollutants in focus, we analyzed the corresponding periods during the previous three years (2015–2016, 2016–2017, and 2017–2018), as measured at THI, using the same instrumentation.

2.2. On-Line Instrumentation

An aerosol chemical speciation monitor (ACSM, Aerodyne Inc., Billerica, MA, USA) was used to obtain, in near-real time (30-min temporal resolution), data on the chemical composition of non-refractory submicron ambient aerosols (NR-PM_1). Specifically, the ACSM, which is practically a compact aerosol mass spectrometer, records concentrations of OA, sulfate, ammonium, nitrate, and chloride, with an effective diameter range of 40–700 nm, while also providing mass spectra of OA [6]. The instrument samples at a flow rate of 3.6 L min^{-1}, through a PM_1 sharp-cut cyclone (SCC 1.109, BGI Inc., Waltham, MA, USA).

Black carbon (BC) concentrations were measured at a 1 min resolution using a 7-λ aethalometer (AE-33, Magee Scientific, Berkeley, CA, USA), sampling at 5 L min^{-1}. The AE-33 [18] records BC concentrations at seven wavelengths by measuring the attenuation of light through particles deposited on a filter tape and calculating the absorption coefficient at each wavelength. A dual-spot measurement approach is followed to compensate for the "filter loading" effect, while a correction for multiple scattering is also applied. Furthermore, through the implementation of the "Aethalometer model" [19], the source-specific BC fractions apportioned to fossil fuel combustion (BC_{ff}) and biomass combustion (BC_{bb}) are calculated automatically by the instrument. All values from the ACSM and the AE-33 were averaged and analyzed at hourly intervals.

Figure 1. Overview of the Attica Peninsula and the GAA, with the two sites in the Athens Basin: THI in Thissio, Central Athens, and PIR in the center of Piraeus, near the passenger port.

2.3. Off-Line Measurements and Additional Data

Chemical composition measurements were performed, in parallel with on-line measurements, on $PM_{2.5}$ quartz fiber filters collected daily on a 24-h basis, using reference-equivalent low-volume samplers: Derenda LVS-PNS-15 at PIR (Comde-Derenda, Stahnsdorf, Germany) and Partisol 2025-D at THI (Thermo Fisher Scientific Inc., Waltham, MA, USA). Filters were analyzed for organic and elemental carbon (OC, EC) and ionic composition. Quantification of OC and EC was performed on filter punches using a thermal/optical Sunset carbon analyzer (Sunset Laboratories Inc., Portland, OR, USA), according to the EUSAAR-II protocol [20]. Nanopure water extracts were analyzed using an ion chromatography system (Dionex DX-500, Thermo Fisher Scientific Inc., Waltham, MA, USA) for major cations and anions, including sulfate, nitrate, ammonium, and chloride [21]. The results from filter-based analyses were used to perform quality control on the ACSM data [12], validating the results for OA and major ions. The covariance between EC and BC on a daily basis was also explored. The impact of wind circulation and transport from sources at the local/medium spatial scale [22] on concentrations at PIR was assessed using bivariate polar and annular (assessment of the diurnal variability) wind plots, according to the methodology of Uria-Tellaetxe et al. [23]. Wind speed and direction data were obtained from a meteorological station, operating at a distance of approximately 2 km from PIR.

3. Results and Discussion

3.1. Comparison between On-Line and Off-Line Measurements

A selection of characteristic scatterplots between daily averaged measurements from on-line and off-line instruments at PIR, for the two campaigns (winter-summer) combined, is presented in Figure 2.

