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Inter-Comparison of Carbon Content in $PM_{2.5}$ and PM_{10} Collected at Five Measurement Sites in Southern Italy

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Abstract: A field campaign was performed simultaneously at five measurement sites, having different characteristics, to characterize the spatial distribution of the carbonaceous content in atmospheric aerosol in Southern Italy during the winter season. Organic carbon (OC) and elemental carbon (EC) were measured at urban (Naples), suburban (Lecce), coastal/marine (Lamezia Terme and Capo Granitola), and remote (Monte Curcio) locations. OC and EC mass concentrations were quantified by the thermal-optical transmission (TOT) method, in 24-h PM_{10} and $PM_{2.5}$ samples collected on quartz fiber filters, from 25 November 2015 to 1 January 2016. The different sites showed marked differences in the average concentrations of both carbonaceous species. Typically, OC average levels (±standard deviation) were higher at the sites of Naples (12.8 ± 5.1 and 11.8 ± 4.6 μg/m^3) and Lecce (10.7 ± 5.8 and 9.0 ± 4.7 μg/m^3), followed by Lamezia Terme (4.3 ± 2.0 and 4.0 ± 1.9 μg/m^3), Capo Granitola (2.3 ± 1.2 and 1.7 ± 1.1 μg/m^3), and Monte Curcio (0.9 ± 0.3 and 0.9 ± 0.3 μg/m^3) in PM_{10} and $PM_{2.5}$, respectively. Similarly, EC average levels (±standard deviation) were higher at the urban sites of Naples (2.3 ± 1.1 and 1.8 ± 0.5 μg/m^3) and Lecce (1.5 ± 0.8 and 1.4 ± 0.7 μg/m^3), followed by Lamezia Terme (0.6 ± 0.3 and 0.6 ± 0.3 μg/m^3), Capo Granitola (0.3 ± 0.3 and 0.3 ± 0.2 μg/m^3), and Monte Curcio (0.06 ± 0.04 and 0.05 ± 0.03 μg/m^3) in PM_{10} and $PM_{2.5}$, respectively. An opposite trend was observed for the OC/EC ratios ranging from 6.4 to 15.9 in PM_{10} and from 6.4 to 15.5 in $PM_{2.5}$ with lower values in urban sites compared to remote sites. Different OC-EC correlations, $0.36 < R^2 < 0.90$, were found in four observation sites. This behavior suggests the contributions of similar sources and common atmospheric processes in both fractions. No correlations were observed between OC and EC at the site of Naples. The average secondary organic carbon (SOC) concentrations, quantified using the minimum OC/EC ratio method, ranged from 0.4 to 7.6 μg/m^3 in PM_{10} and from 0.4 to 7.2 μg/m^3 in $PM_{2.5}$, accounting from 37 to 59% of total OC in PM_{10} and from 40 to 57% in $PM_{2.5}$ with higher percentages in the urban and suburban sites of Naples and Lecce.

Keywords: particulate matter; carbonaceous fraction; organic carbon; elemental carbon; SOC

1. Introduction

Carbonaceous aerosol components, organic carbon (OC) and elemental carbon (EC), account for a large fraction of atmospheric particulate matter (PM) and, on average, contribute to 20–45% of $PM_{2.5}$ and 20–35% of PM_{10} [1,2] across Europe. OC and EC are co-emitted, but in different proportions, depending on the source [3]. Elemental carbon is directly emitted into the atmosphere from the incomplete combustion of fossil fuels, biofuels, and biomass. It has a long photochemical lifetime and this makes it a good indicator for primary anthropogenic air pollution [4,5]. Organic carbon originates from a variety of processes. It can be released into the atmosphere from anthropogenic (fossil fuel combustion, domestic heating and cooking, industrial processes, biomass burning), and biogenic sources (vegetation, wind-lifted biological particles, fires, emissions from marine environments), as primary OC (POC), or produced within the atmosphere by photochemical reactions through gas-to particle conversion of volatile organic compounds, as secondary OC (SOC) [6–8]. Due to their different physical and chemical properties, OC and EC influence the environment and climate in different ways. Depending on their size and composition, carbonaceous aerosol can efficiently scatter and absorb solar radiation and serve as cloud condensation nuclei (CCN), thereby affecting climate [9]. In general, OC mainly scatters light and exerts a negative climate forcing influence [10,11], while EC is one of few aerosol components with strong absorbing properties, from visible to infrared waveband [12,13]. Therefore, EC can increase the solar radiation energy absorbed in the earth-atmosphere system, and regionally it can be an important agent of global warming, similar to CO_2.

Carbonaceous aerosols concentrations in the atmosphere have substantially increased from preindustrial times to the present-day because of increasing anthropogenic activities like human use of coal, oil and other fossil fuels, agricultural and biological burning, and vehicle exhaust emissions. Although carbonaceous aerosols exist in abundance, near source regions their atmospheric lifetimes are about a few weeks [14]; hence, they can be transported over long distances [15], contributing not only to local but even contributing to global air quality and potentially influencing global climate. This is in part due to highly variable temporal and spatial concentrations in the troposphere, caused by dispersion or turbulent mixing and in part due to undiscovered atmospheric transformations, such as heterogeneous oxidation or cloud seeding. In the atmosphere, aerosols become photochemically aged. Complex mechanisms such as condensation, coagulation, cloud processing, and photochemical oxidation processes lead to the formation of secondary aerosols [8].

In recent years, particular attention has been paid to carbonaceous aerosols through systematic studies regarding their abundances, sources, and spatial variations. Nevertheless, the Mediterranean area is a hot spot for air pollution and climate, highly impacted by biomass burning and anthropogenic activities, emitting high concentrations of EC and OC. Only a few observations are available in this crucial area, where these emissions are able to play a significant role in climate, in an environment already highly impacted and sensitive to climate change. An interesting analysis of OC and EC available data in Italy [16] shows data are insufficient in Central and Southern Italy. In this context, an intensive measurement campaign was conducted from November 2015 to January 2016 at five different sites of Southern Italy, to investigate and compare the characteristics and the relative contributions of carbonaceous species (OC and EC) to the PM_{10} and $PM_{2.5}$ mass. Due to the geographical location, this area is affected by local and long-range transport of marine, desert, and anthropogenic aerosols [17,18]. Thus, the comparison among different sites (from coastal, to mountain and urban) within the same geographical region would be a useful tool for exploring long-range transport vs. local emissions in conjunction with aerosol ageing processes. The results obtained were related to the climatic and geographic conditions of the study areas to identify the possible factors affecting the concentrations of carbonaceous species.

2. Method

2.1. Sampling Sites

The carbonaceous content was investigated in daily 24-h $PM_{2.5}$ and PM_{10} samples simultaneously collected at five measurement sites (spread in Southern Italy): Lecce, Lamezia Terme, Capo Granitola, Monte Curcio, and Naples. The first four sites are regional stations of the Global Atmosphere Watch program (GAW-WMO), dedicated to environmental-climate monitoring and activated in the framework of the PON Project I-AMICA (Infrastructure of High Technology for Integrated Climate and Environmental Monitoring (Available online: http://www.i-amica.it/). Figure 1 shows the geographical location of the sampling sites: the urban site of Naples, the suburban site of Lecce, two coastal sites (Lamezia Terme, and Capo Granitola) and the remote (high altitude) site of Monte Curcio. The sites were classified on the basis of their distance from pollution sources, according to criteria proposed by the European Environment Agency [19].

