Airborne Particles during a Firework Festival in Belvedere M.mo, South-Western Italian Coast

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Abstract

The effects of a Summer Firework Festival on the air quality were studied for the first time in a rural area of Southern Italy. The case study analyzes the physical-chemical properties of airborne particles collected during the Note di Fuoco (NDF) Festival, which took place in Belvedere M.mo in 2016. The sampling period was peculiar since in one week three different kinds of events have succeeded: three days during the NDF Festival with the concurrence of the festival and the firework displays, one day with the typical street Market involving food stalls and specialty shops, and three days with no specific events, considered as background conditions. Particulate Matter in different two size fractions ($PM_{2.5}$ and PM_{10}) was simultaneously collected on a daily basis and then chemically analyzed for major and trace metal content as well as for organic and elemental carbon determination. Levels of particles were even below the European air quality limit values. However, the day with the country market and during the three days of the NDF festival, the finer and respirable particulate fraction, $PM_{2.5}$, showed an increase of 46% and 84%, respectively, over the mean concentration values observed during the background days. Both elemental and organic carbon, even in the finer fraction showed an increment up to 30%. All major, and trace elements were found in higher concentrations during the festival with respect to those recorded in days with no events. In our case study, K was recognized as the best fireworks tracer because its level doubled during the festival. Typical firework tracers like Fe, Ti, Mn, Pb and Sr resulted in greater concentrations, up to 50%.

Keywords

Fireworks, Air Quality, Particulate Matter, Tracers

1. Introduction

Fireworks are products of pyrotechnic industry that are displayed throughout the world to celebrate special events (New Years Eve, National Day) as well as traditional and religious festivals. The scale of fireworks displays can vary from as small as a birthday party up to a national day celebration [1] or one-off worldwide events, such as the millennium celebrations in 2000 [2].

Fireworks displays are becoming more frequent and are increasing in both their number and quality [3]. As an example, the Divali Festival in India [4] [5] [6], the Las Fallas, Valencia, in Spain [7], the Festas in the Maltese archipelago [8], the Lantern Festival in Beijing, China [9], and the Firework Festival in Taiwan [3] consume hundreds of thousands of tons of fireworks and firecrackers every year.

The tradition of fireworks in Italy is quite common with greater emphasis in the Southern regions. Nevertheless, in literature there is only well documented study carried out by Vecchi *et al.* (2008) [10] focusing on a firework episode in Milan occurring in correspondence of the World Fifa 2006.

Apart from the benefits provided by the splendid scenes of multicolored lights in the sky and the excitement of continuous brittle and resounding firecracker detonations, the burning of fireworks is a source of airborne pollutants, including O_3 [11] [12], SO_2, NO_2, CO and suspended particulate matter [9]. Fireworks consist of gunpowder and some unique chemical substances that give them their color and effect. Some of these substances include K, Al, Ba, Mn, Cd, Cu, Sr, and other heavy metals that are very harmful to human health [7] [10] [13]. The effects of airborne particulate matter on the environment and human health are strongly dependent on their size and chemical composition [14] [15].

The firework-related recreational pollution episodes during a few hours in the year provide an input of metal burden which is carried in initially dense clouds of extremely fine, easily deeply inhalable particles. Such emissions have been proven to be capable of inducing short-term adverse health effects, especially for asthmatic children and other respiratory-sensitive groups of the population [16] [17]. Firework smoke is indeed known to lead to acute eosinophilic pneumonia [18]. Barium-rich aerosols released from fireworks may be responsible for a significant rise in the number of asthma cases [19]. Majorities of barium compounds released by pyrotechnics are water-soluble and thus, bio-available, which may cause even more significant harm [20]. More recently, a positive and significant relationship was found between particulate oxidative burden and trace metals impact of firework-emitted particles on human health [21].

While for Chinese, Japanese and Indian countries there is a quite large amount of literature describing the physico-chemical characteristics of firework particles and their harmful effects of fireworks on the environment and human health, [3] [6] [22] [23] over the Italian region there are few reference studies [10], especially for the southern Italian part, where fireworks festival usually oc-

cur. To the best of our knowledge, there have been no studies regarding the simultaneous characterization of elemental and carbon content components during a firework festival in Southern Italy. This preliminary study thus provides an opportunity to assess the associated changes in the levels of ambient air pollutants caused by fireworks in a rural area of the south-western Italian coast.

In the complex, this paper reports simultaneous monitoring of 13 elements, as well as Elemental and Organic Carbon (EC and OC) in ambient aerosols collected during the 2016 NDF Festival in the town of Belvedere M.mo, Calabria, South Italy. Relative enhancements of tracer species during the pollution episode were studied, and efforts were made to justify the findings.

2. Materials and Methods

2.1. Sampling Site

As Figure 1 shows, Belvedere M.mo is a small town in the province of Cosenza, part of the Calabria region of Southern Italy. It is located at 39˚37' north and 15˚52' east on the south-western Italian coast, facing on the western side of the Tyrrhenian Sea. On the eastern side there is indeed a stretch of mountain chain which is part of the Pollino massif running parallel to the west coast. Belvedere M.mo experiences a Mediterranean climate with mean temperatures during winter and summer around 11˚C and 25˚C, respectively [24]. Belvedere M.mo has a population more than 9 thousand [25] and it is a rural area without any particular anthropogenic local source, being its economy mainly based on commercial and artisanal activities. The territory includes two distinct areas: the medieval village, which stands on a rocky ledge at 150 m a.s.l. and the most
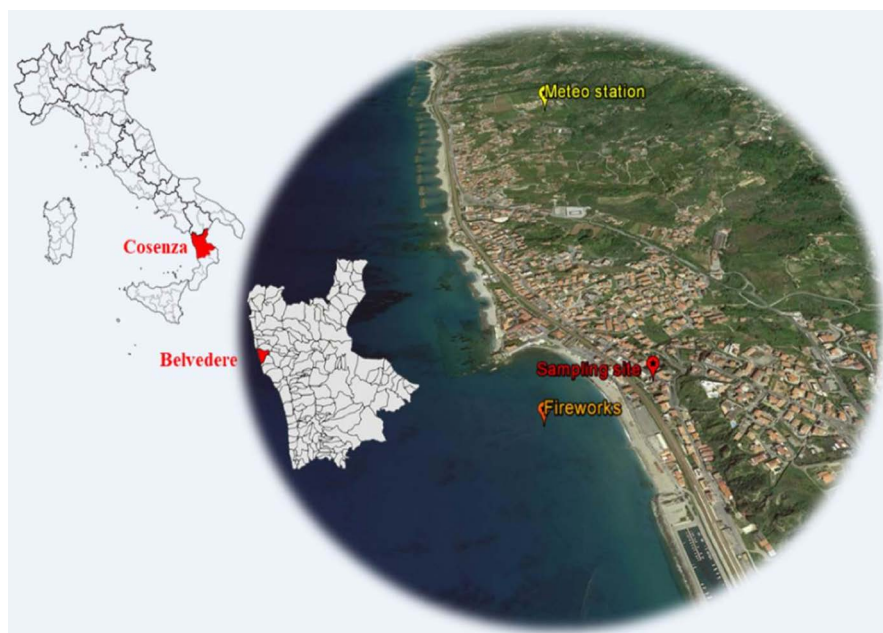

Figure 1. Map showing the contest and location of the Sampling site along with the Meteo station and the little Capo Tirone sea basin where the Firework displays took place.

properly maritime part, developed on the coast at 5 m a.s.l., which include various tourist services. Traditionally, each Wednesday morning, the maritime part of Belvedere is interested by a typical street Market (hereafter referred simply to as "Market") that involves many food stalls and specialty shops resulting in a greater flow of cars and trucks. Since 2007, even in the maritime area, and precisely around the facing sea basin known as Capo Tirone, a great and consolidated firework display Festival took place each summer. The Festival, called Note di Fuoco (NDF), is marked by 3 days off celebration including permanent street food cookers, various kind of artistic performances, and ending each night with an exhibition among the best fireworks companies in the world of fire art. Each year multi-launch stations, with large batteries of fires and simultaneous radio-controlled departures, are arranged over the Capo Tirone basin. During the pyrotechnic show, it is possible to admire the explosion of tons of gunpowder in a great choreography of music, lights and colors, with fan flies that reach an amplitude of aerial fire of over 200 meters. The Festival attracts a large number of tourists and curious.