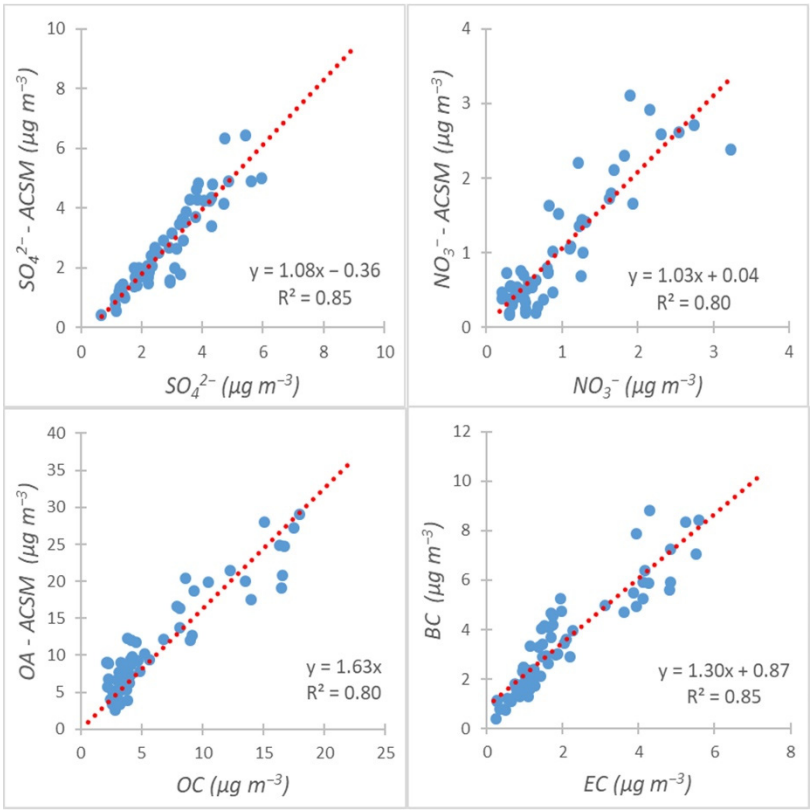

Figure 2. Comparison of 24 h averaged concentrations determined with the on-line instruments and from filter-based analyses, for major fine aerosol species in Piraeus, for the two campaigns combined.

The results of the comparison present an excellent agreement ($R^2 > 0.80$, slopes close to unity, very small intercepts) for sulfate and nitrate between the two methods (this is also valid for ammonium ions, but not for chloride due to the differences between the very fine non-refractory ammonium chloride measured by the ACSM and the coarser water-soluble sodium chloride that participates also in the $PM_{2.5}$ fraction). A very good correlation ($R^2 = 0.80$) was found between OA and OC (forced through the intercept in the figure), with a slope of 1.63. It is expected that the actual OA in $PM_{2.5}$ would be slightly higher due to the small amount of organic particles concentrated in the intermodal range [24]. However, the obtained slope is rather indicative for OA/OC ratios (1.4–1.8) being reported at traffic-impacted urban sites, where freshly organic carbon emissions are less processed to oxygenated compounds of higher molecular weight [25]. Similarly, good correlations were obtained for ACSM components regarding the comparisons at THI (not shown). Black and elemental carbon daily average concentrations at PIR also correlated excellently ($R^2 = 0.85$), although BC tended to record higher concentrations (possibly due to a contribution of non-EC light absorbing particles or a somewhat different mass absorption cross-section for aerosol in Piraeus than the default value used in the aethalometer) [26,27].

3.2. Comparison of Levels between the Two Sites on a Seasonal Basis

Figure 3 displays box-whisker plots for the measured hourly concentrations of aerosol components by season at the two sites.