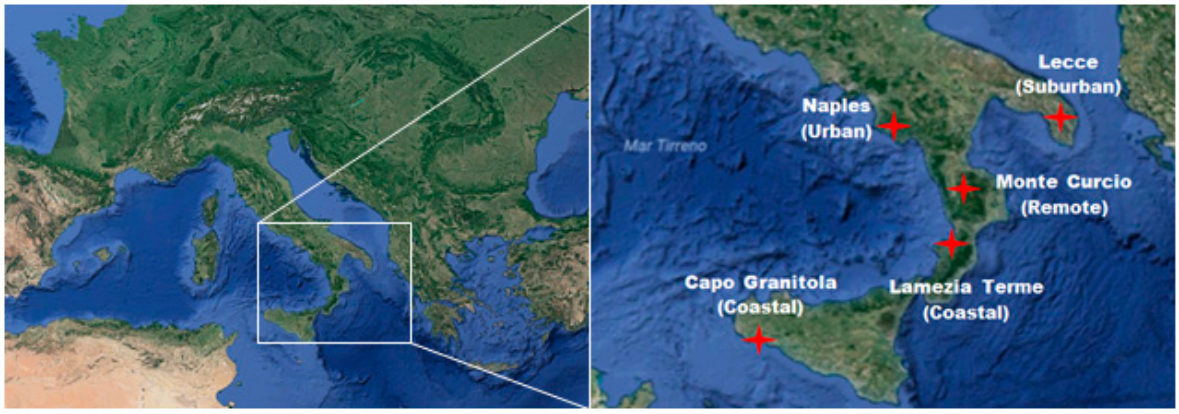

Figure 1. Map of the observation sites over Southern Italy: Naples (urban), Lecce (suburban), Lamezia Terme and Capo Granitola (coastal), Monte Curcio (remote).

Naples-San Marcellino Observatory (40.5° N, 14.0° E; 53 m a.s.l.), located in the centre of Naples (referred to hereafter as the Naples site), is a site within a restricted traffic area, close to the marina, but not distant (about 0.5 km) from very busy roads. It is influenced by multiple sources, e.g., vehicular traffic, port emissions, and biomass combustion. It is also likely that emissions from numerous pizza restaurants located nearby (using wood burning) as well as from garbage accumulation in the town could influence measured PM concentrations. Although the site is within a restricted traffic area, Naples is an urban area strongly influenced by road traffic [20,21]. More details on the site and on concentration levels are given in Riccio et al. [20–22]. Lecce Observatory (ECO, 40.3° N 18.1° E; 36 m a.s.l.) is located inside the University Campus at about 4 km (W-SW) from the urban area of Lecce and about 15 km from South Adriatic Sea [23]. The site is not strongly influenced by local sources, rather by the integrated contributions of traffic inside the University Campus and by diffused emissions of the town of Lecce and near villages, and sometimes by industrial emissions of Taranto (about 80 km in the NW direction) and Brindisi (about 30 km in the NNW direction). More details on the measurement site, on pollution levels and on the main sources can be found in Cesari et al. [24]. Lamezia Terme Observatory (LMT, 38.8° N 16.2° E; 6 m a.s.l.) is located about 10 km from the urban city, 600 m inland from the Tyrrhenian coastline where the breeze system plays a major role in defining local meteorology and natural and anthropogenic air mass transport. Its long and narrow shape create a complex interaction of breezes which develop perpendicularly to the coast, determining an atmospheric circulation variability and the development of vertical structures of the coastal planetary boundary layer. The site is at the end of a natural channel between Thyrrenian and Ionian Seas (respectively W and E directions). The area experiences some pollution coming from the transport

sector (airport, cruises from/to Gioia Tauro and local traffic mainly for E-NE direction), houses, and agriculture. More details on the site can be found in Cristofanelli et al. [25]. Capo Granitola Observatory (CGR, 37.6° N 12.6° E; 5 m a.s.l.) is located only 5 m from the coastline, towards the Strait of Sicily and it is representative of the background conditions of the western Sicily/central Mediterranean basin. It is located in the Torretta Granitola hamlet, Campobello di Mazara municipality, 12 km from Mazzara del Vallo. More details on the site can be found in Cristofanelli et al. [25]. Monte Curcio Observatory (CUR, 39.2° N 16.2° E; 1780 m a.s.l.) is located in a strategic position within the Sila National Park in the Calabria region. It is a high altitude and remote monitoring station located on a southern Apennine mountain peak with a completely free horizon, thus allowing atmospheric monitoring measurements with a large spatial representativeness. Due to its elevation and position in the middle of the Mediterranean basin, around 30 km far from the Tyrrhenian Sea and 60 km from the Ionian Sea, the Monte Curcio station is particularly able to intercept dust plumes from the Saharan desert (similarly to Capo Granitola) as well as volcanic ashes and gases from the Stromboli and Mt. Etna volcanoes (similar to Lamezia Terme), located at around 120 km south-easterly and 220 km south-south-easterly from the atmospheric monitoring site, respectively [26].

2.2. Sample Collection and Analysis

At all the sites, 24-h PM_{10} and $PM_{2.5}$ samples were simultaneously collected, from 25 November 2015 to 1 January 2016. Mass concentration measurements were performed by the β-ray attenuation method, using low volume samplers (2.3 m^3/h) with two channels for automatic sampling and monitoring, one for PM_{10} and one for $PM_{2.5}$ (SWAM 5a Dual Channel Monitor-FAI Instruments). The device measures the attenuation of β-ray across the filter medium which collects particulate matter, and the attenuation of intensity in β-ray is proportional to the amount of material present. Due to technical problems, the sampling at Capo Granitola was carried out only in the first two weeks of the campaign; for the same reason, for a few days there was no sampling at Monte Curcio. The particulate matter was collected on quartz microfiber filters (Whatman Q-grade, diameter 47 mm). The mass concentration measurements by the β-attenuation technique were in very good agreement with those from the standard reference gravimetric method, and the typical uncertainty of the measured daily mass concentration was 0.5–0.6 μg/m^3 [27].

The analysis of Total Carbon (TC = OC + EC), OC, and EC was performed on all filters, pre-fired for 2 h at 700 °C in order to remove any residual carbon contamination, by the thermo-optical method (TOT) using a Sunset Laboratory OC/EC analyser (Sunset Laboratory, Tigard, OR, USA), implementing the EUSAARII temperature protocol [28]. To ensure the accuracy of the OC and EC analysis, the analyser was calibrated (multipoint) using as an external standard a sucrose solution. Blank filters, from each measurement site, were also analysed for correcting the measured concentrations. EC concentrations observed in blank filters were negligible (<0.1 μg/cm^2) for all sites; however, contamination was observed for OC. The corrected OC concentrations were obtained by subtracting the average value of the blank filters obtained at a specific site from the OC measured in each exposed sample at the same site. The average correction was less than 4% for Lecce, Naples, and Monte Curcio sites; about 12% for the Lamezia Terme site; and about 25% for the Capo Granitola site. The uncertainty of the measured OC concentrations was variable between 5% and 6% of measured concentrations at the different sites. The uncertainties of the measured EC concentrations had a larger variability in relative terms: 7.5% of measured concentrations (Lecce), 9% (Napoli), 11% (Lamezia Terme), 20% (Capo Granitola), and 37% (Monte Curcio). The largest relative uncertainty was observed at the lowest concentration.

During the sampling period, meteorological data, including ambient temperature, pressure, relative humidity (RH), wind velocity, and wind direction were also recorded by using automatic weather stations (Vaisala) for all monitoring sites except for Monte Curcio, at which different equipment were used (LSI Lastem). In addition, particle concentration measurements were performed at the four sites of the Global Atmosphere Watch program, being equipped with optical particle counters

(OPC FAI Multichannel Monitor) which classifies particles in 22 size intervals, from 0.28 to 10 μm [27]. The instruments were located close to the PM sampling area.