2.2. Sample Collection

Aerosol particles were collected by 2 distinct sampling monitors on the roof (15 m high) of a building in Belvedere M.mo, far about 130 m from the coastline (see Figure 2). PM_{10} and $PM_{2.5}$ collections were carried out according to European Standards EN-12341:1998 and EN-14907:2005, respectively [26]. Samples were simultaneously collected on 47-mm Whatman quartz microfiber filters, through 2 lower-volume samplers, the Echo *PM*-Instruments (Tecora), each equipped with the proper PM_{10} and $PM_{2.5}$ inlet, and both operating with a flow rate of about 38 L·min^{-1}. The samples and blank filters were kept in polyethylene bags before and after sampling until analysis. Before and after sampling collection, each filter was conditioned under constant temperature (25°C) and relative humidity (50%) for 24 hours, a then weighed using a micro-balance (Gibertini microcrystal model) with 0.1-μg sensitivity. All weight measurements were repeated thrice to ensure reliability, and the average was taken to make the consistency in reading. The net weight collected, obtained as the gross (after sampling) minus the tare (before sampling) filter weight, was divided by the collected standardized sampling volume to obtain the corresponding concentration by the gravimetric method. All the procedures were strictly quality-controlled to avoid any possible contamination of the samples. PM_{10} and $PM_{2.5}$ were monitored over a 24-hours sampling period, from the 29 July to the 4 August 2016. The observing sampling week covered the 3-day period of the NDF Festival (29, 30 and 31 July) and a period following the end of the Festival, including 3 days with no specific events and taken as background (1, 2 and 4 August), and 1 day during which the typical country Market took place (3 August). Starting time was set at midnight of each new day and lasted for 24-hours. The systematic sampling plan, and the Identification coding for the days during and after the NDF
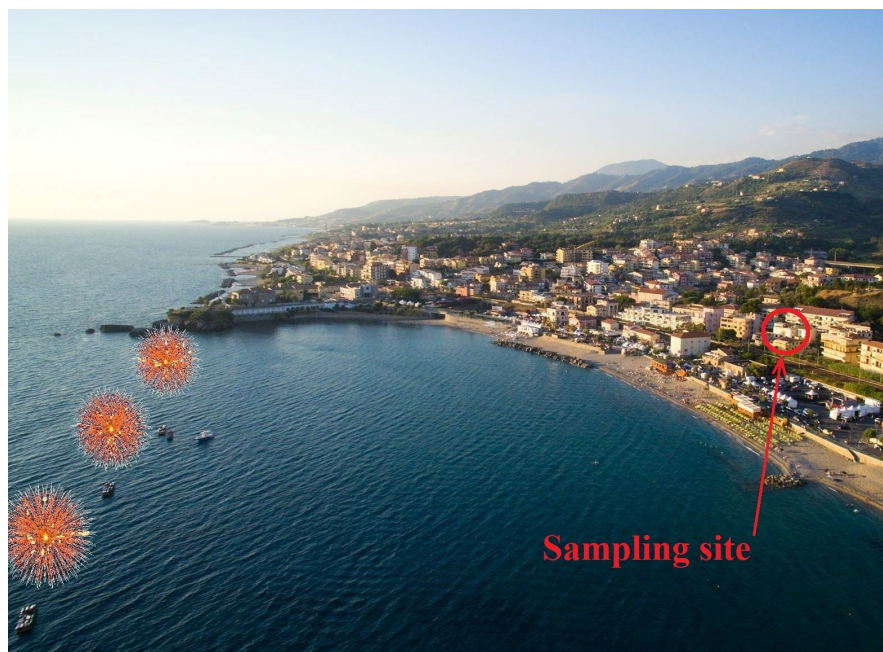
Figure 2. Location of the Sampling site within the little Capo Tirone sea basin where the Firework displays took place.

festival, is presented in **Table 1**. In total, fourteen samples (seven for $PM_{2.5}$ and seven for PM_{10}) were collected along with seven blank filters, which were kept in the same condition as the actual samples. During the sampling period, meteorological data, including wind speed and direction, were obtained by the Arpacal weather station (39˚38'N 15˚51'E) at about 2 km northward from the sampling site (see **Figure 1**). The anemometer is at a height of 12 m above the ground surface.

2.3. Analytical Techniques

2.3.1. EC/OC Measurements

The carbonaceous species are operationally classified into organic carbon (OC) and elemental carbon (EC). EC is mainly derived from incomplete combustion of fossil-fuel, biomass burning and other carbon-contained material. It has a long photo-chemical lifetime and this makes it a good indicator of primary anthropogenic air pollution [22] [27]. 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 photo-chemical reactions through gas-to-particle conversion of volatile organic compounds, as secondary OC (SOC) [28] [29]. The concentrations of the carbonaceous species were determined on one punch (area: 1 cm^2) cut from the quartz fiber filters employed for collecting the 24-h PM_{10} and $PM_{2.5}$ samples. All the filters prior the sampling were pre-fired for 2 h at 700 ˚C in order to remove any residual carbon contamination. The analysis of

Table 1. Sampling plan and Identification coding for the week of aerosol collection.

Sample ID	Influencing Event	Day of Sampling
NDF_2907	1st day of Note Di Fuoco	29 July 2016
NDF_3007	2nd day of Note Di Fuoco	30 July 2016
NDF_3107	3rd day of Note Di Fuoco	31 July 2016
BKG_0108	1st Background day with No event	1 August 2016
BKG_0208	2nd Background day with No event	2 August 2016
MKT_0308	Market day	3 August 2016
BKG_0408	3nd Background day with No event	4 August 2016

Total Carbon (TC = OC + EC), OC, and EC was performed by the thermo-optical method (TOT) using a Sunset Laboratory OC/EC analyzer (Sunset Laboratory, Tigard, OR, USA), implementing the EUSAAR-II temperature protocol [30]. This thermal protocol, characterized by a transmittance optical correction for pyrolysis, has been recently selected as the European standard thermal protocol for the measurements of TC, OC and EC in *PM* samples (EN 16909:2017) [26]. To ensure the accuracy of the OC and EC analysis, the analyzer was calibrated using a sucrose solution as an external standard. Blank filters, from each of the three observed events, were also analyzed for correcting the measured concentrations. EC concentrations observed in blank filters were negligible; however, contamination was observed for OC with an average correction that was about 7%. In this study, the SOC concentration was additionally quantified using the minimum OC/EC ratio methodology proposed by [31]-[37].

2.3.2. Multielement Analysis

PM_{10} and $PM_{2.5}$ filters were digested by using a microwave-assisted protocol in accordance to the EN 14902:2005 standard [26]. This approach is better than the traditional heating procedures, involving heat convection or diffusion phenomena because increase the digestion efficiency and minimize the sample contamination. Each filter was transferred to TFM (tetrafluoromethoxil) vessels with 8 mL of HNO_3, 2 mL of H_2O_2 and 0.2 mL of HF. The vessels were placed in the microwave oven and digested using a three-step temperature-time program in which the temperature was increased to 180 ˚C in 15 min, then to 220 ˚C in 10 min and hold at this temperature for 10 min. Following digestion, the analysis was carried out by Inductively Coupled Plasma Mass Spectrometry, ICP-MS, (7500CE, Agilent) for the elemental content determination. The analytical batch consisted of a set of calibration standards, which were analyzed at the beginning of the run, samples, and a minimum of three blank filter samples whose values were subtracted from each sample. A mid-range calibration standard was measured after every 20 samples to assess instrumental drift throughout the run. A six-point calibration curve covering the range of 0.1 – 1000 μg·L^{-1} was used for quantitative analysis. Internal standardization was performed by on-line addi-

tion of a 200 μg·L^{-1} Rh solution through a Y-connector. The use of internal standard quantitation allows satisfactory and repeatable results to be obtained by ICP-MS, even if instrumental instabilities are observed. The following elements were investigated: Na, Al, K, Fe, Ca, Mg, Ti, V, Cu, Ba, Mn, Pb, Sr, Ni.

3. Results and Discussion

3.1. Meteorological Field Analysis and Characterization

3.1.1. Synoptic Scale

The sampling site is located within the Mediterranean basin. Belvedere M.mo thus experiences meteorological conditions in line with the typical Mediterranean climate [38]. Exactly, we registered no rain in our summer sampling period with high temperature (means around 26˚C) as those typically recorded during the warmest month of July and August in the Mediterranean region [39]. The synoptic chart of NCEP-based 925 mbar geopotential heights (m) during our sampling periods (from 29 Jul until 4 Aug) shows the persistence of an irregular Anticyclone vortex which spans from the Algerian-Libyan desert to the Île-de France and the North of the Alpine region (see **Figure A1** in Supplemental section). When the Libyan anticyclone invades the Mediterranean basin, there is a general subsidence over the region, with a diffusive tropospheric adiabatic warming thus favoring a general accumulation of aerosol in the boundary layer.