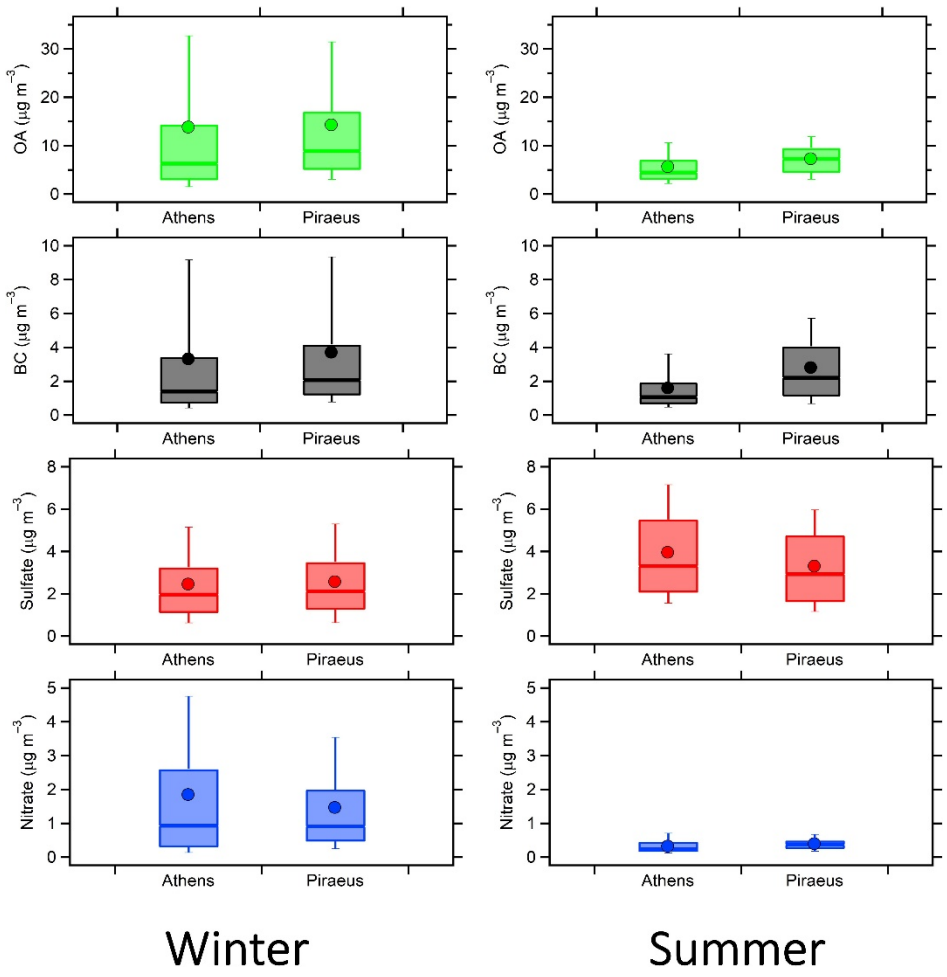

Figure 3. Box-whisker plots for hourly concentrations of on-line measured aerosol components in Athens (THI; 3 years, 2015–2018) and Piraeus (PIR; 2018–2019), for the specified winter and summer periods. Whiskers for 10–90° percentiles, dot for arithmetic mean, box for median and interquartile range.

Concentrations for BC and OA at PIR were, on average, higher than those at THI, something expected in a comparison between a traffic-impacted and an urban background site. However, it has to be noted that this difference is much less pronounced during the winter period. BC concentrations in winter are merely 12% higher on average (compared to 75% during the summer period), while average OA levels are almost comparable in winter (higher by only 3% at PIR). This fact should be mainly attributed to the excessive utilization of biomass burning for heating, which is an effective source over the entire Athens basin [17]. This phenomenon peaks during the month of December—the focus of the analyzed winter period—with extreme levels of hourly OA and BC values being frequently recorded [12]. The differences for OA and BC between the two sites are much more evident for the summer period, where the levels at PIR are significantly higher than at THI (29% and 75% for OA and BC). The deactivation of biomass burning as a source, combined with the decrease of traffic emissions at THI during summer [13], provides an explanation for this disparity. Moreover, the activity (commuting, passenger vehicle traffic and shipping) is substantially increased during summer around the port of Piraeus [28], further explaining the large inter-site differences for BC. As can be seen in Figure 4, while a local impact associated with low-wind nocturnal conditions at PIR explains the higher winter levels, the pattern is different during summer, when an impact of the wider port zone (shipping emissions and traffic in the passenger section of the port) is evident. The smaller inter-site difference for OA against BC, during summer, can be attributed to the fact that a substantial part of OA during the warm period photochemi-

cally evolves as secondary OA [11,12], a process which is less local in character. The enhancement of carbonaceous aerosol levels at locations close to major ports has also been reported by relevant studies using high-resolution instrumentation [29,30].