3. Results

3.1. PM_{10} and $PM_{2.5}$ Concentrations

The temporal variability of the PM_{10} and $PM_{2.5}$ average daily concentrations measured during the campaign at all sites is plotted in Figure 2, while the statistics of the concentrations are shown in Table 1 which reports the average values (±standard deviation), minima (Min), maxima (Max), $PM_{2.5}/PM_{10}$ average ratios, and the number of samples (N). The higher PM_{10} and $PM_{2.5}$ mass concentration values were observed in the urban site of Naples (50.8 ± 21.7 and 37.8 ± 18.0 μg/m^3), followed by Lecce (32.7 ± 13.0 and 25.7 ± 11.6 μg/m^3), Capo Granitola (23.2 ± 8.6 and 10.4 ± 2.6 μg/m^3), Lamezia Terme (10.1 ± 3.8 and 7.2 ± 3.5 μg/m^3) and Monte Curcio (3.4 ± 1.4 and 3.0 ± 1.2 μg/m^3). The results obtained are in general agreement with other aerosol studies conducted in Naples [20,21] and Lecce [29]. The measured PM concentrations are also in the same range of levels reported for other European urban [30], Mediterranean coastal and remote sites [31,32].

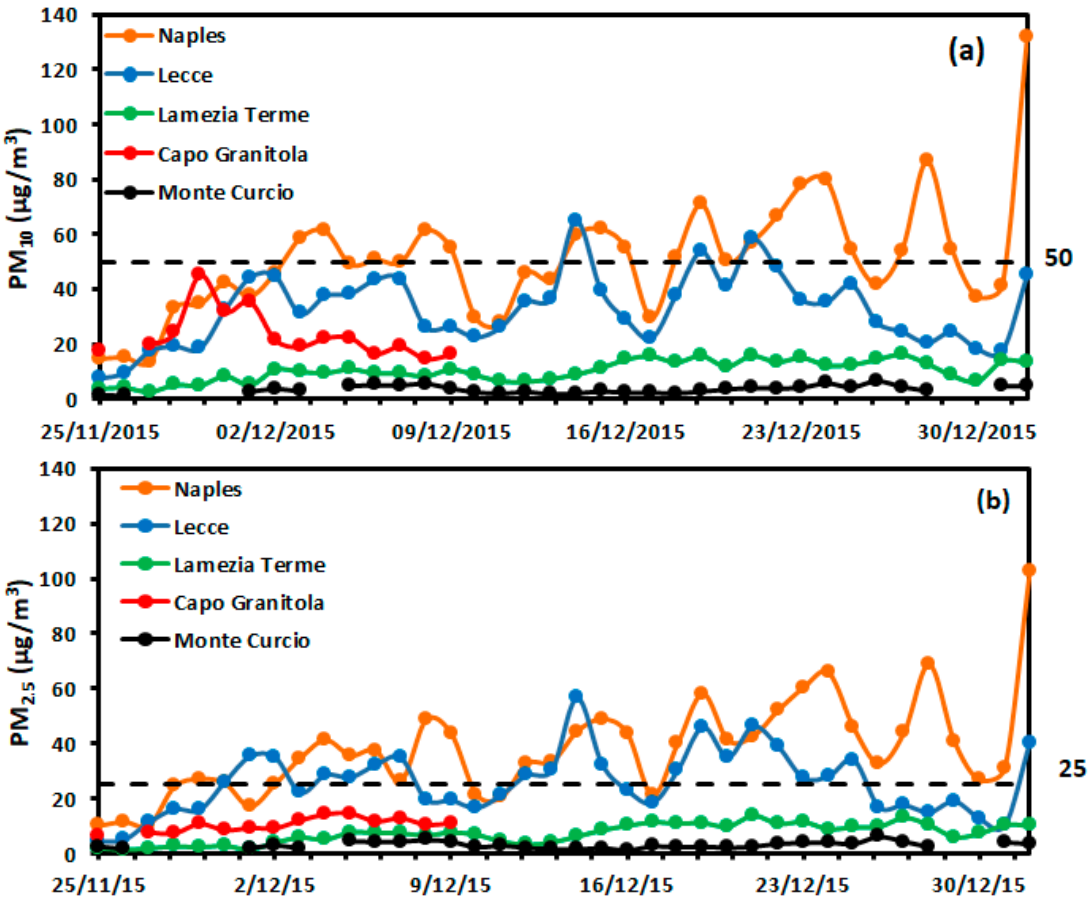

Figure 2. Temporal variability of (**a**) PM_{10} and (**b**) $PM_{2.5}$ mass concentrations during the measuring campaign at the Naples, Lecce, Lamezia Terme, Capo Granitola and Monte Curcio sites. Horizontal dashed lines represent the legislative limit values set in Directive 2008/50/EC for (**a**) the daily PM_{10} concentration that is permitted to be exceeded 35 days per calendar year, and (**b**) the limit for the annual average concentration of $PM_{2.5}$.

Table 1. Number of samples (N), average ± standard deviation (Avg ± Std), minima (Min) and maxima (Max) concentrations for PM_{10} and $PM_{2.5}$ fraction together with $PM_{2.5}/PM_{10}$ average ratios measured during the campaign at each observation site.

Sites	PM_{10} (μg/m^3)				$PM_{2.5}$ (μg/m^3)				$PM_{2.5}/PM_{10}$
	N	Avg ± Std	Min	Max	N	Avg ± Std	Min	Max	
Naples	37	50.8 ± 21.7	13.5	132.1	38	37.8 ± 18.0	10.1	102.5	0.74
Lecce	38	32.7 ± 13.0	7.4	64.9	36	25.7 ± 11.6	4.4	56.6	0.77
Lamezia Terme	38	10.1 ± 3.8	2.5	16.1	38	7.2 ± 3.5	1.4	13.8	0.68
Capo Granitola	14	23.2 ± 8.6	14.5	45.1	14	10.4 ± 2.6	6.1	14.6	0.50
Monte Curcio	31	3.4 ± 1.4	1.1	6.5	31	3.0 ± 1.2	1.2	6.1	0.82

Figure 2 shows that there have been several exceedances of the daily limit value (μg/m^3) for PM_{10} concentrations at the urban site (Naples) and at the suburban site (Lecce); however, no exceedances were observed during the measurement period at the coastal/marine and remote sites. This confirms that Southern Italy continues to be one of the most problematic areas, especially in urban environments, with numerous exceedances [19]. Results also suggest that local emissions and meteorological conditions have a role in determining some of these exceedances. It interesting to observe the high PM mass concentrations recorded on 1 January 2016 at Naples. The PM_{10} and $PM_{2.5}$ daily levels were 132.1 μg/m^3 and 102.5 μg/m^3, respectively, almost 3 times larger than the mean average values registered during the whole sampling campaign. The high PM levels could be due to the burning of fireworks that are traditionally used to celebrate New Year's Day.

As several studies have revealed, the high PM concentrations can be due not only to increased emissions but also to atmospheric circulation and to typical conditions of the winter season, characterized by stagnant weather with a relatively low planetary boundary layer (PBL) height, which leads to accumulation of pollutants and aerosol formation processing [33–37]. Dispersion and transport of lower atmospheric pollutant depend largely on the local PBL structure, and the turbulence is the dominant mechanism mixing particulate matter (PM) and ambient air. By acting as a lid to the pollution vertical mixing extent, PBL height is one of the important factors affecting pollution concentration and large-scale transport [38].

At the same time, the lowest PM concentrations observed in Lamezia Terme and Monte Curcio can be due to the lower anthropogenic emissions and favorable meteorological conditions (such as turbulence, high wind velocity, vertical thermal gradient leading to unstable atmospheric conditions) that promote atmospheric dispersion and dilution of pollutants. In particular, the Lamezia Terme site is characterized by prevalent circulation coming from the sea (western direction) with clean air mainly influenced by sea spray that could potentially contribute to high PM concentrations but lower OC (and especially low EC) concentrations. Monte Curcio, being located at 1780 m a.s.l. and far from pollution sources, is located for most of the time above the mixing layer. Therefore, it can be considered representative of free troposphere conditions.