3.1.2. Local Scale

The local wind field conditions were equally important in affecting aerosol content at our sampling site. Being our sampling site located in a coastal area, the land-sea breeze played an important role in the variations of the aerosol loading over the site. Over the whole week of our observations, wind speed showed a diurnal variation with comparative lower values in the evening, around 1 ms^{-1}, in respect to those recorded during the morning that were double in intensity, around 2 ms^{-1}. Specifically, during the evening, the wind intensity ranged from 0.1 to 2.6 ms^{-1}, characterized over the 73% by "Light Air" and for the 25% of the cases by "Light breeze", expressed as Beaufort scale [40]. The wind intensity was stronger during daylight with values from 0.1 to 3.6 ms^{-1} with a major frequency of the higher scales: 22% of "Light Air", 73% of "Light breeze" and also a 4% of "Gentle Breeze". The wind rose analysis (see **Figure 3**) of all the days during our period of study shows that most winds were onshore (sea breeze) during the day, and then changed direction to blow offshore (land breeze) during the night and till early morning. The prevailing surface winds blow from sea in south-west and west direction. Exactly the opposite direction was observed during nighttime, mainly from land in northeast and east direction, but with weaker wind speed. Being the firework displays arranged around midnight, with the above mentioned wind prevailing direction during nighttime, there could be a reason to suppose that aerosol particle load emitted from fireworks was underestimated since, in respect to our point of sampling, it was measured upwind. However, the vicinity of the sampling site to the coast, where fireworks have been displayed,
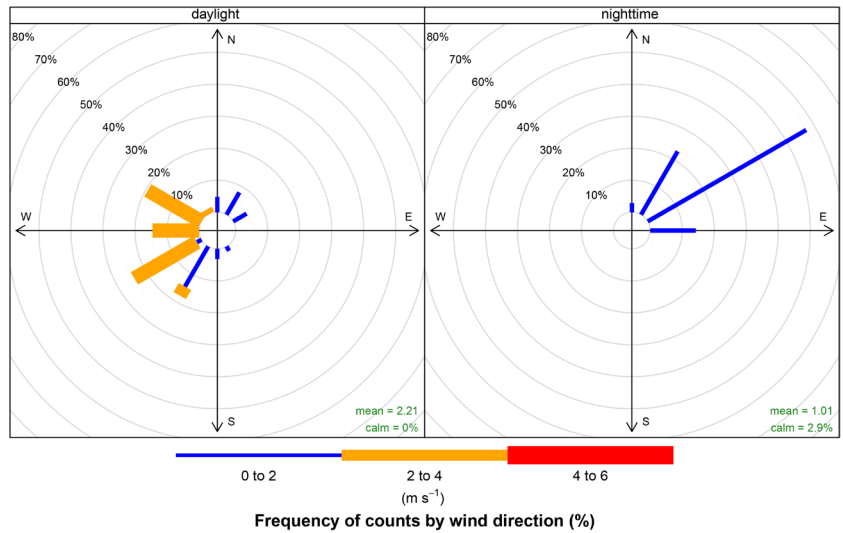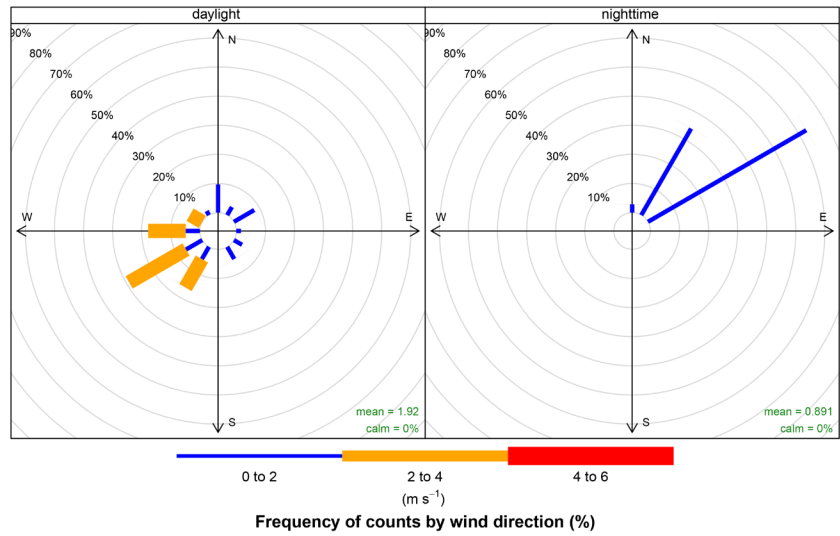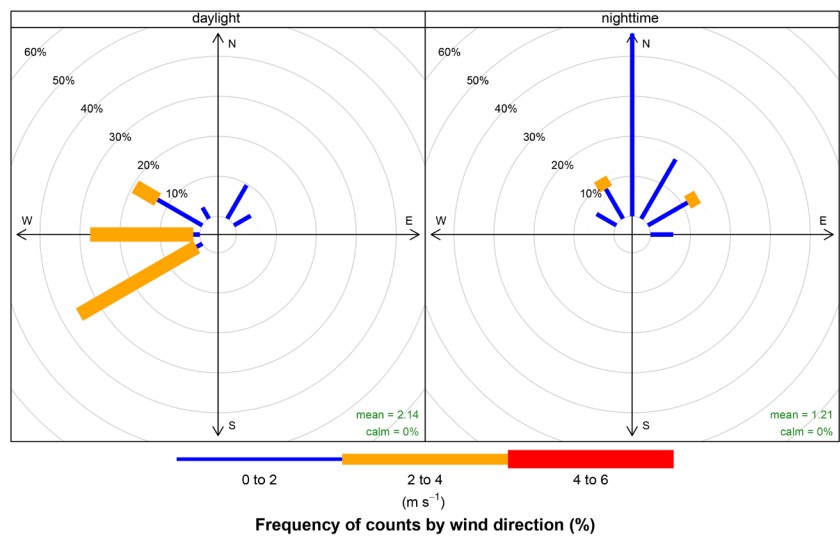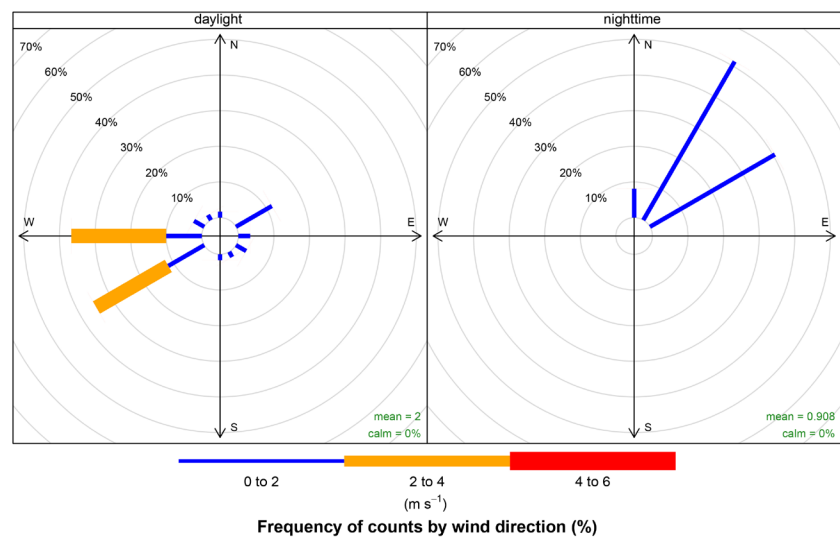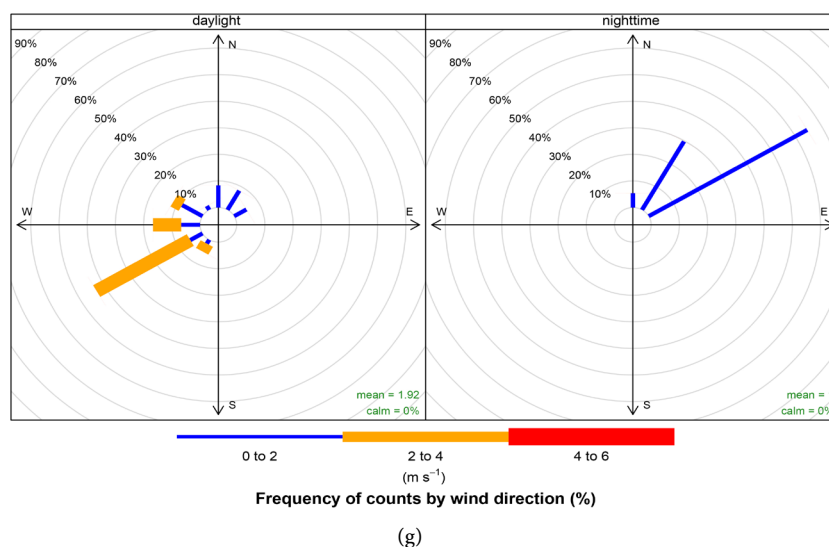
(a)
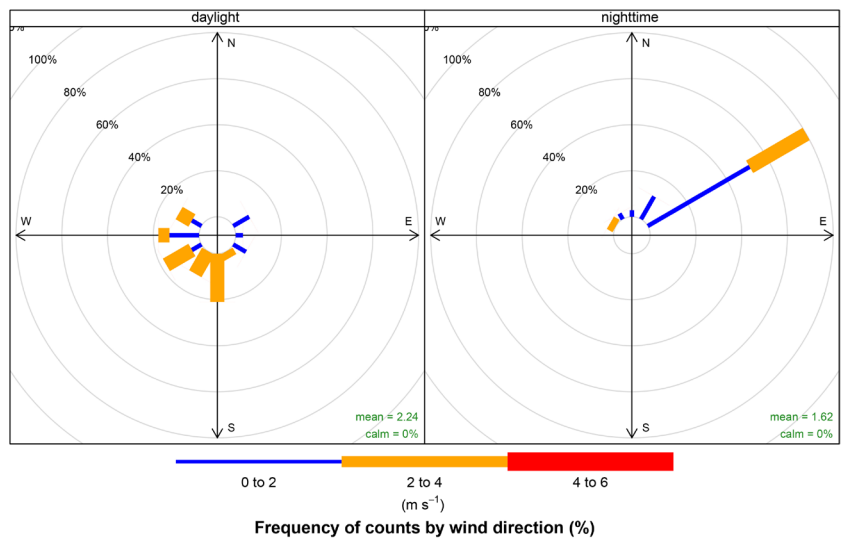
(b)
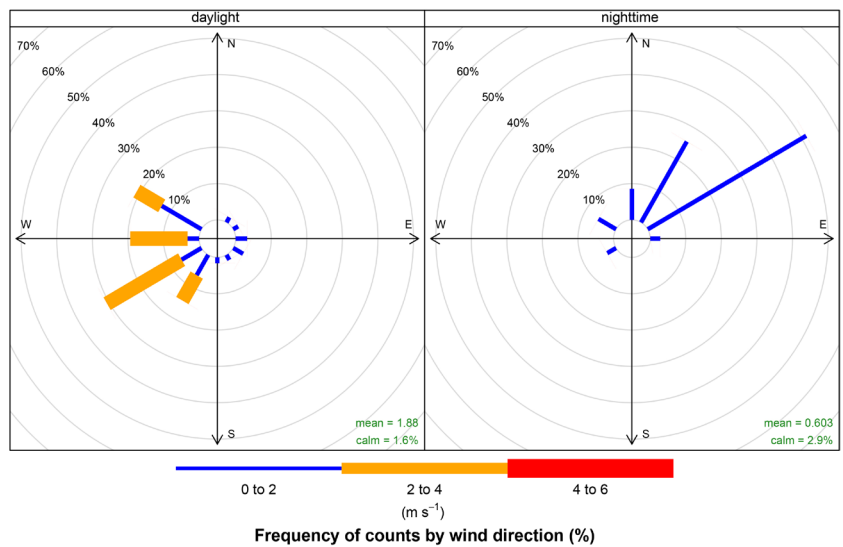
(c)