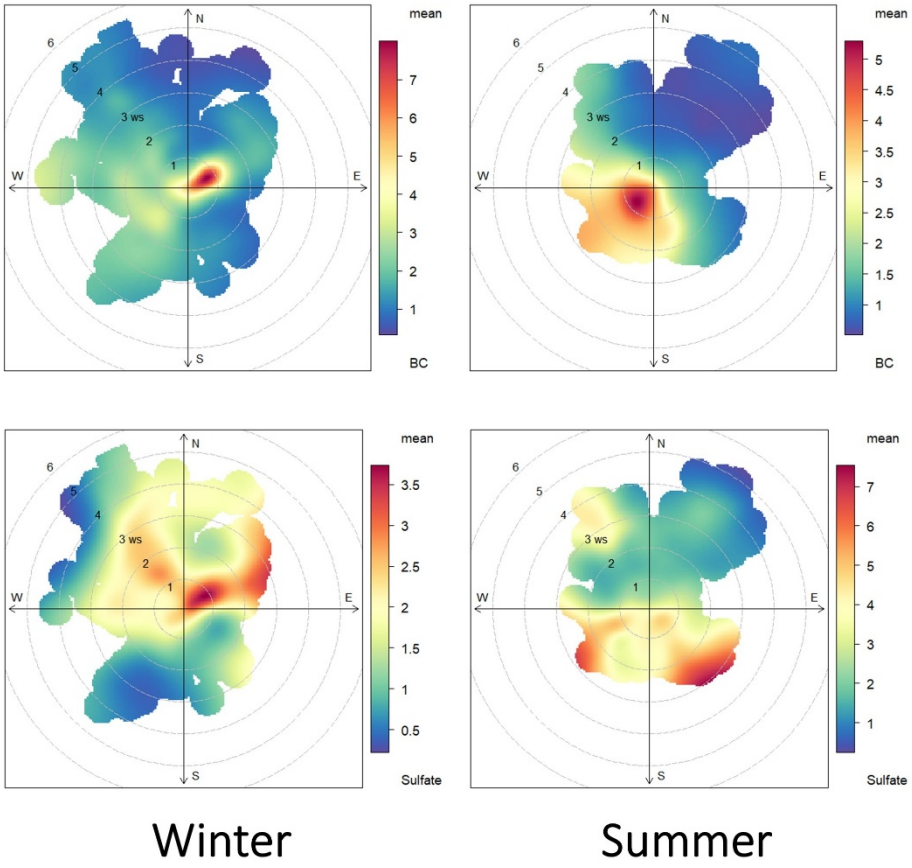

Figure 4. Bivariate polar plots for the relationships between wind direction (angular) and speed (radial), on black carbon (BC) (upper panels) and sulfate (lower panels) concentrations, during the two study periods at PIR.

Different seasonal patterns can be seen for the two major secondary aerosol ions. Nitrate levels are comparable between sites, with high wintertime levels being characterized by peak hourly concentrations during nighttime, which has been associated to the processing of fresh biomass burning emissions, under favorable atmospheric acidity conditions [10]. Nitrate levels largely diminish during summer as the equilibrium shifts to the gas phase under increased ambient temperatures [31]. Levels of sulfate present similarities among the two sites, measured at approximate 2.5 μg m^{-3} on average in winter, and being enhanced during the summer period due to the higher degree of photochemical processing of sulfur oxides at the regional scale. Studies in the Athens basin have indeed verified the regional character of sulfate, with important inter-site correlations reported for secondary sulfate [9]. This is underlined by the larger dispersion of elevated concentrations in the polar plots of Figure 4. However, it is interesting that higher sulfate levels during the summer tend to be associated with winds from the S–SW sectors. At a coastal site like PIR, such winds are related to sea breeze circulation, which in turn is associated with the most elevated fine aerosol concentrations, presenting an enhancement during the midday to early afternoon. Due to the common temporal evolution of sulfate concentrations (which also peak in this timeframe, as discussed in Section 3.3), an association is registered by the wind plot. However, the effect of emissions from heavy oil combustion (shipping activity in the general area of Piraeus, to the south and west of the site), processed to sulfate under favorable conditions, is also considered possible [32]. The observed

patterns for sulfate are to a certain extent reproduced by wind analysis results at the THI site (not shown).

3.3. Short-Term Variability of Concentrations

The mean diurnal variability of concentrations for selected aerosol components at the two sites is presented in Figure 5. OA and BC_{ff}, during winter, present typical bimodal diurnal cycles, indicative of rush-hour traffic emissions in the morning and of evening traffic combined with domestic heating emissions in a shallow nocturnal boundary layer. The effect of heating emissions is readily evident in the diurnal plot of BC_{bb}, with the nighttime contribution of BC_{bb} exceeding 40% of total BC. Interestingly, the nighttime BC_{bb} peaks at THI tend to be higher than at PIR. A 1-h lag in the morning maxima of BC_{ff} concentrations is recorded between the two sites, with PIR peaking before THI due to the earlier intensification of vehicular emissions (commercial-related traffic), as well as the time required for fresh emissions to travel from the urban/commercial center of Athens to the urban background THI location [14].