The $PM_{2.5}/PM_{10}$ average ratios ranged between 0.68 and 0.82, as shown in Table 1, and they show that more than 68% of the PM_{10} is in the form of $PM_{2.5}$. PM_{10} and $PM_{2.5}$ concentrations were well correlated at three sites (Figure 3a), Lecce (R^2 = 0.98), Naples (R^2 = 0.95) and Lamezia Terme (R^2 = 0.88), with a slope varying from 0.81 to 0.88. These results indicate that the two fractions are driven by similar sources and controlled by common processes of transport and dispersion. A slightly lower correlation (R^2 = 0.77) was found at the Monte Curcio site, where the high $PM_{2.5}/PM_{10}$ average ratio of 0.82 shows the predominant contribution of the fine fraction likely due to long-range transport given that no local sources are present nearby this high altitude site. Fine aerosol, coming from industrial areas of continental Europe, can persist in the atmosphere longer and can be transported over a large distance, as already observed in other remote sites [39,40].

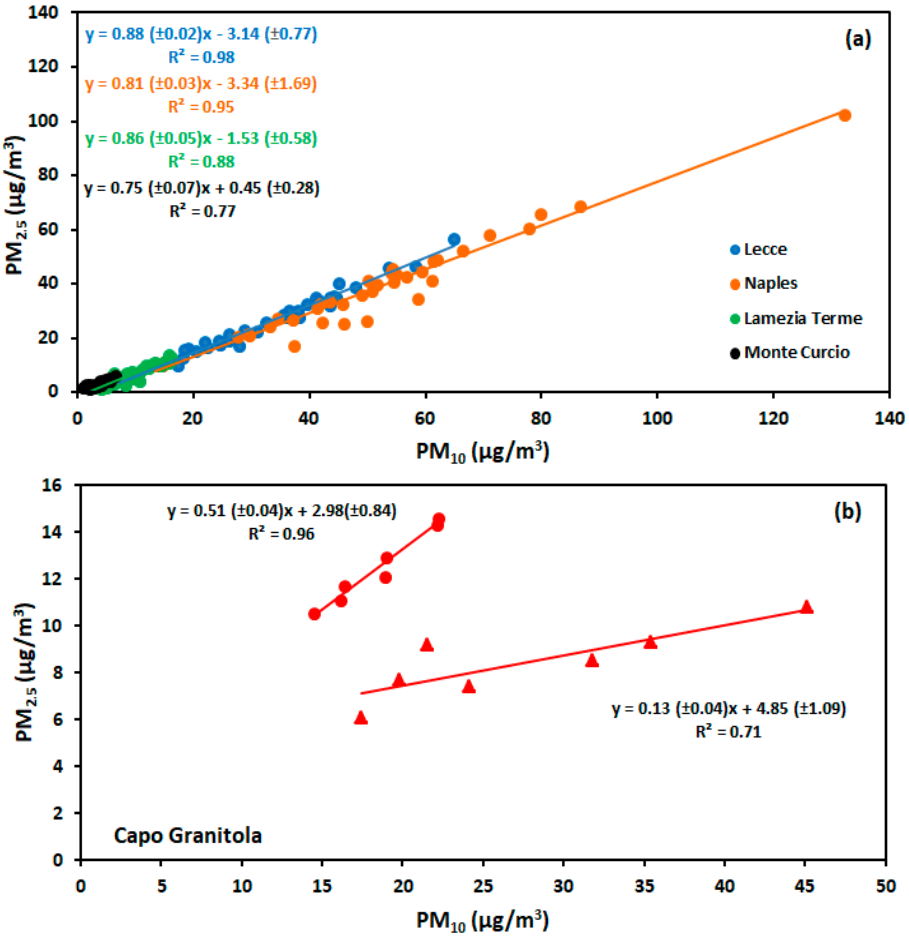

Figure 3. Correlation between PM_{10} and $PM_{2.5}$ mass concentrations at (**a**) the Naples, Lecce, Lamezia Terme, Monte Curcio sites and (**b**) Capo Granitola (triangular and round points represent the samples of two distinct periods: from 25 November 2015 to 2 December 2015 and from 3 December 2015 to 9 December 2015, respectively).

In Capo Granitola, the dataset is more limited compared to the other sites; however, some information could be obtained from the data in Figure 3. At first glance the two fractions seemed completely uncorrelated (R^2 = 0.01); instead, the points are distributed in two distinct periods, from 25 November 2015 to 2 December 2015 and from 3 December 2015 to 9 December 2015 (Figure 3b), with different slopes: 0.3 and 0.7. Both periods were separately well correlated R^2 = 0.96 and R^2 = 0.71, because they were influenced by two main advection pathways characterized by a different kind of air masses, coming from the sea (N-NW) or mainland (E-NE) (see Section 3.5).

3.2. Concentration Levels of OC and EC

Statistics of the TC, OC and EC concentrations, measured during the sampling campaign, are summarized in Tables 2 and 3. The results show a considerable variation of average values (±standard deviation) among the sampling locations.

Table 2. TC, OC, EC, and SOC average concentrations (±standard deviation) in PM_{10} together with the OC/EC, TC/PM, OC/PM, EC/PM and SOC/PM average ratios, for each observation site.

Sites	TC	OC	EC	TC/PM	OC/PM	EC/PM	OC/EC	SOC	SOC/OC
	($\mu g/m^3$)	($\mu g/m^3$)	($\mu g/m^3$)	%	%	%	(min)	($\mu g/m^3$)	%
Naples	15.1 ± 5.2	12.8 ± 5.1	2.3 ± 1.0	31	26	5	6.4 (2.6)	7.6 ± 5.3	52
Lecce	12.2 ± 6.4	10.7 ± 5.9	1.5 ± 0.8	35	31	5	7.3 (2.8)	6.9 ± 4.8	59
Lamezia Terme	4.9 ± 2.3	4.3 ± 2.0	0.6 ± 0.3	48	42	6	6.9 (4.1)	1.7 ± 1.1	37
Capo Granitola	2.6 ± 1.5	2.3 ± 1.2	0.3 ± 0.3	13	11	2	10.0 (4.4)	0.7 ± 0.6	41
Monte Curcio	1.0 ± 0.4	0.9 ± 0.3	0.06 ± 0.04	30	28	2	15.9 (10.0)	0.4 ± 0.1	47

Table 3. TC, OC, EC, and SOC average concentrations (±standard deviation) in $PM_{2.5}$ together with the OC/EC, TC/PM, OC/PM, EC/PM and SOC/PM average ratios, for each observation site.

Sites	TC	OC	EC	TC/PM	OC/PM	EC/PM	OC/EC	SOC	SOC/OC
	($\mu g/m^3$)	($\mu g/m^3$)	($\mu g/m^3$)	%	%	%	(min)	($\mu g/m^3$)	%
Naples	13.7 ± 4.8	11.8 ± 4.6	1.8 ± 0.5	39	33	6	6.4 (2.6)	7.2 ± 4.4	54
Lecce	10.4 ± 5.1	9.0 ± 4.7	1.4 ± 0.7	40	34	6	6.9 (2.6)	5.7 ± 3.6	57
Lamezia Terme	4.7 ± 2.1	4.0 ± 2.0	0.6 ± 0.3	67	57	10	6.5 (3.0)	2.1 ± 1.3	47
Capo Granitola	2.0 ± 1.3	1.7 ± 1.1	0.3 ± 0.2	17	15	2	8.0 (4.0)	0.6 ± 0.4	40
Monte Curcio	0.9 ± 0.3	0.9 ± 0.3	0.05 ± 0.03	33	31	2	15.5 (10.0)	0.4 ± 0.2	48