(d)

(e)

(f)

Figure 3. Wind roses reporting the frequency of counts by wind direction (%), distinguishing daylight from night-time, for each day of our period of study: (a) 29-Jul; (b) 30-Jul; (c) 31-Jul; (d) 01-Aug; (e) 02-Aug; (f) 03-Aug; (g) 04-Aug, 2016.

the elevation and the amplitude of aerial fires of over 200 meters, together with the almost stable atmospheric conditions during night, can confidently support the belief that our aerosol sampling was able to catch in part the products of the firework gunpowder. It is noteworthy that, as an exception in respect to the other days, during the BKG_0208 a clear prevalent direction from the north was recorded, together with the highest wind speed even detected during nighttime, equal to 1.2 ms^{-1}. This wind condition presumably favored the advection to our sampling site of air masses mostly coming from sea thus influencing the aerosol composition with mostly coarse particles such as sea salt [41].

An in-depth analysis of the wind meteorological data-set can further confirm that around midnight, when approximately the pyrotechnic shows were about to start, the local wind intensity was very low (0.1 - 0.4 ms^{-1}) while it was growing (up to 1.2 ms^{-1}) early in the morning, around 7:00 AM local time. The increase in wind speed was concurrently with the change of wind from eastern to western prevalent direction. The calculated ratio of wind speed (RWS-day/night) was even larger than 1.5, implying that the mean wind speed during daylight was even more intense than that recorded during nighttime (see **Figure A2** for more details). Firstly, it could be hypothesized that the stable conditions during nighttime prevented any horizontal diffusion of the aerosols and could, at times, contribute to aerosol stagnation in the local area. Secondly, the stronger wind blowing onshore during daylight otherwise favored both re-suspension and influx of aerosols toward our sampling location.

3.2. Temporal Evolution

3.2.1. Aerosol and Carbon Content

Over the week of our monitoring study the air quality, in respect with aerosol concentrations, resulted to be quite good at Belvedere M.mo, with PM_{10} and

$PM_{2.5}$ levels even below 30 μg·m^{-3} and 20 μg·m^{-3}, respectively (see **Figure 4**). The European health thresholds are in fact set equal to 50 μg·m^{-3}, as daily limit value for PM_{10}, and 25 μg·m^{-3}, as annual limit value for $PM_{2.5}$ [42].

Otherwise, during the study period, an interesting inversion in the finer ($PM_{2.5}$) and coarser ($PM_{2.5-10}$) concentration was observed. By looking **Figure 4** it is evident, in terms of both absolute concentration values and $PM_{2.5}/PM_{10}$ ratio, the prevalence of the finer fraction during the three days of the NDF festival, followed by a net decreasing during the next days. The concentrations of $PM_{2.5}$ showed, in fact, a steady increase starting the first day of the Festival (NDF_2907) from a value of 16 μg·m^{-3} with a share of 56% over the PM_{10} total fraction, reaching the maximum value of 20 μg·m^{-3} and a share of 77% over the PM_{10} the third Festival day (NDF_3107). During days after the end of the Festival, the $PM_{2.5}$ levels dropped around 10 μg·m^{-3} with a share that was even down to 55%. The only nearest sampling site with air quality data collected in the same period of our study is the Lamezia station. This coastal site faces on the Tyrrhenian Sea and is located at about 80 km SSW in respect to Belvedere M.mo [37]. During the same sampling period of our observations at Belvedere, the values recorded at Lamezia station for $PM_{2.5}$ were even lower than 10 μg·m^{-3} [43]. As it can be seen in **Figure 4**, we recorded $PM_{2.5}$ around this same value of 10 μg·m^{-3} during our background conditions. During the Festival the finer particles reached instead a higher level, ranging from 16 to 20 μg·m^{-3}. This comparison highlights the potential influence of the festival on air quality at Belvedere. The
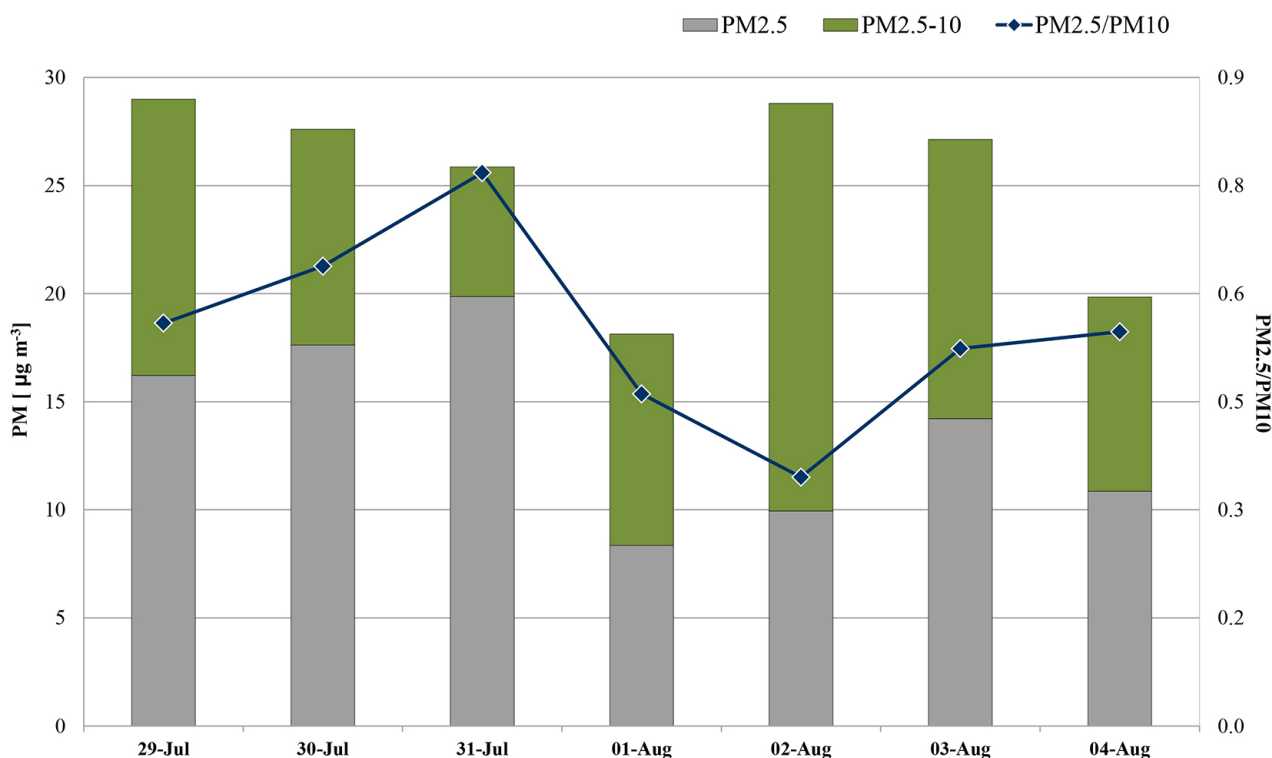
Figure 4. Evolution of concentrations of Fine ($PM_{2.5}$-grey) and Coarse ($PM_{2.5-10}$-green) particles and their ratio over the week of study.

minimum $PM_{2.5}$ contribution, with a value of 35%, was recorded the day with no events (BKG_0208), during which a concomitant raising of the coarser particles, up to 19 μg·m^{-3}, was detected. As an exception over the entire period, a slight increase in $PM_{2.5}$ levels, around 15 μg·m^{-3}, was recorded at our sampling location the day identified as MKT_0308, probably influenced by the greater flow of cars and trucks usually occurring each Wednesday at Belvedere M.mo town during the Market's activity.