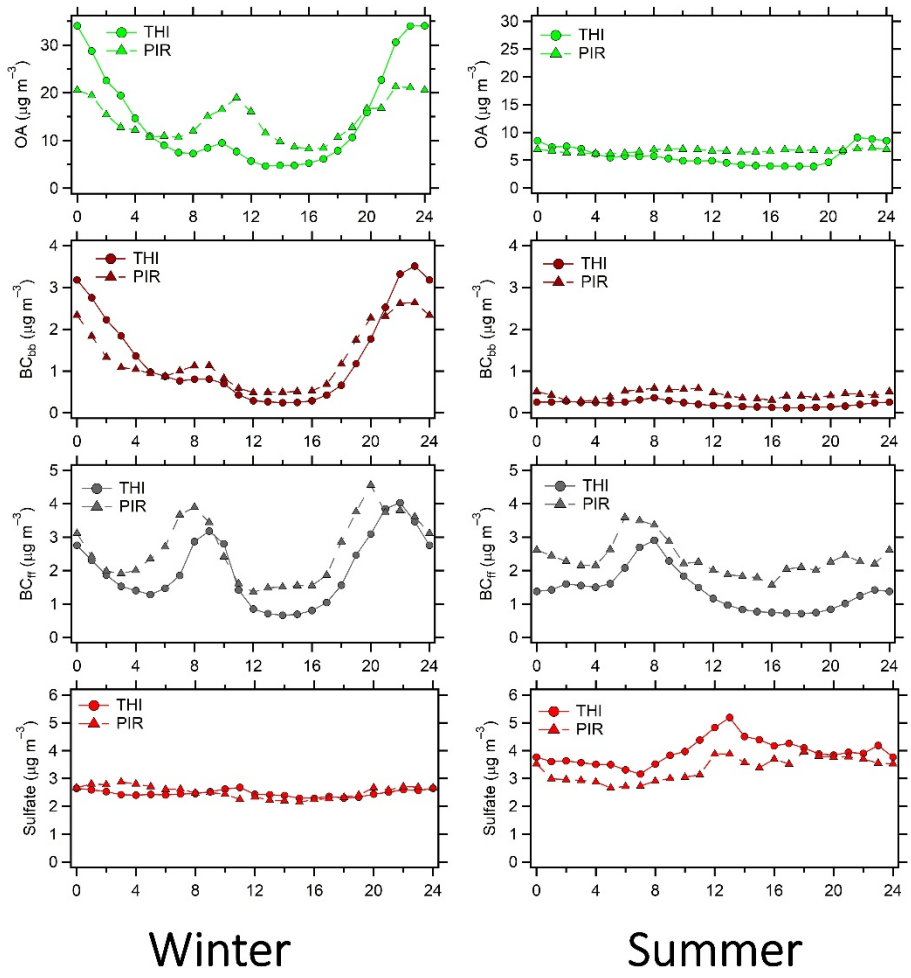

Figure 5. Mean diurnal variability of hourly concentrations of major aerosol components, at the two sites for the examined periods.

OA concentrations during summer present a mostly flat diurnal variability at both sites, indicating an impact of regional processed aerosol that is offsetting local emissions [33]. The summertime diurnal variability of BC_{bb} is insignificant; however, BC_{ff} presents at both sites a unimodal cycle, characteristic of increased traffic contributions of vehicular emissions in the morning (more intense at PIR).

The shape of the BC_{ff} cycle at PIR (compared to THI) indicates that levels tend to persist in the hours following the morning peak, in spite of enhanced dispersion during midday, which is characterized by strong sea breeze or NW synoptic-scale winds, combined with the evolution of the boundary layer (processes that lead to a pronounced midday-afternoon valley at THI) [34]. The BC_{ff} concentrations form an extended plateau up to the evening hours and beyond. This is considered to be related to persistent emissions throughout the day, attributed to the passenger port activity [35]. It can be seen in Figure 6, by inspection of the annular plots which describe the effect of wind direction by hour of the day at PIR, that an enhancement is documented in winter, associated with NW directions (mainly low-wind conditions) during the evening and nighttime (indicative of domestic heating BC emissions). By contrast, during summer, the effect of winds from the general direction of the port zone is again evident and notable throughout the day.