The average OC concentrations, contained in the PM_{10} and $PM_{2.5}$ fractions ranged, respectively, from 0.9 $\mu g/m^3$ to 12.8 $\mu g/m^3$ and from 0.9 $\mu g/m^3$ to 11.8 $\mu g/m^3$, increasing about 14 times from remote to urban sites. The same behavior was found for the EC concentrations but with a larger variability, ranging from 0.06 $\mu g/m^3$ to 2.3 $\mu g/m^3$ (in PM_{10}) and from 0.05 $\mu g/m^3$ to 1.8 $\mu g/m^3$ (in $PM_{2.5}$), increasing more than 36 times from remote to urban sites. The results obtained show similar features with other studies performed in different European sites [41], indicating that the high spatial variability of EC, compared to OC, is due to local primary emissions (traffic, biomass burning for heating), produced from a wider range of sources [16]. The highest OC and EC average values were observed in the urban sites of Naples and Lecce; this indicates that the two environments are strongly affected by anthropogenic emissions. The two sites are influenced by local primary emission from nearby traffic and anthropogenic activities that can emit large amounts of primary aerosols, as well as high quantities of volatile organic compounds, favoring the production of secondary organic aerosol under favorable meteorological conditions. Significantly lower values were found in Lamezia Terme and Capo Granitola, characterized by relatively limited sources, and probably influenced by sea-breeze effects that favor the pollutant's dispersion [42]. The extremely low concentrations measured in Monte Curcio are in good agreement with free tropospheric conditions characterizing a remote site. The TC percentage in the PM fractions was mainly determined by the contribution of the OC mass concentration. Higher TC average percentage values were found in Lamezia Terme (48% and 67%) followed by Lecce (35% and 40%), Naples (31% and 39%) and Monte Curcio (30% and 33%), while very low percentages were found in Capo Granitola (13% and 17%), in the PM_{10} and $PM_{2.5}$ fractions, respectively.

3.3. Relationship between OC and EC Concentrations

The relationship between the OC and EC atmospheric concentrations gives qualitative information regarding the sources contributing to carbonaceous species in PM [43]. If OC and EC are released into the atmosphere by common primary sources, the two carbonaceous species should be well correlated [44]. The scatter plots of OC versus EC concentrations, in both size fractions, are given in Figure 4 using different colors for each site. The solid lines indicate the linear regressions of data. Good correlations were found for the sites of Capo Granitola (R^2 = 0.80, R^2 = 0.90), Monte Curcio (R^2 = 0.76, R^2 = 0.73), and Lamezia Terme (R^2 = 0.76, R^2 = 0.67) in PM_{10} and $PM_{2.5}$, respectively (Figure 4). The weaker correlation (R^2 = 0.36, R^2 = 0.37) observed in Lecce indicates that, in addition to primary sources, other emission sources contribute significantly. At Naples, on the contrary, OC and

EC were not correlated in both size fractions (R^2 = 0.003, R^2 = 0.07). The lack of OC-EC correlation has also been found in other urban areas such as Milan [45] and Thessaloniki [46]. This behavior suggests that the sources of OC are different from those of EC and/or can be the result of the presence of different emission sources, having significantly different OC/EC ratios.

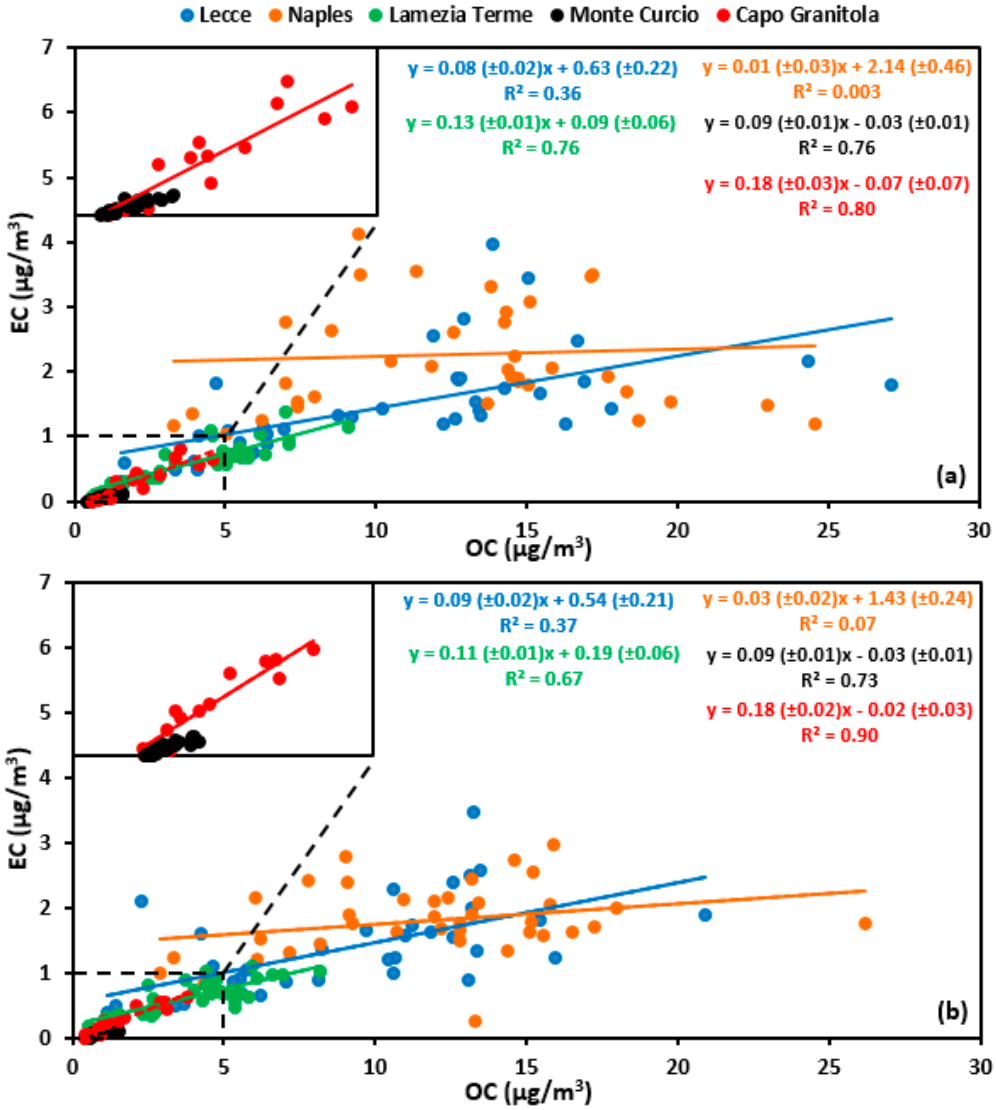

Figure 4. Scatter plot of OC vs. EC in (**a**) PM_{10} and (**b**) $PM_{2.5}$ fractions at all observation sites with linear fits. Dotted lines show in detail the scatter plot of OC vs. EC related to Monte Curcio and Capo Granitola, in both pictures.

At the same time, the OC/EC ratio is strongly source dependent, and provides a valuable tool to obtain information on the emission sources and the transformations of the carbonaceous aerosol [47], identifying the secondary organic aerosol (SOA) formation. Organic aerosol can be emitted directly into the atmosphere as primary particles or it can be of secondary origin. When volatile organic compounds (VOC) are oxidized in the atmosphere, they produce oxidized volatile organic compounds (OVOC) which condense onto pre-existing aerosol forming secondary organic aerosol (SOA) [48]. In general, the OC/EC ratio shows a seasonal variability depending on the sources influencing specific sites (e.g., road traffic, biomass burning) and also influenced by the formation of SOA that depends on atmospheric conditions [16,29,46,49,50]. Therefore, this ratio can range from low values (about 1) in polluted environments to high values (up to 15) in remote locations [16].