For both, directly recorded, *PM* size fractions (PM_{10} and $PM_{2.5}$) Table 2 reports a summary regarding their total mass concentrations along with the values obtained for the carbonaceous species, TC (EC + OC), the results for their relative contribution, their ratios, and also calculations for the Secondary Organic Carbon (SOC) component. Our analysis showed a higher, even if slight, prevalence of TC levels for all the three days of the festival, during which the TC value was up to 4 μg·m^{-3}, reaching the maximum recorded value the third day of NDF with a level of TC equal to 4.68 μg·m^{-3}. Once the Festival finished, the carbon content decreased reaching the minimum value 3.26 μg·m^{-3} the day BKG_0208.

In general, the relationship between the OC and EC atmospheric concentrations gives qualitative information regarding the sources contributing to carbonaceous species in *PM* [44]. If OC and EC are released into the atmosphere by common primary sources, the two carbonaceous species should be well-correlated [45]. The weaker correlation found in $PM_{2.5}$ and PM_{10} (R^2 = 0.56,

Table 2. Mass concentration (*PM*), Total Carbon (TC), Organic Carbon (OC), Elemental Carbon (EC) along with calculations for the carbonaceous species, are reported for both $PM_{2.5}$ and PM_{10} size fractions for each day of our sampling period.

	Sample ID	*PM*	TC	OC	EC	TC/*PM*	OC/*PM*	EC/*PM*	OC/EC	SOC	SOC/OC
		μg·m^{-3}	μg·m^{-3}	μg·m^{-3}	μg·m^{-3}	%	%	%		μg·m^{-3}	%
7*$PM_{2.5}$	NDF_2907	16.22	4.11	3.75	0.36	25.3%	23.1%	2.2%	10.33	1.13	30%
	NDF_2907	17.62	4.13	3.68	0.45	23.5%	20.9%	2.5%	8.23	0.46	12%
	NDF_3107	19.86	4.03	3.68	0.35	20.3%	18.5%	1.8%	10.59	1.18	32%
	BKG_0108	8.36	3.44	3.16	0.28	41.1%	37.8%	3.3%	11.50	1.18	37%
	BKG_0208	9.95	2.97	2.71	0.26	29.8%	27.2%	2.6%	10.46	0.84	31%
	MKT_0308	14.22	3.29	3.03	0.27	23.2%	21.3%	1.9%	11.38	1.11	37%
	BKG_0408	10.86	3.00	2.64	0.37	27.6%	24.3%	3.4%	7.20	0.00	0%
7*PM_{10}	NDF_2907	29.00	4.52	4.05	0.47	15.6%	14.0%	1.6%	8.52	1.15	28%
	NDF_2907	27.61	4.34	3.74	0.60	15.7%	13.6%	2.2%	6.28	0.10	3%
	NDF_3107	25.87	4.68	4.20	0.48	18.1%	16.2%	1.9%	8.73	1.26	30%
	BKG_0108	18.14	3.86	3.43	0.43	21.3%	18.9%	2.4%	8.00	0.81	24%
	BKG_0208	28.75	3.26	2.80	0.46	11.4%	9.8%	1.6%	6.11	0.00	0%
	MKT_0308	27.14	3.60	3.12	0.48	13.3%	11.5%	1.8%	6.45	0.17	5%
	BKG_0408	19.85	3.81	3.35	0.46	19.2%	16.9%	2.3%	7.21	0.51	15%

$R^2 = 0.28$) observed in our dataset indicated that the sources of OC at our sampling site were different from those of EC and/or can be the result of the presence of different emission sources, having significantly different OC/EC ratios.

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 carbonaceous aerosol, identifying the secondary organic aerosol (SOA) formation. In fact, 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). As Table 2 shows, the SOC estimated for our study using the EC tracer method and the minimum OC/EC ratio, was found to be an appreciable component of particle mass with contribution to OC ranging between 3 and 30% in the PM_{10} fraction, with relatively higher values in $PM_{2.5}$ (12% - 37%).

In our study case, the OC/EC ratio showed a considerable variation of values around 10 and 7, for $PM_{2.5}$ and PM_{10}, respectively. These relatively high values suggest a clear prevalence of the OC contribution over EC, which could be attributed to significant local sources with higher OC and lower EC emission rates. During the Festival, meat and pizza cooking systems were widely used on the promenade close to the Capo Tirone sea basin. These cooking methods are all 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. Thus, due to our observations, it could be hypothesize an important contribution of this kind of source over the organic carbon content of particles collected at our sampling location.

It is also interesting to observe the distribution of EC and OC between the fine and coarse particle size fractions. In fact, even if lower values, for both EC and OC levels, were measured for days after the Festival, it is possible to notice an increasing OC/EC ratio in the finer fractions (see Table 2). This occurrence could be explained by the fact that low wind speed observed during the study could help in trapping pollution gases near the surface followed by their secondary transformation and subsequent condensation onto pre-existing aerosols. As a result, concentrations of secondary components may be high, mainly in finer fraction, and in the post-firework period as confirmed by our calculation for the contribution of SOC to the corresponding OC values, and as also observed elsewhere by [9] and by [23].

3.2.2. Major and Trace Elements

Over the whole study period, 7 Major (Na, Al, K, Fe, Ca, Mg, Ti) and 7 Trace (V, Cu, Ba, Pb, Mn, Sr, Ni) Elements were detected. For each of the above mentioned elements Table 3 reports mean, Standard Deviation (SD), minimum (min) and Maximum (Max) values. Elements are ordered following descending mean values obtained for both $PM_{2.5}$ and $PM_{2.5-10}$ particle size fractions.

Table 3. Mean, Standard Deviation (SD), minimum (min), and Maximum (Max) values are reported for Major and Trace elements detected during the study period on both Fine ($PM_{2.5}$) and Coarse ($PM_{2.5-10}$) particle size fractions. Maximum values are highlighted in bold in case they have been recorded during a Festival day.

		$PM_{2.5}$					$PM_{2.5-10}$			
		Mean	SD	min	Max		Mean	SD	min	Max
7*Major Elements [ng·m⁻³]	Na	267	166	101	**590**	Na	650	369	399	**1470**
	Al	14	98	78.7	316	Ca	162	76.6	5.0	232
	K	99.4	54.2	33.4	175	Al	160	103	3.0	279
	Fe	69.1	38.8	27.7	141	Fe	154	48.5	54.6	198
	Ca	68.7	35.9	40.0	111	Mg	134	42.1	87.0	**222**
	Mg	48.8	28.0	16.0	**89.3**	K	70.9	40.0	2.0	**123**
	Ti	11.2	9.1	6.3	28.9	Ti	12.4	7.5	3.4	21.8
%MEs over *PM*		5%	3%	2%	**12%**		13%	5%	5%	19%
7*Trace Elements [ng·m⁻³]	V	3.1	0.9	2.1	4.5	Cu	5.7	2.4	0.9	**7.9**
	Cu	2.8	0.6	1.9	3.5	Ba	4.6	4.4	0.2	10.5
	Ba	2.6	1.2	1.7	4.2	Mn	2.5	1.0	0.9	**3.9**
	Pb	1.5	0.5	0.7	1.9	Sr	1.6	0.8	0.1	2.3
	Mn	1.4	1.0	0.3	2.7	V	0.8	0.6	0.2	**1.6**
	Sr	1.0	0.5	0.6	1.8	Pb	0.4	0.4	0.1	**1.1**
	Ni	1.0	0.3	0.7	**1.3**	Ni	0.2	0.1	0.1	**0.3**
%TEs over *PM*		0.08%	0.02%	0.04%	0.11%		0.13%	0.08%	0.01%	0.24%

Maximum values are further highlighted in bold in case that they have been recorded during a Festival day.

Elements with mean concentration up to 10 ng·m⁻³ in $PM_{2.5}$ or in $PM_{2.5-10}$ were identified as Major Elements (MEs). In our samples, levels varying from a minimum mean value of 11.2 ± 9.1 and 12.4 ± 7.5 for Ti until values of 2667 ± 166 and 650 ± 369 ng·m⁻³ for Na, were observed in $PM_{2.5}$ and $PM_{2.5-10}$, respectively (see Table 3). Mean concentration of the detected MEs was observed to be in the order of Na > Al > K > Fe > Ca > Mg > Ti in the finest fraction while it was Na > Ca > Al > Fe > Mg > K > Ti in the coarser one, thus revealing a prevailing concentration of K in $PM_{2.5}$, which was even larger during the three days of the NDF Festival. The total amount of MEs accounted for 2% - 12% and 5% - 19% of the total $PM_{2.5}$ and $PM_{2.5-10}$ mass concentrations, respectively. As it can be noted by numbers in bold in Table 3, in both $PM_{2.5}$ and $PM_{2.5-10}$, all MEs reached the maximum value in correspondence of the NDF Festival, except for Na and Mg that otherwise peaked during the background day identified as BKG_0208. Dur-

ing this day the wind was more intense in the direction NNW (from the sea) thus favouring a substantial injection of sea spray, of which Na is a tracer, as well as of sandy dust, whose a maker is Mg [41]. Contrarily from the finer fraction, the maximum value of K in the coarser fraction was recorded the day BKG_0108. The different behavior of K in the two particle fractions implies they originated from two sources, in particular, larger K levels in $PM_{2.5}$ during the Festival can be confidently attributed to fireworks being the K itself recognized as a good tracers of the emissions from fireworks [9].