Sulfate levels present a mostly uniform diurnal distribution during the cold period, characteristic of its regional origin [36]. The summer midday peaks displayed in the diurnal cycles at both sites can probably associated to the increased vertical mixing [37] of regional transported sulfate in the Athens basin and the intensification of photochemically produced sulfate at a regional scale [38].

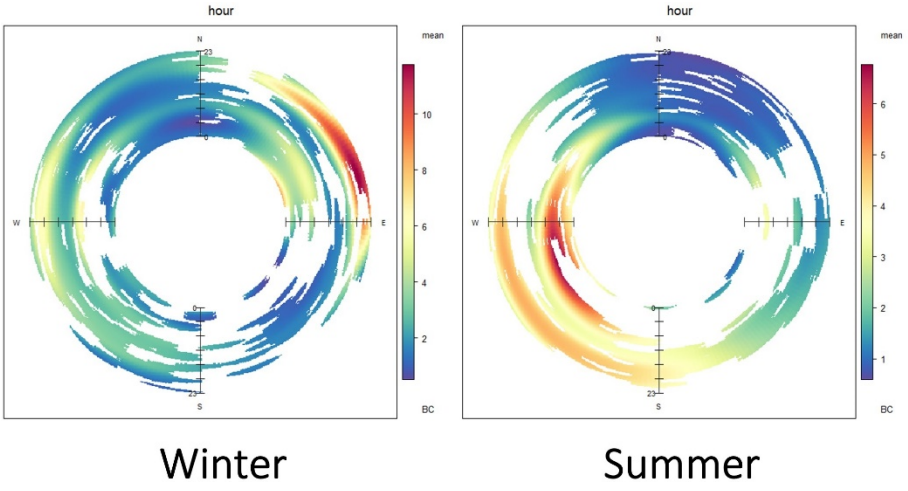

Figure 6. Annular plots examining the associations of wind direction and (BC) concentrations by hour of the day, for the two measurement periods at PIR.

4. Conclusions

In this study, we performed a comparison regarding the temporal variability and sources of fine aerosols in the Greater Area of Athens, as measured at two sites, during selected winter and summer periods, within a four-year span. The two sites are located in areas with distinct characteristics, i.e., at a residential urban background area in the center of Athens (Thissio) and in the center of Piraeus, an area impacted by traffic emissions and by the operation of a major European harbor. Measurements for organic aerosol, major aerosol ions, and black carbon were performed using on-line instrumentation (ACSM and aethalometer). The obtained results highlight, case-wise, interesting disparities but also unexpected similarities on the spatial level. A contiguity of carbonaceous compound (OA, BC) levels among traffic and background locations in the GAA during winter conditions appears to be an important finding and has to be further validated, as it indicates the great impact and spatial uniformity of a season-specific anthropogenic source (biomass burning), which can be regulated through the adoption of pertinent policies. On the other hand, emissions from the port zone and the related traffic activity appear to be an important year-round aerosol source in Piraeus, which maximizes during summer—when concentrations in Thissio remain low—leading to a characteristic seasonal profile. Concentrations of secondary nitrate seem strongly impacted by the rapid processing of local

emissions of nitrogen oxides at both sites during the winter. By contrast, sulfate levels present a more uniform spatial pattern. Wind analysis indicates that the port zone of Piraeus is expected to have a significant impact on levels of primary carbonaceous aerosols, especially in the summer period. The contributions of local sources at the two sites were also translated in the short-term temporal variability of concentrations, with large enhancements for primary pollutants (including source-apportioned BC) recorded during nighttime in winter at both sites (indicative of the spatially effective impact of biomass burning emissions). Moreover, there are indications from the analysis of short-term patterns that there is an enhancement of BC concentrations in Piraeus during summer, which is associated with the operation of the port and leads to increased levels throughout the day, having important implications for exposure of residents and commuters. The present results will be supplemented and expanded by a follow-up study applying positive matrix factorization (PMF) source apportionment analysis on the organic mass spectra available by the ACSM measurements, in order to quantify OA contributions of specific primary sources (such as traffic and biomass burning) and also to differentiate between primary and oxidized secondary OA aerosols.

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