Tables 2 and 3 show the OC/EC values obtained at the five sites in both PM fractions. These OC/EC ratios are in agreement with the average values measured in other stations of similar typology [16], ranging from 6.4 to 15.9 in PM_{10} and from 6.4 to 15.5 in and $PM_{2.5}$. From one side, the mountain site of Monte Curcio was characterized by the highest OC/EC average ratios, 15.9 and 15.5, and this highlights the clear prevalence of the organic carbon species over EC. In clean environments, like Capo Granitola, the emissions of EC are limited, thus the OC/EC ratio tends to be higher [51]. In contrast, the site of Naples (in both fractions), Lamezia Terme (in $PM_{2.5}$), and Lecce (in $PM_{2.5}$) were characterized by the lowest OC/EC average ratios, 6.4, 6.5, and 6.9 respectively. Larger OC/EC ratios were observed at the other sites. The relatively high values suggest a clear prevalence of the organic carbon contribution over EC that could be attributed to significant local sources with higher OC and lower EC emission rates. Local heating systems, particularly in small towns, are often based on the combustion of biomass burning, an important OC source which leads to the increase of the amount of carbonaceous particles of primary origin [52].

3.4. Estimation of SOC Concentrations

Quantifying the contributions of SOC to carbonaceous aerosol is rather difficult mainly because of the complexity of the OC reaction pathways and the vast number of products formed by photochemical and thermal oxidation reactions [53]. There is no simple direct analytical technique to estimate its formation, but there are several complementary techniques based on measurements of ambient aerosol, such as the ratios of organic mass (OM) to organic carbon (OC), loadings of water-soluble OC and level of oxidation from online aerosol mass spectrometry [54]. Nevertheless, it is possible to use an indirect method for quantitative assessment of secondary organic aerosols (SOA), such as the EC trace method [53]. In this study, the SOC concentrations were calculated according to the methodology proposed by [55]. In general, the OC/EC ratio varies considerably from source to source, due to the strengths of the different emission sources, and the presence of a minimum ratio for OC/EC suggests that samples contain almost exclusively primary carbonaceous compounds [56]. In addition, the minimum ratios can be affected by various factors, such as meteorology, local sources and long-range aerosol transport. Under these condition, the organic carbon may still contain small proportions of secondary OC; therefore, this calculation provides a lower limit for the SOC content. The concentrations of secondary organic carbon SOC were estimated in both PM fractions for every sample from:

$$\mathrm{SOC} = \mathrm{OC} - \mathrm{EC} \times (\mathrm{OC/EC})\mathrm{min} \quad (1)$$

where (OC/EC)min is the lowest OC/EC ratio. Average concentrations of secondary organic carbon and its percentage contribution to the ambient OC are summarized in Tables 2 and 3.

Over the whole measurement campaign, the average SOC concentrations ranged from 0.4 to 7.6 $\mu g/m^3$ in PM_{10} and from 0.4 to 7.2 $\mu g/m^3$ in $PM_{2.5}$, accounting from 37 to 59% of the OC in PM_{10} and from 40 to 57% in $PM_{2.5}$. It is interesting to observe that the spatial variability of the ratio SOC/OC is much smaller with respect to the observed variability of SOC and OC concentrations. The SOC/OC values found are comparable with those observed in other sites influenced by different sources. In central Italy, SOC/OC ratios between 44% and 54% were observed at three sites of different typology (rural, urban background, and urban) [57]. In Northern Italy, SOC/OC ratios between 52% (summer) and 76% (winter) were observed at different sites [58]. In Birmingham (UK), an SOC/OC ratio of 59% was observed during winter [59] and the same ratio (59%) was also observed at an urban site in Beijing (China) [60]. These results show that SOC particles observed in this study were an important component of the OC mass in all sites. In particular, the higher percentage of SOC in the OC, observed at the urban and suburban sites of Naples and Lecce, can be attributed to several factors. In winter, the increased emission of volatile organic precursors, together with the stable atmospheric condition and the prolonged residence time, may strengthen atmospheric oxidation of volatile organic compounds.

On the other hand, as regards the other measurement sites, the lower percentage of SOC estimated can be prevalently due to the direct emission in the atmosphere from combustion sources.

3.5. Influence of Meteorological Parameters on Measured Concentrations

To better analyze the role of meteorology on the local aerosol and carbon concentrations, the correlations of the main meteorological parameters with measured concentrations were investigated. Although particulate mass concentrations and their components are controlled primarily by emission sources, meteorological and topographical factors also play a crucial role in their dispersion and diffusion. The average daily values of relative humidity, temperature, and wind velocity for each sampling site during the study period are shown in Table 4.

Table 4. Average values of meteorological parameters collected during the campaign: wind velocity, temperature and relative humidity. In parentheses, the minima and maxima values are reported.

Sites	Wind Velocity (m/s)	Temperature (°C)	Relative Humidity (%)
Naples	1.8 (0.5–5.7)	10.8 (8.7–14.2)	———
Lecce	1.5 (0.2–5.3)	10.0 (4.7–12.5)	79.3 (50.0–87.1)
Lamezia Terme	2.8 (0.8–10.2)	12.6 (9.1–16.6)	70.4 (54.3–84.8)
Capo Granitola	3.6 (0.6–13.7)	13.0 (10.6–15.2)	76.2 (64.2–85.8)
Montecurcio	3.2 (0.2–13.4)	2.8 (−2.2–8.2)	70.9 (29.9–99.0)

The daily average values of the relative humidity (RH) ranged from 50 to 85% in Lecce and Lamezia Terme, from 30 to 100% in Monte Curcio, and from 65 to 85% in Capo Granitola (no data are available for Naples). The higher daily temperature values were measured in Lamezia Terme (9.1–16.6 °C) and Capo Granitola (10.6–15.2 °C) followed by Naples (8.7–14.2 °C), Lecce (4.7–12.5 °C), and Monte Curcio (−2.2–8.2 °C). The results of the regression analysis revealed that relative humidity was not significantly correlated with the carbon concentrations at all sites ($R^2 \cong 0.1$). Temperature was not correlated with carbon concentrations at Monte Curcio, Naples, and Capo Granitola; instead, low correlations (R^2 between 0.2 and 0.3) showed larger OC and EC concentrations at lower temperature in Lecce and Lamezia Terme. This was observed in previous work in Lecce and was associated with the contribution of biomass burning for domestic heating [29].

The statistical analysis of the wind velocity versus the EC and OC data indicated that the wind velocity did not show any correlation with the carbonaceous concentrations for the Naples and Monte Curcio sites, while a slight correlation was found at the Lecce ($0.37 < R^2 < 0.51$), Lamezia Terme ($0.32 < R^2 < 0.48$) and Capo Granitola ($0.75 < R^2 < 0.86$) sites. At these sites, the correlation between the wind velocity and the OC and EC concentrations follows the form of a power law where the carbonaceous mass concentrations decrease with the increase in wind velocities. The wind velocity plays a leading role in the cleansing of the atmosphere from particulate matter in the sites influenced by local sources, affecting the turbulence near the ground. The greater the wind speed, the greater the dispersion of particulates, and hence the lower the mass concentration [61,62].

The wind direction was also considered to assess the relationship between sources and pollutant levels. The wind-rose pictures related to each site are shown in Figure 5. The sites of Naples and Lecce showed one of the most frequent advection pattern, with the wind generally coming from the North and North-Northwest (N-NW) directions, respectively, accounting for 89% of the total observations. In the case of Lamezia Terme and Monte Curcio, the wind blows mainly from two directions: East-Northeast (E-NE) and Southwest-Northwest (SW-NW). However, the two dominant pathways were not characterized by differences in carbonaceous concentrations.