Elements with mean concentration lower than 10 ng·m^{-3} but higher than 1 ng·m^{-3} in $PM_{2.5}$ and/or in $PM_{2.5-10}$ were identified as Trace Elements (TEs). Their amount in our study case varied from 0.04% to 0.1% in $PM_{2.5}$ and from 0.01% to 0.24% in $PM_{2.5-10}$. In the finer fraction, the higher mean concentration was observed for V (3.1 ± 0.9 ng·m^{-3}) and followed by Cu (2.8 ± 0.6 ng·m^{-3}). In the coarser fraction, the larger mean value was otherwise detected for Cu (5.7 ± 2.4 ng·m^{-3}) and followed by Ba (4.6 ± 4.4 ng·m^{-3}). By looking at Table 3 the different order of TE concentrations in $PM_{2.5}$ and $PM_{2.5-10}$, it is possible to notice the larger enrichment of V (range of value: 2.1 - 4.5 ng·m^{-3}) and Pb (0.7 - 1.9 ng·m^{-3}) in the finer fraction in respect with that recorded in the coarser one where values varied from 0.2 to 1.6 ng·m^{-3} and from 0.1 to 1.1 ng·m^{-3} for V and Pb, respectively. Regarding Pb, levels were found to be below the annual limit value set by EU legislation and set to 0.5 μg·m^{-3}. Similarly for Ni, whose target yearly value is equal to 20 ng·m^{-3} while in our samples it was found to be lower than 1.3 and 0.3 ng·m^{-3} in $PM_{2.5}$ and $PM_{2.5-10}$, respectively (see Table 3). It is important to note that in the finer particle mode, with the only exception of Ni, each TE reached the maximum value in correspondence of a day within the NDF festival. The behavior of TEs was different in the coarser particle mode: only Ba and Mn peaked during NDF while the other ones recorded maximum values during a BKG day.

3.3. Events Influence

3.3.1. Aerosol and Carbon Content

Levels of aerosol mass, carbon content and elemental concentration, already presented as temporal evolution over the study period in the previous paragraphs, were further grouped according to the various occurring events (NDF, MKT and BKG), and discussed in terms of their inter-variability.

As Table 4 shows, the $PM_{2.5}$ mean level (17.9 ± 1.8 μg·m^{-3}), obtained as average of the daily $PM_{2.5}$ concentrations recorded during the 3 days of the NDF Festival, was almost double in respect to that revealed at the Background conditions (9.7 ± 1.3 μg·m^{-3}). The value obtained during the Market event was intermediate between the last two ones. Particulate EC and OC in the finer mode both showed higher mean values in correspondence of the NDF event, followed by those recorded the day with Market. Differently, for the coarser fraction it seems that there was not a contributing source during the Festival.

Table 4. Mean and Standard Deviation (SD) for total mass concentration (*PM*) along with EC and OC content obtained over each single event period (Note di Fuoco, Market and Background), and associated with both Fine (*PM*$_{2.5}$) and Coarse (*PM*$_{2.5-10}$) particle size fractions.

Conc [µg·m⁻³]	$PM_{2.5}$					$PM_{2.5-10}$				
	Note di Fuoco		Market	Background		Note di Fuoco		Market	Background	
	(n = 3)		(n = 1)	(n = 3)		(n = 3)		(n = 1)	(n = 3)	
	Mean	SD	Mean	Mean	SD	Mean	SD	Mean	Mean	SD
PM	17.9	1.8	14.2	9.7	1.3	9.6	3.4	12.9	12.5	5.4
EC	0.4	0.1	0.3	0.3	0.1	0.1	0.0	0.2	0.2	0.1
OC	3.7	0.0	3.0	2.8	0.3	0.3	0.2	0.1	0.4	0.3

The percentage variation of aerosol particle levels measured during the Festival itself in respect with those recorded at Background conditions shows a negative variation, around 20%, for *PM*$_{2.5-10}$ mass concentration as well as for its EC and OC content, while for *PM*$_{2.5}$ there was an increment up of 80% for the total mass concentration that was instead about 30% for both EC and OC (see **Figure A3** for more details).

3.3.2. Major and Trace Elements

To better evaluate the influence of the NDF Festival on the elemental particle concentrations, the percentage variation between levels recorded during NDF and BKG days was calculated, highlighting the different behavior of finer and coarser particles (see **Figure A4** for more details).

For *PM*$_{2.5}$-associated elements with the only exception of Na and Ni there was a positive contribution of NDF with an increase up to 50% for Fe, Ti, K within Major and for Mn, Pb, Sr in Trace Elements. Although Fe is not an element typically originated from fireworks, it showed a significant increase during the NDF period. Fe is in fact used to make gold sparks; its oxides are usually used as high-temperature oxidizers in fireworks while Ti is used to provide silvery effects [7].

As known, potassium salts might be one of the major compounds used in fireworks and potassium could serve as a tracer of the emissions from fireworks [9]. Interestingly, in our study K in the fine fraction showed strong correlation with Pb, and Sr (R^2 = 0.86 in both cases), indicating they are largely from fireworks. In fact, Pb could help to achieve a steady and reproducible burning rate as well as to produce crackling micro-stars [3]. Otherwise Sr, in the form of strontium nitrate and strontium sulfate, is employed to give the red color to flares, fires, and stars; besides, Sr atoms also serve as a stabilizer for the mixtures. In contrast to the other trace elements, concentrations of Ni dropped during the Festival. This metal is considered tracer of vehicular (fuel combustion) source. Traffic during NDF was interdicted for security, being thus the probable explanation of the lower values observed for Ni itself during the Festival.

For $PM_{2.5-10}$-associated elements, an important increase ($\Delta > 40\%$) was recorded only for Ba and Al while the others elements showed minor positive variation or even a negative contribution. These results could be explained by the fact that fireworks burning produce mainly finer particles that have much shorter residence times in the atmosphere and will convert through aggregation or coagulation to coarser particles whose levels increased the days before the Festival.

To distinguish the fireworks-induced changes in the elemental compositions of the fine particles from the coarse particles, the $PM_{2.5}$-to-PM_{10} ratios (concentration of element associated with $PM_{2.5}$/concentration of element associated with PM_{10}) for each of the elements identified in this study was further determined. As indicated in **Figure 5** the $PM_{2.5}/PM_{10}$ ratio was higher during the NDF period with respect to the BKG one for all the Major and Trace elements with the only exception of Ba and Ni. This behavior can be explained by considering that the burning of fireworks increased the level of fine aerosol particles, which remained suspended in the air before they coagulated into coarser particles that dropped on the ground. The higher ratio found in this study for K, Pb and V well agrees with that reported by [3].

Although there have been only a limited number of other studies on atmospheric emissions emanating from fireworks, it is clear that such particle emissions have their distinctive physio-chemical composition. The firework tracer elements did not show an increment in the coarser mode neither in the study carried out in Milan and reported by [10], thus confirming that ambient aerosol during fireworks event is preferably confined in the fine fraction.

4. Conclusions

In this study, $PM_{2.5}$ and PM_{10} aerosols were recorded in summer 2016 during the Note di Fuoco Festival to evaluate the general impact induced from the overall Festival itself on the ambient air quality at Belvedere M.mo, a rural area facing on the Tyrrhenian coast of Italy. Elemental and Organic Carbon along with 14 major and trace elements has been measured by the thermo-optical method and ICP-MS, respectively. This paper is designed as a contribution towards understanding the distinctive and unusual chemistry of the anthropogenic aerosol burden created by firework displays together with related influencing sources. The outcomes from this study confirmed that particles induced during the overall period featured by pyrotechnic shows were characterized by a high $PM_{2.5}/PM_{10}$ ratio and contain a complex mixture of different trace metals. Our measurements specifically showed that $PM_{2.5}$ was double during the NDF Festival compared to background conditions. In particular, the analytical results revealed that the concentrations of many of the major and trace elements contributed mainly to the finer, more toxic and inhalable particulate size fraction. Some elements that play an indispensable role in forming the various colours seen during the burning of fireworks, namely K, Cu, Sr, and Ba, were found in higher concentrations. The most notable increases in our study involved Ba, Sr, Pb, and Sb, Mg, Ti showing lesser increases. In this preliminary
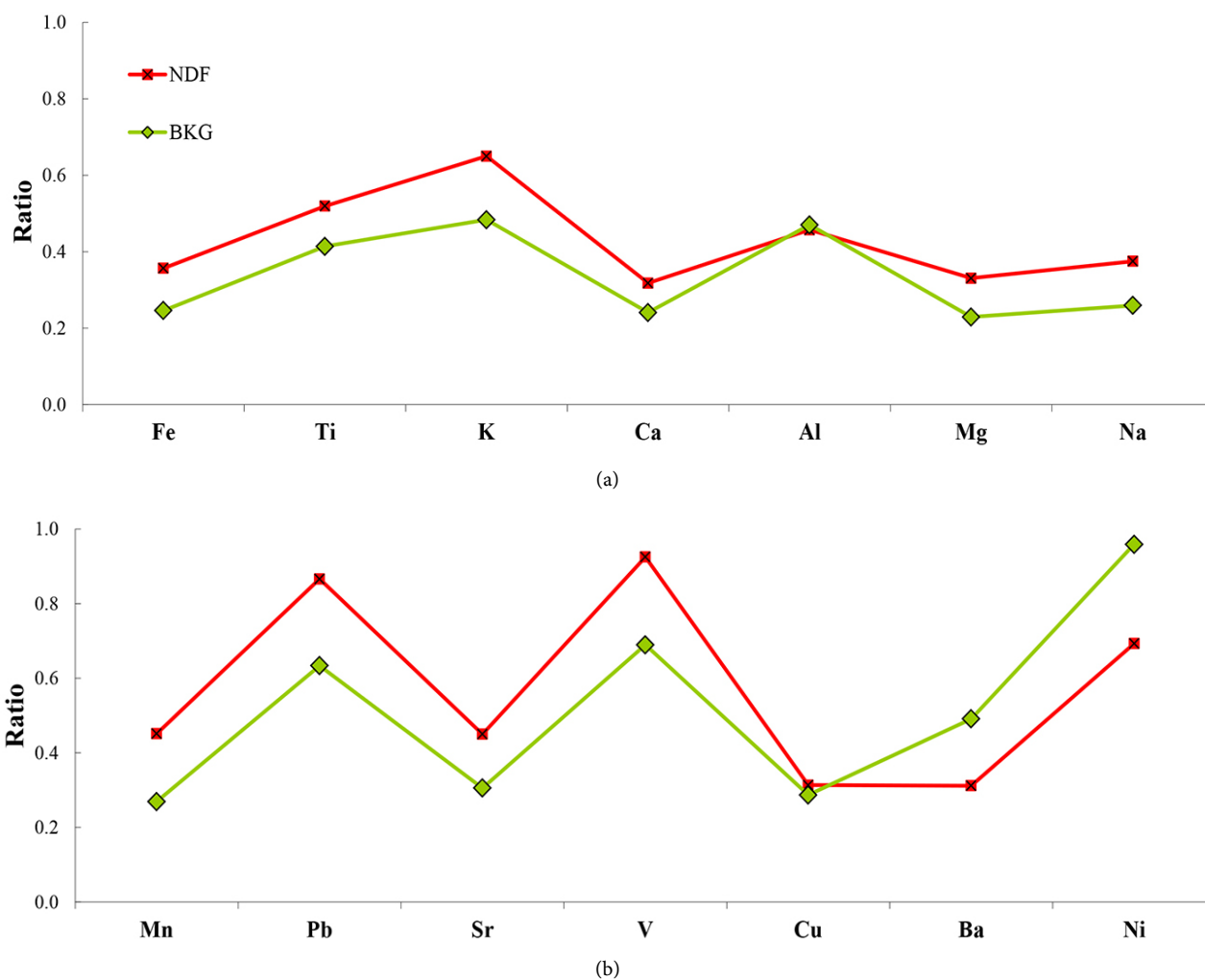
(a)

(b)

Figure 5. Ratio between $PM_{2.5}$ to $PM_{2.5-10}$ corresponding levels for Major and Trace elements.

investigation, we also were able to recognize the likely influence of the cooking street systems which, based on biomass burning, mainly resulted in an increase in organic carbonaceous component of the recorded particles.

As an added value, in a forthcoming study, it will be necessary to sample aerosols variation with a major temporal resolution to be able to check variations in chemicals and distribution of aerosols when the prevailing wind starts deviating from onshore to offshore, due to land and sea breeze which characterizes our sampling location. In such a way, it would also possible to verify the real impact of the firework displays and distinguish it from other contributing sources induced by the Festival itself. In addition to the aerosol physical-chemical composition, it would be useful to monitor also the main primary and secondary gas pollutants such as NO_x, SO_2 and O_3. Taking this into account, it will allow to better understand and characterize mechanisms and processes involved in the increase of pollution load in a rural location, like Belvedere M.mo, that generally recall a huge number of tourists during such kind of summer events.

With these preliminary results in mind, we can affirm that although fire-

work-related recreational pollution episodes are transient in nature, they are generally highly concentrated, and are on average fine enough to be easily inhaled and have a health risk for susceptible individuals. On the other hand, as Clark (1997) has noted, regulating or banning such events would be socially unacceptable; however, adequate knowledge of the scenario is vital to ensure that the sensitive population takes precautionary measures.

Acknowledgements

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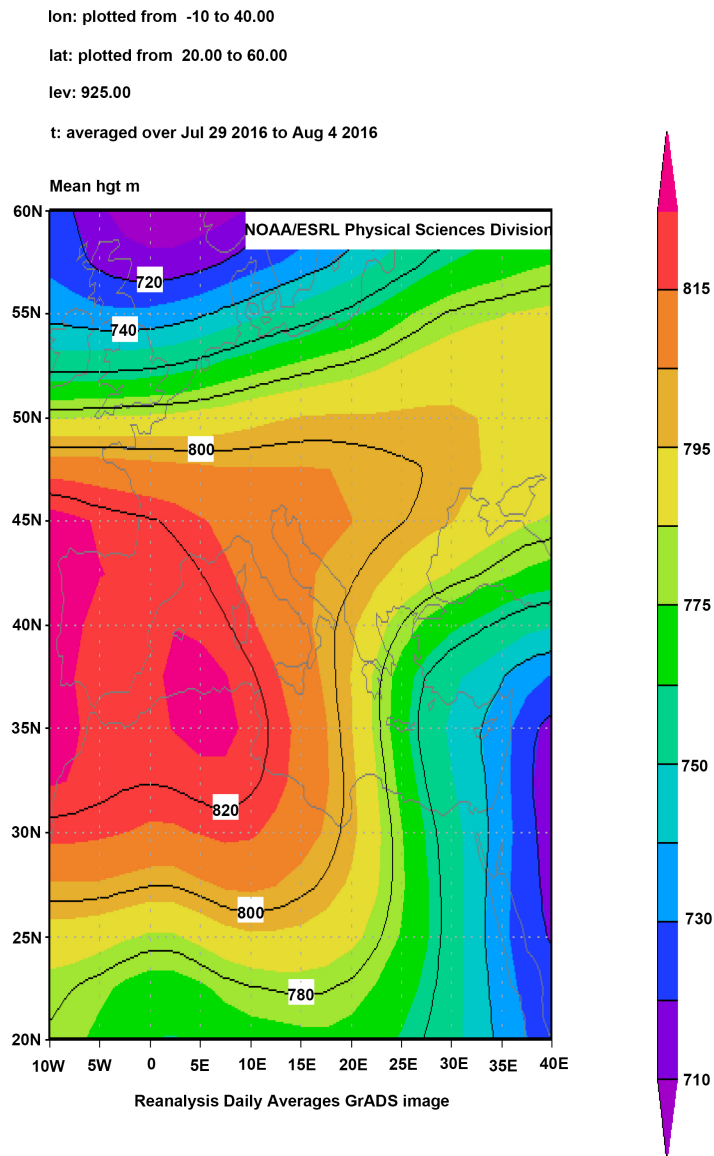
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Appendix A. Supplemental Section