In Capo Granitola, the major prevailing wind directions during the campaign were between WNW-NW to N-NE, which was a peculiar wind distribution (generally NW and SE) at this site [25], with winds from inland generally associated with higher concentrations and more polluted events. Associated with the N-NE wind direction, the OC and EC concentrations were higher than average

(43–59%), while the carbonaceous concentrations associated with wind from the (W-NW) direction were observed to be lower (65–71%), in both size fractions. As has already been noted (Section 3.1), in Capo Granitola it is possible to recognize two distinct periods, from 25 November 2015 to 2 December 2015 and from 3 December 2015 to 9 December 2015. The first period is characterized by WNW-NNW wind direction, indicating possible advection from the sea. The second period is characterized by air mass from the NNE-ENE sector (mainland).

To further investigate the correlation between wind direction and measured PM, OC, and EC concentrations, the concentration roses were produced for each measurement site. Results for Lecce and Naples do not give further information because the wind direction has limited variability during the sampling period (Figure 5). Results for Monte Curcio and Lamezia Terme did not show significant differences in the two main wind direction sectors identified in Figure 5. Results for Capo Granitola (Figure 6) show that the two measurement periods identified are characterized by significantly different concentrations. During the first measurement period, with winds coming from the sea (WNW-NW, in blue in Figure 6), PM_{10} concentrations are larger than those observed in the second period with wind coming from mainland (NNE-ENE, in red in Figure 6). However, OC and EC concentrations in this period are smaller than those measured when wind originated from the mainland, especially for EC.

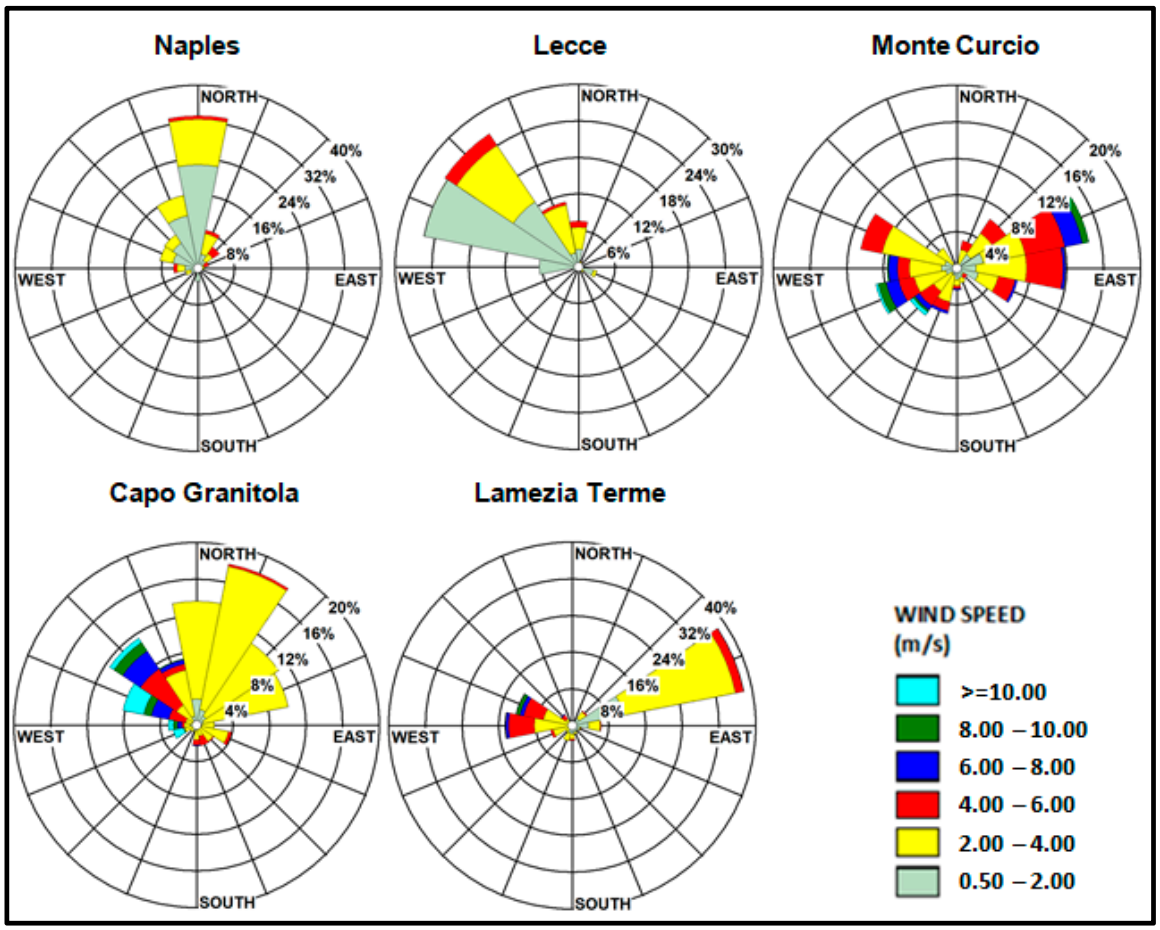

Figure 5. Wind roses of the prevailing wind directions and associated speeds related to each site during the measuring campaign.

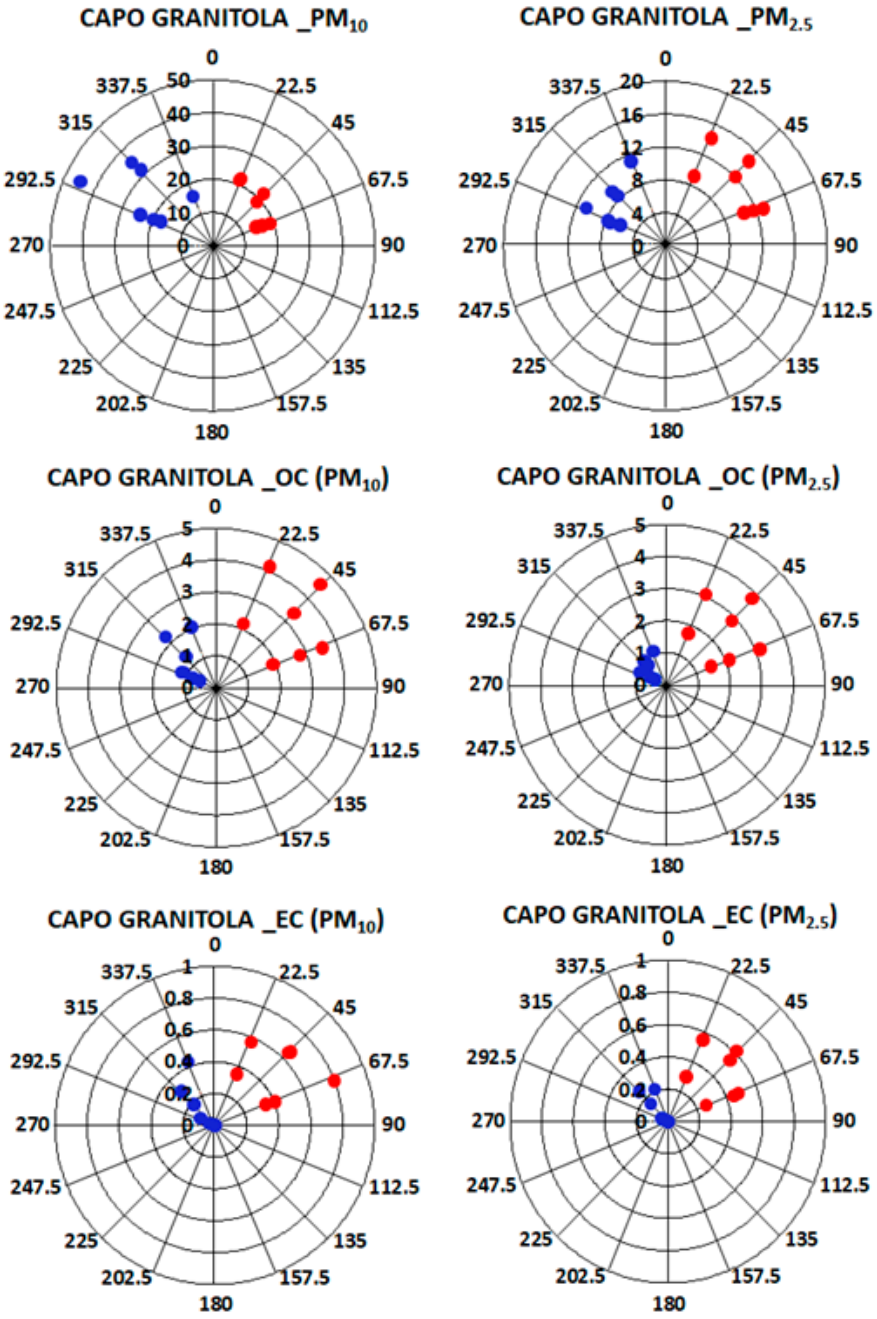

Figure 6. Concentration roses of PM_{10}, $PM_{2.5}$, and associated OC and EC concentrations. Blue and red dots represent the concentrations of the two distinct periods, from 25 November 2015 to 2 December 2015 and from 3 December 2015 to 9 December 2015, respectively.