lon: plotted from -10 to 40.00

lat: plotted from 20.00 to 60.00

lev: 925.00

t: averaged over Jul 29 2016 to Aug 4 2016

Figure A1. NCEP chart showing the geo-potential heights (m) over the whole Mediterranean region and during the study period (from 29 Jun to 4 Aug).
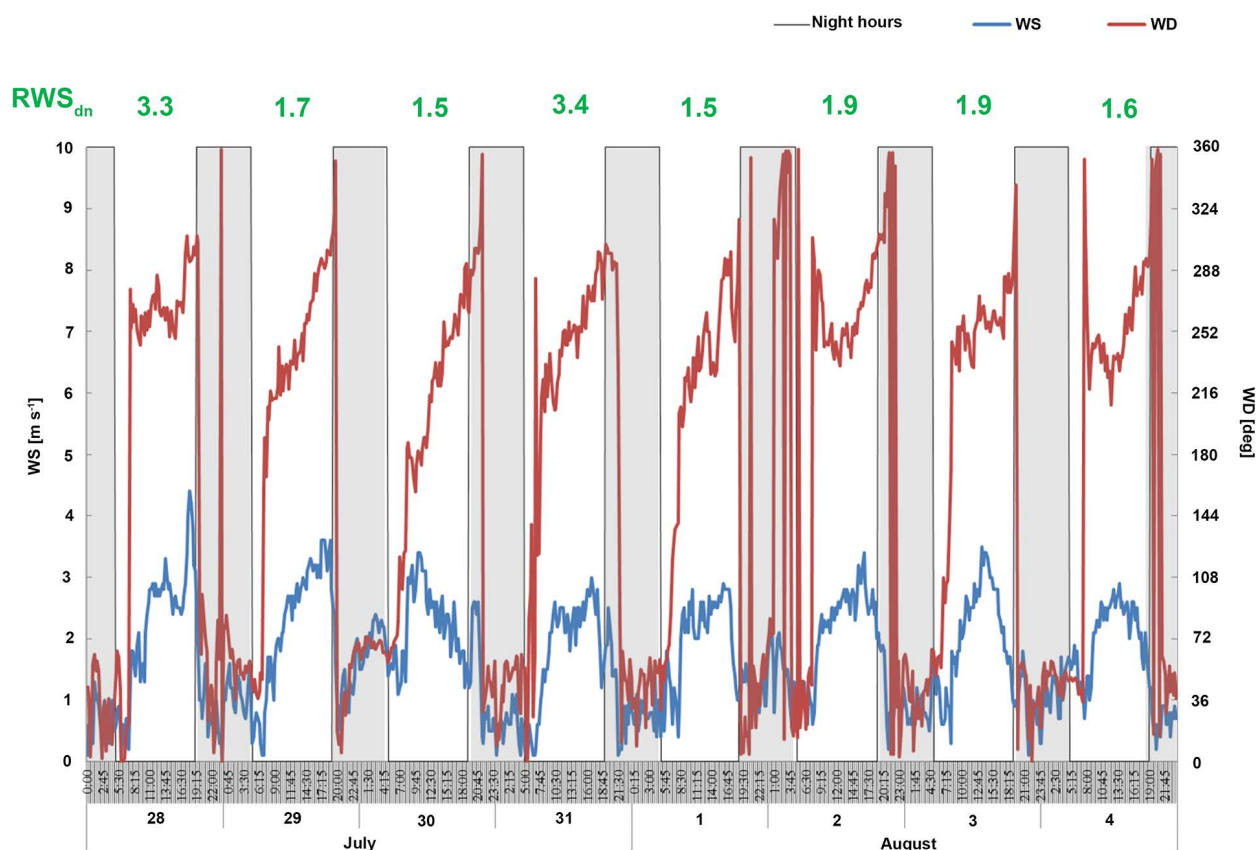
Figure A2. Wind Speed (WS-ms⁻¹) and Wind Direction (WD-degree) over the study period with gray bars highlighting the night hours. The Ratio between diurnal and night mean values of Wind Speed (RWSdn) is also overwritten.
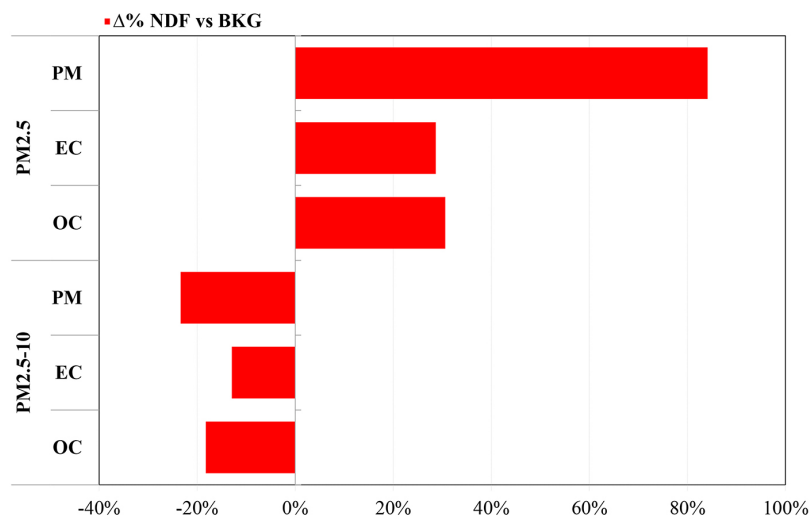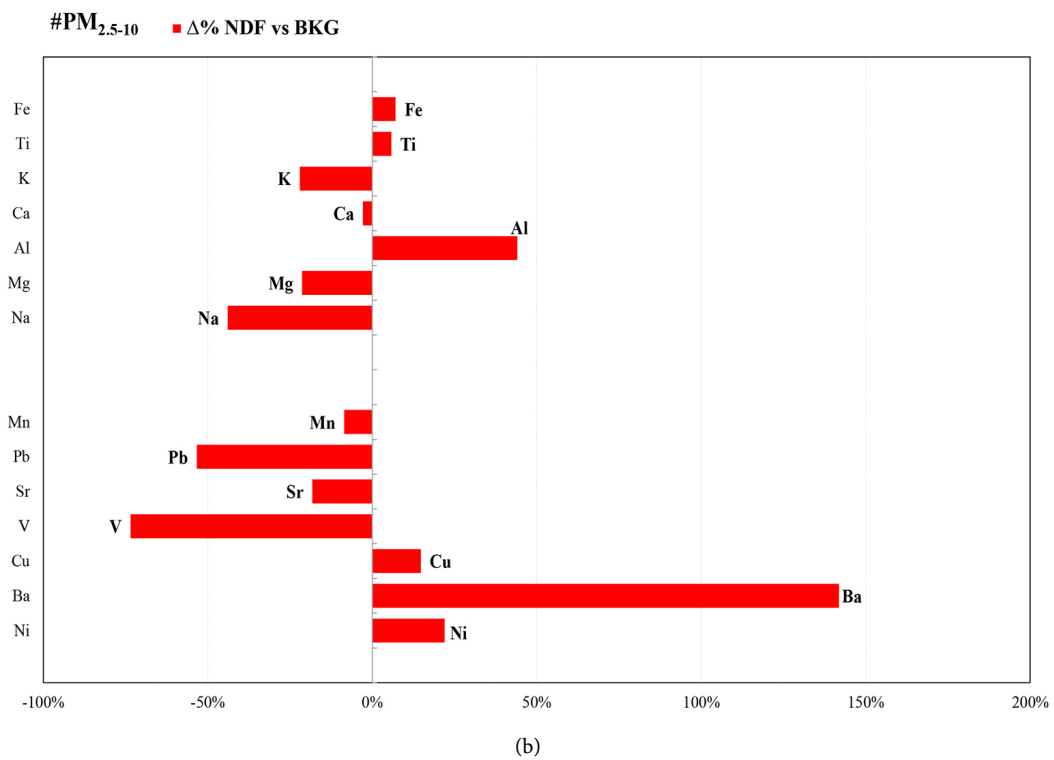

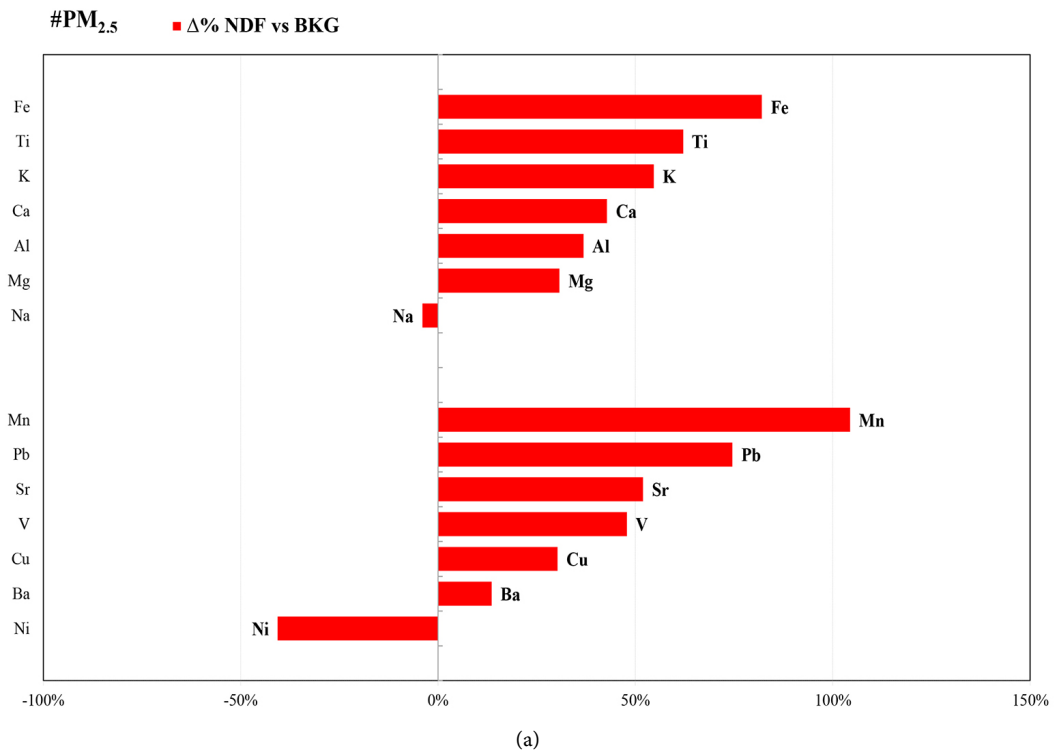**Figure A3.** Percentage variation of *PM*, EC and OC levels recorded during NDF in respect with those observed at BKG, for Fine ($PM_{2.5}$) and Coarse ($PM_{2.5-10}$) size particle fractions.

(a)

(b)

Figure A4. Percentage variation of each detected Major and Trace element level recorded during NDF in respect with that observed at BKG, for Fine (*PM$_{2.5}$*) and Coarse (*PM$_{2.5-10}$*) size particle fractions.