This suggests that the first period is influenced by coarse particles with low carbon content that may be due to a marine contribution that has these characteristics in Southern Italy [18]. Daily trends of coarse particles (diameter > 2.5 μm) and fine particles (diameter < 2.5 μm) number concentrations, obtained by using the OPC and shown in Figure 7, show a larger contribution of coarse particles during the first measurement period. In the second period, air mass advected from the NNE-ENE sector and influenced by mainland and likely by anthropogenic sources, producing particles richer in carbon, may explain the higher measured $PM_{2.5}$, OC and EC concentrations, and the different correlation between $PM_{2.5}$ and PM_{10} shown in Figure 3.

The advection patterns during the two measurement periods in capo Granitola were investigated using air parcel backward trajectories analysis by the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model [63]. Trajectories were computed each day for a 72-h period, which is considered sufficient to represent the synoptic air flows. The trajectories terminated at the Capo Granitola site at 12:00 UTC at an elevation of 500 m above ground level. Figure 8 shows that air mass arriving at Capo Granitola during the sampling campaign could be separated into two advection patterns: that from the sea relative to the first measurement period (blue lines), and that showing advection above the mainland during the second measurement period (red lines). This supports the hypothesis of the presence of a marine contribution during the first measurement period. The average wind velocity near ground level, measured at 5 m from the coastline, was relatively high (6.4 m/s) during the first period compared to the second period (2.4 m/s). Results of the meteorological model MOLOCH (MOdello LOCale in H coordinates) indicate that the wind velocities in open sea are significantly higher during the first measurement period compared to the second one (http://www.isac.cnr.it/dinamica/projects/forecasts/moloch/). Such high wind velocity could favor the breaking of waves in open sea and the formation of sea-spray.

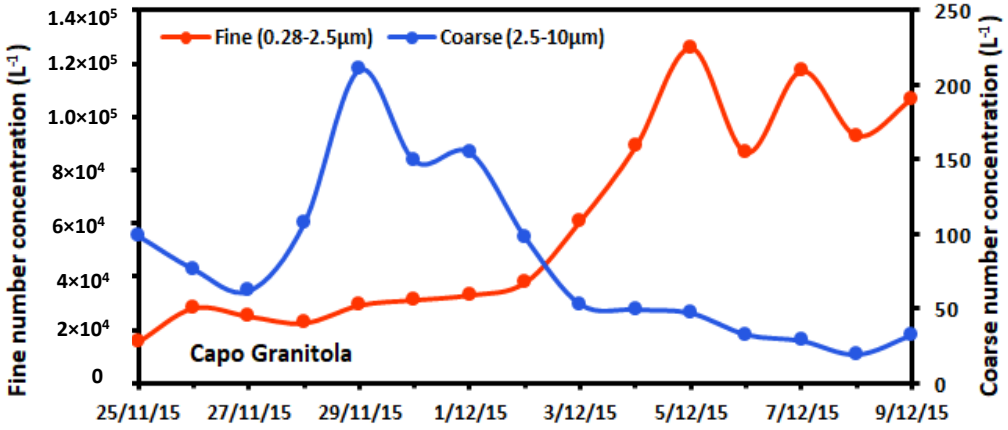

Figure 7. Comparison between trends of coarse and fine daily particles number concentrations for the two size fractions at Capo Granitola during the measuring campaign.

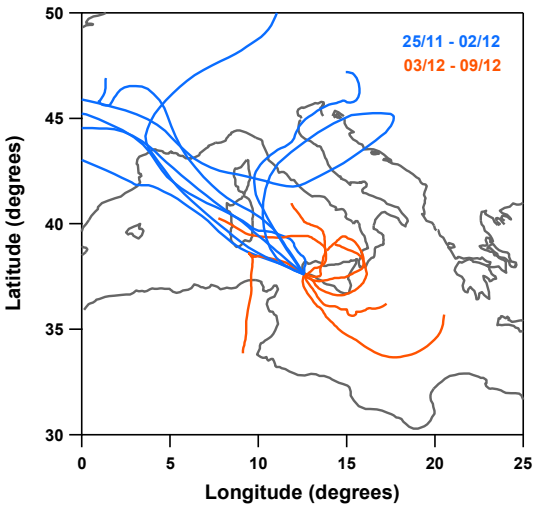

Figure 8. 72-h back trajectories arriving at the Capo Granitola site during the sampling campaign. Blue and red lines represent the back of the two distinct periods, from 25 November 2015 to 2 December 2015 and from 3 December 2015 to 9 December 2015, respectively.

4. Conclusions

In this study, the carbon content in $PM_{2.5}$ and PM_{10} at five stations, characteristic of different Mediterranean basin environments, was investigated. The mass concentration and carbonaceous species (OC and EC) in PM_{10} and $PM_{2.5}$, collected in five sites of Southern Italy, were for the first time investigated in winter during the period November 2015 to January 2016. The sites represented different environments: urban (Naples), suburban (Lecce), coastal/marine (Lamezia Terme and Capo Granitola) and remote/high altitude (Monte Curcio).

Both OC and EC average concentrations were minimal at the remote mountain site and increased in the following order: remote < coastal/marine < suburban < urban (i.e., Monte Curcio < Capo Granitola < Lamezia Terme < Lecce < Naples).

The increasing trend from remote to urban sites was also observed for the $PM_{2.5}$ and PM_{10} concentrations. However, the $PM_{2.5}$ and PM_{10} concentrations observed at the marine site of Capo Granitola are higher than those observed at Lamezia Terme, likely because of a major contribution of sea spray in the coarse fraction considering that the Capo Granitola station is located 5 m from the sea. The $PM_{2.5}$ and PM_{10} concentrations are highly correlated at all sites, with the exclusion of Capo Granitola where significantly different $PM_{2.5}/PM_{10}$ ratios were observed due to air masses coming from the sea or from inland.

The OC and EC concentrations were well correlated at all sites, with the exclusion of the urban site of Naples in which the different trend may be due to local sources with different OC/EC ratios in primary emissions. The OC/EC ratios are generally higher in PM_{10} with respect to $PM_{2.5}$ or comparable (in Naples and Monte Curcio). In addition, the OC/EC ratios were higher at the sites minimally influenced by local combustion/pollution (Monte Curcio and Capo Granitola).

SOC, evaluated using the minimum OC/EC ratio, was mainly present in $PM_{2.5}$ at all sites, and higher SOC/OC ratios were observed at the urban site (Naples) and at the suburban site (Lecce).

No significant correlations were detected between the carbon content and the temperature or relative humidity. Correlation with the wind velocity was observed only at three sites: Lecce, Lamezia Terme, and Capo Granitola. The concentrations measured at the marine site of Capo Granitola seem to be strongly dependent on the wind direction, with an important contribution in the coarse fraction due to the sea spray.

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